Influence of Sintering Temperature on the Microstructure and Property of Low-cost Ceramic Proppants Prepared by Adding Purple Sands

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Abstract: High-strength corundum-mullite based ceramic proppants have been fabricated from 2nd bauxite (62.3wt%Al₂O₃) and purple sands, which were used as main raw materials by solid sintering method, combined with the additive of feldspar and pyrolusite powder. The phase analysis was studied by X-ray diffraction (XRD) and the morphology of specimen was observed by the scanning electron microscopy (SEM). The result showed that the additive of feldspar was beneficial to the formation of internal liquid phase of sample with the sintering temperature increasing, which reduced the pores and promoted the densification of sample. Meanwhile the proper liquid phase resulted in the growth of mullite and promoted the close integration of mullite and corundum, forming the network structure of needle-like mullite. Ultimately the proppants exhibited the optimal performance at 1450 °C with bulk density of 1.59 g/cm³, apparent density of 3.11 g/cm³ and the lowest breakage ratio of 3.76% under 52 MPa pressure.

1. Introduction
Proppant, as a significant material in the hydraulic fracturing process, can increase the amount of oil and gas extraction [1]. Currently, the proppant primarily includes the quartz sand, the resin-coated product and the ceramic proppant. The quartz sand, as a traditional proppant, possesses advantage of low cost, however it is unsuitable to be applied in the deep reservoirs because of its relatively low crush resistance [2]. The resin-coated quartz sand plays a more significant influence compared to that of the quartz sand in terms of resistance crush, but it increases cost in the production process. By contrast, ceramic proppant, as an ideal proppant material, not only meets the demand of lower production cost, but also has higher resistant crushing capability [3].

In previous several literatures have focused on pursuing the higher strength. However, the high-strength ceramic proppant has been successfully synthesized using pure alumina or high-grade bauxite. Zhao et al [4] produced ceramic proppant from pure alumina and BaCO₃, and investigated the effect of BaCO₃ on the breakage ratio. It was found that the lowest breakage ratio and the apparent density were 2.5% (86MPa) and 3.48 g/cm³ respectively. Li et al [5] prepared ceramic proppant by high bauxite. The result displayed that the breakage ratio was 4% under 69 MPa closed pressure and the apparent density was 3.27 g/cm³. However, these above-mention materials were expensive in cost and unfavorable to the large-scale production. Therefore, to choose the low-grade bauxite or low-cost minerals as a substitute for the high-grade bauxite has become urgent.
In this work, we used the low grade bauxite (62.3 wt% Al₂O₃) and low-cost purple sands as main materials to prepare the corundum-mullite based ceramic proppants. Purple sands, as a cheap raw material, belonged to Al₂O₃—SiO₂ system compound. Therefore, adequately using the purple sands as a substitute for bauxite was feasible. Furthermore, the effects of sintering temperatures on the phase evolution, microstructure, apparent density, bulk density and breakage ratio of proppants were investigated.

2. Experimental

2.1. Raw materials

The natural low-grade bauxite and purple sands were (obtained from Yangquan city, Shanxi province, China) used as the starting material, feldspar and pyrolusite powder were selected as additives. Their main chemical components are displayed in Table 1.

| Raw materials       | Al₂O₃ | SiO₂ | Fe₂O₃ | TiO₂ | CaO | MnO₂ | L.O.I |
|---------------------|-------|------|-------|------|-----|------|-------|
| Bauxite             | 62.3  | 12.4 | 5     | 2.8  | –   | –    | 17.5  |
| Purple sands        | 29.26 | 51   | 4.34  | –    | –   | –    | 15.4  |
| Feldspar            | 18.4  | 64.7 | –     | –    | 16.9| –    | 4.28  |
| Pyrolusite powder   | 4.52  | 18.41| 13.43 | 0.05 | 1.82| 56.82|       |

2.2. Preparation of proppants

Firstly, the weight ratios of purple sands, feldspar and pyrolusite powder with regard to the bauxite are of 10 wt%, 2 wt% and 4 wt% respectively. These materials were mixed homogeneously to form small granules by a strong mixing machine (R02, Eirich Co. Ltd, Germany), and then the specimens were dried in an oven. After drying, the homogeneous granules were screened by a set of sieves of 20/26 meshes to gain the desired semi-finished products of 0.85 mm~0.71 mm in diameter. Secondly, these semi-finished products were placed in a high temperature furnace (KF1700, Nanjing Bo Yun Tong Instrument Technology Co. Ltd, China) and sintered through the following process: the semi-finished products were calcinated from the room temperature to the different sintering temperatures (1300 °C, 1350 °C, 1400 °C, 1450 °C and 1500 °C) with a heating ratio of 5°C/min, and were held 2 h from 1300 °C—1500 °C, then cooled to the room temperature naturally. Finally, the sintered granules were sieved by a set of sieves of 20/40 meshes to obtain finish products.

