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Structure, morphology and mechanism research on synthesizing xonotlite fiber from acid-extracting residues of coal fly ash and carbide slag

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HIGHLIGHTS

- We successful synthesized xonotlite fiber from carbide slag and acid residues.
- We find an effective way to deal with millions of tons of solid waste.
- Much longer xonotlite fibers (10–15 μm) were obtained by rapid synthesis.
- The transition steps is C–S–H block, tobermorite needle, and then xonotlite fiber.

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ABSTRACT

Xonotlite fibers have attracted much attention in super thermal insulation and flame retardant fields due to its ultra-light property. In this article, well crystalline xonotlite fibers were successfully prepared from two kinds of industry wastes, carbide slag and acid residues of fly ash respectively, by hydrothermal method. Influences of synthesis parameters, such as hydrothermal temperature, hydrothermal time and Ca:Si ratio, on both crystalline structure and micro morphology of hydrothermal products have been carefully researched. The results show that the formation of xonotlite fiber is remarkably accelerated by alumina impurities in carbide slag. Xonotlite phase could be formed within 24 h, and pure xonotlite fibers with satisfied crystalline degree are obtained after 48 h in this system. It also means that much thinner fibers could be achieved under a certain time. The resultant xonotlite fibers are in 50–300 nm diameter and 10–15 μm length. Moreover, because of relatively large particle size of carbide slag, pectolite intermediate is generated due to the temporary deficient condition of free calcium species. Furthermore, the phase type of product could be effectively controlled by altering Ca:Si ratio under suitable hydrothermal system. And xonotlite phase could be obtained under a wide range of Ca:Si ratio.

1. Introduction

Coal fly ash is one of the solid wastes generated in coal fired power stations. Currently, about 800 million tons of coal fly ash has been generated in the world, and the annual discharge of coal fly ash is more than 4×10^8 tons in China [1–5]. CaC_2 is an acetylide source that was prepared first by Wöhler in 1862 [6]. Due to the low solubility of CaC_2 in organic solvents, consequently, it is mainly used for the production of acetylene gas and as a drying agent in organic synthesis [7,8]. Recently, the calcium carbide (CaC_2) hydrolyzates are generated in the industrial production of ethylene, polyvinyl chloride (PVC) and other products [9–11]. At least 900,000 tons of dry carbide slag is generated from a factory which produces 600,000 tons of PVC from CaC_2 a year in China [12–15]. Nevertheless, the main method for disposal of carbide slag is simply dumping. Millions tons of these solids are accumulated as an industrial waste and result in many environmental problems [12–14]. Accordingly, comprehensive utilization of these industrial wastes is becoming an urgent issue.

With the diminishing of bauxite resources as well as the increase in alumina demand, the high-value industrial utilization of the coal fly ash in alumina recovery has become the main

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development trend. Therefore, it is necessary to discuss the method on how to increase the fly ash utilization and reduce the residues after extracting alumina from fly ash. In a typical acid extracting reaction of alumina from fly ash, the alumina extraction yield could reach 80%. After being filtrated, the filtrate can be further dealt to produce the main-product aluminum oxide. On the other side, the residue attracts our attention because of the amorphous form of SiO_2. It can be used to produce some high-value fiber materials.

Xonotlite, whose chemical formula is $Ca_6Si_6O_{17}(OH)_2$, is a novel kind of ultra-light fiber synthesized from calcium and silicon species, which is widely used in super thermal insulation and flame retardant fields. In previous studies, such material was usually synthesized from chemical sources. If the sources of calcium or silicon could be replaced by industry wastes, the synthesis cost of xonotlite fibers could be significantly reduced. However, such researches on the effects of industry resources are very rear.

Some researches about the crystalline state of xonotlite fiber material have already been published, including the optimum conditions and the addition agents for synthesis [16–19]. Typically, xonotlite generally can be formed via a hydrothermal process by using different kinds of high purity siliceous material and calcareous materials as the raw materials, such as quartz, sodium silicate, calcium oxide, calcium carbonate [20–22]. However, former researches always focused on the temperature, time or additions to the synthesis process, very little effort has been expended towards the study on fiber material involving issues such as the material sources, impurities, the crystalline degree of the fiber material, crystal growth and mechanisms, which is the essence of the synthesis.

