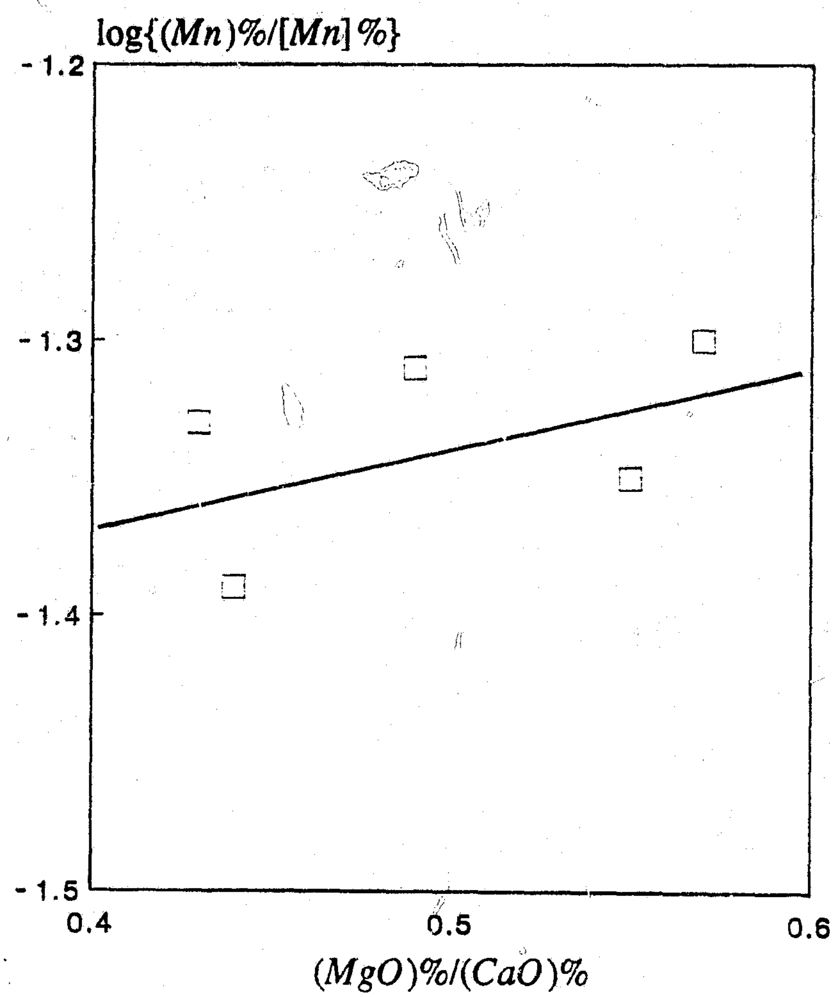

Figure D.2. The effect of the MgO-to-CaO ratio of the slag on the Mn distribution with 5% Al_2O_3 and 4.43% MnO at 1500°C under CO atmosphere.

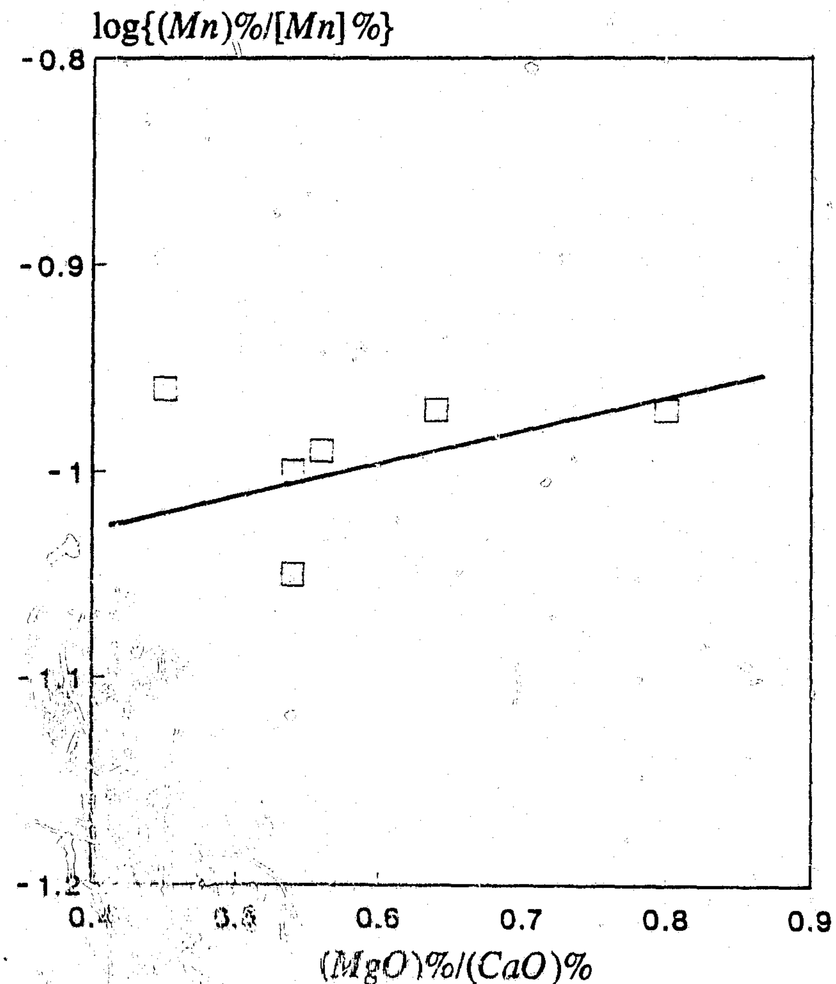

Figure D.3. The effect of the MgO-to-CaO ratio of the slag on the Mn distribution with 5% Al_2O_3 and 9.53% MnO at 1500°C under CO atmosphere.

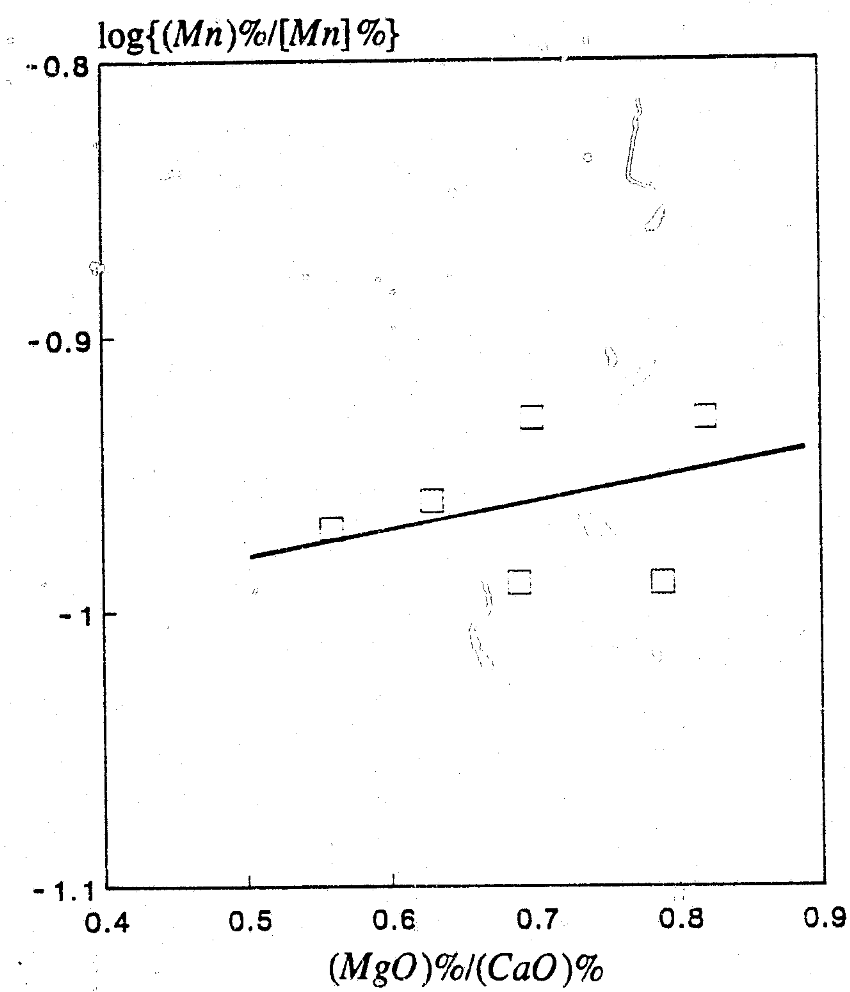

Figure D.4. The effect of the MgO-to-CaO ratio of the slag on the Mn distribution with 5% Al_2O_3 and 10.57% MnO at 1500°C under CO atmosphere.

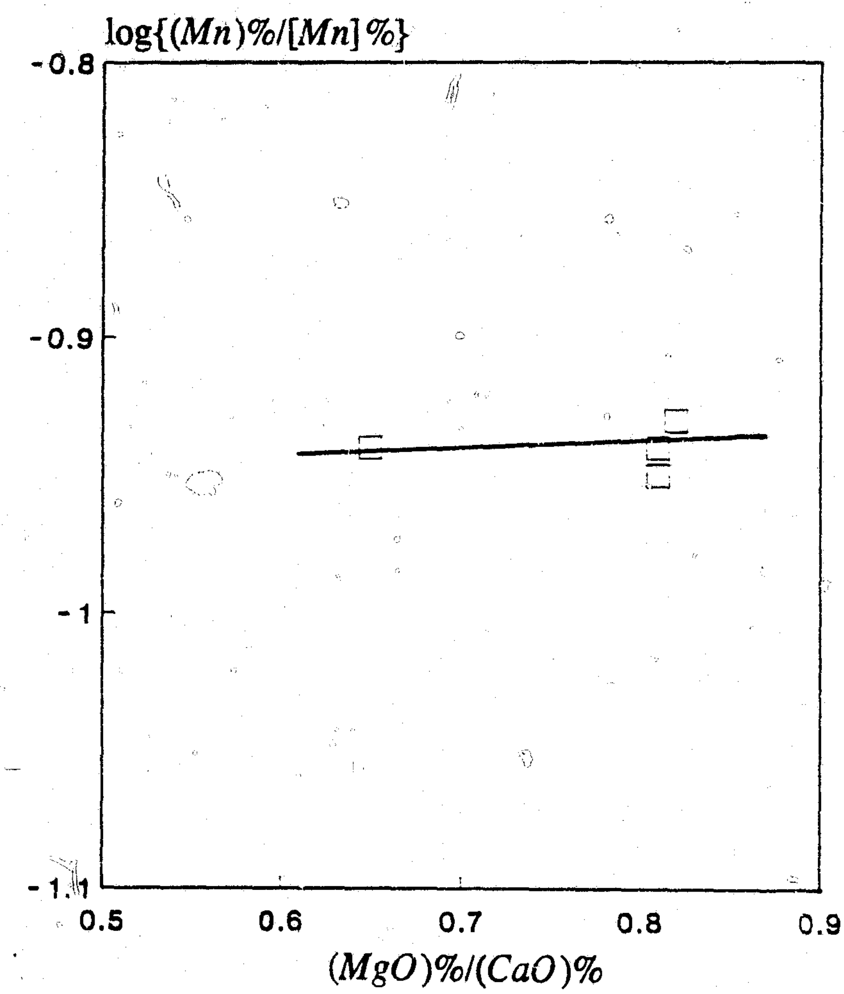

Figure D.5. The effect of the MgO-to-CaO ratio of the slag on the Mn distribution with 5% Al_2O_3 and 11.42% MnO at 1500°C under CO atmosphere.

