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_2O_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_2O_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, $C + H_2O = CO + H_2$ 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_2O, C and CO_2 and CO and H_2O.

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 $Mn + H_2O = MnO + H_2$ gas.

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Tab.1. Calculated equilibrium partial pressure of Mn vapour versus temperature, as reported by Barin [16,17].

Temperature [°C]	Mn Vapour Pressure (Atmospheres)
0	1.65E-47
100	5.36E-33
200	1.22E-24
300	3.22E-19
400	2.02E-15
500	1.28E-12
600	1.81E-10
700	9.06E-09
800	2.09E-07
900	2.78E-06
1000	2.42E-05
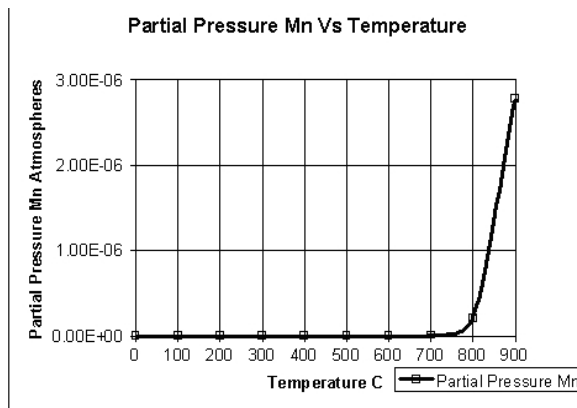
Fig.1. Manganese vapour equilibrium partial pressure showing its substantial increase from ~740°C (Note: Due to graph scaling and resolution there is the illusion that vapour pressure is zero below ~680°C. See data in Table 1).
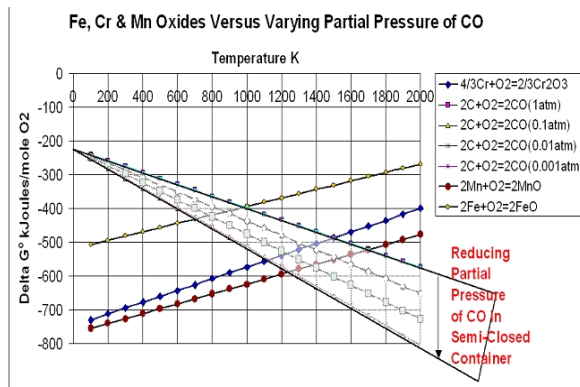

Fig.2. Reducing partial pressures of CO in pore or semi-closed container in relation to Fe, Cr and Mn oxides, as a function of temperature.

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_2O_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.
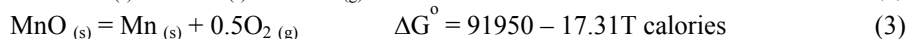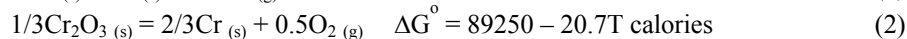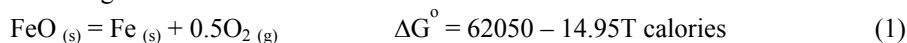
Accordingly sintering will be modelled for a conglomerate of several surface oxidised alloy powder particles surrounding a pore with graphite present and tortuous access to nitrogen-rich atmosphere containing some water vapour and oxygen. Theoretical calculations involve use of several algorithms for 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.
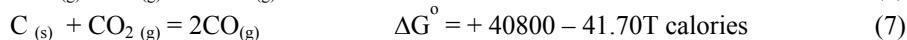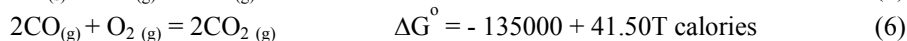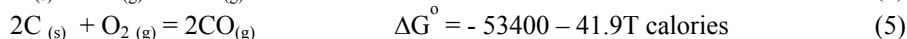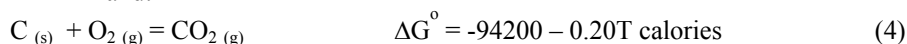
REDUCTION OF OXIDES WITH SOLID CARBON

