

REDUCTION BEHAVIOR OF CHARCOAL COMPOSITE IRON OXIDE PELLETS INCLUDING RESIDUAL VOLATILE MATTER ¹

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Abstract

Japanese cypress were carbonized partly at maximum carbonization temperatures ($T_{C, \max} = 823, 1073$ and 1273 K) in order to obtain semi-charcoal with residual volatile matter (V.M.). Charcoal composite pellets using such semi-charcoal including residual V.M. have been prepared and reduced at reduction temperature (T_R) in N_2 gas atmosphere. Fractional reduction $F(\%)$ after 60 min of the semi-charcoal composite pellet at $T_{C, \max} = 823$ K was 20 % and over 40 % at $T_R = 1073$ and 1173 K, respectively, and was higher than any other pellets. When $T_{C, \max}$ was lower, namely the pellet had more residual V.M., the reduction of iron oxide was more accelerated at $T_R = 1073$ and 1173 K. Fractional reductions $F(\%)$ of all the semi-charcoal composite pellets were over 90 % for 60 min at $T_R = 1273$ K. On the other hand, fractional reduction $F(\%)$ of the semi-charcoal composite pellet at $T_{C, \max} = 1073$ K using semi-charcoal particle with the size of $23 \sim 35 \mu\text{m}$ was 38 % for 60 min and over 90 % for 40 min at $T_R = 1173$ and 1273 K, respectively. As the size of semi-charcoal particle decreased, the reduction of iron oxide increased.

Key words: Ironmaking; Volatile matter; Charcoal; Carbon composite pellet.

¹ Technical contribution to the 7th Japan-Brazil Symposium on Dust Processin-Energy-Environment in Metallurgical Industries and 1st International Seminar on Self-reducing and Cold Bold Agglomeration, September 8-10 2008, São Paulo City – São Paulo State – Brazil

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1 INTRODUCTION

The Kyoto Protocol came into effect in February 2005, and the first agreement period is to begin from 2008. As declared in the Kyoto Protocol, Japan is targeting a 6% decrease in greenhouse gas (GHG) emissions in 2010 compared with the baseline year 1990. However, Japan's total GHG emissions in 2004 were reported as 7.4% increase in comparison with 1990, rising to 1.355 billion tons. In a serious situation, the Japanese steel industry has already targeted a 10.5% decrease in CO₂ emissions of 2010 under a Voluntary Action Plan adopted by the Japan Iron and Steel Federation.^[1] A lot of steel engineer researched various means to decrease reducing agent at blast furnace in order to reduce CO₂ emissions. For example, injection of waste plastics and carbon neutral materials such as biomass into blast furnace is better alternative.^[2,3] Especially, biomass has novel advantage, i.e., no CO₂ emissions, because of carbon neutral. Recently, charcoal composite iron oxide pellets were proposed to decrease CO₂ emissions for the ironmaking. These pellets were promising to decrease the starting temperature for iron oxide reduction in carbon composite iron ore agglomerate under a rising temperature condition, such as in a blast furnace shaft.

On the other hand, we have already studied the novel iron ore agglomerate bearing semi-coal-char including residual volatile matter (V.M.).^[4-6] This semi-coal-char with residual V.M. is obtained when the carbonization of coal under a rising temperature condition is interrupted at a certain temperature, i.e., a maximum carbonization temperature, $T_{C, \max}$. These agglomerates bearing such semi-coal-char have high reducibility at low temperatures and some strength as well. While simple iron ore agglomerate bearing char will start the reduction reaction as solid-solid reaction at somewhat higher temperature, the proposed one will start the reduction reaction as gas-solid reaction at somewhat lower temperature but a little higher than $T_{C, \max}$ under a rising temperature condition.

From these backgrounds, we propose charcoal composite iron oxide pellets including residual V.M. in order to decrease reducing agent at blast furnace and CO₂ emissions. In this work, charcoal composite iron oxide pellets including residual V.M. have been prepared and reduction behavior of these pellets was investigated.