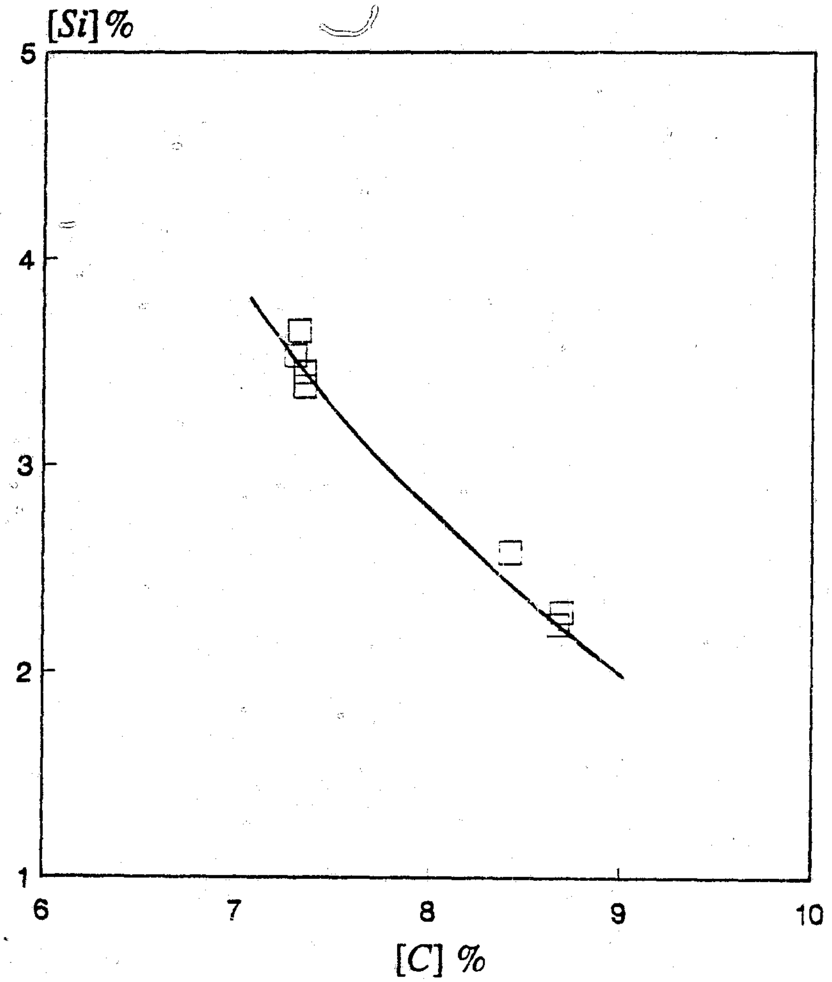

Figure D.6. The effect of the Si content on the C content of the metal phase with Mn:Fe≅7.4 at 1500℃ under CO atmosphere.

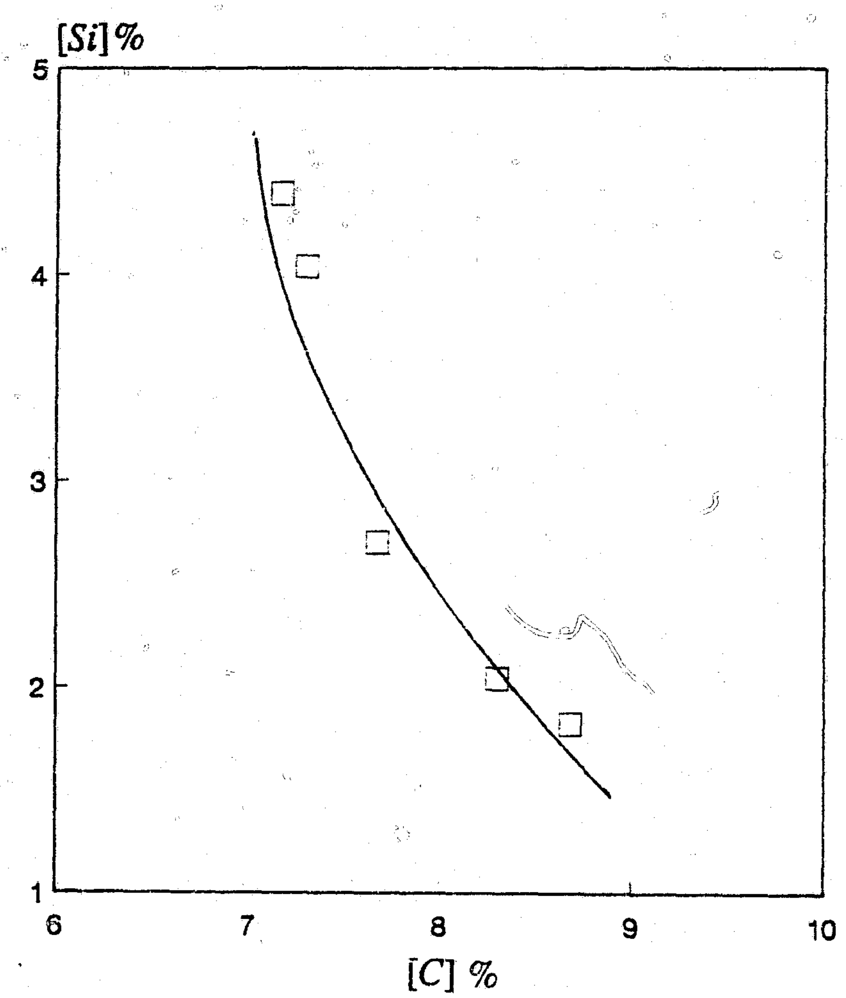

Figure D.7. The effect of the Si content on the C content of the metal phase with Mn:Fe≅ 6.7 at 1500°C under CO atmosphere.

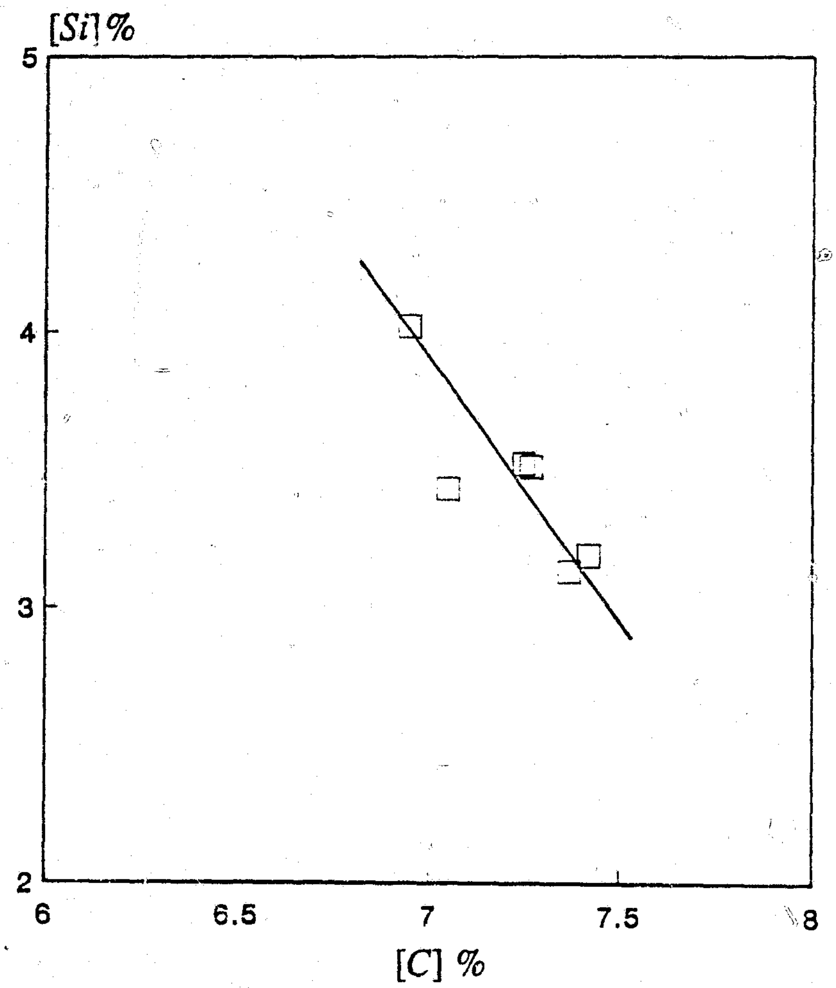

Figure D.8. The effect of the Si content on the C content of the metal phase with Mn:Fe≅3.7 at 1500°C under CO atmosphere.

