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Journal of the European Ceramic Society 26 (2006) 797–801
www.elsevier.com/locate/jeurceramsoc

Fabrication of porous SiO_2/C composite from rice husks

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Available online 3 August 2005

Abstract

Porous SiO_2/carbon composites were fabricated by heating pellets composed of rice husk (RH) powders in small (<74 μm), medium(74–175 μm) and large(150–300 μm) sizes. The contents of the small RH were fixed at 30 mass% and the RH pellets molded at 10, 15, and 30 MPa were heated at 800–1150 °C in an inert atmosphere. The weight loss due to the thermal decomposition of the organic materials in the pellet peaked at 1000 °C, whereas the specimen heated at 1000 °C showed the lowest carbon content and density, 29 mass% and 0.40 g cm^{-3}, respectively. The SiO_2 phase of the specimens were amorphous at 800 and 1150 °C, but a cristobalite phase was visible at 1000 °C. The specimen fire at 1000 °C showed a higher compressive strength than the others, and the large RH particles were seen to increase the strength of the product while an increase in molding pressure decreased the medium pore size, from 17 to 7 μm, and increased the strength, from 0.25 to 3.52 MPa. The specific surface area (SSA) of the specimen peaked at 450 m^2 g^{-1}, at 1000 °C and finally, the mesopore size of the specimens was similar throughout, at ∼2 nm.

Keywords: Carbon; SiO_2; Rice husk

1. Introduction

The rice husk (RH) used, normally a discarded agriculture by-product, consisted of organic materials (e.g. cellulose, hemicellulose and lignin) (61–77 wt.%), ash (mainly amorphous SiO_2) (13–29 wt.%) and water.[1] These components converted to the following useful materials in the course of each treatment. By burning out the organics, a porous SiO_2 with a high specific surface area could be obtained.[2] Moreover, the SiO_2 thus obtained from RH is particularly active and has thus been used as a raw material for the preparation of zeolite[3] and cordierite[4], respectively. Furthermore, SiC whiskers were fabricated based on the reaction between the organic materials and SiO_2 in the RH at a temperature of 1100–1400 °C.[1] On the other hand, porous carbons were formed by heating the RH within an inert atmosphere.[5,6] The molded RH powder tube was changed to porous carbon with a specific surface area (SSA) of 3.4 m^2 g^{-1}. The RH compact was heated under H_2O gas, with an SSA value of 240 m^2 g^{-1}. Furthermore, the RH compact mixed with $ZnCl_2$ compound was heated within a CO_2 atmosphere and the resulting carbon showed high SSA value of 480 m^2 g^{-1}. In spite of these complicated processes, a fresh attempt to simplify the process was recently investigated.[7]

This project also aimed to obtain a porous form of carbon with a high surface area through a simple process using rice husk powder compacts. The powder compacts formed by mixing the RH powders with different particle sizes were carbonized to form a porous SiO_2/carbon composite. In this paper, the effects of the molding pressure and treatment temperature on the features of the product were described.

2. Experimental

Three commercial RH powders (S-RH (<74 μm), M-RH (74–175 μm), and L-RH (150–300 μm) from Daiso Trading Co. Ltd.) were used. Since the rice husk has a shell shape, the commercial large L-RH powder mainly consisted of anisotropic plate-like particles and the S-RH powder was homogeneously mixed with M- or L-RH powders according to a ratio; S/(S + M (or L)) = 0.3 in weight according to the previous work.[8] In order to avoid any change in the size

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doi:10.1016/j.jeurceramsoc.2005.06.013

and structure of the raw RH particles during the mixing process, a special mixer ("Hybrid Mixer", Keyence Co. Ltd.) was used. The mixed powder was pressed into a pellet (Ø 10 mm × 5 mm) under a pressure of 10, 20, or 30 MPa and then placed into an alumina crucible with an alumina cover. This crucible was placed into a larger alumina crucible and covered with graphite powder. The outer crucible was covered with an alumina cover again in order to avoid any combustion of the graphite powder in air. The crucible set was heated at 800–1150 °C for 2 h in air and the rate at which the temperature increased to the treatment temperature was 20 °C/min.

The thermal behavior of the products was evaluated using thermogravimetry (TG) and differential thermal analyses (DTA) in the air flow. The density and shrinkage of the pellet, meanwhile, were calculated using its dimension and weight. The microstructures were observed with a scanning electron microscope (SEM) and the SSA value was measured through the N_2 gas adsorption (BET) method at 77 K. The pore size distribution of the product was measured with a mercury porosimeter (MP) and also calculated using the N_2 gas desorption behavior using the BJH method.

