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Improvement of Coke Strength by Phenolic Resin Coating: Experimental and Theoretical Studies of Strengthening Mechanism

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ABSTRACT

Coke strength is the most important characteristic for retaining permeability in the bed of a blast furnace. In the present study, coke was coated with phenolic resin in order to improve the coke strength, and a nanoindentation method was used to estimate the strength of the coated coke after reaction under CO2 atmosphere. The elastic modulus was measured for the microporous coke substrate,. The elastic modulus of coated coke before reaction was higher than that of uncoated coke. However, after reaction with CO2, the elastic modulus did not necessarily show an improvement in coke strength. The mechanism whereby the resin coating improved coke strength before and after the reaction was considered by a finite element analysis using a mesh superposition technique.

Keywords: Component, coke, phenolic resin, nanoindentation, elastic modulus, mesh superposition method, finite element method

INTRODUCTION

Recently, the degradation of coke quality caused by long-term use of a coke oven has emerged as an important issue to be solved in iron making processes. Furthermore, vast quantities of natural resources are consumed in operating a blast furnace, and a high level of operational efficiency is required in order to reduce the emission of CO_2. Accordingly, high-strength coke is needed for preventing poor permeability of the bed due to fracture and pulverization of coke at the bottom of a blast furnace. To improve coke strength, modification of the microstructure of coke has proved useful. Coke consists of inert and substrate containing various sizes of micropores, such that its material structure is heterogeneous and porous. In iron making processes, three mechanisms are thought to lead to the degradation of coke strength: fracture, that is, propagation of large cracks

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in coke caused by loads in a blast furnace; pulverization, such as surface abrasion of coke in the raceway; and reaction with CO_2 (Hayashizaki *et al*., 2009). These mechanisms are strongly linked to the heterogeneous and microporous structure of coke. Therefore, in this study, coke is dipped into an aqueous solution of phenol resin, and the resin seeps into the micropores to improve coke strength. Conventionally, the drum index and microstrength *index* are used to measure coke quality. Although these indices highlight macroscopic properties of coke, measurements are not always sufficient for evaluation of the heterogeneous microstructure. Consequently, a nanoindentation method has been introduced that can measure the elastic modulus and hardness of a microregion of coke (Mihashi *et al.*, 2002). Improvement of coke strength by phenol resin is investigated through microhardness data obtained under various experimental conditions and through theoretical data from a finite element analysis of the nanoindentation method.

EXPERIMENTAL

Procedure

Coke was provided by Kansai Coke and Chemicals Co., Ltd., and all experimental samples used were fabricated under the same manufacturing conditions and were from the same section of a coke block (16 mm × 16 mm × 5 mm). First, coke is dipped into an aqueous solution of phenol resin (Oshika Co., Ltd; RS-05) at a concentration of 20, 30, or 40 wt % for 1 min. The specimen is then dried at room temperature for 24 h. Second, any moisture remaining in the phenol resin is removed by placing the sample in a drying oven for 3 h at 150 °C. Finally, the reaction between CO_2 and the coated coke is run by using the experimental apparatus shown in Fig.1.

The experimental procedure is as follows:

1. Coke is positioned at the center of a quartz glass pipe (ϕ20 mm) and placed in the furnace.
2. Air in the pipe is replaced with N_2 and the sample is heated to 950 °C.
3. For the reactions, N_2 is replaced with CO_2 (at 50 mL/s) at a given temperature.
4. Reaction with CO_2 proceeds for 1 h, and the gas is replaced by N_2 once more. Finally, the furnace is cooled.
5. Microhardness of coke after the reaction is measured as shown in next section.

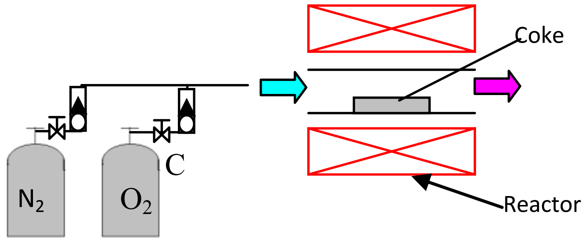


Fig.1: Apparatus for reaction experiments

The effects on elastic modulus of the phenol concentration and of the CO_2 reaction were investigated in two experiments. The conditions for these two experiments are shown in table 1 and 2, respectively.