2 EXPERIMENTAL

2.1 Sample

Japanese cypress (Fixed carbon: 8.12 mass%, V.M.: 90.8 mass%, Ash: 1.05 mass%) as woody biomass and reagent grade hematite Fe₂O₃ (95 mass%, Wako Pure Chemical Industries, Ltd.) as an iron oxide sample were used. Woody biomass generally has more V.M. than coal. Carbonization of Japanese cypress under rising temperature conditions was interrupted at maximum carbonization temperatures, $T_{C, \max} = 823, 1073$ and 1273 K, to obtain semi-charcoal with some residual V.M. The obtained charcoal was mixed with reagent grade hematite Fe₂O₃ in the mass ratio of one to four. Then, Bentonite of 1 mass% was added to the mixture as a binder in order to strengthen. The particle size range of the mixture was regulated as 23~63, 63~75 and 105~150 μm by the sieves. The charcoal composite pellet including residual V.M. was prepared by handrolling.

2.2 Preparation of Semi-Charcoal

Japanese cypress (200 g) as woody biomass was carbonized partly in order to obtain the semi-charcoal with some residual V.M. A schematic draw of experimental apparatus is shown in Figure 1. Chips of the wood were packed in the carbonization reactor. N₂ gas was entered from the top of the reactor, which was heated at 200 K h⁻¹ by a digital thermo-controller. N₂ gas with a constant flow rate of 1.67×10⁻⁵ (m³ s⁻¹ (s.t.p.)) was passed through the packed bed and mixed with the carbonizing gas to determine each gas flow rate.^[7] This outlet gas mixture was filtered through glass wool to remove the tar. The resultant gas was cooled to condense the water vapor. After the water vapor was captured in the condenser, the carbonizing gas without tar was analyzed by the gas chromatograph (GC14B, Shimadzu Corporation).

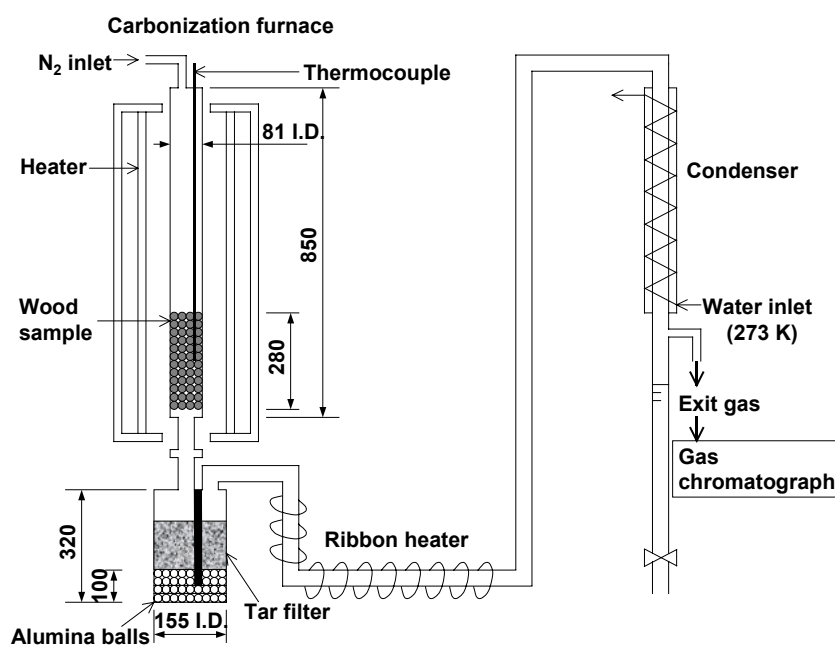


Figure 1. A schematic view of experimental apparatus for carbonization; dimensions in mm.

2.3 Reduction of Iron Oxide

Charcoal composite pellets including residual V.M. were kept at 373 K for 24 h in the air in order to remove water. Then, these formed pellets were reduced at $T_R = 1073, 1173$ and 1273 K in N₂ gas atmosphere in order to investigate the reduction behavior of pellets. After reduction, obtained pellets were analyzed by XRD (RINT2500V, Rigaku Corporation) with CuK α line at 40 kV and 200 mA.

