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The Characteristics of Mechanical Grinding on Kaolinite Structure and Thermal Behavior

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Abstract

The relationship between kaolinite structure and the temperature of thermal transformation of phase was discussed in this paper through grinding and heating treatment. The results show that the structure of kaolinite is destroyed rapidly with increasing mechanical grinding time, and the kaolinite structure collapses completely after 1 h grinding. The temperature of thermal transformation of phase decreases with the destruction of kaolinite structure. This result has a great significance for the utilization of kaolinite associated with coal measures in China.

Keywords: kaolinite; mechanical grinding; thermal behavior

1. Introduction

The crystal structure of kaolinite is deformed mainly along the C-axis after mechanical treatment, which was widely discussed in the middle age of twenty century by many geologists (Grofcsik, 1961; Hinckley, 1963; Miller, 1970; Jack, 1976). Afterwards, some scientists had a further discussion on changing of OH groups and rupture mechanism of the O-H, Al-OH, Al-O-Si and Si-O bonds in ground kaolinite (Adams, 1983; Opoczky, 1990; Kristof et al., 1993; Davies 2001; Ding et al., 2004). Nevertheless, the effects of kaolinite structure changes on the phase transformation in heating treatment have been seldom reported. The kaolinitic rock is a new type of nonmetallic resource associated in the coal measures, which is discovered in the last 20 or 30 years (Liu and Zhang et al., 1997; Li et al., 2001). Recently, many researches on kaolinite rocks in coal measures have been carried out in coalmine districts.

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The pulverizing and calcination are two important steps in the processing kaolinite rocks. It has a great significance to study the effects of pulverizing on the kaolinite structure and temperature of phase transformation in the calcination, as well as to determine the suitable calcination parameters and technology.

2. Materials and Methods

The raw samples of kaolinite used in experiment are from interlayer of coal seam No.4, Shanxi Formation, Lower Permian, Pinglu coalfield, Shanxi province in China. This layer of kaolinite rock is slightly gray, hard, compacted, and has uneven fracture when broken. The relatively huge crystal grains of the kaolinite, which has pseudomorph of feldspar and mica, can be seen under the microscope. This kind of kaolinite rock (so-called tonstein) has been investigated by many geologists, and commonly considered as having volcanic origin, that is, kaolinization of tuffs which had fallen directed into the peat swamps (Williamson, 1970; Liu et al., 1994). The kaolinite content is nearly 100% in this kind of rock, having a chemical analysis of SiO_2 46.38%, Al_2O_3% 37.56%, Fe_2O_3 0.29%, TiO_2 0.48%, CaO 0.15%, MgO 0.2%, K_2O 0.55%, Na_2O 0.1%, and loss on ignition 14.29%. All the samples used in experiments pass through 0.074mm sieve, and its organic carbon was removed by H_2O_2 (concentration: 30%). The planetary mill is made of manganese steel with the volume of 180cm^3 and 150g steel ball (ball diameter range 3.5～8 mm) in it. The ports were rotated at 1500r/min. The intensive cooling of ports with cold running water increased the efficiency of mechanical treatment. Each sample (weights 20g) was ground with planetary mill for 0~2 h respectively. Then, each sample was divided into three parts to be heated at 900℃, 1000℃ and 1400℃ for 1 h, respectively. X-ray diffractograms (XRD) were obtained on D/max-RA diffractometer at a scanning speed meter 4°（2θ）/min using CuKα radition (at 40kV, 100mA). The infrared spectra (IR) is recorded on Perkin-Klmer577 double-beam spectrophotometer. The differential thermal analysis (TDA) is performed with DT-3 Derivatograph.

