

Development of Large-Scale Simulation of Mass Transfer in a Metallurgical Coke with Chemical Reaction

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学位授与番号	11301甲第20399号
URL	http://hdl.handle.net/10097/00135900

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学位論文題目 Development of Large-Scale Simulation of Mass Transfer in a Metallurgical
Coke with Chemical Reaction (化学反応をともなう製鉄用コークス内の
大規模な流体シミュレーションの開発)
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論文内容要約

Chapter 1: Gasification reaction of metallurgical coke largely affects the operation of iron-making process. The metallurgical coke plays a role not only as a reduction agent of iron ore but also as a spacer, which keeps permeability in a blast furnace. In a blast furnace, the coke is degraded by the gasification reaction though the reaction converts the coke to reductants such like H₂ gas and CO gas. Thus, the coke has the possibility to inhibit the permeability. Although a high-strength coke has utilized in a blast-furnace for a stable operation so far, the coke property required for its operation will be changed because the gas atmosphere around coke in the next-generation blast furnace such like COURSE50 [1] is different from that in a conventional blast furnace. The coke degradation needs to be investigated under several reaction condition. Since it is difficult to directly observe the coke degradation in a blast furnace, numerical analysis of mass transfer of gas with heterogeneous reaction was analyzed in a coke model with an assumed uniform porosity in previous studies [2,3]. In addition, Fong et al. developed a coal char model by using X-ray CT, and simulated the gasification of the model with mass transfer [4]. In this thesis, the numerical simulation of mass transfer with chemical reaction such like heterogeneous reaction and homogeneous reaction was performed for a highly resolved coke model developed from X-ray CT images, and then the validity was evaluated.

Chapter 2: Large-scale simulation of mass transfer in a highly resolved coke model with chemical reaction (Simulator for Reaction of Porous Medium, SRPM) was developed. The coke model was developed from X ray CT images, and were classified into either pore or carbon matrix based on Otsu's method [5]. In pore voxels, gas was enabled to diffuse, and CO₂ gasification reaction occurred at the interface between the carbon matrix and pore or gas phase. In addition, it was assumed that gas could not diffuse into voxels of the carbon matrix. The coke model was found to degrade non-uniformly as the reaction progressed, and the areas with highly concentrated carbon matrix voxels remained unchanged. These characteristic areas were derived from the X-ray CT images. Focusing on the concentration distribution of CO₂ at 1573 K, it was found that the change of the rate-controlling step from pore diffusion to chemical reaction by structural change.

Chapter 3: To obtain the kinetic parameter of gasification reaction at the interface between a carbon matrix voxel and a pore voxel in SRPM, the kinetic analysis of CO₂ and H₂O gasification reaction was performed for pulverized metallurgical coke. The results of the scanning electron microscopy observations and CO₂ gas adsorption suggested that the gasification reaction

occurs at the particle surface, and thus the grain model was employed as the gasification reaction model. As a result, the activation energy changed as the reaction progressed and hardly depended on the particle size. The activation energies were 200–260 kJ/mol in CO₂ gasification and 220–290 kJ/mol in H₂O gasification. The frequency factor of H₂O gasification was approximately 10 times larger than that of CO₂ gasification, regardless of the progress of the reaction. At the same activation energy level, the frequency factor showed a higher value with a decrease in the particle size. This result was consistent with the theory of the grain model and indicated that the gasification reaction of the pulverized coke with μm-scale occurs on the surface of the coke particle. Furthermore, the predicted value was in good agreement with the experimental one.

Chapter 4: In SRPM, only gas diffusion was considered as mass transfer to reduce a calculation cost. To validate this assumption, the impact of convection on mass transfer in the 2D coke model developed from a X-ray CT image was numerically investigated. The computational domain is a rectangle mesh in which a 2D coke model with a radius of 20 mm was arranged, and the incompressible Navier-Stokes equation was solved in Reynolds number, Re of 10, 100 and 500. As a result, the Peclet number in a coke model was lower than 0.1 at each Reynolds number, and thus the mass transfer in a porous medium was dominated by gas diffusion.

