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Utilization of waste wood as charcoal absorbent of exhausted gas in iron and steelmaking process.

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A purification system of exhausted gas from refining furnace in iron and steelmaking process is proposed for utilization of waste wood as a charcoal absorbent. This system could solve the problems of both the treatment of heavy metals contained in waste wood and dioxins in the exhausted gas.

The effect of temperature, atmosphere and holding time on the specific surface area and pore size distribution of a charcoal carbonized from Cryptmeria is examined, in order to clarify the carbonization conditions for the charcoal absorbent. The obtained results are as follows. The specific surface area has a maximum at 1073K of carbonizing temperature in N_2+O_2 atmosphere. The high oxygen concentration in carbonizing atmosphere and the long holding time cause the increase of the specific area of the charcoal. The maximum specific surface area of the charcoal in this experiment is $582m^2/g$ which is about 74% of that of commercial activated carbon. The specific surface area is proportional to the reaction ratio between carbon in the charcoal and oxygen in atmosphere. The specific surface area, which is related to the absorption capacity, can be controlled by the reaction ratio.

Key word : waste wood, carbonizing, absorbent, charcoal, exhaust gas treatment.

1. INTRODUCTION

Huge amount of wood material was wasted annually in Japan. The amount[1)] in 1991 was reached 36 million m^3. About 90% of them was incinerated or reclaimed. About 74% of the waste wood came from destroyed houses. Such kind of waste wood contains Copper, Chromium and Arsenic in its as CCA treatment for wood preservation. When they are incinerated or reclaimed, environmental problems will be occurred[2)], such as exhausting Arsenic contained gas and Chromium and Copper contained ash by the incineration, and flowing out of Chromium, Copper and Arsenic contained water from the landfill. Many method[2)] for waste wood treatment have been investigated for solving these problems.

On the other hand, there are many investigations for utilization of wood as microporous carbon such as absorbent[3,4,5)]. Investigators have paid much attention to the utilization of waste wood as charcoal absorbent of exhausted gas in iron and steelmaking process[6)] as shown in Fig.1.

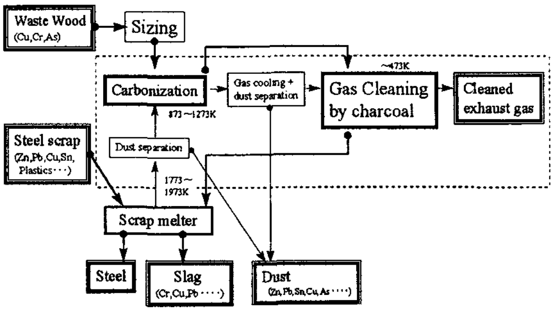

Fig.1 Cleaning system of exhaust gas from iron scrap melter with charcoal from waste wood.

Steel scrap is needed to be used more in the steelmaking industry. The scrap contains plastics, paints and oils, which might produce dioxins during melting the scrap. Although activated carbon is the possible material to remove the dioxins from exhausted gas, it takes high cost. When the charcoal from waste wood can be used as the absorbent instead of activated carbon, it might reduce the cost. Furthermore, the heavy metals, such as Arsenic, Chromium and Copper, from waste wood can be recovered as dust or stabilized into slag in the steel making process. It reduces environmental load.

In this study, the effect of temperature, atmosphere and holding time on the properties of charcoal such as specific surface area and pore size distribution are investigated for producing charcoal absorbent from waste wood in single process under gas flowing condition.

2. EXPERIMENTAL

2.1 Experimental apparatus and material

Figure 2 shows the schematic diagram of the experimental apparatus which is TG-7000VHT produced by ULVAC(SINKU-RIKO).