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

If FeO, Cr_2O_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 enthalpy changes ΔG^O, 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_2O_3 and 1140°C for MnO. The following reactions will be considered:

$$FeO_{(s)} = Fe_{(s)} + 0.5O_{2(g)} \qquad \Delta G^o = 62050 - 14.95T \text{ calories} \qquad (1)$$

$$1/3Cr_2O_{3(s)} = 2/3Cr_{(s)} + 0.5O_{2(g)} \qquad \Delta G^o = 89250 - 20.7T \text{ calories} \qquad (2)$$

$$MnO_{(s)} = Mn_{(s)} + 0.5O_{2(g)} \qquad \Delta G^o = 91950 - 17.31T \text{ calories} \qquad (3)$$

and:

$$C_{(s)} + O_{2(g)} = CO_{2(g)} \qquad \Delta G^o = -94200 - 0.20T \text{ calories} \qquad (4)$$

$$2C_{(s)} + O_{2(g)} = 2CO_{(g)} \qquad \Delta G^o = -53400 - 41.9T \text{ calories} \qquad (5)$$

$$2CO_{(g)} + O_{2(g)} = 2CO_{2(g)} \qquad \Delta G^o = -135000 + 41.50T \text{ calories} \qquad (6)$$

$$C_{(s)} + CO_{2(g)} = 2CO_{(g)} \qquad \Delta G^o = +40800 - 41.70T \text{ calories} \qquad (7)$$

Iron Oxide

$$\Delta G^o_{1013} = 46905.65 \text{ calories} = -(1.987 \text{ x } \ln10) \text{ x } 1013 \log K_p$$

Therefore

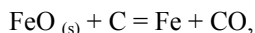$$\log K_p = 46905.65/(-4.575 \text{ x } 1013) = -10.121$$

But

$$K_p = P^{0.5}_{O_{2(eq,T)}}$$

so　　　　$\log P_{O_{2(eq,1013)}}$ = 2 x –10.121 = -20.242

Therefore　　　　$P_{O_{2(eq,1013)}}$ = 5.73 x 10^{-21} atmospheres.

　　　　If it is considered that C is reducing FeO to form Fe + CO, then the pertinent reaction is :

　　　　FeO $_{(s)}$ + C = Fe + CO,

for which

　　　　ΔG^o = 35350 – 35.9T calories = -RTlnK$_p$ = -1016.7

where

　　　　Kp = P $_{CO_{(eq,T)}}$

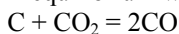Thus　　　　ΔG^o_{1013} = -1016.7 calories = -4.575 x 1013 log P $_{CO_{(eq,1013)}}$
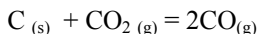
and so:

　　　　log P $_{CO_{(eq,1013)}}$ = 0.21938

　　　　P $_{CO_{(eq,1013)}}$ = 1.657 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_2 pressure must be exerted by:

　　　　C + CO_2 = 2CO

for which:

　　　　C $_{(s)}$ + CO_2 $_{(g)}$ = $2CO_{(g)}$

ΔG^o = + 40800 – 41.70T calories = -RTlnK$_p$ = -1442.1　　　　(7)

where $K_p = \left(\dfrac{\rho^2 CO}{\rho CO_2} \right)_{eq,T}$

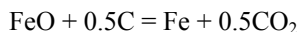Thus　　　　ΔG^o_{1013} = -1442.1 calories = - 4.575 x 1013 log K$_p$

or　　　　$\log \left(\dfrac{\rho^2 CO}{\rho CO_2} \right)_{eq,1013}$ = 0.3112

Hence

　　　　log P_{CO_2} = 2 log P_{CO} - 0.3112 = (2 x 0.21938) - 0.311 = 0.12759

　　　　P $_{CO_{2(eq,1013)}}$ = 1.34 atmospheres.