In this research, a novel preparation method for xonotlite fiber material using acid residue and carbide slag was developed for the first time, aimed at finding an effective way to deal with millions of tons of residue and carbide slag, synchronously seeking a cheap raw material to prepare xonotlite. The hydrothermal time, hydrothermal temperature and the Ca/Si molar ratios, were analyzed and evaluated by XRD and SEM analysis. The crystalline process has been tracked from 12 h to 72 h. A model of xonotlite fiber material formation process was set up based on the experimental results. The industry sources accelerate the generation process of xonotlite fiber, which is expected to be environmentally and economically benign.

2. Experimental section

2.1. Materials

The carbide slag was sampled from a factory for polyvinyl chloride production by calcium carbide acetylene method in Inner Mongolia Province of China. The acid residue was collected from a pilot plant in Inner Mongolia Province of China which is acid-extracting alumina from circulating fluidized bed (CFB) fly ash. We collected the carbide slag and acid residues for different times. About 10 kg carbide slag and acid residues were collected each time. Then carbide slag and acid residues were stored immediately in PVC zip lock bags to prevent contamination. Prior to use, acid-extracting residues of CFB fly ash were successive washing to remove the unreacted acid and later filtered. The acid residue and carbide slag were dried at 105 °C for 3 h in an oven.

The chemical composition of carbide slag and acid residues were given in Table 1, which was determined at The First Geological Survey, Changchun, Jilin, China. Three replicates of the samples were conducted and the average data were reported. The uncertainty was estimated to be within ±3% for the chemical components analyzed. As can be seen in Table 1, main chemical components of acid residues is silica, the sum of silica account for more than 50 wt.%; main chemical components of carbide slag is calcium oxide, the sum of calcium oxide account approximate to 60 wt.%. These unique characteristics make suitable raw materials for xonotlite synthesized. All other chemicals are analytical grade reagents and commercially available.

2.2. Xonotlite preparation

Because of alumina extraction yield could reach 80%, there is still a part of alumina in the acid residue. It has a great influence on synthesis of xonotlite as reported by Mitsuda and Taylor [23]. The Al/(Si + Al) molar ratio beyond 0.15 is difficult to form xonotlite. Therefore, in the synthesized process, the first reaction is pretreatment of acid residues, which can dissolve silica in alkali solution and remove most of alumina by a hydrothermal reaction. The acid residue and 3 mol/L sodium hydroxide solution were fully mixed by stirring with Si/Na molar ratio of 1:2. The mixture was sealed in a closed container at 95 °C for 2 h. Then filtered, the filtrate was used for synthesized xonotlite and named as siliceous material. The silica and alumina concentration of siliceous material are 85–101 g/L and 4–5.4 g/L respectively.

The second reaction is pretreatment of carbide slag, which can remove the unreacted carbon. The carbide slag was calcined at 700 °C for 2 h, then hydrated in distilled water of 50 °C and stirred for 2 h, to prepare $Ca(OH)_2$ suspension and named as calcareous material.

The calcareous material was homogeneously mixed with siliceous material, and then the mixture was transferred into an autoclave with inner volume of 500 ml. The hydrothermal treatment proceeded under the following conditions: the CaO/SiO_2 molar ratio of 0.8–1.2, the concentration of silica is 34–38 g/L, temperature range of 200–260 °C, reaction time of 12–60 h, stirring rate of 100 rpm for heat preservation and cooled down naturally. At the end, the product was separated by filtration, washed several times with distilled water and then dried at 100 °C for 8 h. The overview of the process is shown in Fig. 1. All experiments were conducted in duplicate and the mean data were reported.

2.3. Characterization of materials

The crystalline phases in the acid residues and synthesized samples were characterized using XRD (DX-2700, Dandong Fangyuan, Dandong, China) with Cu Kα radiation. The acceleration voltage was 35 kV, and the electrical current was 25 mA. The scans ranged from 5° to 50° at 5°/min. Morphology of acid residues and the products were examined by scanning electron microscope (SEM).

3. Results and discussion

3.1. The effect of hydrothermal temperature

In this section, we focus on the structure and phase changes of synthesized samples. As L. Black and S Shaw have pointed out, the reaction temperature strongly affects the nucleation process and crystal growth process of xonotlite [24,25]. So we choose different temperatures to synthesize the fiber materials.

Fig. 2 shows XRD patterns of the samples synthesized at 200 °C, 220 °C, 240 °C and 260 °C for 48 h when Ca:Si = 1.0 (molar ratio). As can be seen, a well-crystallized 11 Å tobermorite (PDF No. 45-1480)