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Effect of mineral matter on structure and dielectric properties of chars

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ABSTRACT

The study was undertaken to investigate the changes of mineral matters in coal during heat treatment and its effect on structure and dielectric properties of generated chars. An acid treatment method was adopted to remove mineral matters in coal for preparing chars at 850–1600 °C using an electric furnace. Dielectric properties of coal chars were determined with the transmission/reflection method. Also, phase structure of coal chars was examined by X-ray diffraction (XRD). Significant transformation was found in the presence of mineral matters during heat treatment. Especially the process of creating silicon carbide (SiC) above 1300 °C in carbothermal reduction played a catalytic role on char structure. Consequently, dielectric properties were improved with the increase of structural ordering. These results could be instructive for the application of mineral matters in microwave technique at higher temperatures.

1. Introduction

Microwave has been a normal technique widely used for coal processing and comprehensive utilization, such as coal grindability, desulfurization, pyrolysis and measurement for the residual carbon content in combustion products [1–5]. These applications are based on microwave absorbing properties of the compositions of coal, including organic matters and mineral matters. In particular, some metal oxides like cupric oxide and ferriferous oxide etc., important components in mineral matters, have been clarified effective to assist heating or pyrolysis owing to the ability of absorbing microwave [6,7].

Mineral matters in coal were found to play important roles on coal combustion or gasification [8–10]. Moreover, In the process of heat treatment, the changes and chemical reactions among mineral matters could accelerate or hinder structural evolution of coal chars [11–13]. Hence one can see that mineral transformation should affect the microwave attenuation under various conditions. However, the effect of mineral matter seemed not to be considered, although Peng et al. [14] and Binner et al. [15] have shown microwave absorption capability of coal during pyrolysis below 900 °C. Furthermore, few researches have been done on the effect of mineral matter on microwave absorption over 1000 °C, as the changes of mineral matters and the effects at higher temperatures could markedly differ from those at relative low temperatures.

In this paper, an acid treatment method was introduced to remove mineral matters in a selected coal. The transformation of mineral matter was examined with X-ray diffraction, from comparison of chars produced from coals before and after demineralization. Dielectric properties, evaluating the action of coal char on microwave, were measured with the transmission/reflection method. The effect of mineral matter on dielectric properties was discussed. The results could expand applications of mineral matters in coal utilization referring to microwave treatment.

2. Experimental

2.1. Sample properties and char preparation

A bituminous coal from Shanxi Province in Northeast China was selected for this study. The proximate analysis and ultimate analysis, chemical compositions of coal ash were listed in Table 1 and Table 2, respectively.

Acid treatment has been adopted as a common method for the effect of mineral matter in many studies [10,16]. What's more, the process of acid treatment was considered to take negligible effect on crystal structure of coal or coal char [17]. Here an acid treatment method was also carried out to understand the effect of mineral matter. The procedure was as follows: 10 g coal samples were weighed out from raw coal ground through a 200 mesh sieve and put into a 150 ml plastic beaker with 6 M hydrochloric acid (HCl). The slurry was stirred for 12 h at the environmental temperature of 60 °C, which was built in a thermostatic water bath. Afterwards, 100 ml of 4 M hydrofluoric acid (HF) was injected into the plastic beaker and stirred for another 12 h. Then 100 ml of 6 M HF was added to the solution for next 12 h. After the

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Table 1
Proximate and ultimate analyses of raw coal (wt%, db).

Proximate analysis (%, dry basis)			Ultimate analysis (%, dry basis)				
Ash	Volatile	Fixed carbon	C	H	N	S	O
12.27	34.45	53.28	71.46	3.96	0.96	0.26	11.09

Table 2
Chemical composition of coal ash (wt%).

Ash component (%)									
SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	TiO_2	K_2O	Na_2O	P_2O_5
43.6	14.58	13.26	18.82	2.5	4.53	0.62	1.12	0.51	0.46

reaction, the acid washed coal was filtered with deionized water from unreacted excess acid mixtures, until no chloride or fluoride ion was detected. Demineralized coal was finally obtained after drying at 50 °C in a vacuum oven for 6 h. The ash content in demineralized coal reached below 1%.

After acid treatment, an electric furnace was utilized to produce coal char by fast heating mode. The temperature in electric furnace was firstly controlled to rise from room temperature with a heating rate of 10 °C min^{-1}. The tube reactor was preheated to the set temperature (850–1600 °C). Then about 2 g coal samples were put into the constant temperature zone quickly and held for 10 min in nitrogen atmosphere. After that, char samples were got out for rapid cooling in nitrogen flow. Both raw coal and demineralized coal were subject to heat treatment between 850 °C and 1600 °C with an interval of 150 °C.