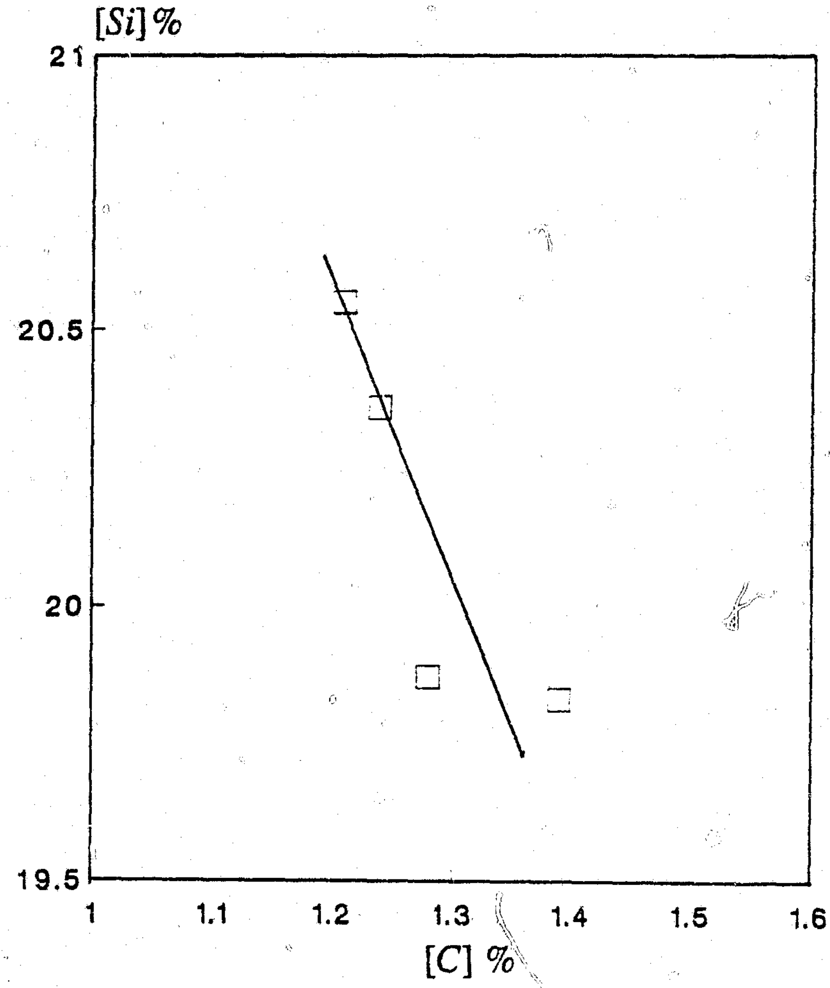

Figure D.9. The effect of the Si content on the C content of the metal phase with Mn:Si≅2.9 at 1500°C under CO atmosphere.

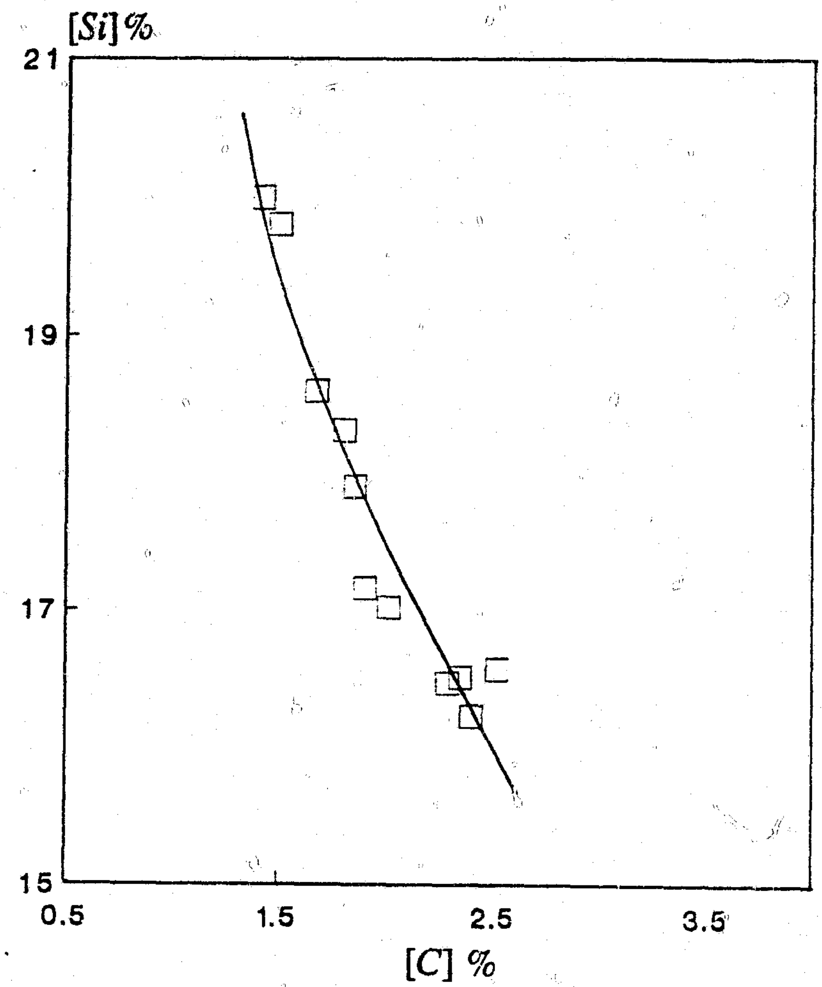

Figure D.10. The effect of the Si content on the C content of the metal phase with Mn:Si≅3.5 at 1500°C under CO atmosphere.

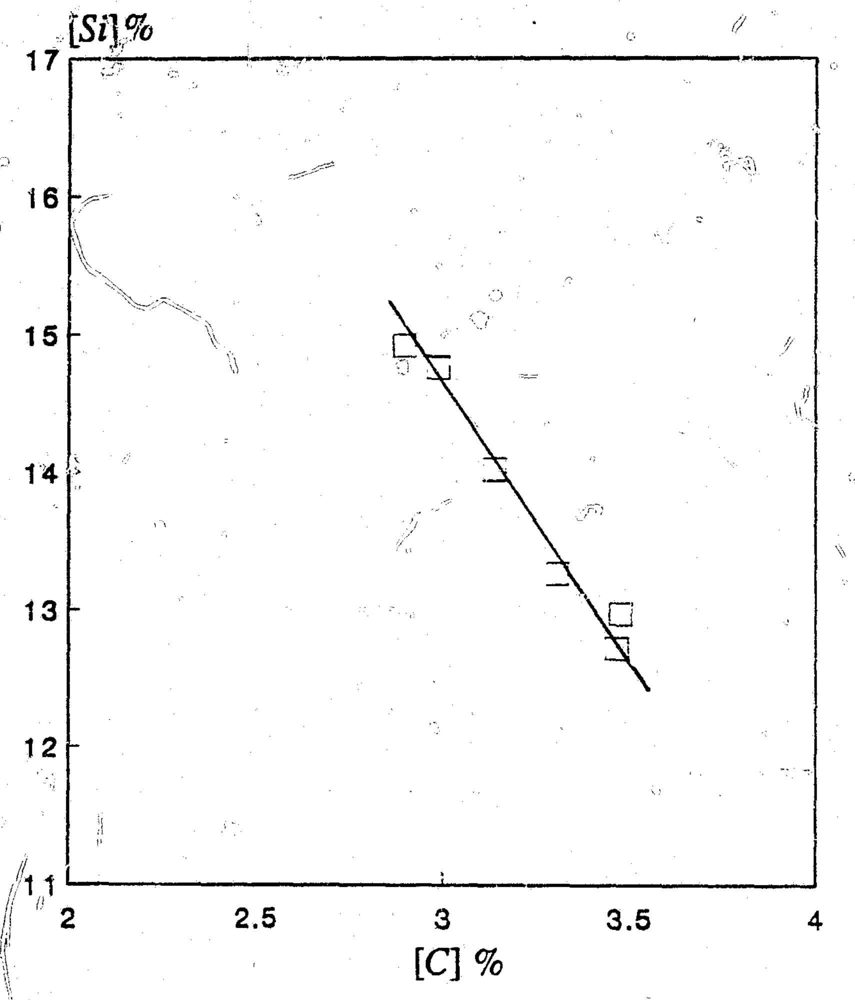

Figure D.11. The effect of the Si content on the C content of the metal phase with Mn:Si≅4.5 at 1500°C under CO atmosphere.

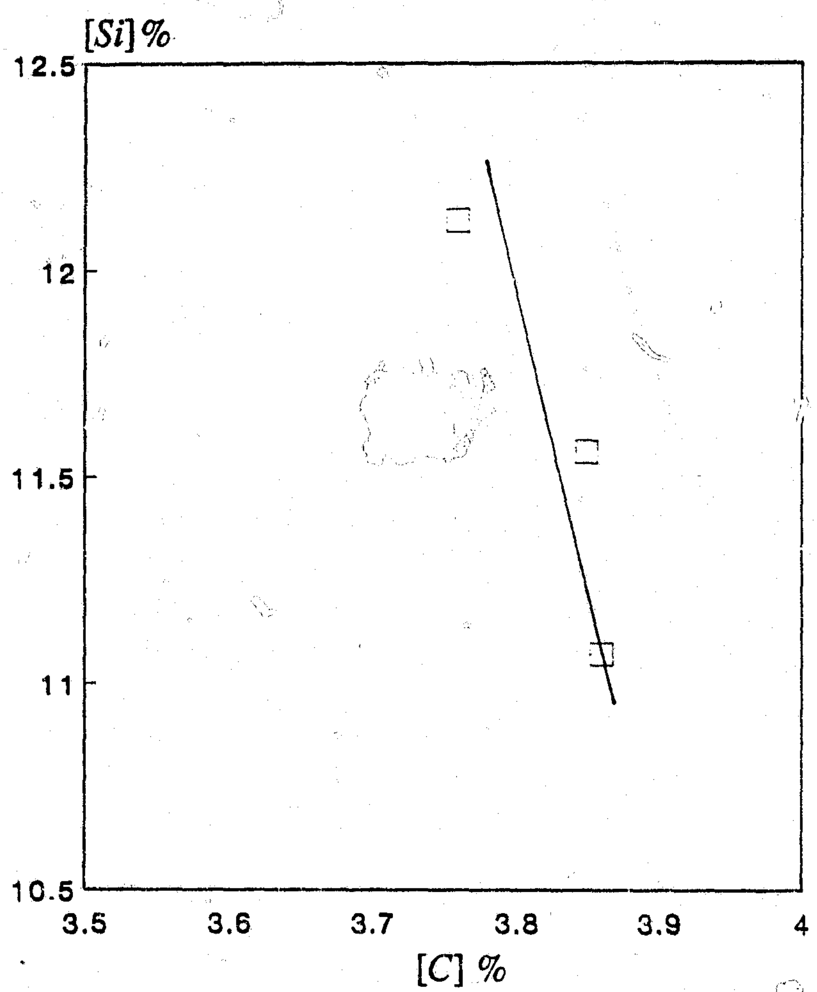

Figure D.12. The effect of the Si content on the C content of the metal phase with Mn:Si≅5.6 at 1500°C under CO atmosphere.