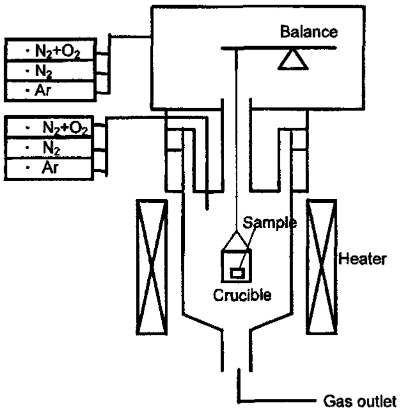

Fig.2 Schematic diagram of experimental Apparatus

This apparatus measures the change in weight of a sample with controlling the temperature and the atmosphere.

Investigators have paid attention to Cryptmeria which is produced most as wood material in Japan. The sample is 10mm cube from air dried Cryptmeria. The ratio of the contained water is 13.1% by the absolute dried method.

2.2 Experimental method

3 species of the samples were placed in a alumina crucible after measuring its weight. The crucible was hung on a balance, then the gas (N_2 or N_2+O_2) was introduced to control the atmosphere of the samples. The samples were heated to a temperature with 100K/min in order to carbonizing. They were kept at the temperature for a period, then they were cooled rapidly to the room temperature. The weight of the carbonized samples (charcoal) was measured just after the cooling. The experimental conditions, such as the carbonizing temperature, the atmosphere and the holding time, are listed in Table I.

Table I Experimental Conditions.

Atmosphere	Temperature (K)	Holding time
N_2	673 - 1273	10 min - 10 hr
N_2+O_2:0.1%	673 - 1273	10 min - 10 hr
N_2+O_2:1%	673 - 1273	10 min - 5 hr
N_2+O_2:10%	1073	10 min

The gas flow rate was 1000cm^3/min. not to be interfered by volatile gas during carbonizing of wood. The inner volume of the apparatus is about 900cm^3. N_2 and N_2+O_2(1% and 20%) was mixed to control the gas composition. The purity of the N_2 and N_2+O_2 gas was more then 99.99%. The oxygen concentration of N_2 gas is less than 10 ppm.

Specific surface area, pore size distribution, pore volume and mean pore diameter were measured for the obtained charcoal. The specific surface area was measured with Shimadzu Frosorb II-2300 based on the adsorption isotherm of N_2 gas(BET 1point method[7]). The sample was cut under 3mm before the measurement. Macro pore size distribution(180μm-3mm), pore volume and mean pore diameter were determined by mercury intrusion porosimetry (Shimadzu model AUTOPORE 9200).

3. RESULTS AND DISCUSSION

3.1 Effect of temperature on specific surface area and pore size distribution

Figure 3 shows the relationship between the carbonizing temperature and the specific surface area. The specific surface area of the charcoals which was carbonized in N_2 atmosphere is increasing to 873K of carbonizing temperature, then decreases. The specific surface area of the charcoals which was carbonized in N_2+O_2 atmosphere is increasing to 1073K of carbonizing temperature, then decreases. The tendency of the effect of temperature on specific surface area is agree with the results by I. Abe et al[8], that is the maximum absorption capacity, which is related to the specific surface area, of the charcoals from Chamaecyparis and Nara oak for benzene at carbonization temperature of 1123K.

The pore size distribution of the charcoals is shown in Fig. 4. This figure indicates that the diameter of macro pore of 0.5 - 5.0 μm decreases with increasing of carbonizing temperature. The pore volume decreases with increasing of temperature from 873K to 1273K, as shown in Fig.5. The decrease of the specific surface area in higher temperature is caused by the thermal shrinkage. In lower temperature, the reason of lower specific surface area is considered to be insufficient progress in carbonization.

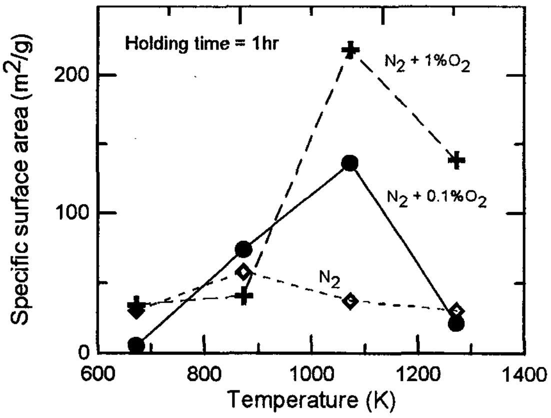

Fig.3 Effect of carbonization temperature on specific surface area of charcoals.

