論文の内容の要旨

論文題目

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）

氏名

スンカル　アフメット　セミヒ

This study investigates the thermodynamic properties of the ferroboron alloys and boron oxide containing slags, which coexist in a carbothermic ferroboron process. This study is composed of 6 chapters.

In the chapter 1, a detailed introduction was given for ferroboron alloys. Most common production methods were paid some special attention. Basic points about carbothermic reduction and metallothermic reduction processes, their initial process design parameters were mentioned. After introducing the common practices, a deeper look into the ferroboron production were given and most important problems of the current production trends were discussed.

In addition, previous studies on these problems were mentioned in detail. It was seen that the literature lacks the required reliable and complete data for ferroboron processing. Therefore, construction of a thermodynamic database for ferroboron production processes was taken as the main objective of this study. In order to achieve this goal, this study was divided into two major parts: the thermodynamics of Fe–B based liquid ferroboron alloys and the thermodynamics of B_2O_3-bearing slag systems.

In chapter 2, the thermodynamic properties of the Fe–B alloy systems were investigated experimentally. As the experimental method, chemical equilibration with liquid Ag was selected. However, because of a lack of reliable data on the Ag–B system in the 1773–1873 K range, the properties of B in liquid Ag were examined as preliminary experiments. The solubility of B at 1273 K, 1773 K and 1873 K was measured as 0.055 ± 0.003, 0.149 and 0.305 ± 0.0075, respectively. The activity coefficient of B at infinite dilution in Ag, $\gamma^{o}_{B\,in\,Ag}$, with respect to solid standard state was determined to be 194 and 172 at 1773 K and 1873 K respectively, for solutions of B concentration less than 0.01 at. %.

After finding the properties of B in the Ag–B system, Fe–B binary alloys were examined for the activities of the components at 1773 K and 1873 K. Activity vs. composition relations were clarified and it was seen that the binary Fe–B system deviates considerably in the negative direction for both components at these temperatures. The excess Gibbs energy of the alloys at 1873 K was also calculated to compare the degree of deviation with other binary Fe–X alloys. At the same time, the activity coefficient of B at infinite dilution, $\gamma^{o}_{B\,in\,Fe}$, and self interaction parameter of B in Fe, $\varepsilon^{B}_{B\,in\,Fe}$, were calculated at 1773 K and 1873 K.

After clarifying the properties of the Fe–B binary system, investigations were expanded to the Fe–B–C ternary system to determine the effect of C on the properties of the B at 1873 K. Initially, the C solubility was determined as a function of B and a strong inverse relation was found. Following this, the activities of B and Fe were measured and isoactivity curves of B and Fe were drawn for the liquid Fe–B–C alloys at 1873 K. Following the activity calculations, the effect of C on B was mathematically expressed by the interaction parameter of C on B at C saturation as $\varepsilon_{B\ Csatd.}^{C} = 11.8 \pm 0.4$. This value was considered to be in excellent agreement with the solubility and reported data.

Before finalizing the experiments on the Fe–B based alloys, the solubility of C in the Fe–B–Si–C quaternary alloys was determined at 1873 K. It was found that the addition of Si into Fe–B–$C_{satd.}$ alloys results in a further decrease in the C solubility. Therefore, it was concluded that elemental Si can be used to reduce the C content of the melts without any refining process.

In chapter 3, B_2O_3-containing binary slag systems were investigated at 1873 K by chemical equilibration method using Cu as the reference metal. The thermodynamic properties of B_2O_3-bearing slags were of primary importance in ferroboron processing; therefore, three binary systems i.e., MgO–$BO_{1.5}$, CaO–$BO_{1.5}$ and SiO_2–$BO_{1.5}$, were evaluated in terms of thermodynamic properties, for their potentials as alternative raw materials.

Experiments were performed using Fe–B–$C_{satd.}$ alloys and Cu as reference metals under 1 atm CO atmosphere in graphite crucibles at 1873 K. Even though initial experiments utilized Fe–B–$C_{satd.}$ alloys as the reference metal phase for activity measurements in the MgO–$BO_{1.5}$ and CaO–$BO_{1.5}$ binary systems, because of the limitations arising from the use of these reference alloys, the reference melt was replaced by Cu to perform experiments within complete $BO_{1.5}$ range.

To measure the properties of slags by this method, the properties of B in the liquid Cu–B system became necessary at 1873 K. Therefore, the properties of B in Cu phase were measured and compared with the published data and they exhibited quite good agreement. The self interaction parameter of B in Cu phase $\varepsilon_B^B = -1.75$ and the activity coefficient of B at infinite dilution $\ln \gamma_B^o = 1.92$ were calculated and the temperature dependences of these properties were shown in mathematical expressions.

$$\ln \gamma_B^o = -\frac{10706}{T} + 7.58 \qquad \text{and} \qquad \varepsilon_B^B = -\frac{8485}{T} + 2.54$$

After investigating the Cu–B binary alloys, the measurements of the $BO_{1.5}$ activities were continued in the MgO–$BO_{1.5}$ and CaO–$BO_{1.5}$ systems at 1873 K under 1 atm CO atmosphere. From the measured data of $BO_{1.5}$ activities, the activities of the other components were calculated by Gibbs-Duhem integration.

