CARBOTHERMIC REDUCTION OF OXIDES DURING NITROGEN SINTERING OF MANGANESE AND CHROMIUM STEELS

S. C. Mitchell, A. Cias

Abstract
To interpret nitrogen sintering of chromium and manganese steels without the formation of deleterious oxides, but with manganese and carbon modifying the local microclimate, the role of the volatile Mn and carbothermic reactions were considered. Reduction of Cr$_2$O$_3$ by Mn vapour is always favourable. CO is an effective reducing agent, however, whereas at atmospheric pressure it will reduce FeO at ~730°C, temperatures some 500 and 700°C higher, i.e. above those for conventional sintering, are necessary for reducing Cr$_2$O$_3$ and MnO, respectively. Accordingly partial pressures must be considered and the sintering process is modelled at a conglomerate of several surface oxidised alloy particles surrounding a pore with graphite present and a tortuous access to the nitrogen-rich atmosphere containing some water vapour and oxygen. The relevant partial pressures were calculated and reduction reactions become thermodynamically favourable from ~200°C. Kinetics, however, dictates availability of CO and the relevant reactions are the water-gas, C + H$_2$O = CO + H$_2$ from ~500°C and the Boudouard, C + CO$_2$ = 2CO, from ~700°C. Discussion of sintering mechanisms is extended to processing in semi-closed containers, also possessing specific microclimates.

Keywords: PM chromium and manganese steels, nitrogen sintering, carbothermic reduction of oxides

INTRODUCTION
Šlesár et al, who have recently reexamined sintering of Fe-C [1], noted the critical importance of its initial stages, including removal of particle surface oxides, formation of sinter necks, dissolution of carbon, pore elimination and density development. They conducted isothermal sintering experiments in the temperature range 600-1200°C and complemented these with EDX, tensile testing, micrography and fractography. Kremel et al [2] went on to examine Astaloy CrM-C sintered in N$_2$-20% H$_2$ with additional dilatometric/degassing experiments. The importance of carbothermic reactions was stressed and general correlations with reducing reactions proposed. Most recently Bocchini [3], when reviewing controlled atmospheres in the “proper” sintering of carbon steels, considered equilibrium constants of relevant reactions, including those between CO$_2$ and H$_2$O, C and CO$_2$ and CO and H$_2$O.

Concurrently Mitchell et al [4-13] examined Fe-Cr-Mn-Mo-C systems, including sintering in nitrogen in semi-closed containers, with special reference to the volatile Mn [14], as shown in Table 1 and Fig.1, as well as carbothermic reactions. It is also to be noted [15] that Mn + H$_2$O = MnO + H$_2$ gas.
Tab.1. Calculated equilibrium partial pressure of Mn vapour versus temperature, as reported by Barin [16,17].

<table>
<thead>
<tr>
<th>Temperature [°C]</th>
<th>Mn Vapour Pressure (Atmospheres)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1.65E-47</td>
</tr>
<tr>
<td>100</td>
<td>5.36E-33</td>
</tr>
<tr>
<td>200</td>
<td>1.22E-24</td>
</tr>
<tr>
<td>300</td>
<td>3.22E-19</td>
</tr>
<tr>
<td>400</td>
<td>2.02E-15</td>
</tr>
<tr>
<td>500</td>
<td>1.28E-12</td>
</tr>
<tr>
<td>600</td>
<td>1.81E-10</td>
</tr>
<tr>
<td>700</td>
<td>9.06E-09</td>
</tr>
<tr>
<td>800</td>
<td>2.09E-07</td>
</tr>
<tr>
<td>900</td>
<td>2.78E-06</td>
</tr>
<tr>
<td>1000</td>
<td>2.42E-05</td>
</tr>
</tbody>
</table>

Fig.1. Manganese vapour equilibrium partial pressure showing its substantial increase from ~740°C (Note: Due to graph scaling and resolution there is the illusion that vapour pressure is zero below ~680°C. See data in Table 1).

Fig.2. Reducing partial pressures of CO in pore or semi-closed container in relation to Fe, Cr and Mn oxides, as a function of temperature.
On examination of thermodynamics of reduction reactions involving metal oxides on alloy powder particles, it is evident that, Fig.2, whereas CO at atmospheric pressure will reduce FeO at ~730°C, temperatures some 500 and 700°C higher than those for conventional sintering are necessary for reduction of Cr$_2$O$_3$ and MnO, respectively. It should be recalled that the sintering pressure is usually just above 1 atmosphere and the predominant partial pressures are usually of nitrogen and hydrogen. Accordingly for proper analysis of the relevant reactions, partial pressures must be considered and Fig.2 illustrates the effect of reducing the partial pressure of the 2C + O$_2$ reaction by 1, 2 and 3 orders of magnitude.