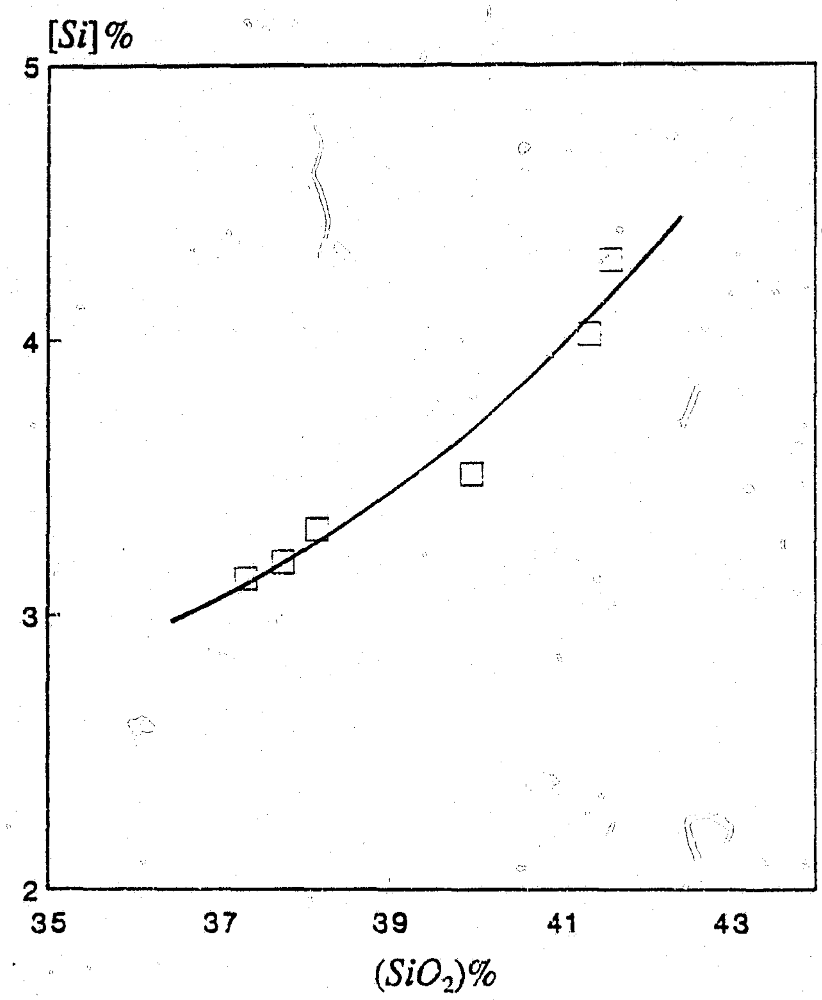

Figure D.13. The effect of the SiO_2 content of the slag phase on the Si content of the metal phase with Mn:Fe≅3.7 at 1500℃ under CO atmosphere.

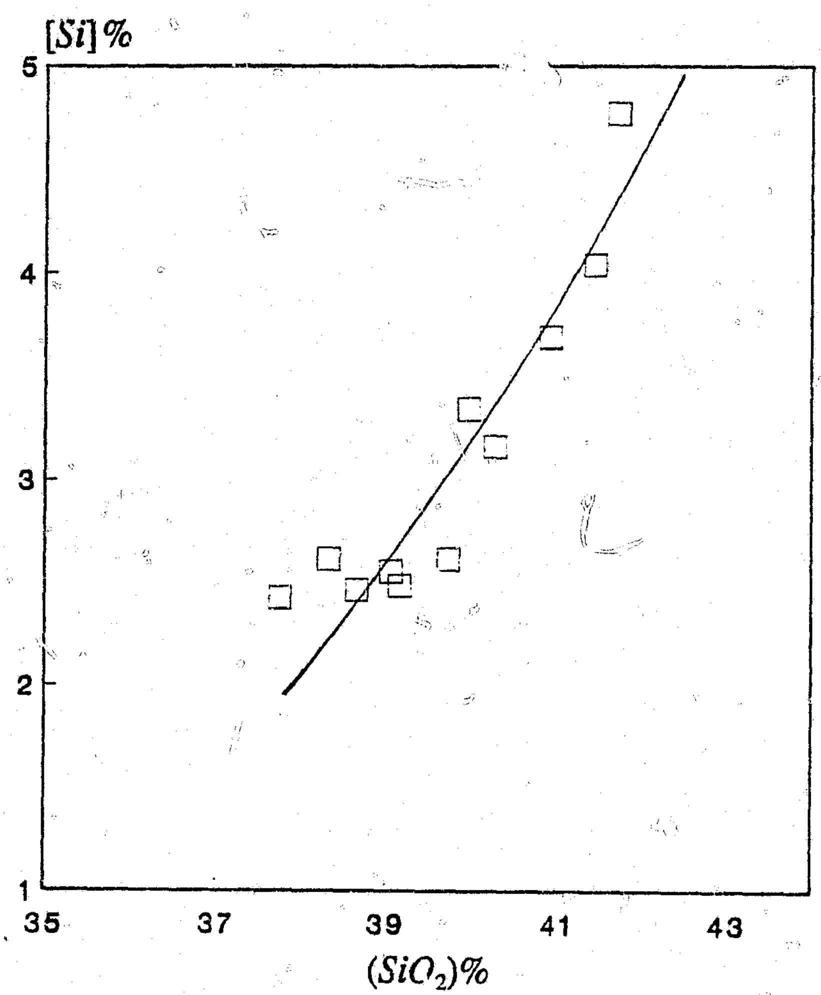

Figure D.14. The effect of the SiO_2 content of the slag phase on the Si content of the metal phase with Mn:Fe≅5.5 at 1500°C under CO atmosphere.

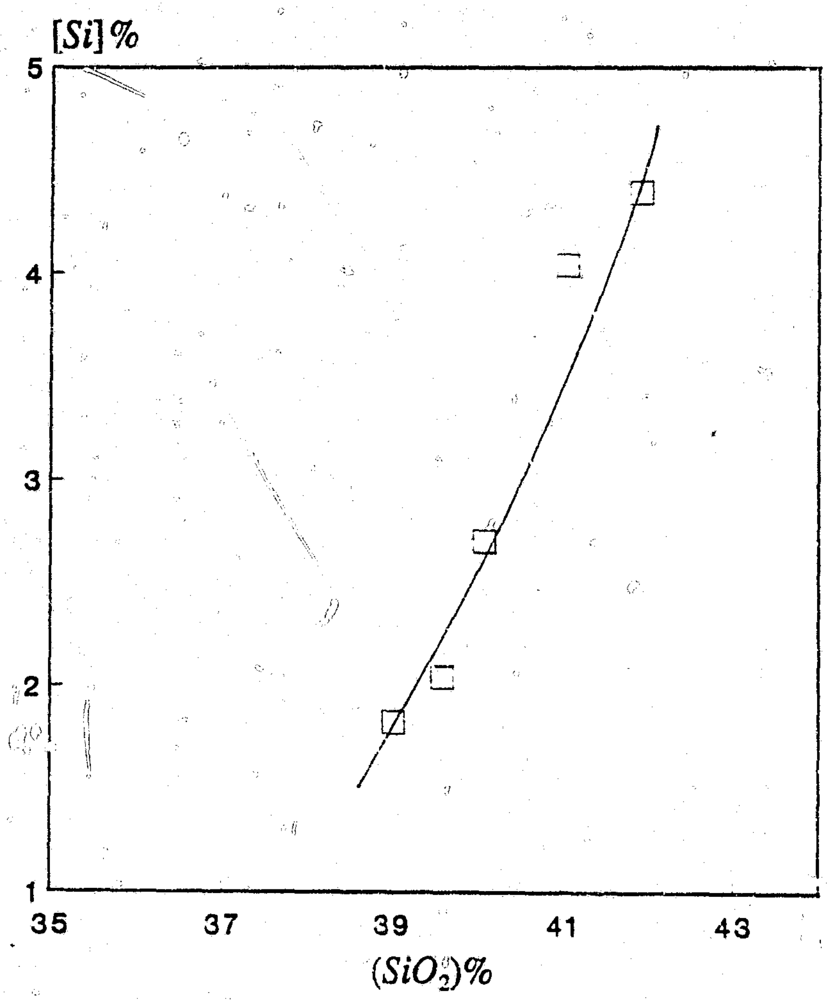

Figure D.15. The effect of the SiO_2 content of the slag phase on the Si content of the metal phase with Mn:Fe≅6.7 at 1500°C under CO atmosphere.

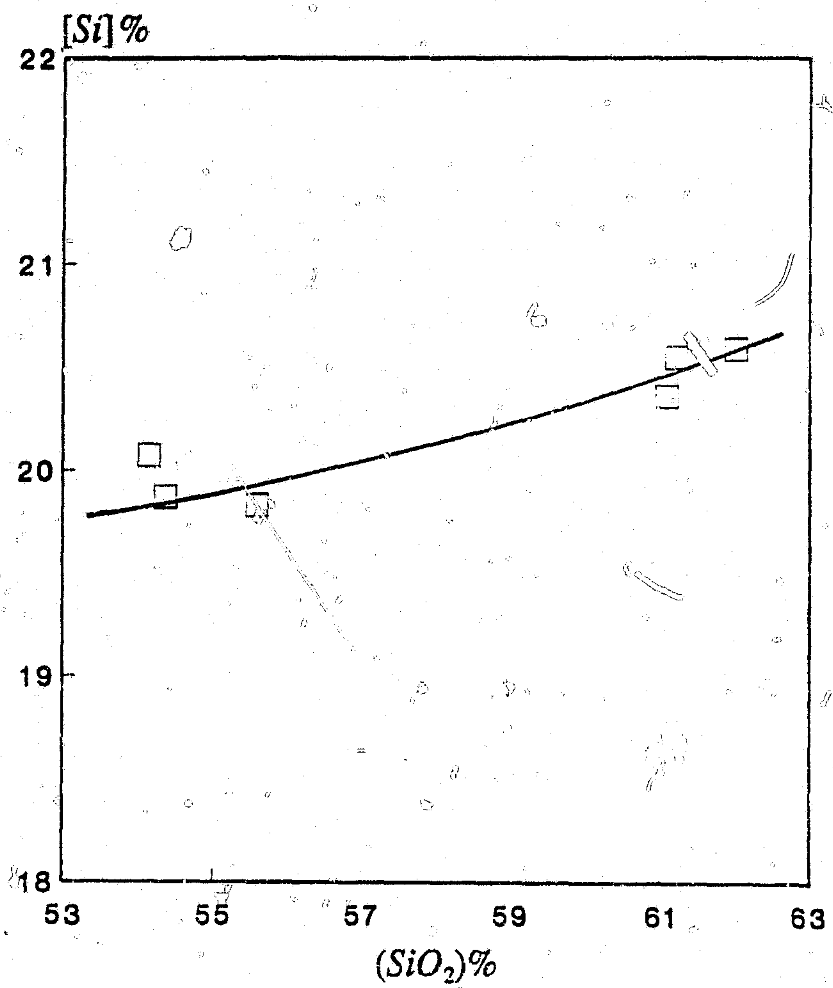

Figure D.16. The effect of the SiO_2 content of the slag phase on the Si content of the metal phase with Mn:Si≅2.9 at 1500°C under CO atmosphere.