Measurement

The nanoindentation method can measure microscopic properties, such as the elastic modulus and hardness of a microregion (Mihashi *et al.*, 2002). In this study, coke strength was evaluated on a microcompression tester (Shimadzu Co.; MCT). A triangular pyramid indenter with an angle of 115° is loaded against a sample, and after being held at the lowest position for 5 s, the indenter is unloaded (Fig. 2). The loading speed and maximum load are 207.4 mN/s and 500 mN, respectively. The elastic modulus is calculated from the tangent line to the unloading curve at the holding point. Because the tip of the indenter is small (1 µm) and can be aimed at a designated position, and because the tester has a microscope, this method can distinguish between the substrate and micropores, as shown in Fig.3 (Ueoka *et al.*, 2007). The elastic modulus of only micropores (Komatsu *et al.*, 2010) is measured 50 times, and the average value of the distribution is calculated to estimate the coke strength of the microregion.

TABLE 1
Conditions for phenol concentration experiments

Experiment	1-1	1-2	1-3
Conc. of Phenol resin [wt %]	20	30	40

TABLE 2
Conditions for CO_2 reaction experiments

Experiment	2-1	2-2
Conc. of Phenol resin [wt %]	0	30

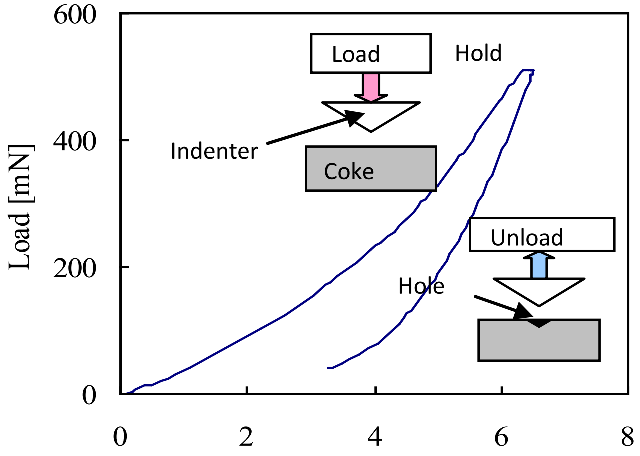


Fig.2: Load–displacement curve for nanoindentation method

CALCULATION

To establish the improvement in the elastic modulus of coke coated by phenol resin, a finite element analysis with mesh superposition (Takano & Uetsuji, 1999; Asakuma *et al*., 2001) that can consider both macro- and micro-structural behavior simultaneously is applied to a model having complex microstructural geometry similar to that of coke. The analysis uses two independent finite element meshes; a fine local mesh and a rough global mesh for the overall domain. In the method, the local mesh is overlaid onto an arbitrary portion of the global mesh (Fig. 4). Here, Ω^G denotes the global domain, Ω^L $\left(\Omega^L \subset \Omega\right)$ is the arbitrary local domain, and Γ^{GL} represents the boundary between Ω^L and Ω^G. For the calculations in this study, the local mesh is overlaid around the tip of the indenter, because loading by the indenter does not affect the stress distribution away from this point. Accordingly, the total number of mesh

