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# Production of iron/carbon composite from low rank coal as a recycle material for steel industry

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## Abstract

Utilization of low rank coal is indispensable to qualify the future demand of energy. Low rank coal, however, has several disadvantages such as small calorific value, so we should develop a new technology of using effectively it. On the other hand, as for the steel manufacturing process, we must think about an effective utilization of iron sludge and scrap from the standpoint of recycle. In this paper, we presented a new method to produce an iron/carbon material by utilizing a large amount of functional groups in low rank coal which can be used as an iron recycling media to revolving furnaces. The method is as follows: The low rank coal was oxidized for 2 h at 70 °C by nitric acid to introduce a large amount of carboxyl functional group and was impregnated by $FeCl_3$. Through pyrolyzing the Fe-impregnated coal pure iron crystal/carbon composite was successfully produced above 760 °C. As an option, $Fe_2O_3$ or $Fe_3O_4$/carbon composite was also successfully produced by the oxidation or gasification of it at low temperature. The irons in these composites were reduced by carbon with evolving CO and $CO_2$ at high temperature. Thus, it is clarified that the proposed method is attractive for producing a recycle material for the iron melting furnace prior to revolving furnaces from waste iron using low rank coal.

*Keywords:* Low rank coal; Iron and carbon composite; Recycling iron material

## 1. Introduction

Recently, construction of a sustainable society based on recycle technology has been stressed in a worldwide. In general, utilization of natural energies such as solar, biomass, etc. is believed to overcome the issues of energy resources and environment. These energies have to be used by an advanced technology, however, the amounts supplied is too small. To develop the society of human being in the 21st century, the fossil energy will be used efficiently with environmental protections. On the other hand, stable supply of bulk materials is also important to keep an industrial society. Iron is the most popular and indispensable product to support our life. To achieve a sustainable development in the steel industry, two problems about iron making will be qualified: one is a reasonable management for the variety of resources in the steel-making process having no blast furnace including a shortage of bituminous coal, and the other is a difficulty of scrap recycling containing trace elements such as copper. Under these situations, utilization of low rank coal is also indispensable to qualify the future demand of energy. Low rank coal, however, has several disadvantages such as small calorific value, so we should develop a new technology of using effectively it. On the other hand, we must think about an effective utilization of iron sludge and scrap in steel making processes.

For steel making, the utilization of iron carbide has been studied as an alternative source of virgin iron to dilute large amounts of scrap [1–5]. An advanced co-production process by the steam gasification of iron carbide has been proposed to achieve an environmentally benign energy and material production technology [6]. The reaction of iron carbide with steam is very attractive to produce pure iron and hydrogen simultaneously. It was reported that 94% of carbon

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conversion and 80% of pure Fe was successfully obtained by the gasification of iron carbide with 10% of steam at 1100 K under a rapid heating [7]. Thus, iron carbide is expected to be an active material for the co-production, but the pure resources such as methane should be required. Focusing the recycle of waste iron and a feedstock for iron melting process prior to revolving furnace, it is desired to produce an alternative carbon/iron complex expect for iron carbide. Otsuka et al. [8–10] prepared to the low rank coal exchanged by $FeCl_3$, and found that the iron/carbon compound was formed during pyrolysis. The result gives an instructive suggestion that ion-exchanged Fe was converted into iron/carbon complex through the decomposition of functional groups of low rank coal. However, the amount of Fe impregnated was small because of the limitation of both the amount of carboxyl functional groups and the hydrophobic property of aromatics portion in coal. The increase in the amount of Fe impregnated is necessary to utilize the material for bulk iron/carbon composite.