Thus, if the reaction is considered to be

　　　　FeO + 0.5C = Fe + $0.5CO_2$

then the CO_2 pressure must be lower than 1.34 atmospheres. For this reaction

　　　　ΔG^o = + 14950 – 15.05T calories = - 295.65 = -RTlnK$_p$
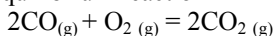
where

$$Kp = P^{0.5}{}_{CO_2(eq,T)}$$

Thus $\Delta G^{o}{}_{1013} = -295.65$ calories $= - 4.575 \times 1013 \log P^{0.5}{}_{CO_2(eq,T)}$

From which $\log P_{CO_2(eq,873)} = 0.12759$

or

$P_{CO_2(eq,1013)} = 1.34$ 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

$$\Delta G^{o} = - 135000 + 41.50T \text{ calories } = -RT\ln K_p. \tag{6}$$

where

$$K_p = \left(\frac{\rho^2 {}_{CO_2}}{\rho^2 {}_{CO}\ \rho_{O_2}} \right)_{eq,T}$$

$$\Delta G^{o} = - 92960.5 \text{ calories}$$

and hence

$$\log \left(\frac{\rho^2 {}_{CO_2}}{\rho^2 {}_{CO}\ \rho_{O_2}} \right)_{eq,1013} = 20.05847$$

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

$P_{O_2\ (eq,\ 1013)} = 5.72 \times 10^{-21}$ 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

$$\Delta G^{o}{}_{1373} = 89250 - 20.7T \text{ calories } = -RT\ln K_p \tag{2}$$

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_2O_3 to form Cr + CO, then the pertinent reaction is :

$1/3Cr_2O_{3\,(s)} + C = 2/3Cr + CO$ for which

$$\Delta G^o = 89250 - 20.7T \text{ calories} \tag{2}$$
$$-26700 - 20.9T \qquad\qquad 1/2 \text{ of} \qquad\qquad (5)$$
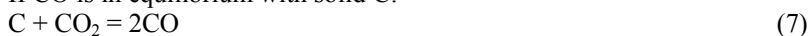$$= 62550 - 41.6T = -RT\ln K_p$$

i.e.

$$\Delta G^o_{1373} = 5433 \text{ calories} = -4.575 \times 1373 \log P_{CO_{(eq,1373)}}$$

and

$$P_{CO_{(eq,1373)}} = 0.136 \text{ atmospheres.}$$

This says that for reduction of Cr_2O_3 to proceed spontaneously at 1373K that CO pressure must be less than 0.136 atmospheres.

If CO is in equilibrium with solid C:

$$C + CO_2 = 2CO \tag{7}$$

and

$$\Delta G^o_{1373} = -16454 \text{ calories} = -4.575 \times 1373 \log K_p$$
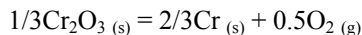
or

$$\log\left(\frac{\rho^2 CO}{\rho CO_2}\right)_{eq,1373} = 2.62$$

i.e.

$$P_{CO_{2(eq,1373)}} = 0.000045 \text{ atmospheres.}$$

Thus if the reaction is considered to be

$$1/3Cr_2O_{3\,(s)} = 2/3Cr_{(s)} + 0.5O_{2\,(g)}$$

then the CO_2 pressure must be lower than 0.000045 atmospheres. For this reaction

$$\Delta G^o = +89250 - 20.70T \text{ calories} = -RT\ln K_p - 47100 - 0.10T$$

1 mole of C $\therefore$ 1/2 of (4) + 42150 - 20.8T Calories = $-RT\ln K_p$ …. Resultant formula

and

$$P_{CO_{2(eq,1373)}} = 0.000047 \text{ atmospheres, in full agreement with the above.}$$

For CO and CO_2 in equilibrium with the solid C at 1373K:

$$\Delta G^o_{1373} = -78020 \text{ calories} = -4.575 \times 1373 \log K_p$$

and hence

$$P_{O_{2\,(eq,\,1373)}} = 4.4 \times 10^{-20} \text{ atmospheres, in close agreement with above.}$$

This tells us that, at 1373K for Cr_2O_3, Cr and C to be in equilibrium with a gaseous atmosphere, this atmosphere must be of composition

$P_{CO} = 0.1365$ atmospheres

$P_{CO_2} = 0.00005$ atmospheres.

