学 位 論 文 内 容 の 要 旨

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学 位 論 文 題 名

Ethanol-Assisted Ironmaking using Mild-Dehydrated Goethite Ore
(マイルドか焼したゲーサイト鉱石を用いるエタノール製鉄)

The depletion of high-grade iron ore encourages us to utilize the low-grade ore (i.e., goethite) more effectively. On the other hand, the shortage of coal, as well as the mitigation of high CO_2 emission, need more intensive utilization of an alternative carbon source. Bioethanol as derived from biomass, regarded as a renewable and carbon-neutral resource, is a promising candidate as a reducing agent for ironmaking. Introducing ethanol to reduce iron ore through the chemical vapor infiltration (CVI) process is attractive as aiming for low-temperature reduction. This study describes the process intensification of the previous proposes CVI process. The new process has been proposed named as ethanol-assisted ironmaking.

Chapter two describes the several aspects to intensify in the previously-proposed CVI ironmaking. As reported in the study, there were three proposed processes involved in CVI ironmaking: (1) production of porous hematite ore, (2) production on carbon composite (CVI) ore through integrated pyrolysis-tar decomposition, and (3) reduction of the CVI ore. Vacuum dehydration successfully intensified the process 1 in reducing time on goethite dehydration to 1 h generating the similar porous hematite ore properties as in 24 h under atmospheric condition. On the other hand, the processes utilizing the inexpensive low-grade coal combined with renewable materials (i.e., biomass) or waste plastic (i.e., polyethylene) in process two are also investigated. It was concluded that the synergetic effect of combined coal-biomass or coal-PE improves the pyrolysis performance to increase decomposition reactivity of heavy tar. More heavy tar decomposed to light tar, gas, and deposited carbon in the ore. However, carbon contents from those methods were still not enough from the requirement for a perfect reduction process.

Chapter three describes the new ironmaking process called ethanol-assisted ironmaking. The porous hematite ore from mild-dehydrated goethite ore has been successfully reduced by charging ethanol (C_2H_5OH) under the heating conditions. In the experiments, ethanol was dropwise added to the mild-dehydrated, porous iron ore beds at heating conditions using the temperature-program. As a result, the ethanol was soon decomposed to CO and H_2, which then reduced the iron oxides. Porous iron ore acts as a suitable catalyst for ethanol decomposition as it simultaneously reduces to metallic iron. Interestingly, iron oxides were reduced at a lower temperature, compared to conventional coal-based ironmaking in the blast furnace. Metallic Fe was obtained at only 750^oC, showing a reduction degree of 81%, due to the contribution of hydrogen reduction. The longer charging time of ethanol promotes the higher reduction degree as well as sufficient compositions of reducing gas (H_2 - CO) for the reduction process. The results of experiments using different iron ores revealed the general rule that the higher CW content in ore makes the larger surface area of the iron ore by mild-dehydration, causing higher reactivity in the reduction process. The results appealed that mild-dehydrated iron ore is good raw materials of ethanol-assisted ironmaking, due to its nanopores. This process demonstrates an intensification of the previously-proposed CVI process from three-step become two-step processes by combining process 2 and 3.

Chapter four describes the kinetic analysis of simultaneous ethanol decomposition and iron reduction. The kinetic study is necessary for understanding the mechanism of the simultaneous ethanol decomposition – iron reduction process. There were 8 main reactions involved: (1) decomposition of ethanol, (2) decomposition of methane, (3) steam reforming of methane, (4) water gas shift, (5) Boudoard reaction, (6) direct reduction by C, (7) indirect reduction of iron oxide by CO, and (8) iron reduction by H_2. Curve fitting methods were conducted with satisfying results (R^2 higher than 0.90) calculating 24 parameters consisting reaction rate constants, activation energies, and diffusion factors. Interpretation on obtained parameters of the diffusion factors shows that the reaction of gases inside pore might be inhibited by carbon deposition on the pore surface of iron ore.

Chapter five describes the exergy analysis and presents a feasibility study on the proposed ethanol-assisted ironmaking process. Applying a high exergetic and renewable reducing agent like ethanol for ironmaking would be attractive. There are four processes involved in the proposed ethanol-assisted ironmaking: (1) Goethite ore mild-dehydration, (2) Porous ore reduction by ethanol, (3) Hot metal – slag separation, and (4) Ethanol recovery. From the viewpoints above, ethanol-assisted ironmaking is an attractive method to solve problem-related resource, environment, and energy in future ironmaking industry.