Experiment and Thermodynamic Optimization of the MnO-SiO_2-"TiO_2"-"Ti_2O_3" system for Application to Steel Production

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ABSTRACT

Phase equilibria of the system MnO-SiO_2-"TiO_2"-"Ti_2O_3" under controlled atmosphere have been measured in the temperature range from 1200°C to 1550°C and in the range of log pO_2 (atm) from -7.2 (pCO/pCO_2 = 1) to -16.6 (C-CO equilibration). High-temperature equilibration, quenching and electron probe microanalysis (EPMA) were employed to obtain equilibrium compositions of liquid and several solid solutions. It was found that phase equilibria is strongly dependent on the oxygen partial pressure. No ternary compounds or ternary solid solutions were observed. Based on the newly obtained phase diagram data with a number of reliable thermodynamic data in literatures, a thermodynamic optimization of phase diagram and thermodynamic properties of the MnO-SiO_2-"TiO_2"-"Ti_2O_3" systems at 1 bar pressure are presented. The molten oxide phase was described by the Modified Quasichemical Model. The Gibbs energies of several solid solutions (spinel, pyrophanite, pseudobrookite, manganosite and rutile) were modeled with the Compound Energy Formalism. Furthermore, inclusions chemistry of Mn/Si/Ti deoxidized steel was studied through thermodynamic computation and compared with experimentally reported data. Inclusions evolutions in Mn/Si/Ti containing steels by thermodynamic prediction were in good agreement with the experimental data.

Scope of Present Study

Motivation

Thermodynamic database development for oxide inclusion systems and application in steelmaking process

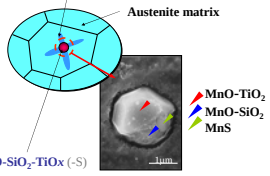
"Oxide Metallurgy"

Inclusion Utilization in HSLA steel

Si/Mn/Ti steel (HSLA steel)

- Play as nucleation site for Intra Granular Ferrite transformation
- Fine distribution
- High sulfide capacity
- Formation of Mn-depleted zone

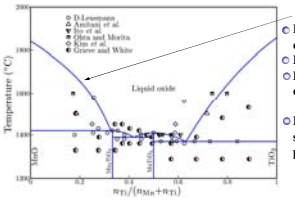
"MnO-SiO_2-TiO_2-Ti_2O_3"



Accurate phase equilibria as well as thermodynamic database for the MnO-TiO_2-Ti_2O_3-SiO_2 system are required.

Previous Studies in MnO-SiO_2-"TiO_2"-"Ti_2O_3" System

Reported phase diagram of the MnO-"TiO_2" system

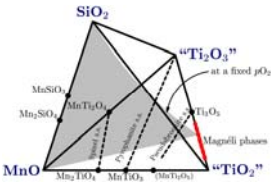


- Experimental results are not consistent with each other.
- Effect of pO_2 was not considered.
- Existence of solid solutions were not considered.
- Phase diagram in the MnO-SiO_2-TiO_x system is rare and oxygen partial pressure was not controlled.

Complete phase diagram in the wide range of pO_2 and temperature has not been known for MnO-TiO_x and MnO-SiO_2-TiO_x systems !

Phases in MnO-SiO_2-"TiO_2"-"Ti_2O_3" System

4 binary, 6 ternary systems



Phase equilibria is strongly dependent on oxygen partial pressure.

Experimental and Thermodynamic Modeling

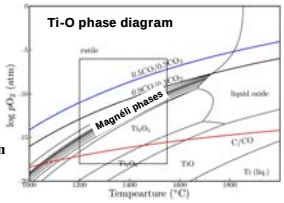
Phase diagram in MnO-SiO_2-"TiO_2"-"Ti_2O_3" quaternary system under controlled oxygen partial pressure

Experimental Condition

- Pt or Mo crucible
- CO/CO_2 or C/CO equilibration
- T = 1200 ~ 1550°C

MnO-TiO_2-Ti_2O_3
pCO/pCO_2 = 1, 9 and C/CO equilibrium

MnO-SiO_2-TiO_2-Ti_2O_3
pCO/pCO_2 = 1 and C/CO equilibrium

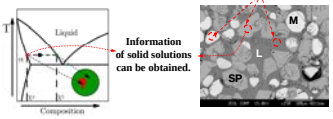


Experimental Method

- High Temperature Equilibration
- Quenching and Polishing
- Examination samples using microscope

