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Preparation and characterization of low-density mullite-based ceramic proppant by a dynamic sintering method

Jinzhou Zhao, Zuolei Liu *, Yongming Li

State Key Laboratory of Oil and Gas Reservoir Geology and Exploitation, Southwest Petroleum University, Chengdu, Sichuan 610500, China

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ABSTRACT

Low-density mullite-based ceramic proppants were prepared from bauxite (49.74 wt% Al_2O_3), soft-clay and manganese dioxide by a dynamic sintering method. The apparent density and breakage ratio of specimens were systematically investigated as a function of sintering temperature. The morphology structure and phase composition of specimens were investigated by scanning electron microscopy (SEM) and X-ray diffraction (XRD). The results show that the proppants were composed of acicular mullite and glass phases. The proppants prepared from calcined bauxite showed a better performance than the proppants prepared from natural bauxite. With increasing sintering temperature properly, the proppants showed an enhanced crystallinity and a denser microstructure, and the proppants sintered at 1355 °C had the best performance with 2.792 g/cm^3 of apparent density and only 3.22% of breakage ratio under 52 MPa.

1. Introduction

Hydraulic fracturing has been widely used to increase the oil and gas production, especially in low permeability oil and gas well. In hydraulic fracturing operation, proppants are transported with fracturing fluid at high pressure to the fractures underground over a distance of several kilometers. The high pressure fluid and proppants then create fractures in the rock. When the hydraulic pressure is removed, the proppants remain in the fractures and hold them open, improving the oil and gas fracture conductivity [1]. In addition, the low-density proppants, compared to the high-density proppants, can be more effectively carried to the fracture [2]. Thus, the ideal fracturing material is a low-density high-strength proppants.

In previous research works, many types of ceramic proppant were prepared from the main raw materials of high-alumina bauxite (> 60 wt% Al_2O_3) or pure alumina by static sintering [3–5]. However, these raw materials are expensive. To the best of our knowledge, no study has been reported on the low-density mullite-based ceramic proppant prepared from low-alumina bauxite (< 50 wt% Al_2O_3) as the raw material by a dynamic sintering method. In the present work, the low-density mullite-based ceramic proppants were prepared from the low-alumina bauxite (49.74 wt% Al_2O_3) by a dynamic sintering method and the effects of sintering temperature on the apparent density, breakage ratio, and structural properties were investigated.

2. Material and methods

Preparation of proppants: Natural bauxite was used as the starting material. First, the bauxite was calcined at 1200 °C for 1 h using a muffle furnace. Second, a kaolin clay and manganese dioxide (AR) were used as additives. The weight ratios of clay and manganese dioxide with respect to the calcined bauxite were of 3 wt% and 4.0 wt %, respectively. They were milled together in water with a planetary ball mill for 36 h. After drying, the dried lumps were crushed and passed through a sieve with an aperture size of 60 mesh. Third, the spherical green bodies with 18–25 mesh were prepared by a homogeneous mixture (d_{50}—1.2–1.8 μm) in a sugar-film coating machine. Lastly, they were sintered in a high-temperature rotary corundum tube furnace. In the sintering process of proppants, the rotating corundum tube made they continuously roll in the corundum tube. The rotation rate of corundum tube is 3 r/min in the sintering experiment. The proppants spent approximate 45 min in the hot zone of the furnace under air atmosphere in the procedure. A-specimens and B-specimens were prepared from calcined bauxite and natural bauxite, respectively.

Characterization: The apparent density and breakage ratio under 52 MPa pressure are determined by the Chinese Petroleum and Gas Industry Standard (SY/T 5108-2006). Apparent density is determined by Archimedes' method and calculated with the following formula: $\rho = M/V$, where M is the weight of specimens (g) and V is

* Corresponding author. Tel.: +86 28 83033228.
E-mail address: zuoleiliu822@163.com (Z. Liu).

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the volume of specimens (cm^3). The diameter of the breakage ratio measuring cylinder is 50.8 mm, which meets the SY/T 5108-2006 standard of between 30.1 mm and 76.2 mm. Breakage ratio is calculated by the following formula: $\eta = W_c/W_0 \times 100\%$, where W_c is the weight of crushed specimens (g) after testing and W_0 is the weight of the specimens (g) before testing.

Chemical analyses of the raw material were done by the Chinese Nonferrous Metals Industry Standard (YS/T 575-2007). Phase identification was done by XRD. The microstructure of specimens was observed by SEM. To reveal the grain of mullite, specimens were etched by a hydroflouric–hydrocholoric acid solution of 12 wt% HCl+3 wt% HF prepared according to SY/T 5108-2006 specifications.

3. Results and discussion

The chemical analysis (loss free basis) indicates that the composition of the bauxite used in the present study is 49.74 wt% Al_2O_3, 43.61 wt% SiO_2, 2.36 wt% CaO, 2.53 wt% TiO_2 and 1.76 wt% Fe_2O_3. The content of Al_2O_3 in this bauxite is significantly lower than that in the bauxite used in common proppants as main raw materials [3,4], which makes the proppants more beneficial economically.

Fig. 1 shows the XRD patterns of natural bauxite, calcined bauxite and specimens. The amount of cristobalite has disappeared in A-specimens and B-specimens, which is due to amorphization. A-specimens and B-specimens had the same XRD patterns. But, compared with calcined bauxite (b), they exhibited the higher (120) and (210) peaks and the smaller values of full width at half-maximum (FWHM), which indicates a higher crystallinity of the mullite (PDF no. 01-082-0037). It is suggested that manganese dioxide promoted the growth of mullite grain. The theoretical density of mullite and corundum is 3.16 g/cm^3 and 3.98 g/cm^3, respectively. The density of mullite based proppants should be lower than that of common ceramic proppants (3.1–3.4 g/cm^3) mainly composed of mullite and corundum.