Accordingly sintering will be modelled for a conglomerate of several surface oxidised alloy powder particles surrounding a pore with graphite present and tortuous access to nitrogen-rich atmosphere containing some water vapour and oxygen. Theoretical calculations involve use of several algorithms for calculating reaction energies [18,19] and the availability of HSC Chemistry for Windows [19] allows, in some instances, speedy theoretical calculations. The enthalpy, H, entropy, S and heat capacity, Cp data used for the HSC calculations are taken from the most reliable recent sources available and should therefore be more consistent with external (absolute) scales. This ensures that the accuracy is adequate for most thermo-chemical calculations.

**REDUCTION OF OXIDES WITH SOLID CARBON**

**Assumptions:**
- total pressure is ~ 1 atmosphere
- nitrogen is inert at sintering temperature.

If FeO, Cr$_2$O$_3$ and MnO are to be reduced by solid carbon, then the maximum pressure of active gases which can be tolerated in the system can be calculated at absolute temperature T, by considering free enthalphy changes $\Delta G^0$, where Kp is the equilibrium constant. Temperatures chosen, with reference to Fig.2, were: 740°C (1013 K), also considered by Danninger et al [1,2], for FeO, 1100°C for Cr$_2$O$_3$ and 1140°C for MnO. The following reactions will be considered:

\[
\begin{align*}
\text{FeO} (s) &= \text{Fe} (s) + 0.5\text{O}_2 (g) \quad \Delta G^0 = 62050 - 14.95T \text{ calories} (1) \\
\frac{1}{3}\text{Cr}_2\text{O}_3 (s) &= \frac{2}{3}\text{Cr} (s) + 0.5\text{O}_2 (g) \quad \Delta G^0 = 89250 - 20.7T \text{ calories} (2) \\
\text{MnO} (s) &= \text{Mn} (s) + 0.5\text{O}_2 (g) \quad \Delta G^0 = 91950 - 17.31T \text{ calories} (3)
\end{align*}
\]

and:

\[
\begin{align*}
\text{C} (s) + \text{O}_2 (g) &= \text{CO}_2 (g) \quad \Delta G^0 = -94200 - 0.20T \text{ calories} (4) \\
2\text{C} (s) + \text{O}_2 (g) &= 2\text{CO} (g) \quad \Delta G^0 = -53400 - 41.9T \text{ calories} (5) \\
2\text{CO}(g) + \text{O}_2 (g) &= 2\text{CO}_2 (g) \quad \Delta G^0 = -135000 + 41.50T \text{ calories} (6) \\
\text{C} (s) + \text{CO}_2 (g) &= 2\text{CO} (g) \quad \Delta G^0 = +40800 - 41.70T \text{ calories} (7)
\end{align*}
\]

**Iron Oxide**

\[
\Delta G^0_{1013} = 46905.65 \text{ calories} = - (1.987 \times \ln10) \times 1013 \log K_p
\]

Therefore

\[
\log K_p = 46905.65/(-4.575 \times 1013) = -10.121
\]

But

\[
K_p = P_{\text{O}_2(\text{eq,T})}^{0.5}
\]
so \[ \log P_{O_2(eq,1013)} = 2 \times -10.121 = -20.242 \]

Therefore \[ P_{O_2(eq,1013)} = 5.73 \times 10^{-21} \text{ atmospheres.} \]

If it is considered that C is reducing FeO to form Fe + CO, then the pertinent reaction is:
\[
\text{FeO}_2 (s) + C = \text{Fe} + \text{CO},
\]
for which
\[ \Delta G^o = 35350 - 35.9T \text{ calories} = -RT \ln K_p = -1016.7 \]
where
\[ K_p = P_{CO(eq,T)} \]
Thus \[ \Delta G_{1013}^o = -1016.7 \text{ calories} = -4.575 \times 10^2 \log P_{CO(eq,1013)} \]
and so:
\[ \log P_{CO(eq,1013)} = 0.21938 \]
\[ P_{CO(eq,1013)} = 1.657 \text{ atmospheres.} \]

This implies that for reduction of FeO to proceed spontaneously, CO pressure must be less than 1.657 atmospheres.