After Experiment

EPMA measurement for equilibrium compositions of phases



Thermodynamic Modeling and Optimization

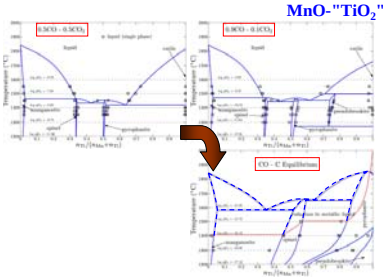
- Systems
  - **Binary**
    MnO-SiO_2, SiO_2-TiO_2, SiO_2-Ti_2O_3, **TiO_2-Ti_2O_3**, **MnO-TiO_2**, **MnO-Ti_2O_3**
  - **Ternary**
    SiO_2-TiO_2-Ti_2O_3, **MnO-TiO_2-Ti_2O_3**, **MnO-SiO_2-TiO_2**, **MnO-SiO_2-Ti_2O_3**
    3 binary and **3 ternary** systems were optimized in the present study.
    3 binary and 1 ternary systems were taken from **FactSage** database.
- Solutions and Models

Molten Oxide	$(Mn,SiO_2,TiO_2,TiO_{1.5})$	: Modified Quasichemical Model
Manganosite	$(Mn,TiO_2,TiO_{1.5})$	: Henrian solution
Spinel	$(Mn^{2+})^T[Mn^{2+},Ti^{4+},Ti^{3+}]^2O_4$	: Compound Energy Formalism
Pyrophanite	$(Mn^{2+},Ti^{3+})^A[Ti^{4+},Ti^{3+}]^BO_3$	: Compound Energy Formalism
Pseudobrookite	$(Mn^{2+},Ti^{3+})^A[Ti^{4+},Ti^{3+}]^B{}_2O_5$	: Compound Energy Formalism
Rutile	$(TiO_2,TiO_{1.5})$	: Henrian solution

All thermodynamic calculations and optimizations were performed by FactSage™

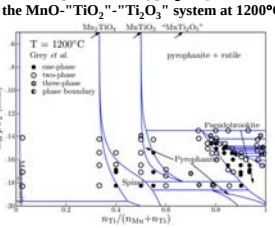
Results – Selected experimental results with thermodynamic calculation (lines)

MnO-"TiO_2"-"Ti_2O_3" system



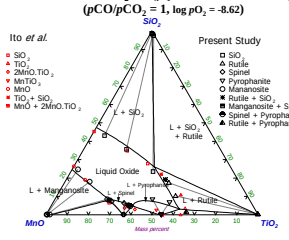
As pO_2 decreases, phase equilibria changes dramatically.
Pseudobrookite s.s. appears at low pO_2.

Composition vs log pO_2 diagram in the MnO-"TiO_2"-"Ti_2O_3" system at 1200°C

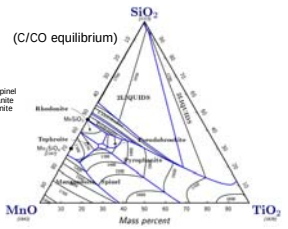


MnO-SiO_2-"TiO_2"-"Ti_2O_3" system

MnO-SiO_2-TiO_x system at 1400°C (pCO/pCO_2 = 1, log pO_2 = -8.62)

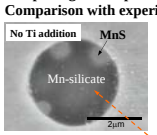


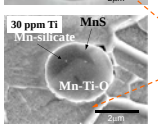
Liquidus projection of the MnO-SiO_2-TiO_x system

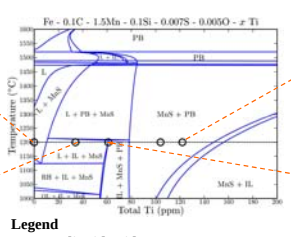


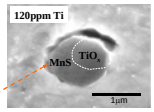
Application – Inclusions Evolution in Mn-Si-Ti containing Steels

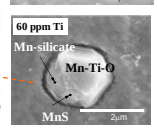
Morphologies and phases of inclusions in steels varying Ti content
Comparison with experimental data by Kim *et al.*, ISIJ Int., (2002)





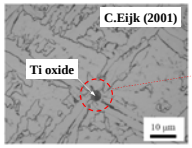




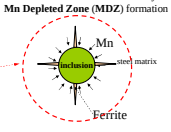


Legend
L: liquid oxide
IL: pyrophanite s.s. ($MnTiO_3$-Ti_2O_3)
PB: pseudobrookite s.s. ($MnTi_2O_5$-Ti_3O_5)

Oxide Metallurgy
Intra Granular Ferrite (IGF) formation using non metallic inclusions as nucleation site

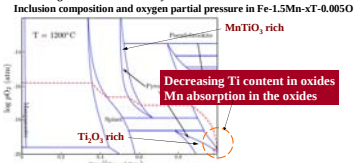


Austenite → IGF transformation by **Mn Depleted Zone (MDZ)** formation



Mn is one of austenite stabilizing element so MDZ results in ferrite transformation around the inclusion.

Phase diagram of the Mn-Ti-O system at 1200°C
Inclusion composition and oxygen partial pressure in Fe-1.5Mn-xT-0.005O



Amount of Mn absorbed into TiO_x from steel matrix (Fe-0.1C-1.5Mn-0.1Si-0.02Ti-0.005O-0.007S) at each temperature