2.2. Dielectric property measurement

The interaction between dielectric material and microwave comes down to the relative dielectric permittivity, which is the primary index and often given in the plural form (formula (1)) owing to the alternating electromagnetic field in microwave:

$$\varepsilon_r = \varepsilon'_r - j\varepsilon''_r \tag{1}$$

Where ε_r', the real part of complex permittivity represents stored energy in the dielectric body, while ε_r'', the imaginary part of the complex permittivity symbolizes microwave energy consumption by dielectric loss, and j is the imaginary unit. In addition, the dielectric loss tangent $\tan\delta_e$ is also an important index for evaluating microwave property, which is from the relationship between the imaginary part and the real part of complex permittivity and expresses the rapidity of energy loss per period:

$$\tan\delta_e = \frac{\varepsilon''_r}{\varepsilon'_r} \tag{2}$$

Overall, the influence of dielectric material on microwave energy can be intuitively described from dielectric properties (ε_r', ε_r'', $\tan\delta_e$) to a large extent.

In order to investigate dielectric properties of coal char, a vector network analyzer (Model 5244A, Agilent, USA) was applied to measure ε_r' and ε_r'' on the basis of Nicholson-Ross-Weir (NRW) transmission/reflection method. Coal sample was introduced into paraffin wax matrix to mold a cylindrical die with 7.00 mm outer diameter, 3.04 mm inner diameter and 2.00 mm height. Then a text fixture containing the cylindrical die was connected to coaxial cables for building transmission network. The mixing ratio of char sample with paraffin wax is a vital ingredient for the comparison of dielectric parameters of chars, due to different mineral contents of chars. Whereas carbon is suggested to perform much more dielectric loss relative to mineral matters in chars. So, the amount of char samples was adjusted to a same carbon level in the coaxial test fixture for each measurement, which was assigned in a 2:3 ratio. No matter how changes the mineral contents, we keep the same mass carbon for test. The changes of microwave signals within transmission cables, owing to storage and loss from char sample in the cylindrical die, would be monitored and processed for ε_r' and ε_r'' by vector network analyzer. The $\tan\delta_e$ value was then derived from formula (2). Dielectric properties of coal char were acquired in 2–18 GHz frequency range.

2.3. XRD technique

As a conventional technique in the research field of crystallography, X-ray diffraction (XRD) has been utilized for coal and relevant carbonaceous materials [16,17], which was also employed in this study for analysis of crystalline structure and mineral transformation in coal char. A small amount of char powder was first compressed on a slide glass, and then placed in X-ray diffractometer (Model XRD-6000, Shimadzu, Japan), which was operated at omega/2theta (2θ-ω) linkage symmetric scanning. The copper target was bombarded by high-velocity electrons at 40 kV and 30 mA, and the induced X-ray source of Kα1 was used to radiate char sample in a step scan mode with 0.2° $step^{-1}$ over the angular 2θ range of 5-65°. XRD profiles were manipulated with an accessory software package for further evaluation of char structure and mineral transformation.

3. Result and discussion

3.1. Dielectric properties of coal char

Fig. 1 shows dielectric properties (ε_r', ε_r'', $\tan\delta_e$) of chars generated at 850 °C, 1300 °C and 1600 °C from raw coal and demineralized coal. From Fig. 1a, it can be seen that ε_r' for 850 °C char remain relatively stable over the whole frequency range, while the values for raw coal char are larger than those for demineralized coal char at the same frequency, but the curves of ε_r'' and $\tan\delta_e$ for two coal chars are very close to each other. As for 1300 °C, the differences of dielectric properties between coal char from two different ways become dramatized. The values of ε_r', ε_r'' and $\tan\delta_e$ for raw coal chars are clearly greater than those for demineralized coal chars under the same conditions, except ε_r' values over 15 GHz, as shown in Fig. 1b. Meanwhile, these curves evidently perform gradual reduction for dielectric properties along measuring frequency, in comparison with those for chars at 850 °C. Dielectric properties of raw coal char and demineralized coal char at 1600 °C in Fig. 1c show a similar relationship, supporting the behaviors in Fig. 1b.

With an increase in frequency, the phenomenon that dielectric properties gradually decrease conforms to dielectric relaxation and polarization behavior exhibited by solid media [18,19]. From this point on, coal char generated at higher temperature shows the trend toward developing typical and uniform dielectric. Moreover, mineral matters in raw coal were testified to boost dielectric properties of the generated char, as shown in Fig. 1. In other words, the presence of mineral matter indeed plays a significant role during heat treatment on dielectric properties of coal char. Dielectric properties of typical material have been revealed to link with structure characteristic, so raw coal char and demineralized coal char would be next inspected for structural changes and the related effect of mineral matter.

3.2. Char structure and mineral transformation

XRD profiles of chars generated from raw coal and demineralized coal are shown in Fig. 2. The evolutions of carbon and mineral matter, the basic two potions in coal, can be found in Fig. 2a. As temperature increases from 850 to 1600 °C, the peak profile corresponding to 002 lattice planes in graphite crystal tends to become shaper and higher, and the peak central line shifts to a position with a larger diffraction