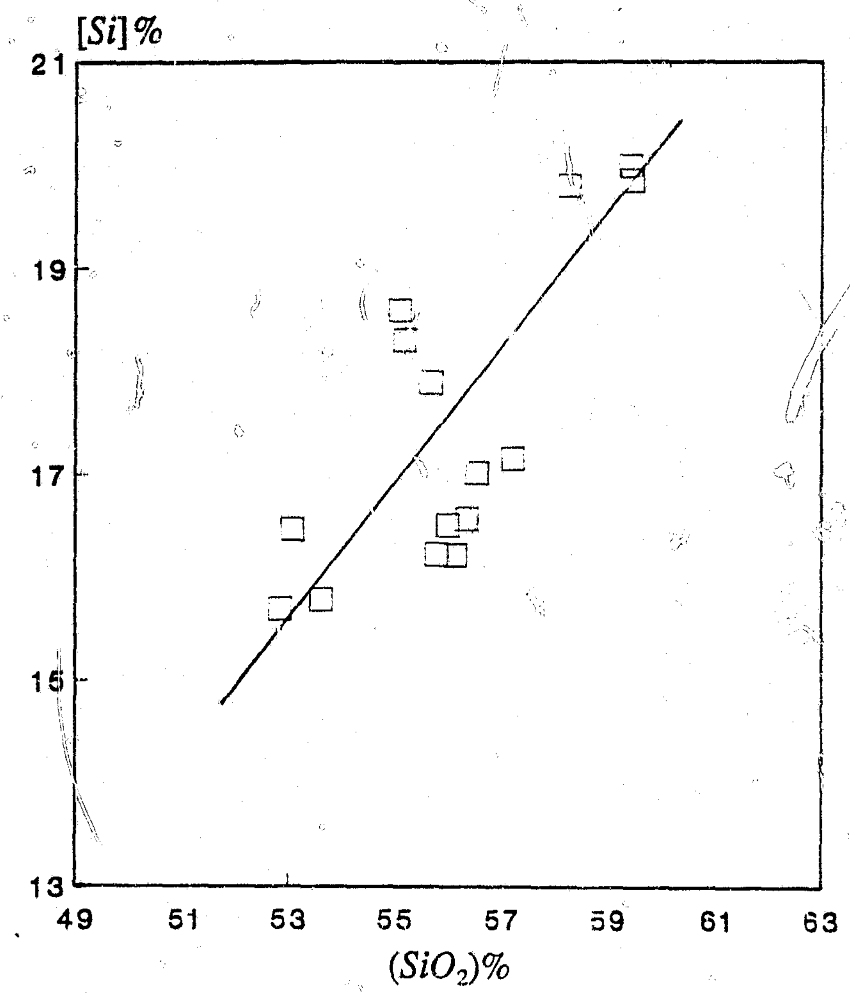

Figure D.17. The effect of the SiO_2 content of the slag phase on the Si content of the metal phase with Mn:Si≅3.5 at 1500°C under CO atmosphere.

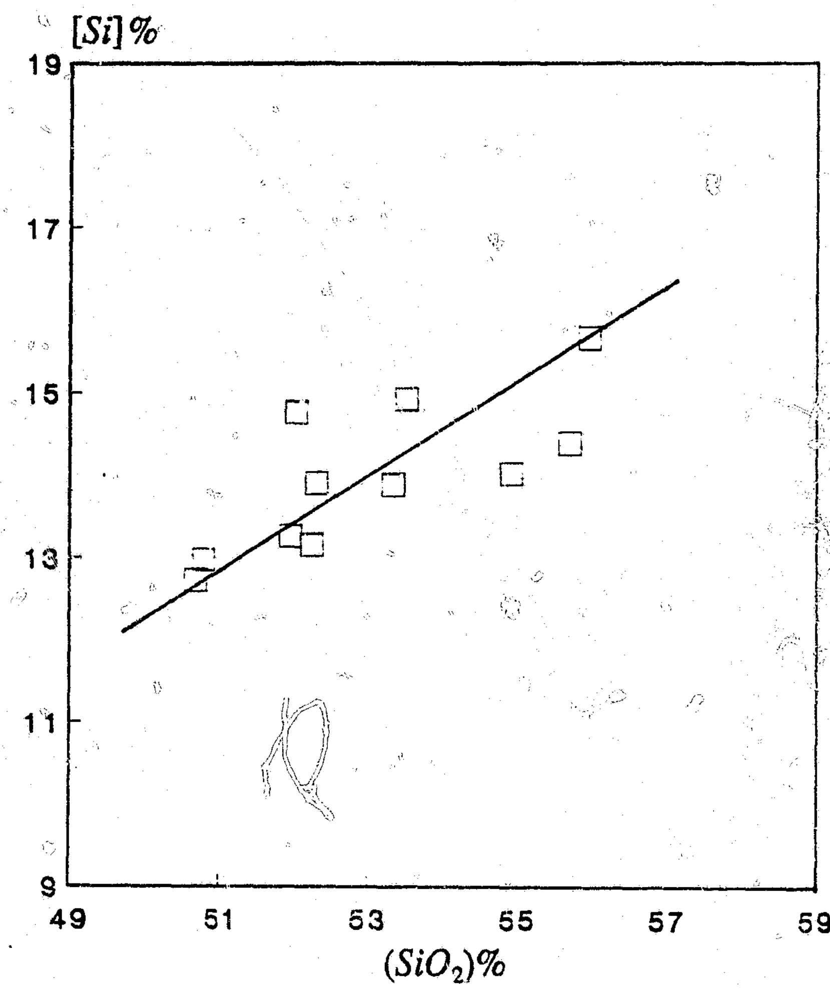

Figure D.18. The effect of the SiO_2 content of the slag phase on the Si content of the metal phase with Mn:Si≅4.5 at 1500°C under CO atmosphere.

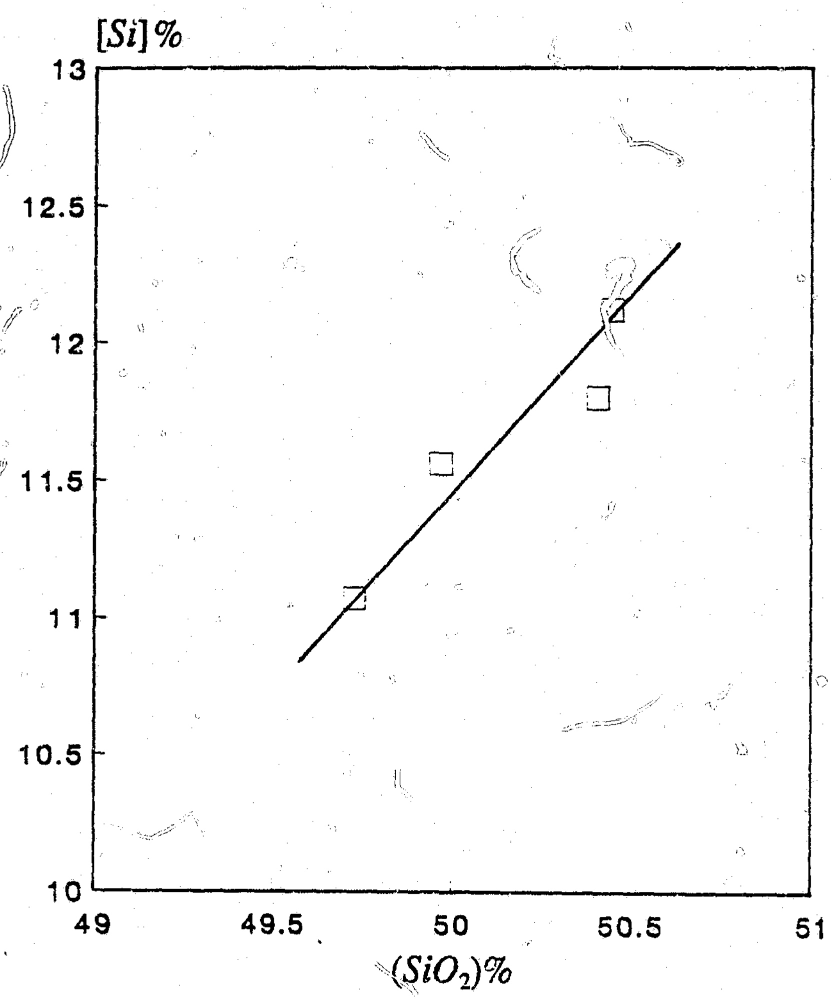

Figure D.19. The effect of the SiO_2 content of the slag phase on the Si content of the metal phase with Mn:Si≅5.6 at 1500°C under CO atmosphere.