If CO is in equilibrium with solid C, then a CO pressure must be exerted by:
\[
\text{C} + \text{CO}_2 = 2\text{CO}
\]
for which:
\[ \text{C}_2 (s) + \text{CO}_2 (g) = 2\text{CO}(g) \]
\[ \Delta G^o = +40800 - 41.70T \text{ calories} = -RT \ln K_p = -1442.1 \]

or \[ \log \left( \frac{\rho^2 \text{CO}}{\rho \text{CO}_2} \right)_{eq,1013} = 0.3112 \]

Hence
\[ \log P_{\text{CO}_2} = 2 \log P_{\text{CO}} - 0.3112 = (2 \times 0.21938) - 0.311 = 0.12759 \]
\[ P_{\text{CO}_2(eq,1013)} = 1.34 \text{ atmospheres.} \]

Thus, if the reaction is considered to be
\[
\text{FeO} + 0.5\text{C} = \text{Fe} + 0.5\text{CO}_2
\]
then the CO pressure must be lower than 1.34 atmospheres. For this reaction
\[ \Delta G^o = +14950 - 15.05T \text{ calories} = -295.65 = -RT \ln K_p \]
where
\[ K_p = P^{0.5}_{CO_2(eq,T)} \]
Thus
\[ \Delta G^o_{1013} = -295.65 \text{ calories} = -4.575 \times 1013 \log P^{0.5}_{CO_2(eq,T)} \]
From which
\[ \log P_{CO_2(eq,873)} = 0.12759 \]
or
\[ P_{CO_2(eq,1013)} = 1.34 \text{ atmospheres, in full agreement with the above.} \]

CO and CO\(_2\), which are in equilibrium with the solid C, give rise to an oxygen pressure via the equilibrium reaction
\[ 2CO(g) + O_2(g) = 2CO_2(g) \]
for which
\[ \Delta G^o = -135000 + 41.50T \text{ calories} = -RT\ln K_p. \quad (6) \]

and hence
\[ \log \left( \frac{\rho_{CO_2}}{\rho_{CO} \rho_{O_2}} \right)_{eq,T} = 20.05847 \]
Thus
\[ \log P_{O_2} = 2 \log P_{CO_2} - 2 \log P_{CO} - 20.05847 \]
\[ = (2 \times 0.12756) - (2 \times 0.2194) - 20.05847 \]
\[ = -20.242 \]
and so
\[ P_{O_2(eq,1013)} = 5.72 \times 10^{-21} \text{ atmospheres, in agreement with above.} \]

This tells us that at 1013K, for FeO, Fe and C to be in equilibrium with a gaseous atmosphere, this atmosphere must be of composition:
- \( P_{CO} = 1.65 \) atmospheres
- \( P_{CO_2} = 1.34 \) atmospheres
- \( P_{O_2} = 5.72 \times 10^{-21} \) atmospheres,
and, if the total pressure of the reactive gases is less than \( 1.65 + 1.34 = 2.99 \) atmospheres, then spontaneous reduction of FeO will occur. At equilibrium at 1013 K, the \( P_{CO}/P_{CO_2} \) ratio in the atmosphere is \( 1.65/1.34 = 1.23 \). It should be stressed, however, that the principal constituent of the ~ 1 atmosphere is nitrogen and that equilibrium is not attained. In reality the partial pressure of CO is considerably lower. The \( P_{CO}/P_{CO_2} \) ratio, however, noting that due to the Boudouard reaction converting CO\(_2\) to CO, this ratio will be at least equal to, or probably larger than, 1.23.

**Chromium Oxide**

\[ \Delta G^o_{1373} = 89250 - 20.7T \text{ calories} = -RT\ln K_p \quad (2) \]
Therefore
\[ \log K_p = 60829/(-4.575 \times 1373) = -9.684 \]
and, following the methodology for iron oxide, above:

\[ p_{O_2(eq,1373)} = 4.3 \times 10^{-20} \text{ atmospheres}. \]

If it is considered that C is reducing Cr\(_2\)O\(_3\) to form Cr + CO, then the pertinent reaction is:

\[
\frac{1}{3}\text{Cr}_2\text{O}_3(s) + C = \frac{2}{3}\text{Cr} + \text{CO}
\]

for which

\[
\Delta G^\circ = 89250 - 20.7T \text{ calories} \quad (2)
\]

\[-26700 - 20.9T \quad 1/2 \text{ of} \quad (5)
\]

\[ = 62550 - 41.6T = -RT\ln K_p \]

i.e.

\[ \Delta G_{1373}^\circ = 5433 \text{ calories} = -4.575 \times 1373 \log P_{CO(eq,1373)} \]

and

\[ P_{CO(eq,1373)} = 0.136 \text{ atmospheres}. \]

This says that for reduction of Cr\(_2\)O\(_3\) to proceed spontaneously at 1373K that CO pressure must be less than 0.136 atmospheres.