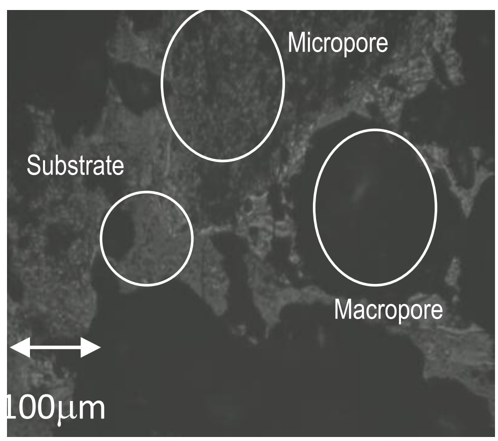


Fig.3: Image of coke surface

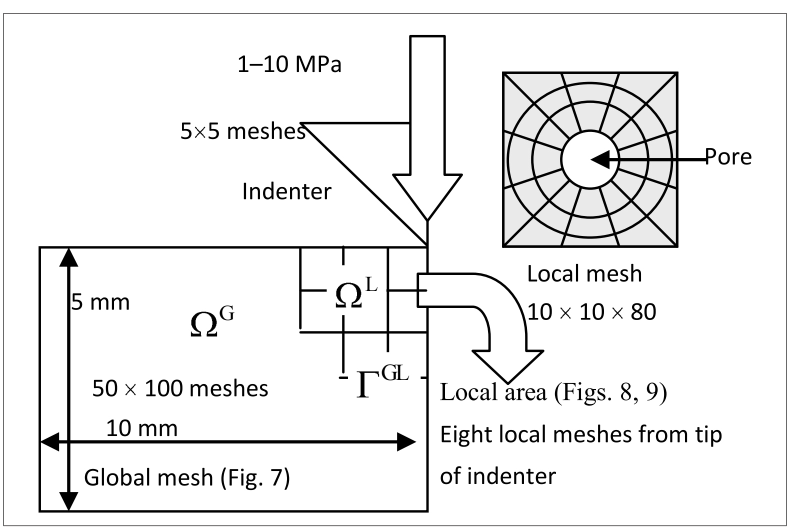


Fig.4: Superposition mesh method

points and the computational costs are reduced, while the accuracy for the heterogeneous structure is maintained. This method has been previously applied to finite element analysis of nanoindentation (Panich & Sun, 2004). For modeling, a parabolic relation between the displacement and load, as shown in Fig. 2, is simulated. Although, in reality, the coke structure is heterogeneous, within the model pores are located regularly and the porosity is systematically changed. Displacement data for various porosities and pore shapes are quantitatively estimated to examine the coating effect, since agreement between the experimental and simulated data is difficult to achieve. Moreover, concentration of the stress distribution around pores, which is a primary factor that affects coke strength, is carefully investigated for each porosity and pore shape through the advantage gained by using the superposition mesh technique.

RESULTS AND DISCUSSION

Elastic modulus

Elastic modulus distributions and average modulus values for the experimental conditions in Table 1 are shown in Fig. 5. For all cases, the average elastic modulus of the substrate with coated micropores is higher than that of the uncoated coke.

In addition, the elastic modulus distributions and averages for the conditions in table 2 are shown in Fig. 6. The average values for both coated and uncoated coke decrease after reaction with CO_2. However, the improvement and sustainability of the elastic modulus from the coating are not confirmed, because a large proportion of the phenol resin evaporates at high temperature.

