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Structural order and dielectric properties of coal chars

Liang Xu, Haiyu Liu *, Yan Jin, Baoguo Fan, Xiaolei Qiao, Bo Jing

College of Electrical and Power Engineering, Taiyuan University of Technology, Taiyuan 030024, China

HIGHLIGHTS

- This work investigated structure changes and dielectric properties of coal chars.
- The crystallite array of coal chars was more ordered with increasing temperature.
- The complex permittivity of coal chars depended on treatment temperature.
- The crystallite structure was responsible for dielectric properties of coal chars.

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ABSTRACT

For studying the influence of the structural evolution on the dielectric properties, X-ray diffraction and Raman spectroscopy were used to examine the phase and the degree of crystallite structure of coal chars prepared in the temperature range of 850–1600 °C. Additionally, structural changes were visualized by high-resolution transmission electron microscopy. The dielectric properties were measured in the 2–18 GHz frequency range using the transmission/reflection method. Generally, the fraction of carbon ordering of coal chars increased, while more parallel-aligned aromatic layers were presented, confirming that the crystallite structure of coal chars became ordered with increasing temperature. The dielectric properties of chars were found strongly dependent on heat-treatment temperature. Increasing temperature could produce higher values of the real part and imaginary part of the complex permittivity. Although mineral matters in coal chars were also observed to transform during heat treatment, the conversion of inorganic matters might have a marginal effect on the complex permittivity. As a result, it is reasonable to conclude that the dielectric properties primarily result from the crystallite structure of coal chars. Furthermore, the dielectric loss may contribute much more than the magnetic loss to the further application of microwave technology.

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1. Introduction

Carbon content in fly ash is a major concern for combustion efficiency of a coal-fired boiler in the power plant. High unburned carbon levels mean poor combustion and cause substantial loss of energy. Real-time monitoring enables carbon content of fly ash to be kept at a reasonable level to improve economic efficiency. Based on much stronger microwave absorption of carbon than other oxides (e.g., SiO_2, Al_2O_3, Fe_2O_3, CaO, MgO) in fly ash, microwave technique [1–5] has great application potentials for on-line determination of unburned carbon in fly ash. Since unburned carbon is produced from coal particles of incomplete combustion, coal char undergoes a complex succession of physicochemical evolution during the combustion process [6–10], which governs the degree of char burnout and carbon structure [11–17]. In circulating fluidized bed boilers the temperature of coal combustion is controlled at 850–950 °C for deep desulfurization, while coal combustion is performed in the temperature range of approximately 1200–1600 °C in most pulverized coal utility boilers. The formation of coal chars with a variety of crystallite is dominated by heat conditions in boilers.

It is well known that coal consists of crystallite phases that are randomly arranged, called turbostratic structure. The evolution of coal char structure properties has been extensively studied not only in combustion but also in pyrolysis and gasification processes [10,18–23]. Hurt and co-workers [12,24] previously compared the evolution of char structure between laboratory-prepared chars and residual carbon from pulverized-coal combustion. Residual unburned chars had been found a high degree of crystallinity than laboratory-prepared chars. Although the growth of regions of turbostratic order developed even in such a short combustion time

* Corresponding author. Tel.: +86 13466871287.
E-mail address: liuhaiyu@tyut.edu.cn (H. Liu).

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of 100 ms, true graphitization was not observed under peak temperature of 1527 °C in their experiments. Feng et al. [25] found that the increase of heat treatment time and temperature improved the fraction of the organized carbon of Australian coal chars but nearly did not change the carbon crystallite size at 850–1150 °C, in agreement with the study of Davis et al. [24]. Meanwhile, the organized carbon structure of ash-free coal chars kept unchanged, which was the result of the loss of catalytic action from the inorganic matter in the coal chars. Emmerich [26] found that the coalescence increase of the crystallites along the *a*-axis and the *c*-axis was depend on the temperature range and the carbon used. The coalescence increase dominated after 1350 °C for the graphitizable chars compared with non-graphitizable chars until 2500 °C. Through microscopic structure of chars pyrolyzed at 400–1500 °C by Yoshizawa et al. [27], the average number of stacking layers per stack had been found maximize around 800 °C, which exhibited the influence of swelling on the char structure. Thus, it can be seen from the above discussion that the growth of regions of carbon structure appears to occur during heat treatment. But the inconformity between different studies also presents the evidence that the evolution of crystallite structure is depend on the specific process of heat treatment, as well as the behavior of inorganic matter in coal chars [25,28,29].