2.3. Characterization

The bulk density, breakage ratio and apparent density were tested according to the Chinese Petroleum and Gas Industry Standard (SY/T 5108-2014). The apparent density was calculated using the well-know Archimedes formula: ρ=M/V, where M represented the mass of test proppants and V denoted the volume of the specimens. The breakage ratio formula was expressed by η=W_c/W_o, here W_c was the mass of specimens after testing and W_o was the mass of specimens before testing. The breakage ratio was evaluated under 52MPa closed pressure. Different phases were analyzed by XRD (X’Pert PRO, Philips Co. Ltd, Holland). The microstructures of the proppants were viewed through SEM (FESEM, S-4800, Hitachi, Japan).

3. Results and discussion

Figure 1 displays the microstructures of sample at different sintering temperatures. From figure 1(a), it can be seen that the sample contains a large number of needle-like grains and the structure of sample is loose. When the sintering temperature reaches at 1350 °C, the needle-like grains are transformed to rod-like grains. For the sample with sintering temperature of 1400 °C, as can be observed that the size of rod-like grains increases further, the rod-like grains are coalesced by a small amount of liquid phase.
Furthermore, with the sintering temperature increasing to 1450°C, the rod-like grains grow through the plate-like grain matrix to form reticular structure during to grains anisotropically grow. For the sample with sintering temperature of 1500°C, it is obvious that a quality number of liquid phase is generated, which leads to disappearance of the grain boundary. The results illustrate that the sintering temperature can boost the growth of mullite and the moderate liquid phase is beneficial for the formation of network structure of sample.

To judge the above-mentioned microstructure of grains, the patterns of XRD of samples are represented in figure 2. A comparison of the XRD patterns observes that the phases of sample are composed of corundum and mullite respectively. It is confirmed that the needle-like grains and the rod-like grains are mullite, the plate-like grains was corundum. These morphologies have been reported in many literatures [6-9].

![XRD patterns of samples at different sintering temperatures.](image)

**Figure 1.** SEM images of samples at different sintering temperatures: (a) 1300 °C, (b) 1350 °C, (c) 1400 °C, (d) 1450 °C, (e) 1500 °C.

**Figure 2.** XRD patterns of samples at different sintering temperatures.
Figure 3 shows the relationship between bulk density, apparent density and sintering temperature. Both the bulk density and apparent density shows an upward tendency as the sintering temperature rises, which indicates the sample gradually becomes densification. Simultaneously, it is also worthwhile to note that the ascent rate of bulk density and apparent density are relatively fast at 1400—1450 °C.

As known, the bulk density is associated with the densification of sample. The densification of sample is mainly depended on liquid phase formation which is filled the pores. However, the ascent rate of bulk density is relatively slow in the sintering temperature range of 1300—1400 °C. This can be explained that the sample is sintered by solid state sintering. The diffusion mass transfer, as the main model of mass transfer of sample, forms surface tension in the sintering stage. The particles are indented distance by the surface tension, resulting in open pores reducing. However, further increasing the sintering temperature to 1400—1450 °C, it is remarkably seen that the structure trends to densification. This is due to the components of additives of feldspar and pyrolusite powder, such as Na₂O, K₂O, CaO, MgO and MnO₂, which is beneficial to liquid phase formation along with the sintering temperature increases. Meanwhile, during to alkaline-oxides can reduce the viscosity of liquid phase [10]. The mass transfer pattern of sample is transformed to flow and mass transfer. However, the rate of flow and mass transfer is faster than that of diffusion mass transfer, which accelerates densification of sample [11]. Therefore the ascent rate of bulk density is relatively fast at 1400—1450 °C.

With regard to the apparent of sample, it is correlated with the internal porosity. At a low sintering temperature, the surface temperature of sample is relatively high, which accounts for the rate of surface diffusion faster that that of volume diffusion. With the sintering temperature increasing, the rate of volume diffusion is faster than that of surface diffusion, which leads to the internal porosity constantly eliminating. Therefore the apparent density shows upward tendency. However, it can be seen that the sintering temperature is up to 1450 °C or higher temperature, the apparent density remains unchanged, which can be explained that the internal pores are nearly inexistence.

![Figure 3. Bulk density and apparent density of samples at different sintering temperatures.](image)

The relationship between the breakage ratio and temperature is shown in figure 4. The breakage ratio decreases firstly and then increases with the increasing of temperature, reaching the lowest value of 3.76 % at 1450 °C. It can be accounted for two aspects: (a) The liquid phase is generated by adding the additive of feldspar and pyrolusite powder, accelerating densification of sample. (b) The needle-like mullite anisotropically grows to form the network structure. Chen et al [10] has demonstrated the mullite whisker was beneficial to improve the strength of sample. However, it is noticeable that the sintering temperature exceeds to 1450 °C, the breakage ratio of sample decreases. It can be explained that the liquid phase is so excessive that the strength of sample reduces.
4. Conclusion
High-strength corundum-mullite based ceramic proppants were synthesized by solid state sintering method. Adding feldspar is helpful to form the liquid-phase, which promotes the growth of corundum and mullite, decreasing the pore and boosting to the dense structure. The proppant sintered at 1450 °C shows an apparent density of 3.11 g/cm³, bulk density of 1.59 g/cm³ and the lowest breakage ratio (3.76 %) under 52 Mpa pressure, meeting the requirement of Gas industry standard SY/T 5108-2014. Compared with the proppants were fabricated by the raw material of high-alumina bauxite (>70 wt %), the proppant in this work displays the better resistance crush.

5. References
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