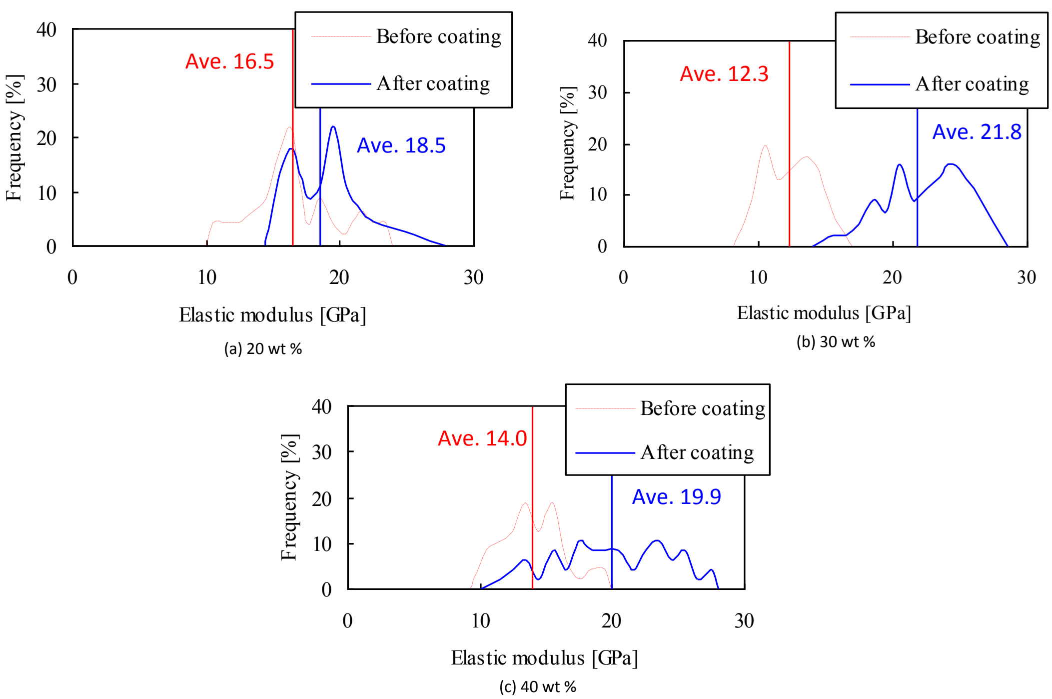


Fig.5: Effect of phenol concentration on elastic modulus

Simulation

Fig.7 shows an example of the von Mises stress distribution in the global mesh when the load produced by the indenter is 5 MPa and the porosity, ρ, of the local mesh is 50%. Stress in the global mesh concentrates around the tip of indenter, and the fine stress distribution of the overlaid local mesh is shown in Fig. 8 for cases when ρ = 50%, 40%, and 30 %. This change in the porosity corresponds to increased resin coating. Fig.8 shows that a decrease in porosity does not greatly influence the stress distribution around pores, because the pores are assumed to be perfect circles (Ueoka *et al*., 2007). When this analysis is applied to the model for studying the improvement in the elastic modulus caused by coating, the elastic modulus of coated coke with ρ = 40% and 30%, respectively, is 1.33- and 1.86-fold greater than that for ρ = 50%. For experiments 1-1, 1-2, and 1-3 in table 1, the increases in the elastic modulus are 1.12-, 1.77-, and 1.42-fold greater than that without coating, respectively. Therfore, the change in the porosity of the coke surface is a direct result of the coating, and if the initial porosity is 50%, the porosity is improved by about 20%. On the other hand, the theoretical elastic modulus of the coated coke after reaction with CO_2 when ρ = 40% and 50% is 0.72- and 0.53-fold greater than that for ρ = 30%, and for experiments in Table 2, the values are both 0.68 of those before the reaction. Thus, the porosity around the coke surface is predicted to increase by 20% as a result of the reaction. Hence, the superposed model can handle porosity changes caused by both

