Thermodynamic Properties of Ferroboron Alloys and B_2O_3 Bearing Slags

Fe-B系合金及びB_2O_3含有スラグの熱力学的性質

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1- Introduction

1.1- FERROALLOYS

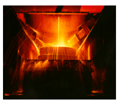
Why Ferroalloys ?

- Alloys of iron with some element other than carbon.
- Used to "carry" reactive elements to Fe-based alloy systems.
- The lowest-cost alloying additives for high temperatures.
- Produced by Carbothermic or Aluminothermic reductions.

Why Ferroboron?

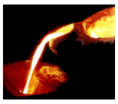
- Used in technologically advanced materials.
- Ferroboron alloys have glass-forming ability.
- Can make permanent magnets
- Can change the properties of important alloys by small amounts.
  Provides steel with a wide hardenability
  Provides wear resistance to hard-facing cast irons

Steels



RE-Fe-B Magnets
Amorphous Metallic Glasses

Cast Irons

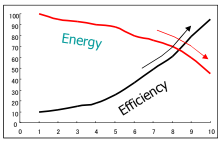


1.2- TARGET of the STUDY

COMMON PROBLEMS

B_2O_3 + 2Fe + 2Al (or C) → 2FeB-**Al** **(or C)** + Al_2O_3 + (or CO)

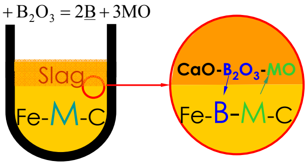
Carbothermic Reduction	Metallothermic Reduction
high % C ΔH >> 0 high energy requirement	high % Al ΔH << 0 high B_2O_3 losses



A new process proposal cover:

- A new reducing agent other than C or Al, like Si.
- A new B source by which utilization of B can be improved.
- An alternative slag treatment by which simultaneous reduction of B_2O_3 and dissolution of B in Fe.

$3\underline{M} + B_2O_3 = 2\underline{B} + 3MO$



1.3- STRATEGY

- Experiments were planned in two main topics;
  - Fe-B based metallic phase
  - B_2O_3-containing slags.
- A stepwise experimentation strategy was considered to determine the properties of both Fe-based alloys and B_2O_3-containing slags.
- Investigated systems
  - **Fe – B**
  - **Fe – B – O**
  - **Fe – B – Si**
  - **Fe – B – C**
  - **Fe – B – C – Si**
  - Low temperatures (~1373 – 1623 K)
  - Low boron contents (< 20 at. % B)

target

derivation of complete thermodynamic data

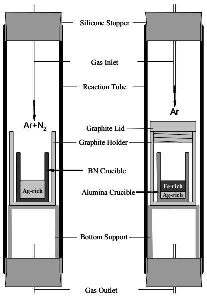
Ag-B → Fe-B → Fe-B-C
Fe-B ⇣ Fe-B-Si ⇢ Fe-B-Si-C
Fe-B-C ↓ Fe-B-Si-C
B_2O_3 containing slags ↑ Fe-B-Si-C

3-1 Results & Discussion / Ag-B & Fe-B SYSTEMS

Experimental method

liquid - liquid equilibration with Ag

$$\underbrace{RT\ln a_B}_{inAg} = \underbrace{RT\ln a_B}_{inFe}$$

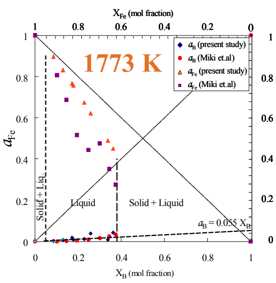


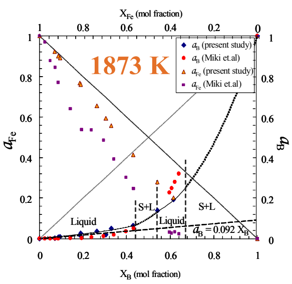
Procedure

alloy preparation → equilibration (@ HT, 18 h) → chemical analysis (ICP: B, Fe, Si; LECO: C)

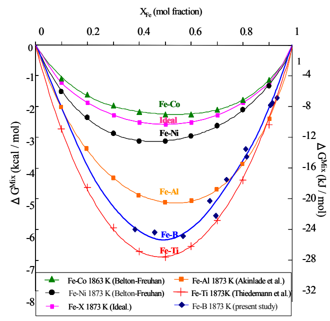
- Liquid – liquid equilibration method was selected
  If properties of any component are known in one phase, properties of the other phase can be calculated.
- Silver and copper were selected as the reference melt

- max. B solubility in $Ag_{(l)}$ were found to be **0.149** and **0.305 at. %** at 1773 and 1873 K.
- Under changing atmospheres (**0.01** < P_{N_2} < **0.5**), activity coefficients of B at infinite dilution wrt solid standard state were calculated as
  $\gamma^{o,(Ag)}_{B(s)}$ = *194* at 1773 K and $\gamma^{o,(Ag)}_{B(s)}$ = *172* at 1873 K.
- Activity coefficient of B at infinite dilution wrt liquid standard state, was also found as **0.055** and **0.092** for 1773 and 1873 K.



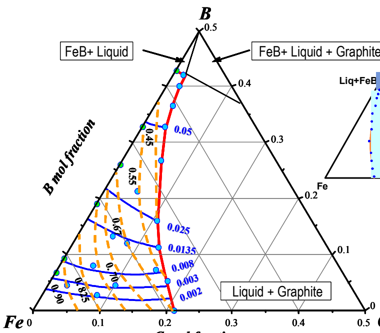


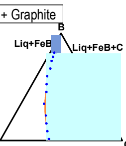
- Using previous findings of the Ag-B system, activities of B were measured from B content in Ag phase, wrt. pure liquid reference state.
- Activities of B and Fe were measured and significant negative deviations from ideality were observed for both constituents.
- Self interaction parameter of B in liquid Fe was also found as **2.49** and **2.86** for 1773 and 1873 K

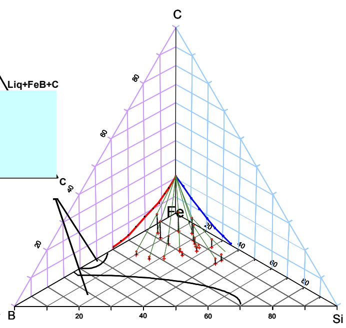


3-2 Results & Discussion / Fe-B-C, Fe-B-Si-$C_{satd.}$ & B_2O_3-bearing SYSTEMS

- The ternary Fe-B-C system isoactivity curves for B and Fe were constructed.
- The effect of C on B and Si was found at 1873 K and the C solubility was inversely proportional to B and Si contents.
- Interaction parameter of C on B at C saturation was evaluated as **11.8 ± 0.4** .







- The MgO-B_2O_3, CaO-B_2O_3 and SiO_2-B_2O_3 binary slags systems were thermodynamically investigated in their liquid states at 1873 K
- Strong negative deviations were observed for all systems, implying the different natures of pure components.
- For a favorable ferroboron conversion from slag to metal phase, slag must have a high activity coefficient of $BO_{1.5}$

$$\frac{X_B}{X_{BO_{1.5}}} = \left(\frac{\gamma_{BO_{1.5}}}{\gamma_B} \cdot K\right) \quad and \quad L_B = \frac{X_B}{X_{BO_{1.5}}}$$

- Among three binary slag systems MgO-based slags are more likely to yield higher B amounts in Fe-alloys.