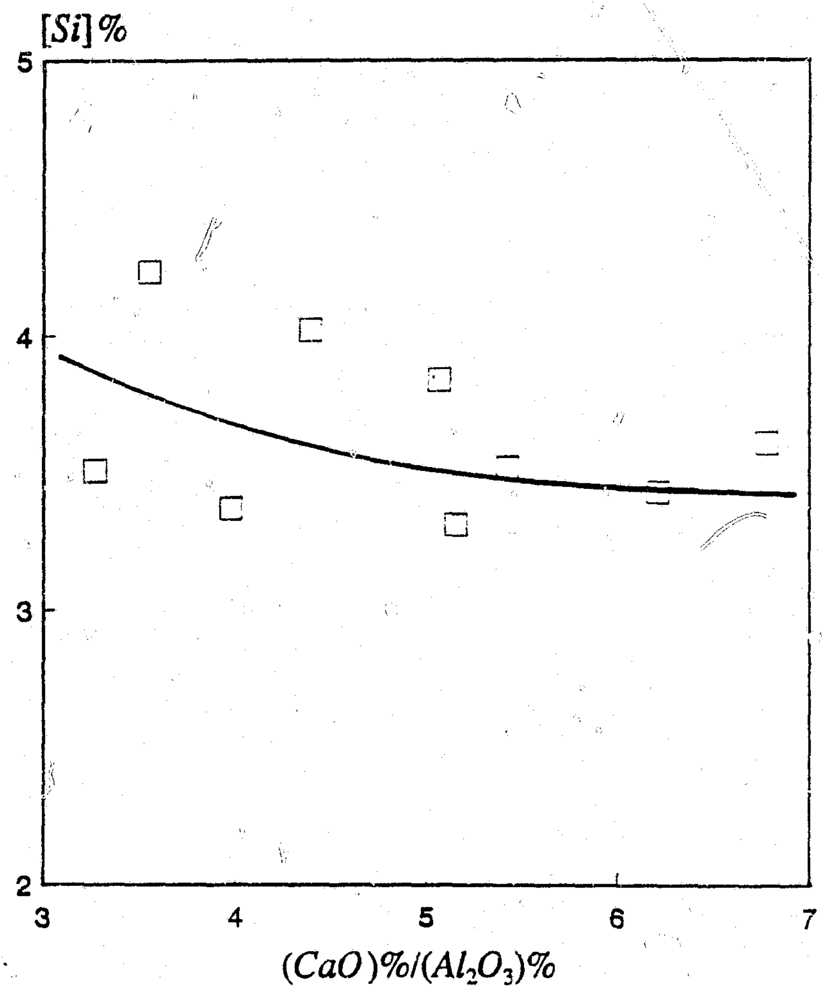

Figure D.20. The effect of the CaO-to-Al_2O_3 ratio of the slag phase on the Si content of the metal phase with Mn:Fe≅3.7 at 1500°C under CO atmosphere.

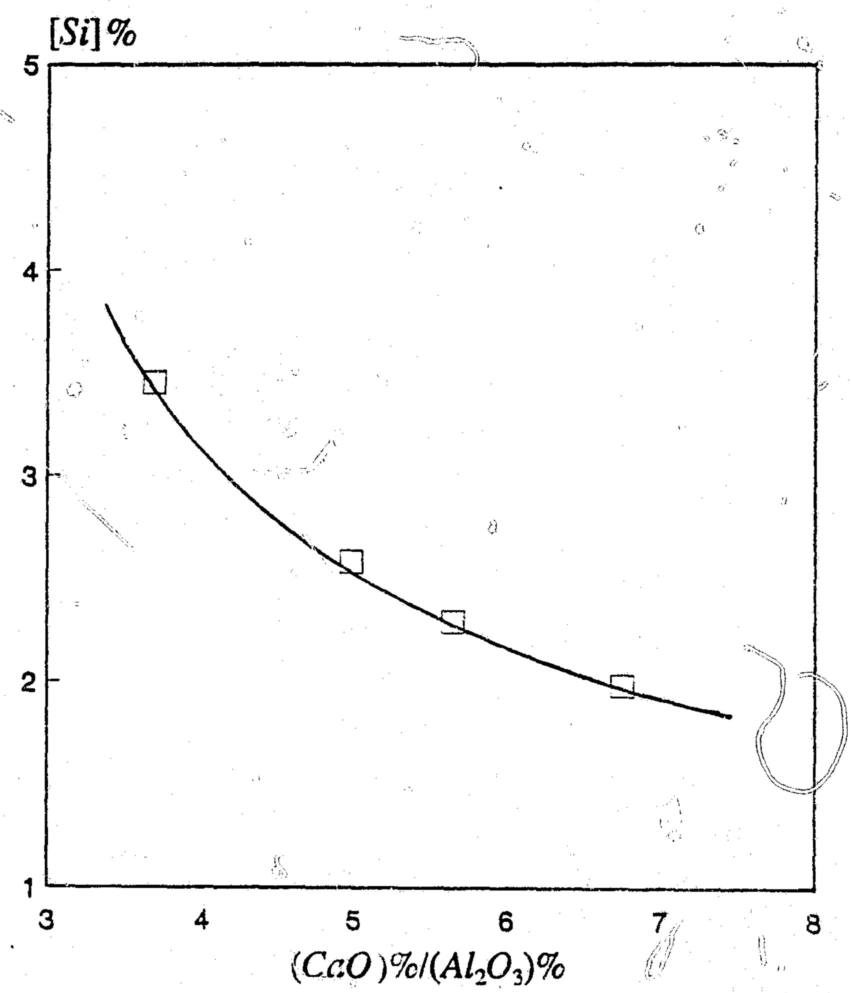

Figure D.21. The effect of the CaO-to-Al_2O_3 ratio of the slag phase on the Si content of the metal phase with Mn:Fe≅7.4 at 1500°C under CO atmosphere.

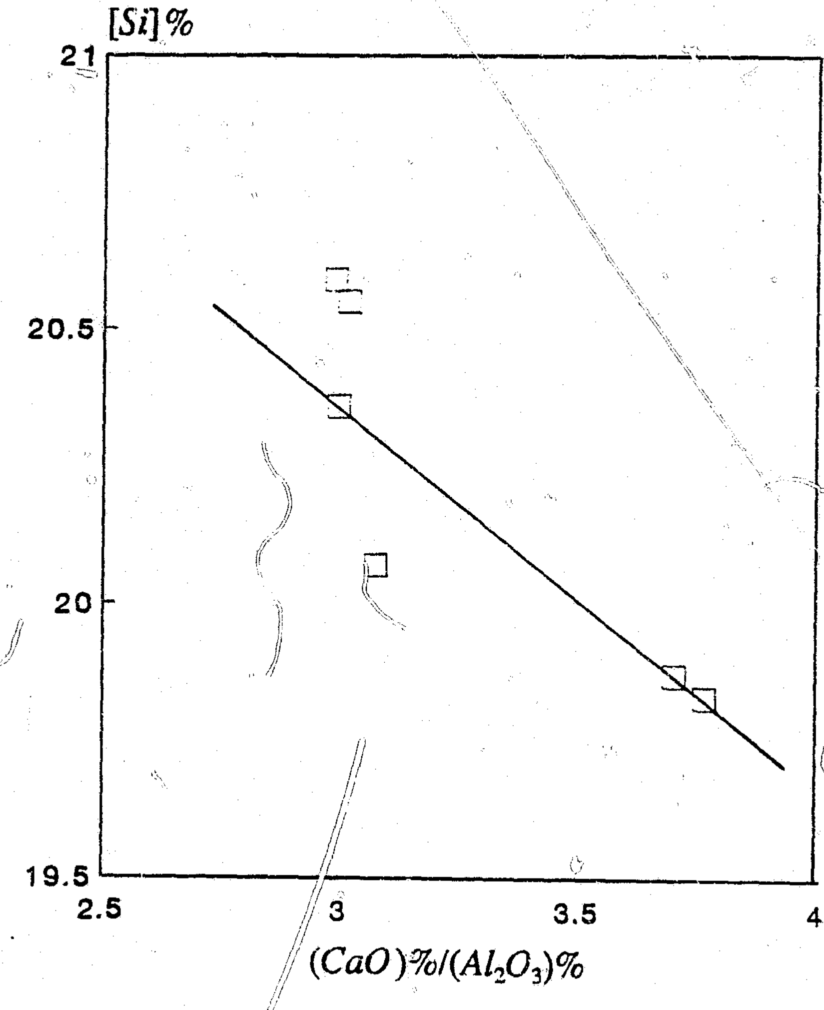

Figure D.22. The effect of the CaO-to-Al_2O_3 ratio of the slag phase on the Si content of the metal phase with Mn:Si≅2.9 at 1500℃ under CO atmosphere.

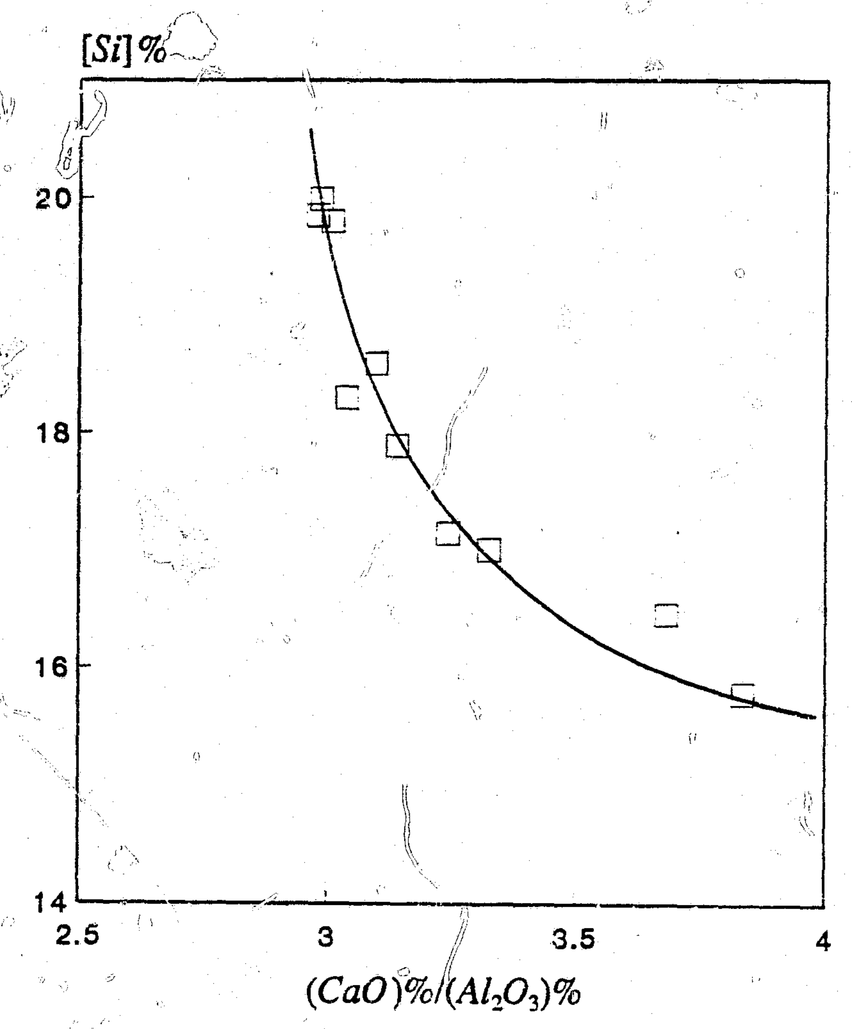

Figure D.23. The effect of the CaO-to-Al_2O_3 ratio of the slag phase on the Si content of the metal phase with Mn:Si≅3.5 at 1500°C under CO atmosphere.