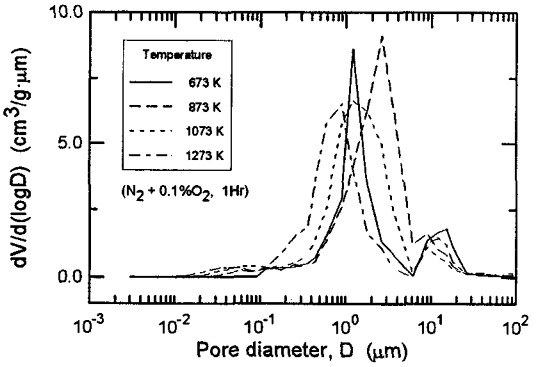

Fig.4 Pore size distribution of charcoals.

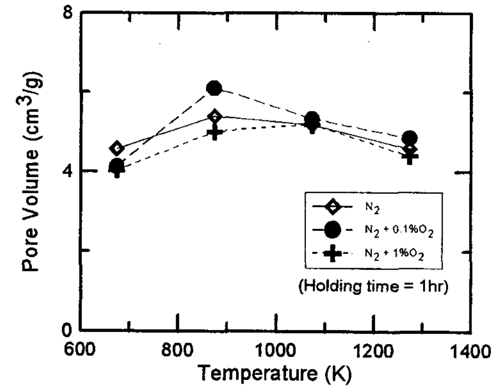

Fig.5 Effect of carbonization temperature on pore volume.

3.2 Effect of carbonization atmosphere and holding time

The carbonization of the samples was carried out in N_2+O_2 (0 - 10%) atmosphere at 1073K for 10, 60 and 300 minute. Figure 6 shows the effect of oxygen concentration in the atmosphere on the specific surface area of the charcoals. Figure 6 indicates that the specific surface area increases with increase of oxygen concentration and increase of holding time.

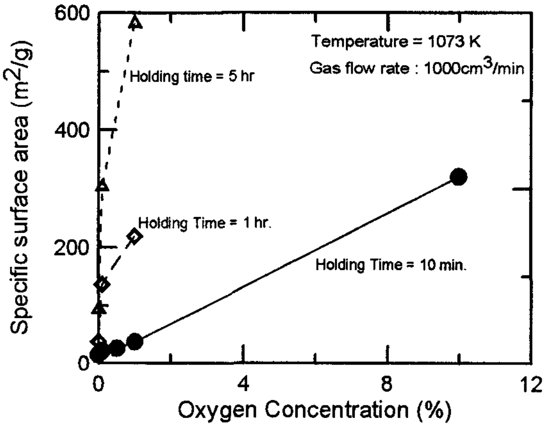

Fig. 6 Effect of oxygen concentration on the specific surface area of charcoals.

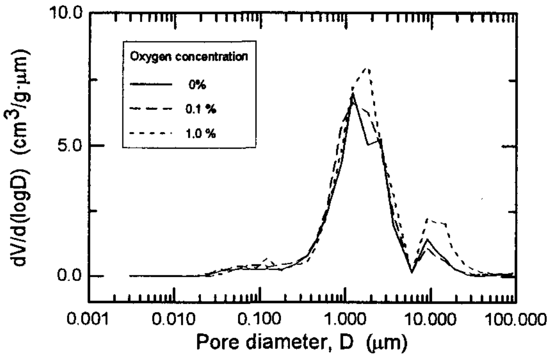

Fig.7 Pore size distribution of charcoals.
(Holding time : 1 hr, Holding temperature : 1073K, Gas flow rate : 1000cm³/min)