3. Results and Discussion

3.1 The effect of grinding time on the kaolinite structure

It can be found that the peaks of kaolinite in the diffractograms decrease in the strength and become wide in the shape with the increasing grinding time. This indicates that the crystallinity of kaolinite decreases and the kaolinite structure is destroyed gradually with the grinding. It can also be found that the diffractograms of original sample and those be mechanically treated at different time shows a rapid deterioration of the kaolinite structure during being ground. All peaks of kaolinite disappear after 1 h grinding, reflecting the complete destruction of the crystal structure. TDA and IR can also confirm the distortion of kaolinite crystal caused by grinding. Both of the endothermic peak strength (500℃ to 700℃) and temperature decrease with increasing of grinding-time due to dehydroxylation. The endothermic peak is almost vanished after 1 h grinding. It indicates that the dehydroxylation increases with the grinding time and almost completed after 1 h. The temperature of the exothermic peak (850 to 1050 ℃) decreases with the grinding time for the deformation of Si-O-Al bonds reduced with mechanical forces, while the strength of exothermic peak (850℃ to 1050 ℃) is nearly unchanged. From the IR spectra of high band,it shows that the absorption band of OH stretching (3695 cm^{-1}, 3654 cm^{-1}, 3621 cm^{-1}) is rapidly reduced. Almost all absorption bands vanished after 1 h grinding. From the IR spectra of lower frequency district, it shows that the absorption band of Si-O stretching (1115 cm^{-1}, 1032 cm^{-1}, 1006 cm^{-1}, 697 cm^{-1}, 469 cm-1 and 433 cm^{-1}), Al-OH stretching (921 cm^{-1} and 935 cm^{-1}), Si-O-Al stretching (796 cm^{-1}, 756 cm^{-1}) are also rapidly reduced, and all absorption bands disappear after 1 h grinding. The disappearance of absorption band at 921 cm^{-1} and 936 cm^{-1} suggests a break down of Al-OH bonds. The alteration of Si-O stretching and the disappearance of the Al-O-Si bands indicate the distortion of tetrahedral and octahedral layer (Kristof et al., 1993; Frost and Tran 1996; Adersson et al., 1998).

3.2 The phase transformation of ground kaolinite

The XRD spectra of ground kaolinite heated under different temperature are shown . For the products under 900 ℃, the grinding time has a little effects on the phase transformation of kaolinite . A little new phase (spinel) is formed for the raw material and the sample ground for 2 h. The grinding time has great effects on the phase transformation of kaolinite when it was heated under 1000℃. The obvious and strong peaks of mullite appeared for the sample ground for 1 h., but no new phase is formed in the spectrum of raw material and sample ground for 2 h. Both the raw kaolinite and the ground one will be transformed to mullite when they are heated under 1400℃, thereinto the mullite peaks from raw kaolinite are sharper and stronger than that from the samples ground for 1 h and 2 h.

3.3 Explanation for phase transformation of kaolinite

It shows that 1 h grinding is favourable for the phase transformation of kaolinite. It can be related to the structure changes when ground. The authors believe that a transition structure maybe exist between crystalline and non crystalline kaolinite when grinding for 1 h. It is the transition structure that makes kaolinite easier be transformed to mullite. This transition structure may be destroyed when grinding for more than 1 h, so a higher temperature will be needed for the kaolinite to be transformed to mullite. The temperature as higher as 1400℃ is enough for all forms of kaolinite to be transformed to mullite. The well crystallinity of mullite transformed from raw kaolinite under 1400℃ may be related to the order arrangement of Si and Al ions in the kaolinite structure. The kaolinite structure was destructed after being ground for 1 h and 2 h produced poor crystallinity of mullite under 1400 ℃.

4. Summary

The structure of crystal network of kaolinite would breakdown after certain mechanical grinding. The grinding process can reduce the temperature of transformation from kaolinite to mullite. One hour grinding makes kaolinite transformed to mullite under 1000℃. In contrast, raw kaolinite need a temperature as high as 1200℃ to 1400 ℃ for this transformation. This study is very significant for the intensive utilization of kaolinitic rocks in coal-bearing strata not only in theory but also in practical application.

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