$P_{O_2} = 4.4 \times 10^{-20}$ atmospheres,

and, if the total pressure of the reactive gases is less than 0.1365 + 0.00005 = 0.13655 atmosphere, spontaneous reduction of Cr_2O_3 will occur.

At equilibrium at 1373K, the P_{CO}/P_{CO_2} ratio in the atmosphere is 0.1365/0.00005 = 2.7 x 10^3.

Manganese Oxide

$$\Delta G^o_{1413} = 91950 - 17.31T \text{ calories} = -RT\ln K_p \qquad\qquad (3)$$

Therefore at 1413K

$$\log K_p = 67491/(-4.575 \times 1413) = -10.44$$

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:

MnO$_{(s)}$ + C = Mn + CO for which

$$\Delta G^o_{1413} = 91950 - 17.31T \text{ calories} \qquad\qquad (3)$$
$$-26700 - 20.9T \qquad\qquad\qquad 1/2 \text{ of } (5)$$
$$= 65250 - 38.21T = -RT\ln K_p$$

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.
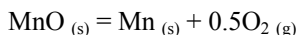
If CO is in equilibrium with solid C and CO_2

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

and

$$P_{CO_{2(eq,1413)}} = 0.00000052 \text{ atmospheres.}$$

Thus if the reaction is considered to be

MnO$_{(s)}$ = Mn$_{(s)}$ + 0.5O$_{2 (g)}$

then the CO_2 pressure must be lower than 0.00000052 atmospheres. For this reaction

$$\Delta G^o = +91950 - 17.31T \text{ calories} \qquad\qquad (3)$$
$$-47100 - 0.1T \qquad\qquad 1 \text{ mole of C} \therefore 1/2 \text{ of } (4)$$
$$+44850 - 17.41T \text{ Calories} = -RT\ln K_p \text{ ....}\quad \text{Resultant formula}$$

and $P_{CO_{2(eq,1413)}} = 0.00000055$ 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

$$2CO_{(g)} + O_{2 (g)} = 2CO_{2 (g)} \qquad\qquad (6)$$

for which

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

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 atmospheres

P_{O_2} = 1.41 x 10^{-21} 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 x 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 ~ 700°C. Similarly carbon can always be converted to CO_2 (Fig.4).
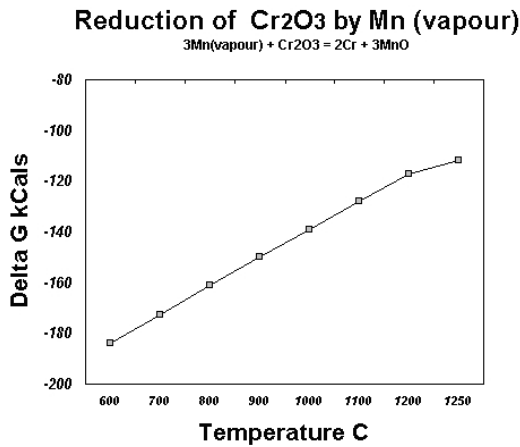