The pore size distribution is shown in Fig. 7. The pore size distribution of the macro pore seems to be independent on the oxygen concentration. The increase of the specific surface area can be due to growth micro or mezzo pore. Oxygen in atmosphere can activate charcoal(carbon) and produce micro and mezzo pore by the reaction (1),(2),(3).

$$C + O_2 = CO_2 \qquad \text{----(1)}$$

$$2C + O_2 = 2CO \qquad \text{----(2)}$$

$$C + CO_2 = 2CO \qquad \text{----(3)}$$

The charcoals carbonized in N_2 atmosphere have very low specific surface area as shown in Fig. 3. This is attributed to less reaction with oxygen which activates carbon and insufficient growth of micro and mezzo pore. N_2 gas was flowed with enough rate to exhaust water and volatiled substance from wood during its carbonization.

Oxygen has much effect on enlargement of the specific surface area of charcoals. However, the yield of charcoals decreases with increase of both oxygen concentration in atmosphere and holding time as shown in Fig. 8. Thus excess the oxygen concentration and holding time must decrease the yield of charcoals unnecessarily.

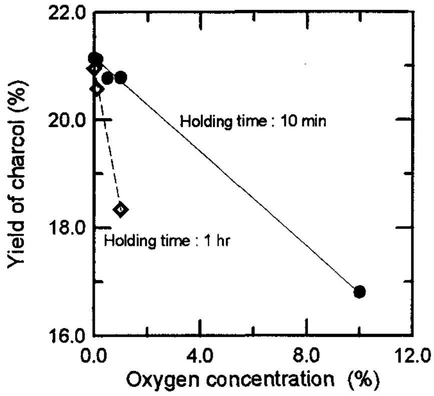

Fig.8 Relationship between oxygen concentration in carbonizing atmosphere and yield of charcoals.
(Holding temperature : 1073K, Gas flow rate : 1000cm³/min)

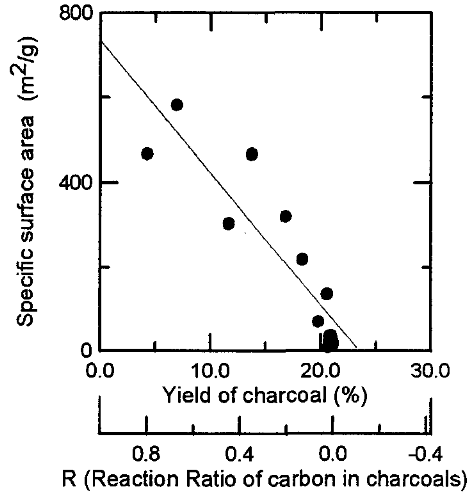

Fig.9 Relationship between the yield and the specific surface area of charcoals.
(Holding temperature : 1073K, Gas flow rate : 1000cm³/min)

Figure 9 shows the relationship between the yield and the specific surface area. We assume that 21% of the yield is the yield of the charcoal without any reaction with oxygen and charcoal. Less than 21% of the yield means that carbon in the charcoal react with oxygen. The reaction ratio of the carbon with oxygen, R, is expressed in eq.(4)

$$R = (21 - Xy) / 21 \qquad \text{----(4)}$$

where Xy is the yield of the charcoal.

The reaction ratio R is indicated in x axis in Fig. 9. R has liner relationship with the specific surface area well. Thus the specific surface area can be estimated with the reaction ratio of the carbon by controlling oxygen concentration and reaction time. Equation (5) is obtained for relationship between the reaction ratio, R, and the specific surface area, S_A, by the method of least squares.

$$S_A = 661 \cdot R + 74.4 \qquad \text{----(5)}$$

3.3 Effect of carbonization time on thermal shrinkage

Carbonization was carried out in N_2 atmosphere at 1073K, in order to estimate the effect of carbonization time on the thermal shrinkage. The specific surface area is shown in Fig. 10. Figure 11 shows the pore size distribution of macro pore.