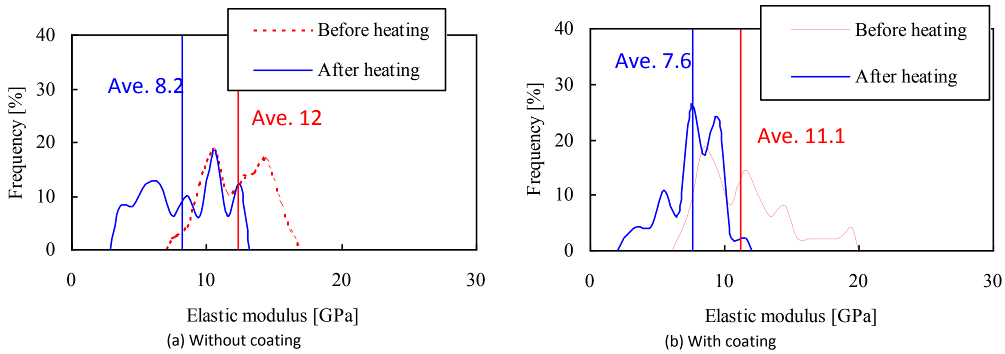


Fig.6: Effect of coating on elastic modulus after reacting with CO_2

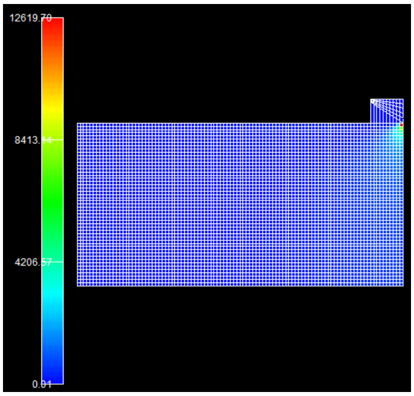
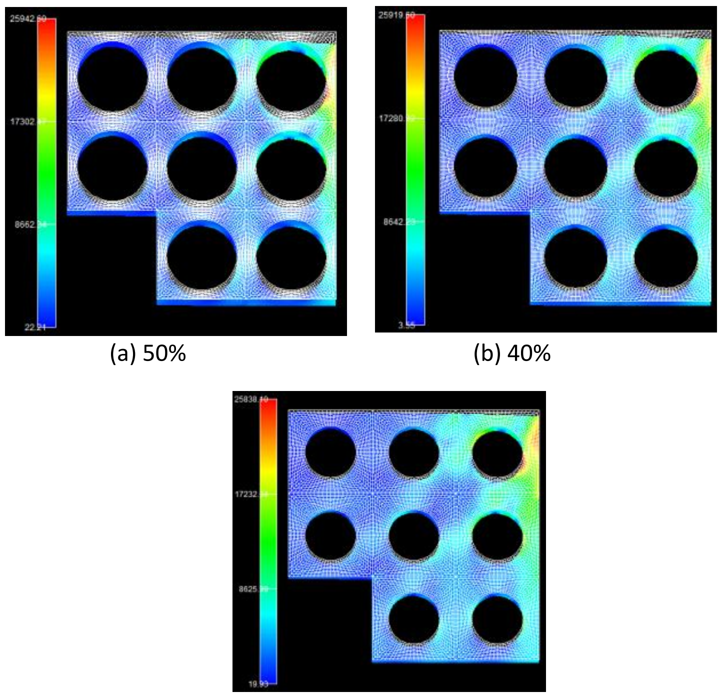


Fig.7: Stress distribution of global mesh

the reaction and the coating. Comparison between experimental and simulated nanoindentation data will be useful for evaluating surface modifications of coke.

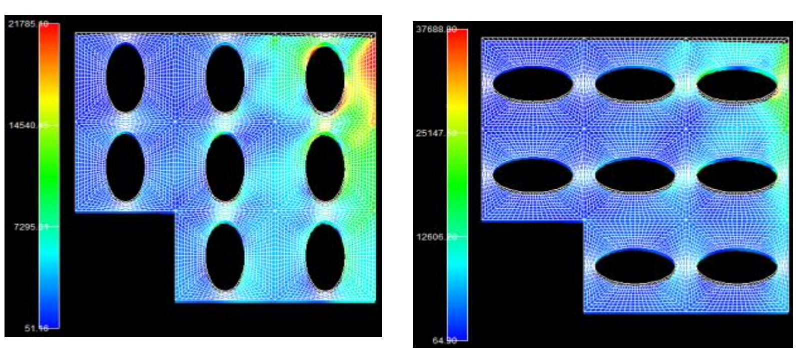
Finally, the effect of pore shape on the stress distribution is analyzed. The stress distributions when a local mesh with vertical or horizontal eliptical pores is overlaid around the tip of indenter are shown in Fig. 9. The stress concentration is greater around the vertical pores than the horizontal ones. Thus, changes not only in the porosity but also in the pore shape by the coating and reaction are essential for improvement of the elastic modulus in microregions.



(a) 50% (b) 40%

(c) 30%

Fig.8: Stress distribution of local mesh for changing porosity



(a) Vertical pores (b) Horizontal pores

Fig.9: Stress distributions for elliptical pores

CONCLUSION

Coke was coated with phenol resin in order to improve the mechanical strength of the coke. The elastic modulus of coke coated with various concentrations of phenol was measured in microregions by a nanoindentation method. Although the elastic modulus was increased by coating before reaction with CO_2, the phenol resin coat was not effective in improving the coke strength observed after the reaction. The mesh superposition technique was useful for evaluating the heterogeneous microstructure of coke, such as the porosity and pore shapes, and proved to be an accurate tool for predicting changes in the elastic moduli of microregions.

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