3. Results and Discussion

3.1. RH Powder Compact

The density of the RH pellet increased with the molding pressure as shown in Fig. 1; 0.95–0.97 g cm^{-3} (10 MPa), 1.02–1.04 g cm^{-3} (15 MPa) and 1.06–1.10 g cm^{-3} (30 MPa). The increase in density between 10 and 15 MPa was larger than that between 15 and 30 MPa. The specimen from the (S + L) mixture powder showed a lower density than that from the (S + M), due to the anisotropic structure of the L-RH particles, which disturb the particle packing during molding. This difference in density changed the pore structure of the pellet and thus the decomposition procedure of the organic compounds in the RH pellet was also inevitably subject to change. This process also led to change in the characteristics of the SiO_2/C products as described below.

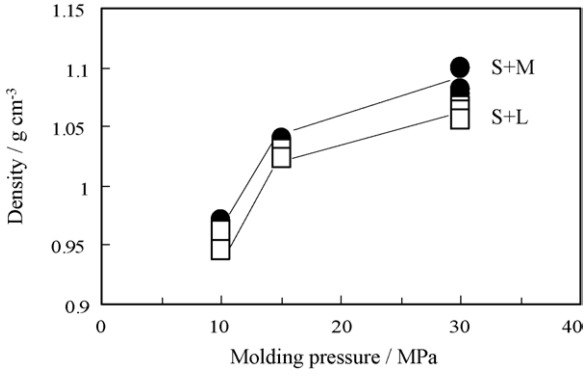

Fig. 1. Dependence of pellet density on molding pressure and raw powders.

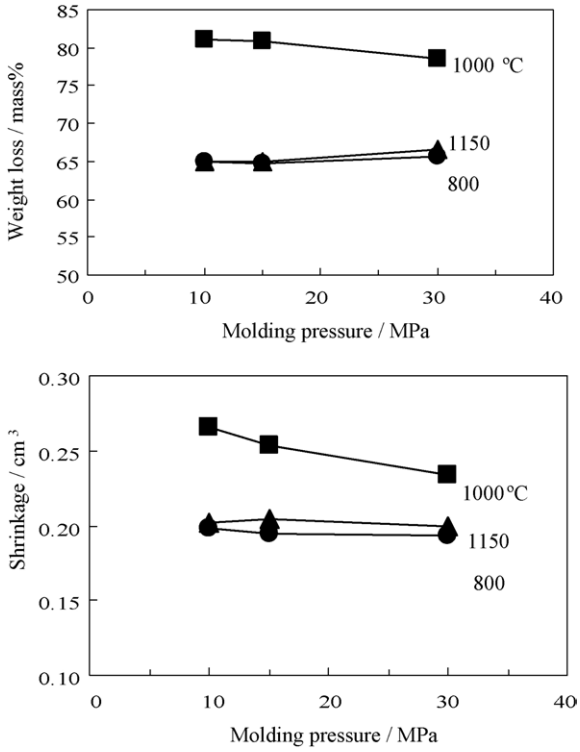

Fig. 2. Dependence of weight loss and shrinkage of (S + M) pellets on molding pressure and treatment temperature.

3.2. Formation of the SiO_2/C composite

The organic compounds decompose when heated in an inert atmosphere and partly change to H_2O, CO, CO_2, and volatile compounds,[9] remaining carbon and SiO_2. This volatilization decreases the weight of the RH pellet following heat-treatment. The change in the weight loss and the shrinkage of the (S + M) pellet with the molding pressure and the treatment temperature are depicted in Fig. 2. The weight losses at 800 and 1150 °C took place almost independently of the pressure, ∼65 mass%, but that at 1000 °C slightly decreased with the molding pressure, from 81 to 78 mass%. According to the previous project,[8] the weight loss became almost constant at 600 °C, ∼60 mass%, with a value is similar to those recorded at 800 and 1150 °C. However, the weight loss and shrinkage of the pellet at 1000 °C were far higher than those recorded at 800 and 1150 °C. Also the (S + L) pellets showed similar behavior to those in Fig. 2. In this project, the products at a temperature of 1000 °C showed different characteristics compared to those prepared at other temperatures and this behavior will be further discussed later.

The porous SiO_2/C composites were fabricated by heating the (S + M) or (S + L) pellets within an inert atmosphere. The density of the resulting pellets varied from 0.40 to 0.67 g cm^{-3} as shown in Fig. 3. In this project, the density increased with increasing molding pressure, but the heat-treatment temperature was more effective. The pellets heated