Fig.3. The thermodynamically favourable reduction reaction of chromium oxide by manganese vapour.
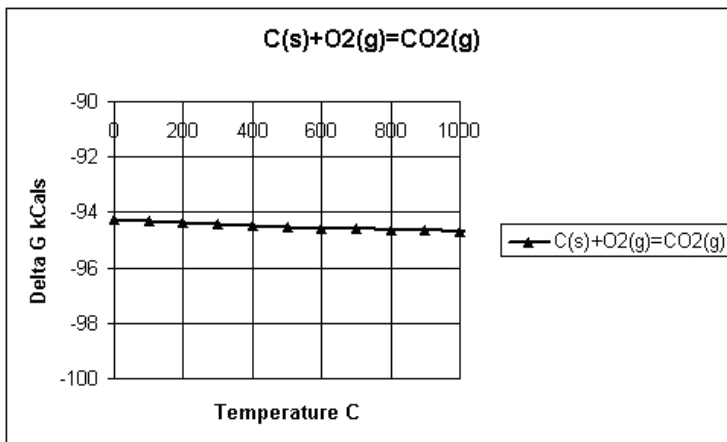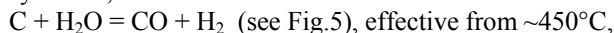

Fig.4. The (permanently) thermodynamically favourable conditions for formation of carbon dioxide from solid carbon.

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,

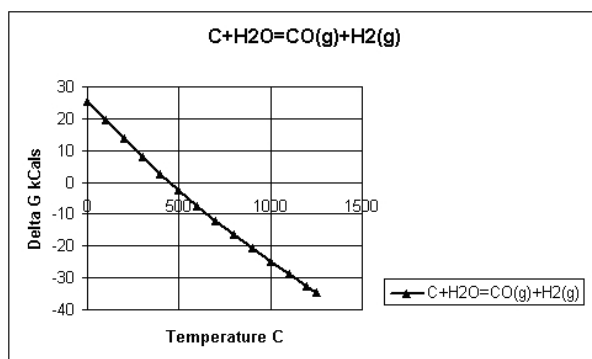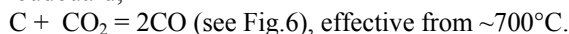$C + CO_2 = 2CO$ (see Fig.6), effective from ~700°C.

Fig.5. The carbon-water vapour reaction becoming thermodynamically favourable at ~450°C.
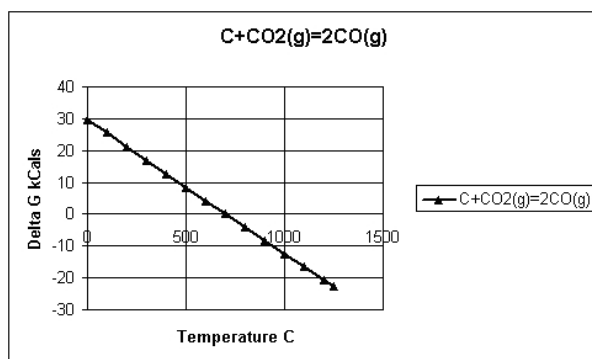

Fig.6. The Boudouard reaction becoming thermodynamically favourable at ~700°C.

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 $C(s)+O_2(g)=CO_2(g)$ and on reaching ~600°C the CO_2 is rapidly reduced by carbon to form 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 pCO/pCO_2 at given oxygen potential and temperature - to favour reduction of difficult oxides (e.g. Cr and Mn) at lower temperatures than would be the case for pure CO.

From the calculations it can be seen that at temperatures above 900°C the amount of CO_2 is negligible and hence the total pressure of carbonaceous gases is approximately equal to the partial pressure of CO. The amount of CO is negligible below ~500°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 CO_2 to CO, which improves the CO/CO_2 ratio. The partial pressure of 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 % MnO can be ideally dissolved into liquid iron [21]. Now, interrupted quench sintering experiments [22] indicate that transient liquid phase exists locally inside 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 FeO, Cr_2O_3 and MnO by solid carbon at 740, 1100 and 1140°C, respectively. The analyses derive the maximum pressures of O_2, CO and CO_2 which can be tolerated in the system and also the P_{CO}/P_{CO_2} ratios. For the oxide of iron it evaluates to 1.23, of chromium to 2.7×10^3 and of manganese to 33×10^3 with 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 CO were considered. The critical reactions were identified as $C + H_2O = CO + H_2$, effective from ~450°C, and the Boudouard, $C + CO_2 = 2CO$, effective from ~700°C. Additionally it was shown that from ~700°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.

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