If CO is in equilibrium with solid C:

\[ C + CO = 2\text{CO} \quad (7) \]

\[ \Delta G_{1373}^\circ = -16454 \text{ calories} = -4.575 \times 1373 \log K_p \]

or

\[ \log \left( \frac{\rho^2\text{CO}}{\rho\text{CO}_2} \right)_{eq,1373} = 2.62 \]

i.e.

\[ P_{CO_2(eq,1373)} = 0.000045 \text{ atmospheres}. \]

Thus if the reaction is considered to be

\[ \frac{1}{3}\text{Cr}_2\text{O}_3(s) = \frac{2}{3}\text{Cr} (s) + 0.5\text{O}_2 (g) \]

then the CO\(_2\) pressure must be lower than 0.000045 atmospheres. For this reaction

\[ \Delta G^\circ = + 89250 - 20.70T \text{ calories} = -RT\ln K_{p}\text{CO}_2 - 47100 - 0.10T \]

1 mole of C \(\cdot\) 1/2 of (4) + 42150 - 20.8T Calories = -RT\ln K_p \quad \ldots \quad \text{Resultant formula}

and

\[ P_{CO_2(eq,1373)} = 0.000047 \text{ atmospheres}, \text{ in full agreement with the above.} \]

For CO and CO\(_2\) in equilibrium with the solid C at 1373K:

\[ \Delta G_{1373}^\circ = -78020 \text{ calories} = -4.575 \times 1373 \log K_p \]

and hence

\[ P_{O_2(eq,1373)} = 4.4 \times 10^{-20} \text{ atmospheres}, \text{ in close agreement with above.} \]

This tells us that, at 1373K for Cr\(_2\)O\(_3\), Cr and C to be in equilibrium with a gaseous atmosphere, this atmosphere must be of composition

\[ P_{CO} = 0.1365 \text{ atmospheres} \]

\[ P_{CO_2} = 0.00005 \text{ atmospheres}. \]

\[ P_{O_2} = 4.4 \times 10^{-20} \text{ atmospheres}, \]

and, if the total pressure of the reactive gases is less than 0.1365 + 0.00005 = 0.13655 atmosphere, spontaneous reduction of Cr\(_2\)O\(_3\) will occur.
At equilibrium at 1373K, the $P_{CO}/P_{CO_2}$ ratio in the atmosphere is $0.1365/0.00005 = 2.7 \times 10^3$.

**Manganese Oxide**

\[ \Delta G_{1413}^o = 91950 - 17.31T \text{ calories} = -RT\ln K_p \]  (3)

Therefore at 1413K

\[ \log K_p = \frac{67491}{(-4.575 \times 1413)} = -10.44 \]

and, following the methodology for iron and chromium oxides, above:

\[ P_{O_2(eq,1413)} = 1.3 \times 10^{-21} \text{ atmospheres.} \]

If it is considered that C is reducing MnO to form Mn + CO then the pertinent reaction is:

\[ \text{MnO} + C = \text{Mn} + \text{CO} \]

for which

\[ \Delta G_{1413}^o = 91950 - 17.31T \text{ calories} \]  (3)

\[ -26700 - 20.9T \quad \text{1/2 of (5)} \]

\[ = 65250 - 38.21T = -RT\ln K_p \]

and

\[ P_{CO(eq,1413)} = 0.0182 \text{ atmospheres.} \]

This says that for reduction of MnO to proceed spontaneously at 1413K that CO pressure must be less than 0.0182 atmospheres.