3 RESULTS AND DISCUSSION

3.1 Carbonization of Japanese Cypress

In order to obtain the semi-charcoal with some residual V.M., Japanese cypress was carbonized from room temperature to $T_{C, \max} = 823, 1073$ and 1273 K at 200 K h⁻¹, and kept at $T_{C, \max}$ until arrival time of 6 h. These obtained variations of main gas flow rates with carbonization time are shown in Figures 2-4. It is found

these figures that releasing of H_2 gas starts from carbonization temperature $T_C = 800$ K, and the flow rate reaches the maximum point at $T_{C, \max} = 1073$ K. H_2 gas flow rate gradually decreases over $T_C = 1073$ K. From these results, H_2 gas is considered to be released mostly about $T_C = 1073$ K. On the other hand, CO and CO_2 flow rates are rising at $T_C = 573$ K, and their peaks are observed at about $T_C = 873$ K. Then, CO_2 gas is hardly released at high carbonization temperatures over $T_C = 1173$ K. In Fig. 4, releasing of CO_2 gas gradually starts from $T_C = 573$ K, and stops over 1073 K. CH_4 gradually increased from $T_C = 573$ K to $T_C = 873$ K. $C_2H_4 + C_2H_6 + C_3H_8$ gases were released slightly from $T_C = 673$ K to $T_C = 873$ K.

Total gas volumes generated by carbonization are calculated by integrating these gas flow rates, and are shown in Figure 5. H_2 gas was released more than any other gas at $T_{C, \max} = 1273$ K. H_2 gas volume at $T_{C, \max} = 823$ K was very little. The higher $T_{C, \max}$ was, the more H_2 gas was released. Both CO and CO_2 gases were released more than any other gases at $T_{C, \max} = 823$ K. Volumes of CO and CO_2 gases were equal to each other at all $T_{C, \max}$. The volume of CH_4 gas was less than that of CO and CO_2 .

From these results, it was found that the semi-charcoal retained much V.M., mainly H_2 , at $T_{C, \max} = 823$ K and that the semi-charcoal with some residual V.M. could be prepared by controlling $T_{C, \max}$ in the carbonization.

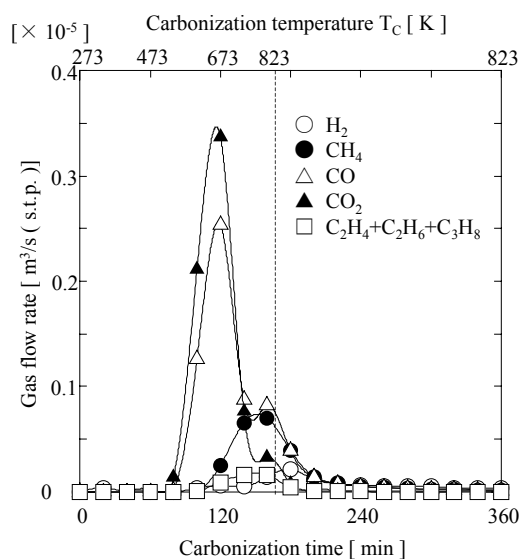


Figure 2. Variations of gas flow rates with carbonization time using Japanese cypress at $T_{C, \max} = 823$ K.

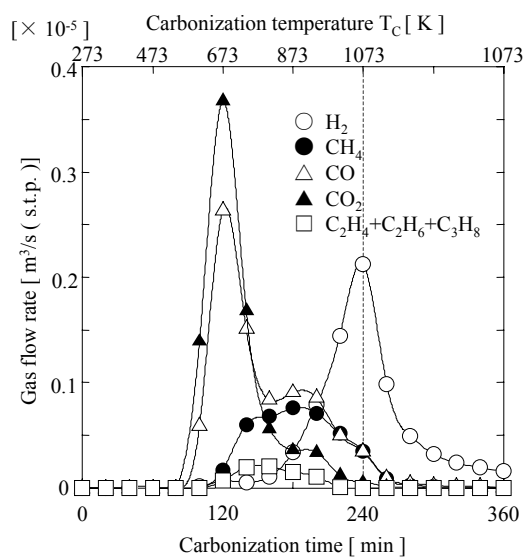


Figure 3. Variations of gas flow rates with carbonization time using Japanese cypress at $T_{C, \max} = 1073$ K.