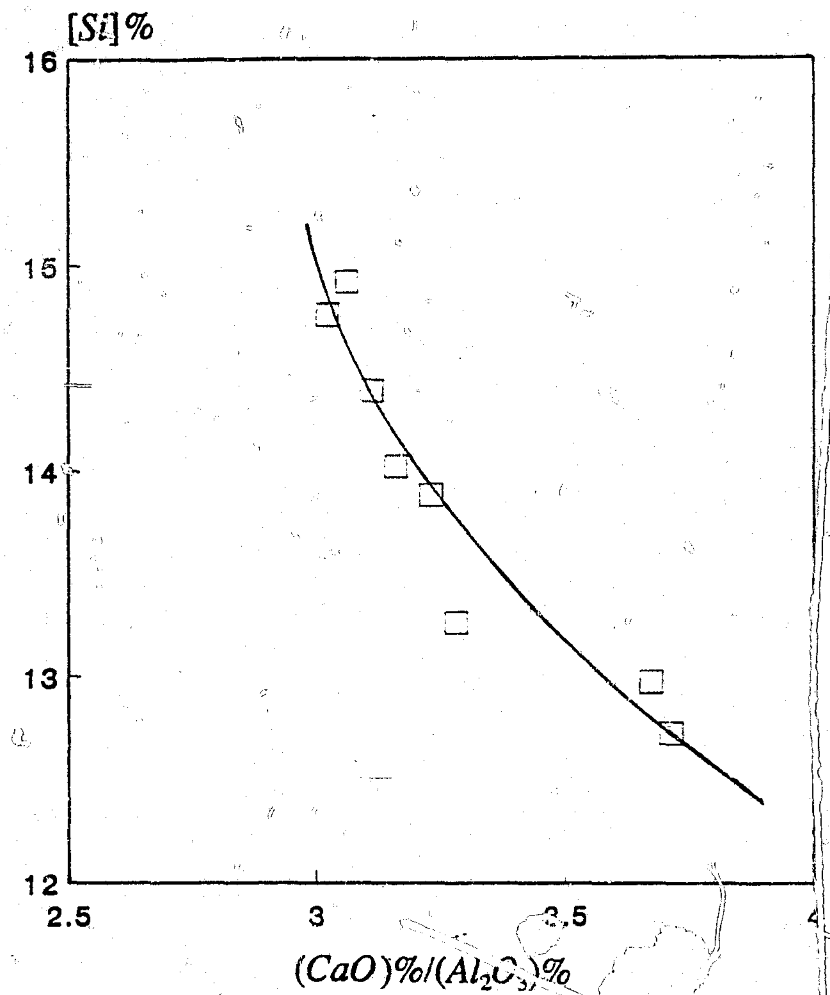

Figure D.24. The effect of the $CaO-Al_2O_3$ ratio of the slag phase on the Si content of the metal phase with Mn:Si≅4.5 at 1500°C under CO atmosphere.

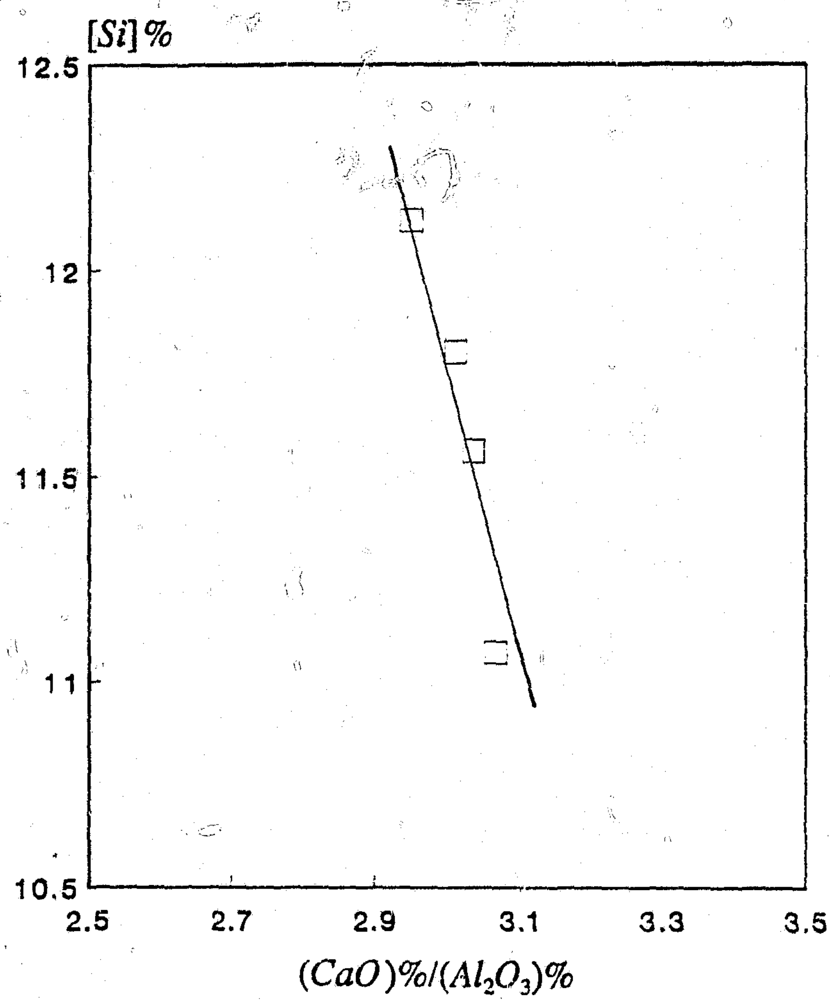

Figure D.25. The effect of the CaO-to-Al_2O_3 ratio of the slag phase on the Si content of the metal phase with Mn:Si≅5.6 at 1500°C under CO atmosphere.

APPENDIX E

APPENDIX E.1 Errors in the measurement of a_{Mn} in Pt-Mn binary system

The formation of MnO from its elements at 1500°C can be written as[123]:

$$Mn(s) + \frac{1}{2}O_2(g) = MnO(s) \quad \Delta G^0 = -128791.49 \quad J/m \text{...........}(E.1)$$

and the free energy of reaction (E.1):

$$\Delta G^0 = -RTln\frac{a'_{MnO}}{\sqrt{p'_{O_2}}\gamma_{Mn}X_{Mn}} \text{...........}(E.2)$$

rearranging the equation (E.2):

$$\frac{\Delta G^0}{RT} = -\ln a'_{MnO} + \frac{1}{2}\ln p'_{O_2} + \ln X_{Mn} + \ln\gamma_{Mn} \text{...........}(E.3)$$

and,

$$\ln\gamma_{Mn} = \frac{\Delta G^0}{RT} + \ln a'_{MnO} - \frac{1}{2}\ln p'_{O_2} - \ln X_{Mn} \text{...........}(E.4)$$

finally:

$$\ln\gamma_{Mn} = \frac{\Delta G^0}{RT} + \ln\frac{a'_{MnO}}{\sqrt{p'_{O_2}}X_{Mn}} \text{...........}(E.5)$$

The manganese activities in Pt-Mn binary system were calculated through the equation (E.5). Therefore, $\ln\gamma_{Mn}$ values are subject to errors made in ΔG^{0}[121], temperature (T), gas composition (p'_{O_2}), a'_{MnO}[15] and analysis of Mn in Pt-Mn binary alloy (X_{Mn}). These errors arise from two different sources which are numerical or random errors and systematic errors. The random errors are due to temperature fluctuations, gas composition variations and analysis of Mn in Pt-Mn binary alloy. However, the systematic errors arise from the error in a'_{MnO} and ΔG^0 of reaction (E.1) which has different values at three different temperatures.

Taking the experiment 3 and 6 in Table VI, 6 and 7 in Table VII and 1 and 10 in Table VIII as the examples, the errors were estimated at 1300°, 1400° and 1500°C at the lowest and highest p_{O_2} values obtained at these temperatures.

(i) 1300°C, p_{O_2} = 3.98x10^{-8} atm:

Temperature:
Fluctuation of temperature about 1300°C and inherent thermocouple error is ± 2°C or ± 0.04 or 0.4 % in $\ln\gamma_{Mn}$.

Gas composition:
Error arising from analysis or calibration and reading of flowmeters is ± 0.192 or 1.87 % in $\ln\gamma_{Mn}$.

Analysis of Mn in Pt-Mn alloy:
± 0.022 or 0.21 % in $\ln\gamma_{Mn}$.

ΔG^{o} value:

$\pm$ 0.96 or 9.36 % in $\ln\gamma_{Mn}$.

a'_{MnO} value:

2 % in $\ln\gamma_{Mn}$.

The total maximum error in $\ln\gamma_{Mn}$ is 14 % at 1300°C and p_{O_2} value of 3.98×10^{-8} atm.

(ii) 1300°C, p_{O_2} = 5.54×10^{-11} atm:

Temperature:

Fluctuation of temperature about 1300°C and inherent thermocouple error is $\pm$ 2°C or $\pm$ 0.04 or 0.5 % in $\ln\gamma_{Mn}$.

Gas composition:

Error arising from analysis or calibration and reading of flowmeters is $\pm$ 0.04 or 0.49 % in $\ln\gamma_{Mn}$.

Analysis of Mn in Pt-Mn alloy:

$\pm$ 0.168 or 0.22 % in $\ln\gamma_{Mn}$.