If CO is in equilibrium with solid C and CO$_2$

\[ \Delta G^o = + 40800 - 41.70T \text{ calories} = -RT\ln K_p \]  (7)

and

\[ P_{CO_2(eq,1413)} = 0.00000052 \text{ atmospheres.} \]

Thus if the reaction is considered to be

\[ \text{MnO} = \text{Mn} + 0.5\text{O}_2 \]

then the CO$_2$ pressure must be lower than 0.00000052 atmospheres. For this reaction

\[ \Delta G^o = + 91950 - 17.31T \text{ calories} \]  (3)

\[ + 47100 - 0.1T \quad \text{1 mole of C : : 1/2 of (4)} \]

\[ + 44850 - 17.41T \text{ Calories} = -RT\ln K_p \quad \text{Resultant formula} \]

and

\[ P_{CO_2(eq,1413)} = 0.00000055 \text{ atmospheres, in full agreement with the above.} \]

CO and CO$_2$, which are in equilibrium with the solid C, give rise to an oxygen pressure via the equilibrium

\[ 2\text{CO}_g + \text{O}_2(g) = 2\text{CO}_2(g) \]  (6)

for which

\[ \Delta G^o = -135000 + 41.50T \text{ calories} = -RT\ln K_p \]  (6)

and

\[ \log P_{O_2} = (2 \times -6.26) - (2 \times -1.74) -11.812 \]

\[ = -20.852 \]

and

\[ P_{O_2(eq,1413)} = 1.41 \times 10^{-21} \text{ atmospheres, in close agreement with above.} \]

This tells us that, at 1413K for MnO, Mn and C to be in equilibrium with a gaseous atmosphere, this atmosphere must be of composition:

\[ P_{CO} = 0.0182 \text{ atmospheres} \]
\[ P_{CO_2} = 0.00000055 \text{ atmospheres} \]
\[ P_{O_2} = 1.41 \times 10^{-21} \text{ atmospheres}, \]
and, if the total pressure of the reactive gases is less than \(0.0182 + 0.00000055 = 0.01820055\) atmospheres, then spontaneous reduction of MnO will occur.

At equilibrium at 1413 K, the \(P_{CO}/P_{CO_2}\) ratio in the gas is \(0.0182/0.00000055 = 33.1 \times 10^3\).

**DISCUSSION**

In extending the processing analysis of Mn steels to Cr-Mn alloys in nitrogen, it is necessary to consider the reaction of \(Cr_2O_3\) with Mn vapour. Figure 3 shows that it is always favourable and accordingly the availability of Mn (determined by its vapour pressure, Fig.1, and Table 1) will be controlling. Useful reaction rates are expected from \(\sim 700^\circ\text{C}\). Similarly carbon can always be converted to \(CO_2\) (Fig.4).

Fig.3. The thermodynamically favourable reduction reaction of chromium oxide by manganese vapour.

Fig.4. The (permanently) thermodynamically favourable conditions for formation of carbon dioxide from solid carbon.
In an EU Copernicus project [6] 3% Mn - 0.6% C steel specimens, covered only by alumina powder, were sintered at 1140°C in flowing 75% hydrogen/25% nitrogen, with a dewpoint of -60°C. It was noted that the specimens showed a dull, oxidised surface, but that the internal microstructure was free of oxides. If one considers that the inter-connected porosity is best represented by a tortuous path, then it follows that the flowing atmosphere can only have limited effect on the climate within the central pores and have greater effect at the surface. The inner pores then can be represented as individual semi-closed containers.

For equilibrium the CO/CO\(_2\) ratio will vary dramatically with temperature due to the Boudouard reaction and the partial pressure of CO will be in balance with the partial pressure of oxygen and CO\(_2\). It has now been shown that in the atmosphere of predominantly nitrogen, the reduction reactions for Fe, Cr, Mn become thermodynamically favourable from ~200°C, inconsistent with experimental observations. Kinetics, essentially availability of CO, needs to be considered and the two relevant reactions are the water-gas:

\[ C + H_2O = CO + H_2 \] (see Fig.5), effective from ~450°C,

and the Boudouard,

\[ C + CO_2 = 2CO \] (see Fig.6), effective from ~700°C.