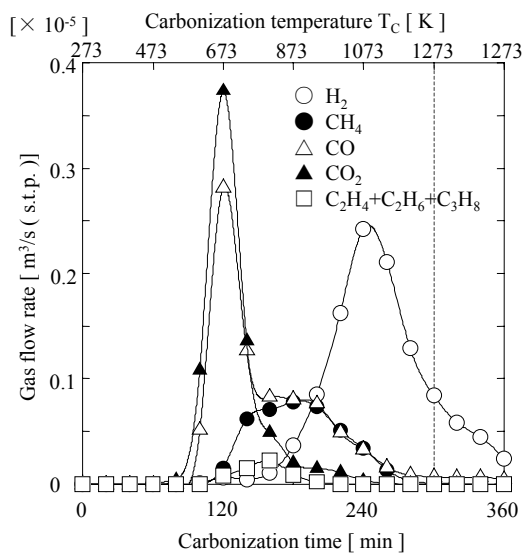


Figure 4. Variations of gas flow rates with carbonization time using Japanese cypress at $T_{C, \max} = 1273$ K.

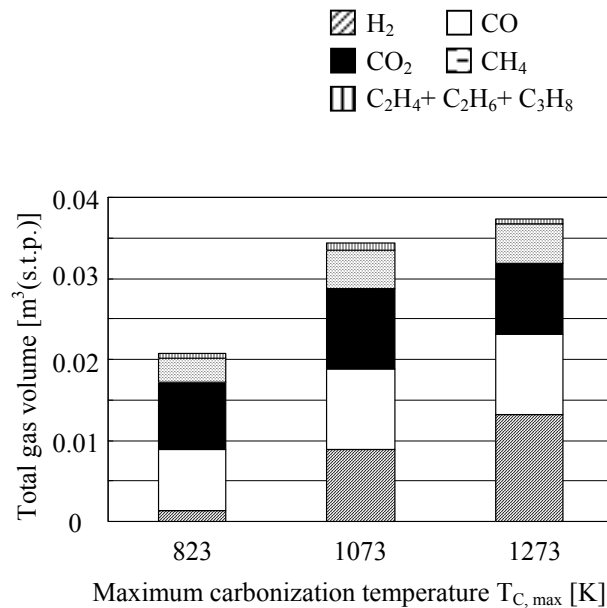


Figure 5. Total gas volume generated by the carbonization of Japanese cypress as a function of $T_{C, \max}$.

3.2 Reduction Behavior of Semi-charcoal Composite Iron Oxide Pellets

In order to investigate the fractional reduction $F(\%)$, charcoal composite iron oxide pellets including residual V.M. obtained at $T_{C, \max} = 823, 1073$ and 1273 K were reduced at $T_R = 1073, 1173$ and 1273 K in N_2 gas atmosphere. The relationship between fractional reduction $F(\%)$ and reduction time at $T_R = 1073$ K is shown in Figure 6. Fractional reduction $F(\%)$ of the semi-charcoal composite pellet at $T_{C, \max} = 823$ K was 20 % for 60 min and was higher than any other pellets by 7~8 %. Figure 7 shows the relationship between fractional reduction $F(\%)$ and reduction time at $T_R = 1173$ K. Fractional reduction $F(\%)$ of the semi-charcoal composite pellet at $T_{C, \max} = 823$ K was 40 % for 60 min and was also higher than any other pellets. This result was similar to the result obtained at $T_R = 1073$ K. From these results, when $T_{C, \max}$ was lower, namely the pellet had more residual V.M., the reduction of iron oxide was much enhanced. Furthermore, the relationship between fractional reduction $F(\%)$ and reduction time at $T_R = 1273$ K is shown in Figure 8. Fractional reductions $F(\%)$ of semi-charcoal composite pellets at $T_{C, \max} = 823, 1073$ and 1273 K were over 90 % for 60 min and indicated the same behavior at $T_R = 1273$ K. From these results, these reducibility of semi-charcoal composite pellets were high and were not dependent on residual V.M. at $T_R = 1273$ K.

On the other hand, in order to investigate the influence of particle size, semi-charcoal composite pellets at $T_{C, \max} = 1073$ K using semi-charcoal particle with sizes of 23~35, 63~75 and 105~150 μm were reduced at $T_R = 1173$ and 1273 K in N_2 gas atmosphere. The relationship between fractional reduction $F(\%)$ and reduction time at $T_R = 1173$ K is shown in Figure 9. Fractional reduction $F(\%)$ of semi-charcoal composite pellet using semi-charcoal particle with the size of 23~35 μm was 38 % for 60 min and was higher than any other pellets. Figure 10 shows the relationship between fractional reduction $F(\%)$ and reduction time at $T_R = 1273$ K. Fractional reduction $F(\%)$ of semi-charcoal composite pellet using semi-charcoal particle with

the size of 23~35 μm was over 90 % for 40 min and was also higher than any other pellets. This result was similar to the result obtained at $T_R = 1173\text{ K}$. From these results, when the size of semi-charcoal particle was smaller, the reduction of iron oxide was much enhanced at $T_R = 1173$ and 1273 K .