Chapter 5: To quantitatively evaluate the temperature dependency of coke degradation by CO₂ gasification reaction in a blast furnace, SRPM for the coke model with approx. 200 million voxels developed from X-ray CT images was performed at the reaction temperatures of 1373, 1573, 1773 and 1973 K. At high reaction temperature, the gas concentration of CO₂ was high in the external area of the analytical object, and the coke matrix voxels vanished mainly in this area. Focusing on the effectiveness factor of a porous catalyst, the rate-controlling step at initial stage was chemical reaction at 1373 K but pore diffusion at over 1573 K. Focusing on the structure of a coke model, although the frequency distribution of local porosity showed unimodal regardless of the progress of reaction, the standard deviation calculated from the distribution was changed by reaction. The change rate of the standard deviation by reaction seemed to be larger at high reaction temperature than at low reaction temperature. The logarithm of the change rate hardly depended on reaction temperature under 1573 K but was proportional to the inverse of the temperature over 1573 K. This chapter quantitatively showed that SRPM is enabled to express the temperature dependency of coke degradation, and rate-controlling step affects the coke structure after reaction largely.

Chapter 6: To evaluate the validity of SRPM, the reaction rate and the structural change by gasification reaction obtained from SRPM were compared with these of experiment. For the experiment, the cylindrical coke samples with a radius of 20 mm were gasified with CO₂ gas or H₂O gas at 1373 K until the conversion reached 0.2 by using the experimental apparatus for coke gasification, in which the sample was suspended from an electric balance located at the top. Also, SRPM for the coke model developed from the X-ray CT images of the coke sample before reaction was conducted under the similar condition to the experiment. As a result, the reaction rate obtained from SRPM almost corresponded with the experimental one in each gasification. However, the prediction accuracy of H₂O gasification was lower than that of CO₂ gasification. Especially, in H₂O

gasification, the calculated reaction rate was significantly higher than the experimental one until the conversion of 0.1 because the reaction rate constant was significantly large in this initial stage.

Chapter 7: To implement homogenous reaction such like water gas shift reaction in SRPM, the net reaction rates of water gas shift reaction obtained from kinetic analysis based on detailed chemistry in a perfectly stirred reactor at 1373 K were learned by neural network. The neural network had 6 hidden layers with 200 nodes and 200 biases, and the ReLU (Rectified Linear Unit) was employed as an activation function between the hidden layers. While there were some differences at the initial and final stages, the mole fractions of CO₂ predicted by machine learning and those predicted by the detailed chemistry broadly corresponded to each other. Thus, our neural network expressed the net reaction rate of water gas shift reaction. Also, the effect of water gas shift reaction on H₂O gasification reaction was investigated by SRPM. Under the condition that only H₂O and N₂ existed on all the boundary ($X_{CO}: X_{CO_2}: X_{H_2}: X_{H_2O}: X_{N_2} = 0.0: 0.0: 0.0: 0.1: 0.9$), the reaction rate of H₂O gasification was not significantly different between with and without water gas shift reaction. This is because the water gas shift reaction is an exothermic reversible reaction, and the production of CO gas and H₂O gas is more favorable than that of H₂ and CO₂ at 1373 K. Therefore, the effect of the water gas shift reaction on H₂O gasification of coke was small under the condition that only H₂O gas and N₂ gas existed.

Chapter 8: The Large-scale simulation of mass transfer with heterogeneous reaction for a pore-resolved coke model (SRPM) expressed coke degradation obtained from a lab-scale experiment, and thus has potential to elucidate coke degradation in a blast furnace. Since the homogenous reaction was also considered by using neural network, SRPM has flexibility to the next-generation blast furnace such like the hydrogen-injection blast furnace and the oxygen blast furnace.

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