Apparent density and strength are an important performance metric of any proppants. Variation of apparent density and breakage ratio with sintering temperature is shown in Fig. 2. It can be seen that the proppants prepared from calcined bauxite showed

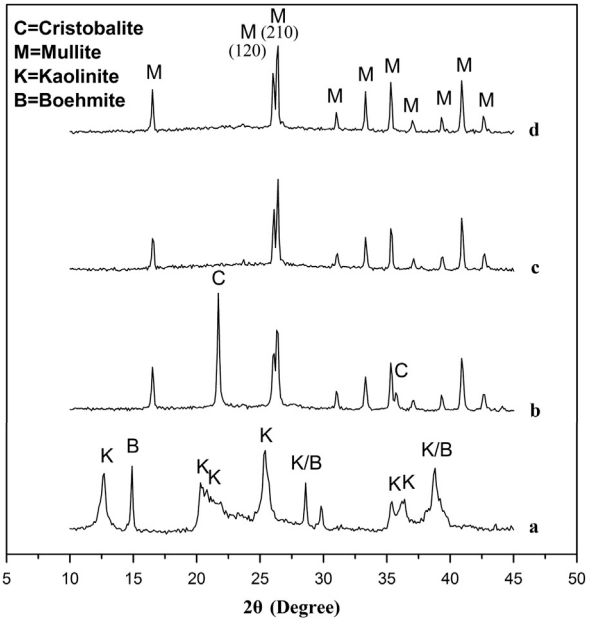

Fig. 1. XRD patterns of (a) natural bauxite, (b) bauxite calcined at 1200 °C, (c) A-specimens sintered at 1200 °C and (d) B-specimens sintered at 1200 °C.

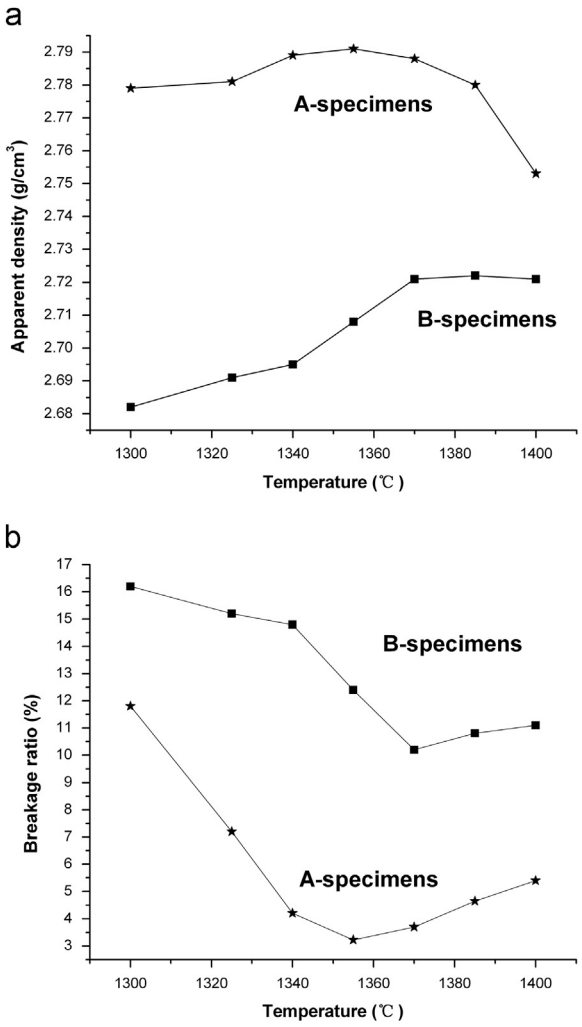

Fig. 2. Apparent density (a) and breakage ratio (b) under 52 MPa pressure with sintering temperature.

the higher density and lower breakage ratio than the proppants prepared from natural bauxite. Natural bauxite underwent a series of phase transformations as the temperature was raised from room temperature to 1200 °C. Fig. 1(a) shows that the major crystalline phase of natural bauxite was kaolinite and boehmite. Crystal water can be formed from kaolinite and boehmite in natural bauxite at the temperature from 400 °C to 700 °C [6,7]. The steam can decrease the compactness of proppants in the early of sintering procedure. In the sintering process of proppants, the reaction between the glass phase and alumina, derived from boehmite, to form secondary mullite occurred when the main raw material is natural bauxite. In previous research works [8], it was proved that this reaction is detrimental to the densification. As can been seen in Fig. 1(b), there was little diffraction peak of alumina. It is indicated that the reaction to form the secondary mullite was complete in the calcining process of natural bauxite. Thus the formation of crystal water and the reaction to form the secondary mullite were avoided in the sintering process of proppants when the main raw material is calcined bauxite. As can been seen in Fig. 1(a) and (b), A-specimens showed a more compact structure than B-specimens. This may be the main reason why a higher breakage ratio was observed in B-specimens.

With regard to A-specimens, it is found in Fig. 2(a) that the apparent density increased with sintering temperature up to 1355 °C followed by a decrease in density with sintering temperature up to 1400 °C. Meanwhile, Fig. 2(b) shows that the breakage