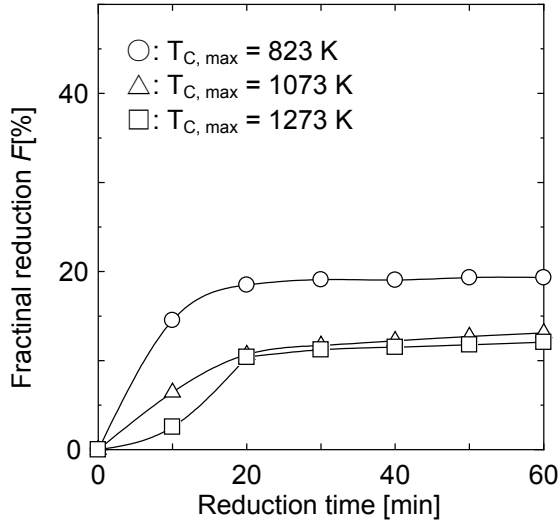


Figure 6. Reduction curves of semi-charcoal composite pellets at $T_R = 1073\text{ K}$ in N_2 gas atmosphere.

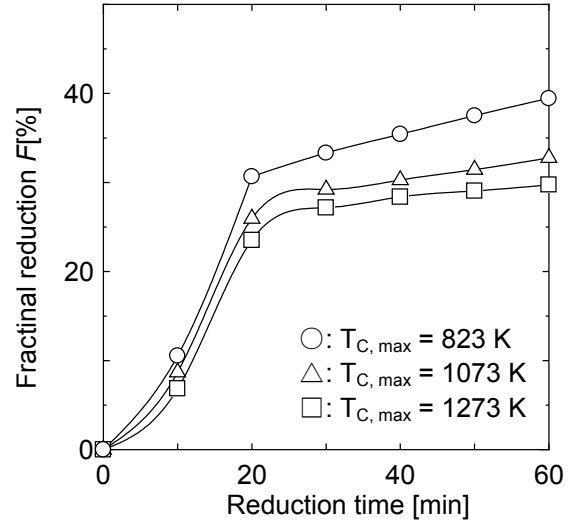


Figure 7. Reduction curves of semi-charcoal composite pellets at $T_R = 1173\text{ K}$ in N_2 gas atmosphere.

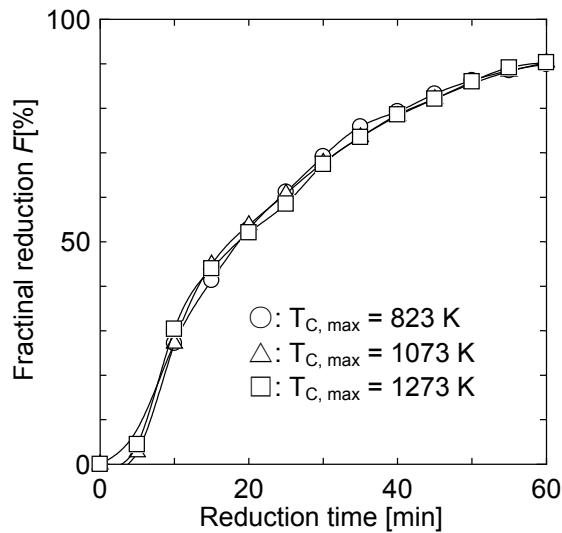


Figure 8. Reduction curves of semi-charcoal composite pellets at $T_R = 1273\text{ K}$ in N_2 gas atmosphere.