We have presented a new treatment method by nitric acid [11,12]. Through the pretreatment much carboxyl groups were introduced at the rate of 4 mol of COOH per 1 mol of aromatic ring, and the hydrophilic property significantly increased. From this viewpoint, we proposed a new method to produce iron/carbon composite which was combined low rank coal as a carbon resource with $FeCl_3$ as a dissolved scrap and sludge with waste acids. We impregnated a large amount of $FeCl_3$ in the brown coal pretreated in nitric acid, and tried to prepare an iron/carbon composite through the pyrolysis of the oxidized brown coal impregnated $FeCl_3$. The pre-gasification with air or steam prior to the pyrolysis was also conducted to prepare various types of iron/carbon composites. By examining the change in the weight, gas formation, and the form of iron during the pyrolysis of the prepared samples, the validity of the proposed method for a recovery of pure iron was clarified.

## 2. Experimental

### 2.1. Samples

### 2.1.1. Preparation of the oxidized coal by nitric acid

An Australian brown coal (Morwell, MW) was used as a raw coal. The coal was ground into fine particles of less than 74 μm, and dried in vacuo at 343 K for 24 h prior to use. The oxidation of the coal was performed as follows: 20 ml of aqueous 4 mol/l nitric acid was added to 1 g of coal, and then the mixture was stirred for 4 h at 70 °C. This oxidized coal is abbreviated to NO. The oxidized coals were dried in vacuo at 60 °C for 24 h prior to use. Table 1 lists the ultimate analyses of the raw coal and NO.

Table 1
Ultimate analysis of raw coal and oxidized coal for MW (wt% daf)

| | C | H | N | O |
|---|---|---|---|---|
| Raw coal | 67.1 | 5.1 | 0.7 | 27.1 |
| NO | 54.2 | 3.7 | 4.5 | 37.6 |

### 2.1.2. Preparation of iron impregnated coal

First, 1 g of NO is mixed to 30 ml of 3.35 M $FeCl_3$ aqueous solution were mixed and heated in a water bath kept at 80 °C. After retaining for 5 or 6 h in the bath, the sample was filtrated with adding distilled water, and finally the sample was dried in a vacuo for 5–6 h. Thus prepared sample, NO impregnated $FeCl_3$, is abbreviated to NO-IE. The NO ion-exchanged by 1 M NaOH aqueous solution was also prepared, and then the coal impregnated $FeCl_3$ was prepared in the same manner. This sample is abbreviated to NO-IE (NaOH). Next, in order to change the ratio of iron to carbon and the form of iron compound, the sample, NO-A, which gasified NO-IE at 350 and 400 °C with air for 10–15 min, and the sample, NO-S, gasified at 700 °C with the steam for 10 min were prepared, respectively.

### 2.1.3. Production of iron/carbon composites through pyrolysis

The oxidized coal and the iron-impregnated coals were pyrolyzed in a helium gas using a thermogravimetric analyzer (Shimadzu Co. Ltd, TG50) directly connected to a mass spectrometer (Shimadzu Co. Ltd, QP5000). About 40 mg of samples were heated from 110 to 1200 °C at the rate of 20 K/min, and several kinds of iron/carbon composites were prepared by changing a final temperature. At that time, the weight change and the formation rates of gases (CO, $CO_2$, $H_2O$, $CH_4$, and Cl) were measured continuously. The product yield of each component during the pyrolysis was represented based on dry and ash free (daf) sample. Ultimate analyses of the samples and their pyrolyzed chars were measured using a CHN analyzer (Yanaco, MT-6). The forms of iron in the iron/carbon composites were also identified from XRD patterns measured using an X-ray diffractometer (Shimadzu Ltd, XD-610).

## 3. Results and discussion

### 3.1. Pyrolysis of the coal impregnated $FeCl_3$

Fig. 1 shows the weight change and the accumulated amounts of gases evolved during the heating of each sample at rate of 20 K/min under nitrogen atmosphere, where X is defined by the weight change per daf sample basis including Cl. The oxidized brown coal by nitric acid (NO) decomposed gradually into inorganic gases up to ca 700 °C as shown in Fig. 1(a). The tar formation suppressed as compared with that of raw coal [12]. The oxidation by nitric acid introduces many hydrogen bonds by carboxyl groups in the brown coal. This causes the decomposition of them between carboxyl groups into ester, resulting in the evolution of much inorganic gas at