Any water vapour in the furnace atmosphere is quickly consumed by the reaction

\[ C+H_2O = H_2(g)+CO(g) \]

and this small amount of hydrogen becomes available for reduction of iron oxide during the heating cycle. The oxygen in the atmosphere is consumed by the
reaction \( \text{C(s)} + \text{O}_2(g) = \text{CO}_2(g) \) and on reaching \(~600^\circ\text{C}\) the \( \text{CO}_2 \) is rapidly reduced by carbon to form \( \text{CO} \) according to the Boudouard reaction. It must be remembered that the furnace atmosphere is largely composed of nitrogen and hence the combined partial pressure of the carbonaceous gases is considerably less than 1 atmosphere. This affects the equilibrium ratio \( \text{pCO}/\text{pCO}_2 \) at given oxygen potential and temperature - to favour reduction of difficult oxides (e.g. \( \text{Cr} \) and \( \text{Mn} \)) at lower temperatures than would be the case for pure \( \text{CO} \).

From the calculations it can be seen that at temperatures above \( 900^\circ\text{C} \) the amount of \( \text{CO}_2 \) is negligible and hence the total pressure of carbonaceous gases is approximately equal to the partial pressure of \( \text{CO} \). The amount of \( \text{CO} \) is negligible below \(~500^\circ\text{C} \), so that the reverse must apply.

It is well established that graphite reacts directly with both oxygen and water vapour - to both dry the atmosphere and reduce the amount of available oxygen \([20,21]\). Also manganese vapour reacts with both oxygen and water \([10,15,20]\) to dry the atmosphere and generate additional hydrogen, which is then available for early reduction of iron oxides.

As the temperature rises, the Boudouard reaction becomes the principal agent in reducing manganese and chromium oxides due to the conversion of \( \text{CO}_2 \) to \( \text{CO} \), which improves the \( \text{CO}/\text{CO}_2 \) ratio. The partial pressure of \( \text{CO} \), as stated above, is proportional to the oxygen partial pressure, which has been lowered dramatically, and hence favourable conditions for reduction have been generated on a local basis [microclimate].

By use of a semi-closed container all the above advantages are retained, but with the extra bonus that surface oxidation is also reduced, because the flowing atmosphere can no longer easily interact with the components' surfaces.

It is also relevant to point out that it has long been known that, at a liquid metal/solid interface, 1 % \( \text{MnO} \) can be ideally dissolved into liquid iron \([21]\). Now, interrupted quench sintering experiments \([22]\) indicate that transient liquid phase exists locally inside \( \text{Fe/Mn/C} \) compacts, as pores are always larger than the size of the starting manganese donor powder and that the pore morphology shows significant internal smoothing. This alloying reduces the thermodynamic activity of manganese dramatically and allows reduction of oxides at much lower temperatures and higher oxygen partial pressure than would otherwise be the case.

**CONCLUSIONS**

Thermodynamic calculations [for an atmosphere predominantly of nitrogen] were carried out for reduction of \( \text{FeO} \), \( \text{Cr}_2\text{O}_3 \) and \( \text{MnO} \) by solid carbon at 740, 1100 and 1140\(^\circ\text{C}\), respectively. The analyses derive the maximum pressures of \( \text{O}_2 \), \( \text{CO} \) and \( \text{CO}_2 \) which can be tolerated in the system and also the \( \text{P}_{\text{CO}}/\text{P}_{\text{CO}_2} \) ratios. For the oxide of iron it evaluates to 1.23, of chromium to \( 2.7 \times 10^3 \) and of manganese to \( 33 \times 10^3 \) with \( \text{CO} \) partial pressures being 1.65, 0.1365 and 0.0182 atmospheres, respectively.

Thermodynamics thus indicates favourable conditions for carbothermic reduction of oxides of iron, chromium and manganese at conventional sintering temperatures.

Equilibrium, however, is then not attained and the reactions and kinetics of production of \( \text{CO} \) were considered. The critical reactions were identified as \( \text{C} + \text{H}_2\text{O} = \text{CO} + \text{H}_2 \), effective from \(~450^\circ\text{C}\), and the Boudouard, \( \text{C} + \text{CO}_2 = 2\text{CO} \), effective from \(~700^\circ\text{C}\). Additionally it was shown that from \(~700^\circ\text{C}\) there is ready availability of manganese vapour to encourage the direct reduction of chromium oxide earlier in the sintering process than would normally be expected when only the carbothermic reduction mechanism is available.
Acknowledgements

The work described forms part of ongoing collaboration between the groups at the University of Bradford and the Krakow Academy of Mining and Metallurgy. Partial financial assistance was provided by NATO Science for Peace Project SfP 972395 and the Polish Science Research Committee under contract no. 11.11.110.491.

REFERENCES

[18] Roine, A.: HSC Chemistry 5.11, Outokumpu Research Oy, Pori, Finland