Anyway, the crystallite structure of coal chars varies during combustion and pyrolysis, and its changes may have notable effects on the electromagnetic parameters of resultant carbon, which further leads to the performance of reliability of microwave measurement. The changes in the dielectric properties are essential and highly necessary for the microwave application. However, very few researches have been reported involved in the influence of structural ordering of coal chars on the dielectric properties.

Herein, in the present work, coal chars were prepared at different temperatures, covering the main heat-treatment range of pulverized coal combustion. For investigating the dielectric properties of coal chars, electromagnetic parameters including the complex permittivity and the complex permeability, were measured by the transmission/reflection method. The crystallite structure of coal chars was characterized by X-ray diffraction (XRD) technique. Raman spectroscopy (RS) analysis was additionally performed to reveal the degree of carbon ordering. The technique of high-resolution transmission electron microscopy (HRTEM) was also employed to provide supporting evidence through visualization of structural changes.

2. Experimental procedure

2.1. Raw coal and preparation of coal char samples

Pulverized coal originating from a utility boiler was selected for this investigation. Proximate analysis and ultimate analysis of the raw material are presented in Table 1. Table 2 summarizes the chemical composition of coal ash.

Coal chars were prepared at various temperatures by a horizontal tube furnace. The furnace reactor was electrically preheated at a heating rate of 10 °C/min to the temperature range of 850–1600 °C. About 2 g coal powder was spread uniformly in an alundum copple and then pushed into the center of the heated tube. After held at the desired temperature for 60 min, the coal in the copple was freely cooled to room temperature and char samples were collected for the following tests. The entire process was strictly performed under a nitrogen atmosphere.

2.2. XRD analysis

A shimadzu diffractometer, model XRD-6000, was applied to record X-ray intensity scattered from char samples and to determine the phase and crystal structure of coal chars. Cu Ka radiation (40 kV, 30 mA) was used as the X-ray source. Char samples were scanned in a velocity of 8° per minute and a step size of 0.2°, over the 2theta angular range of 5–65°.

2.3. RS technique

The Raman spectrum of char samples was acquired by Renishaw confocal microprobe Raman spectroscopy (inVia). A high-power pulsed argon ion laser was used as the excitation light source with a laser beam of 514 nm exciting line, corresponding to the grating of 1800 line/mm. The laser power at the sample surface was controlled at about 2 mW. The spectrum was recorded in the range of 800–2000 cm^{-1}.

2.4. HRTEM observation

High-resolution transmission electron microscopy (HRTEM) images of char samples were captured using a JEM-2100F (JEOL) field emission transmission electron microscopy operated at an accelerating voltage of 200 kV. Before examination, the dispersions and dilution of sample were carried out with ethanol, treated with ultrasonic waves at ambient temperature for 15 min, and then dried onto copper grids for preparation.

2.5. Dielectric properties

The dielectric properties of coal chars were probed on the basis of the coaxial transmission/reflection line theory. Char samples were uniformly mixed with dissolved paraffin at a weight ratio of 1:1 and die-pressed into a toroidal shape with 7.0 mm outer diameter, 3.04 mm inner diameter and approximately 2.0 mm thickness. The test ring was fixed to the input section of reflection access of an Agilent N5244A vector network analyzer, and electromagnetic parameters, i.e., the complex permittivity and the complex permeability were determined in the range of 2–18 GHz. The test apparatus is clearly shown in Fig. 1.

3. Results and discussions

3.1. Phase and crystal structure of coal chars by XRD

Phase qualitative analysis can be made from XRD patterns of chars prepared at different temperature. As shown in Fig. 2, there are two major aspects of changes observed during heat treatment. The diffraction intensity, of the main peak corresponding to the (002) reflection of graphite, is very low but becomes higher with increasing temperature, indicating coal chars composed of turbostratic structure carbon, especially for those generated at relatively low temperature, while increasing temperature encourages

Table 1
Proximate and ultimate analysis of raw coal.

Sample	Proximate analysis (%, mass, ad)			Ultimate analysis (%, mass, daf)				
	Volatile	Ash	Fixed carbon	C	H	N	S	O
Raw coal	34.49	7.43	53.28	78.63	3.79	2.28	0.25	10.66

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