The specific surface area increases and the yield of the charcoals decreases gradually with increasing the carbonization time as shown in Fig.10. However, the pore size distribution seems not to change with the time as shown in Fig. 11, except 10 minute carbonization. 10 minute is insufficient for carbonization. No thermal shrinkage is seems to be occurred with increase of holding time. The carbonization can proceed with time, then micro and mezzo pore could growth gradually. Future investigation of micro and mezzo pore distribution is needed to clarify these phenomena.

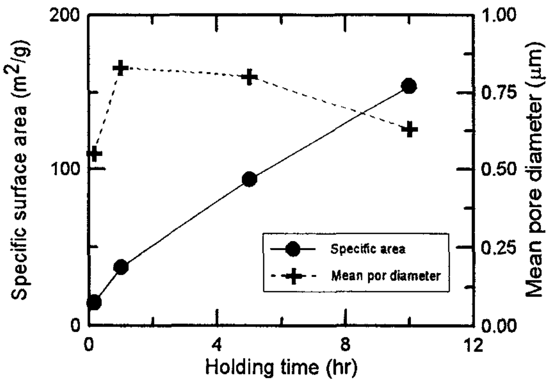

Fig.10 Effect of carbonization time on specific surface area and mean pore diameter of charcoals.
(Holding Temperature = 1073K, N_2:100%)

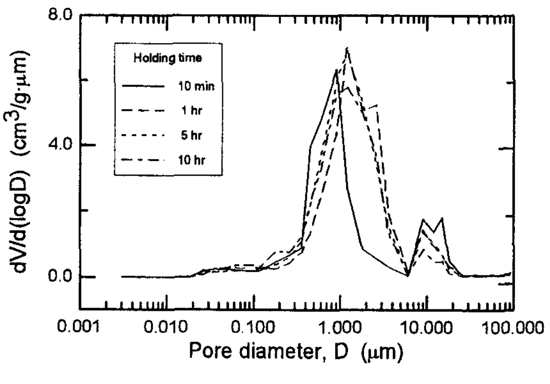

Fig. 11 Pore size distribution of charcoals.
(Holding Temperature = 1073K, N_2:100%)

3.4 Comparison of the charcoals with activated carbon.

We measured the specific surface area, the pore size distribution, the pore volume and the mean pore diameter for an activated carbon on the market with the same method for the charcoal samples obtained. The results are listed in Table II. Comparing the results, the maximum specific surface area of the charcoals obtained is 582 m^2/g which is about 74% of that of the activated carbon.

Table II Specific surface area, pore volume and mean pore diameter of activated carbon.

Specific surface area (m^2/g)	Pore volume (cm^3/g)	Mean pore diameter (μm)
785.7	0.33	0.025

4. CONCLUSIONS

A purification system of exhausted gas from refining furnace in iron and steelmaking process is proposed for utilization of waste wood as a charcoal absorbent. The effect of temperature, atmosphere and holding time on the specific surface area and pore size distribution of a charcoal carbonized from Cryptmeria is examined, in order to clarify the carbonization conditions for the charcoal absorbent. The obtained results are as follows.

(1) The specific surface area of the charcoal carbonized in N_2+O_2 and N_2 atmosphere has a peak at the carbonizing temperature of 1073K and 873K respectively. The reason of this tendency is considered to be insufficient carbonization at low temperature and thermal shrinkage of the charcoal at high temperature from the results of the pore size distribution.

(2) The high oxygen concentration in carbonizing atmosphere causes the increase of the specific area of the charcoal. The oxygen is considered to activate and produce micro and mezzo pore of the charcoals.

(3) The good linear relationship between the specific area of charcoals and the reaction ratio of carbon with oxygen during carbonization is obtained.

(4) The maximum specific area of the charcoal in this experiment is 582 m^2/g which is about a 74% of that of commercial activated carbon.

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