ΔG^{o} value:

$\pm$ 0.96 or 12.71 % in $\ln\gamma_{Mn}$.

a'_{MnO} value:

2 % in $\ln\gamma_{Mn}$.

The total maximum error in $\ln\gamma_{Mn}$ is 16 % at 1300°C and p_{O_2} value of 5.54×10^{-11} atm.

(iii) 1400°C, p_{O_2} = 4.47x10^{-7} atm:

Temperature:
Fluctuation of temperature about 1400°C and inherent thermocouple error is ± 2°C or ± 0.024 or 0.25 % in $\ln\gamma_{Mn}$.

Gas composition:
Error arising from analysis or calibration and reading of flowmeters is ± 0.265 or 2.72 % in $\ln\gamma_{Mn}$.

Analysis of Mn in Pt-Mn alloy:
± 0.017 or 0.17 % in $\ln\gamma_{Mn}$.

ΔG^o valua:
± 0.880 or 9.04 % in $\ln\gamma_{Mn}$.

a'_{MnO} value:
2 % in $\ln\gamma_{Mn}$.

The total maximum error in $\ln\gamma_{Mn}$ is 14 % at 1400°C and p_{O_2} value of 4.47x10^{-7} atm.

(iv) 1400°C, p_{O_2} = 2.35x10^{-10} atm:

Temperature:
Fluctuation of temperature about 1400°C and inherent thermocouple error is ± 2°C or ± 0.024 or 0.36 % in $\ln\gamma_{Mn}$.

Gas composition:
Error arising from analysis or calibration and reading of flowmeters is ± 0.110 or 1.67 % in $\ln\gamma_{Mn}$.

Analysis of Mn in Pt-Mn alloy:
± 0.018 or 0.29 % in $\ln\gamma_{Mn}$.

ΔG^o value:
± 0.880 or 13.34 % in $\ln\gamma_{Mn}$.

a'_{MnO} value:
2 % in $\ln\gamma_{Mn}$.

The total maximum error in $\ln\gamma_{Mn}$ is 18 % at 1400°C and p_{O_2} value of 2.35×10^{-10} atm.

(v) 1500°C, $p_{O_2} = 5.19\times10^{-6}$ atm:

Temperature:
Fluctuation of temperature about 1500°C and inherent thermocouple error is ± 2°C or ± 0.023 or 0.37 % in $\ln\gamma_{Mn}$.

Gas composition:
Error arising from analysis or calibration and reading of flowmeters is ± 0.167 or 1.86 % in $\ln\gamma_{Mn}$.

Analysis of Mn in Pt-Mn alloy:
± 0.021 or 0.23 % in $\ln\gamma_{Mn}$.

ΔG^o value:
± 0.803 or 8.92 % in $\ln\gamma_{Mn}$.

a'_{MnO} value:
2 % in $\ln\gamma_{Mn}$.

The total maximum error in $\ln\gamma_{Mn}$ is 13 % at 1500°C and p_{O_2} value of 5.19×10^{-6} atm.

(vi) 1500°C, p_{O_2} = 4.99×10^{-11} atm:

Temperature:
Fluctuation of temperature about 1500°C and inherent thermocouple error is ± 2°C or ± 0.035 or 0.76 % in $\ln\gamma_{Mn}$.

Gas composition:
Error arising from analysis or calibration and reading of flowmeters is ± 0.218 or 4.76 % in $\ln\gamma_{Mn}$.

Analysis of Mn in Pt-Mn alloy:
± 0.01 or 0.22 % in $\ln\gamma_{Mn}$.

ΔG^o value:
± 0.805 or 17.57 % in $\ln\gamma_{Mn}$.

a'_{MnO} value:
2 % in $\ln\gamma_{Mn}$.

The total maximum error in $\ln\gamma_{Mn}$ is 25 % at 1500°C and p_{O_2} value of 4.99×10^{-11} atm.

APPENDIX E.2 Errors in the measurement of a_{MnO} in slags

In this study, the activity values of MnO in ferromanganese slags were calculated through the equation (E.6) below:

$$a_{MnO} = \sqrt{p_{O_2} \; / \; p'_{O_2}} \; a'_{MnO} \quad \text{(E.6)}$$

Therefore, a_{MnO} values are subject to errors made in p_{O_2} =p, p_{O_2}' =p' and $a'_{MnO}=a'$. The standard deviation is thus given by:

$$\sigma a = \sqrt{\Sigma\left[\left(\frac{\sigma a}{\sigma x}\right)^2 \sigma x^2\right]} \quad \text{.......(E.7)}$$

where x is successively each of the previously named independent variables. If the equation (E.7) is written in the log form,

$$\ln a = \frac{1}{2}\ln p - \frac{1}{2}\ln p' + \ln a' \quad \text{.......(E.8)}$$

it is seen that

$$\frac{\sigma a}{\sigma p} = \frac{1}{2}\frac{a}{p} \quad \text{.......(E.9)}$$

$$\frac{\sigma a}{\sigma p} = -\frac{1}{2}\frac{a}{p}, \quad \text{.......(E.10)}$$

$$\frac{\sigma a}{\sigma a'} = \frac{a}{a}, \quad \text{.......(E.11)}$$

Therefore,

$$\frac{\sigma a}{a} = \frac{1}{2}\sqrt{\left(\frac{\sigma p}{p}\right)^2 + \left(\frac{\sigma p'}{p'}\right)^2 + 4\left(\frac{\sigma a'}{a'}\right)^2} \quad \text{.......(E.12)}$$

There are two different error sources in the measurement of MnO activities in the slags. The first group is numerical or random errors due to temperature fluctuations, gas composition variations and the analysis of manganese in Pt-Mn alloy and MnO in slag. However, the systematic errors arise from the error present in the relationship between p'_{O_2} and mass per cent of manganese in Pt-Mn alloys equilibrated with pure MnO and from small errors in a'_{MnO}.

Numerical (random) errors:

Taking the experiment 63 in Table X as an example, the following random errors arise in the determination of MnO activities:

Temperature:
Fluctuation of temperature about 1500°C and inherent thermocouple error is ± 2°C or 0.?6 % or ± 0.02 in log p_{O_2}.

Gas composition:
Error arising from analysis or calibration and reading of flowmeters is 0.7 % or ± 0.04 in log p_{O_2}.

Analysis of Mn in Pt-Mn alloy:
2 % or ± 0.02 in log p'_{O_2}.

Analysis of MnO in slag:
1.5 % (accuracy of X-ray fusion method)

Slag composition apart from MnO:
Negligible.

Oxygen in commercial gases and diffusion of oxygen into the gas train and reaction tube:
Negligible at partial pressures of oxygen involved.

To the errors mentioned above (random errors) must be added the errors (systematic errors) in the relationship between manganese concentration of the Pt-Mn binary alloy and the partial pressure of oxygen in equilibrium with pure MnO as determined by Abraham and his co-workers[10] and the error in a'_{MnO} as determined by Davis and Richardson[15]. The first of these contribute an error of 0.10 in the log p'_{O_2} and an error of ± 0.02 is estimated for a'_{MnO}. Therefore the total error in the log p'_{O_2} is 0.12 and 0.06 in log p_{O_2}. This assumes that errors in the values taken for the $CO+CO_2$ equilibrium at 1500°C are negligible.

Calculation of the total error on MnO activity values:
From the equation (E.12), therefore:

$$\frac{\Sigma a}{a} = \frac{1}{2}\sqrt{(0.06\times 2.303)^2 + (0.12\times 2.303)^2 + 4\times(0.02)^2} \quad \text{......}(E.13)$$

$$\frac{\Sigma a}{a} = \frac{1}{2}\sqrt{0.026 + 0.064 + 0.002} \quad \text{......}(E.14)$$

$$\frac{\Sigma a}{a} = 0.16 \quad \text{......}(E.15)$$

Therefore, the absolute error in the determination of a_{MnO} value in slag is 16 per cent plus the error of about 1.5 per cent in the determination of the MnO content of the slag (X-ray fusion method) and the error of 5.6 % from ΔG^0 of reaction (50). This leads to a total error of 23 per cent in the determined MnO activity value. In other words, it does appear that the values of a_{MnO} are correct to about ± 23 per cent. It should be noted that the error computed for a single activity determination is a maximum absolute error and includes both random and systematic errors as mentioned above. A previous study[9] on a_{MnO} values in slags estimates a total error of 22 per cent which is in very good agreement with the present study. Richardson and his co-workers[52,53], however, quote inaccuracies of 8 and 12 per cent for the binary and ternary systems respectively from their error estimates. However, this is found to be optimistic by the present investigator. Consideration of the error calculation shows that the random error due to temperature fluctuations, gas composition variations and analysis of manganese in Pt-Mn binary alloy and MnO in slag amount only to about 2.8 per cent. An average scatter of about 2 per cent about the curves drawn through the points is consistent with this conclusion. On the other hand, the systematic error of about 18 per cent arises from the error present in the relationship between p'_{O_2} and mass per cent of manganese in Pt-Mn alloys equilibrated with pure MnO, error in ΔG^0 of reaction (50) and from small errors in a'_{MnO}. Because the highest oxygen partial pressure used in the determination of MnO activities in this study were 4.76×10^{-7} atm, a'_{MnO} never fell below 0.99

per cent, therefore the correction for the non-stoichiometry of MnO is small compared to the errors of the measurements.

APPENDIX E.3 Errors in silicon and manganese activities from the slag-metal equilibrium study

In slag-metal equilibrium experiments, a_{Si} values were calculated through equation (88). Therefore, a_{Si} values are subject to errors made in K and a_{SiO_2}. First of these contributes an error of about 11 %. a_{SiO_2} values were calculated through Gaye's slag model[89] pertinent to a very good agreement between the results of the present study and the slag model. An error of 5 % is estimated from the a_{SiO_2}values which leads to a maximum error of about 16 % in a_{Si} values.

On the other hand, a_{Mn} values were calculated through equation (91). Therefore, a_{Mn} values are subject to errors made in K and a_{MnO}. The error from a_{MnO} is 23 % and an error of 8.5 % is estimated from K value. Both of these errors leads to a maximum error of about 21 % on calculated a_{Mn} values.

The errors on a_{Si} and a_{Mn} values arise from the systematic errors such as errors on K and a_{SiO_2} or a_{MnO} respectively.

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