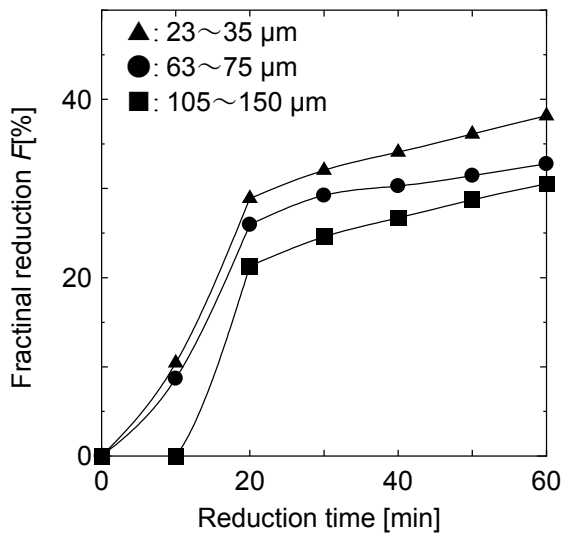


Figure 9. Reduction curves of semi-charcoal composite pellets at $T_{C, \max} = 1073$ K using semi-charcoal particle with sizes of 23~63, 63~75 and 105~150 μm at $T_R = 1173$ K in N_2 gas atmosphere.

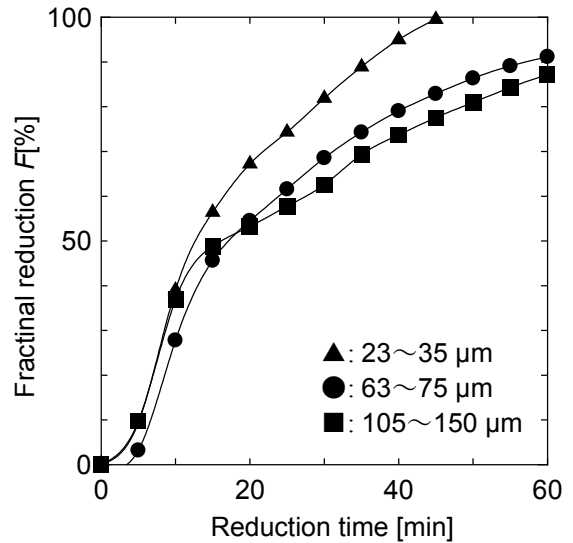


Figure 10. Reduction curves of semi-charcoal composite pellets at $T_{C, \max} = 1073$ K using semi-charcoal particle with sizes of 23~63, 63~75 and 105~150 μm at $T_R = 1273$ K in N_2 gas atmosphere.

In consideration of these results, charcoal composite iron oxide pellets including residual V.M. could be prepared and the reduction behavior was clarified. These results lead to the possibility of novel iron ore agglomerates.

4 CONCLUSIONS

Charcoal composite iron oxide pellets including residual V.M. have been prepared and the reduction behavior of these pellets was investigated. These results obtained are summarized as follows:

- (1) The semi-charcoal obtained at $T_{C, \max} = 823$ K retained much V.M. Most of V.M. was H_2 .
- (2) Fractional reduction $F(\%)$ of semi-charcoal composite pellet at $T_{C, \max} = 823$ K was 20 % for 60 min and was higher than any other pellets by 7~8 % at $T_R = 1073$ K.
- (3) Fractional reduction $F(\%)$ of semi-charcoal composite pellet at $T_{C, \max} = 823$ K was over 40 % for 60 min and was also higher than any other pellets at $T_R = 1173$ K.
- (4) When $T_{C, \max}$ was lower, namely the pellet had more residual V.M., the reduction of iron oxide was more accelerated at $T_R = 1073$ and 1173 K.
- (5) Fractional reductions $F(\%)$ of semi-charcoal composite pellets at ($T_{C, \max} = 823, 1073$ and 1273 K) were over 90 % for 60 min at $T_R = 1273$ K. The reducibility of semi-charcoal composite pellets was high and did not depend on residual V.M. over 1273 K.
- (6) Fractional reduction $F(\%)$ of semi-charcoal composite pellet at $T_{C, \max} = 1073$ K using semi-charcoal particle with the size of 23~35 μm was 38 % for 60 min at $T_R = 1173$ and over 90 % for 40 min at $T_R = 1273$ K, respectively, and was higher than any other pellets.
- (7) When the size of semi-charcoal particle was smaller, the reduction of iron oxide was much enhanced at $T_R = 1173$ and 1273 K.

Acknowledgement

This work was supported by research promotion fund for iron and steel from the Iron and Steel Institute of Japan.

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