The alkaline-earth borate systems, MgO–$BO_{1.5}$ and CaO–$BO_{1.5}$, showed similar complex behaviors. At low $BO_{1.5}$ concentrations, both systems deviated in negative direction indicating the alkaline-earth oxides had higher affinity for $BO_{1.5}$ and isolate the species, $(BO_3)^{3-}$, whereas with an increase in $BO_{1.5}$ composition beyond $X_{BO1.5} > 0.5$, the deviation drastically shifted from negative to positive. This significant change was attributed to the formation of more complex ions and finally the beginning of the formation of the polymeric borate network.

As the third binary system, SiO_2–$BO_{1.5}$ binary melts were investigated. However, after initial experiments, significant Si dissolution in the Cu phase was observed. Thus, to perform the measurements, the effect of Si on B in the ternary Cu–B–Si alloys was evaluated by controlled dissociation of B into various Cu–Si alloys equilibrated with BN under fixed N_2 pressure. The first- and second-order interaction parameters of Si on B were calculated as $\varepsilon_B^{Si} = -0.61$ and $\rho_B^{Si} = -14.53$.

After determining the properties of B in the Cu–B–Si ternary system at 1873 K, activities of $BO_{1.5}$ and SiO_2 were measured and calculated, respectively. This system showed a strong negative deviation, implying a strong interaction between the two components in liquid state.

In order to make a comparison between these three binary systems for ferroboron processing, the concept of B partition ratio was introduced. According to this pre-evaluation, the raw material with the highest $\gamma_{BO1.5}$ was expected to yield the highest B dissolution. The highest $\gamma_{BO1.5}$, i.e., the lowest B partition and thus the highest B recovery was expected from MgO–$BO_{1.5}$ slags, the next highest from CaO–$BO_{1.5}$ and the lowest from SiO_2–$BO_{1.5}$.

In chapter 4, as the third part of the experiments, this study was extended to the ternary slag systems with the introduction of SiO_2 to the MgO–$BO_{1.5}$ and CaO–$BO_{1.5}$ slags because the presence of Si in the metal phase, and hence, its resulting oxide SiO_2 will lead the formation of ternary slags. Like in binary system, experiments were performed by chemical equilibration method under controlled C–CO equilibrium at 1873 K.

The results showed that both ternary systems exhibited considerable negative deviations within the investigated range. Although binary systems of alkali-earth borates exhibited similar behavior, the effect of SiO_2 was noticeably different in each system. In the MgO–$BO_{1.5}$–SiO_2 system, the activity of $BO_{1.5}$ decreased to a minimum value for slags containing about 5–10 mass % SiO_2. With an increase of the SiO_2 beyond 30 mass %, the effect of SiO_2 leveled off. On the other hand, in the CaO–$BO_{1.5}$–SiO_2 system, at low $BO_{1.5}$ compositions, the addition of SiO_2 caused a slight increase in activity up to 25 mass % SiO_2 indicating a preferential interaction between CaO and SiO_2. Beyond this point, the activity of $BO_{1.5}$ reached a constant value and becomes virtually independent of SiO_2 or CaO content for an almost constant $BO_{1.5}$ composition. For this system, the 15–25 mass % SiO_2 composition range was considered to be the composition having the highest $BO_{1.5}$ activity.

Based on the activity measurements in two ternary slag systems, SiO_2 was found to be highly effective in altering the $BO_{1.5}$ activity in both systems, even at small amounts because of its ability to change the behavior of $BO_{1.5}$; this was especially evident in the MgO–$BO_{1.5}$–SiO_2 system. In the light of the results, the addition of SiO_2 was expected to be disadvantageous in yielding higher B recovery in ferroboron processing.

In chapter 5, a detailed evaluation of the possible applications of the measured data was performed. Based on the experimental findings and some processing assumptions, the initial criteria for alternative B_2O_3-bearing material selection were proposed. Furthermore, the alternative materials, selected among natural boron minerals, were evaluated in terms of process efficiency by considering the method of reduction, the production scale and the final product specifications.

Also, the conditions to obtain highest B recovery from these candidate minerals were evaluated. As effective process parameters, the raw material, i.e., the initial slag composition, the final product composition and the partial pressure of CO; hence, the final slag composition were selected. It was found that among these process parameters, the starting material had the highest impact on the process efficiency. Also, a decrease in the partial pressure of CO by applying vacuum had a significant positive effect on B recovery. Morevoer, as the last and least effective method, lowering the B content in metal phase resulted in a slight increase in the B recovery.

Eventually, in chapter 6, the results of the experiments of Fe–B based alloys and B_2O_3-containing slags were summarized. Based on the findings throughout this research, it was concluded that this study contains the reliable, fundamental thermodynamic research, scientific insight and its applicable data of a ferroboron production process. This research is expected to have a direct impact on the improvement of the current carbothermic ferroboron production.