

Effect of Sintering Temperature on the Microstructure and Mechanical Properties of Low-Cost Light-Weight Proppant Ceramics

K Y Wang¹, H J Wang¹, Y Zhou¹, Y Q Wu¹, G M Li¹ and Y M Tian^{2*}

¹ School of Materials Science and Engineering, Taiyuan University of Science and Technology, Taiyuan 030024, China

² Shanxi Engineering Vocational College, Taiyuan 030009, China
E-mail: wangkaiyue8@163.com

Abstract: In this paper, the low-cost light-weight proppant ceramics were prepared with the solid wastes of coal gangue as the raw materials, and the effect of sintering temperature on the apparent porosity, bulk density, bending strength, microstructure and phase composition were investigated. The results showed that the ceramics, sintered at 1350°C, has the best performance with the bending strength of 85MPa, bulk density of 2.7 g/cm³ and apparent porosity of 18%. These properties of ceramics were very close to that of the bauxite-sintered, and thus the gangue were very probably selected for the preparation of proppants that involved in the exploitation of coalbed methane.

1. Introduction

Coalbed methane, known as "Mashgas", is a kind of high-quality chemical and energy resources. Shanxi Province is a large province of coal resources in China, and the reserves of coalbed methane are up to 10.39 trillion cubic meters, especially for two large mines of Qinshui and Hedong [1-3]. When the air concentration of coalbed methane exceeds 5%, it will explode in the case of fire. Therefore, coalbed methane has to be exploited before the coal mining. In order to achieve the industrial gas production, more than 96% of coalbed methane takes advantage of the hydraulic fracturing methods [4]. In the process of hydraulic fracturing, the proppants consist of spherical ceramic particles, which can resist the fracture closure to create the gas channel, and thus their performance directly determines the success or failure of hydraulic fracturing operations [5]. As the main raw material of proppant preparation, bauxite has become scarce and expensive [6]; thus, the need for a replacement is increasingly urgent.

The mechanical properties of the proppant are directly proportional to the content of alumina in the raw material. With the alumina content is increased, the mechanical properties of proppant are increased while the cost of proppant is greatly increased together [7]. Moreover, the density of proppant increased with the increase of alumina content, and then the proppants are not easy to be carried by the fracturing fluids which usually results in the accumulation of proppants at the gas pipeline clogging [8-9]. Compared with oil exploration, coalbed methane locates at the shallower and softer stratum, resulting in lower requirements for the volume density and the crush ratio of the proppants [10-11]. Hereby, a mineral with less Al₂O₃ is a better selection to reduce production costs. A major solid waste in the Shanxi province of China, coal gangue (~20.7 wt% Al₂O₃) has been used mainly for building cement but rarely for ceramics [7]. In this paper, the low-cost light-weight proppant ceramics were prepared with the solid wastes of coal gangue as the raw materials, and the



effect of sintering temperature on the apparent porosity, bulk density, bending strength, phase composition and microstructure were investigated.

2. Experimental

2.1 Raw materials

The starting materials of coal gangue were obtained from the Changqing Fracturing Proppant Co. Ltd., Yangquan, Shanxi, China. The coal gangue consists of 20.7 wt% Al_2O_3 , 65.7 wt% SiO_2 , and 13.6 wt% other oxides. In this paper, the bauxite powder was also involved which were usually selected for proppants. The chemical composition analysis of the bauxite powder is 60 wt% Al_2O_3 , 13.8 wt% SiO_2 , and 26.2% other oxides.

2.2 Experimental procedure

The raw material powder were milled into micrometer-size by a roll crushing mill and a QLM series jet airflow mill. Following that, homogeneous mixtures could be obtained by being ball-milled in an absolute ethanol medium for 6 h and then dried in an oven at 120°C for 36 h. The dried lumps were crushed, sieved through screening (100#) to break up agglomerates, and then compressed into $30\text{mm} \times 6\text{mm} \times 4\text{mm}$ bodies by a press machine under 15MPa pressure holding for 30s. Afterwards, the black bodies were dried at 120°C for 5 h and then sintered in a KBF1700 electron furnace in air at 1200, 1250, 1300, 1350, and 1400°C at holding times of 2 h, respectively. Lastly, the samples were cooled down to 400°C at a heating rate of $5^\circ\text{C}/\text{min}$ and furnace-cooled to room temperature.

2.3 Characterization

The bulk density D and apparent porosity P were determined in accordance with the American Society for Materials Standards ASTM C373, and calculated by using the formulas (1) and (2), respectively, where m_0 is the mass of the samples; m_1 is the mass of sample floating in the water after 24h water boiling and cooling-down to room temperature; m_2 is the mass of sample with the saturated water.

$$D = \frac{m_0}{m_2 - m_1} \times 100\% \quad (1)$$

$$P = \frac{m_2 - m_0}{m_2 - m_1} \times 100\% \quad (2)$$

The bending strength of ceramics was measured by a YDW-10 flexural testing machine. Values of the results were obtained from the average of at least 5 bars. Thermal properties of the raw materials were studied simultaneously by thermogravimetry (TG) and differential-scanning calorimetry (DSC) (METTLER TOLEDO 3+). The test was performed from 50 to 1300°C at a flowing nitrogen atmosphere with a heating rate of $10^\circ\text{C}/\text{min}$. X-ray powder diffraction (XRD, Philips Co. Ltd, Holland) was performed to identify the phase composition of the specimens by using Ni-filtered $\text{Cu K}\alpha$ radiation with a scanning speed of $0.02^\circ/\text{step}$. The microscopic morphology of the specimens was observed by field-emission scanning-electron microscopy (SEM, S-4800).

3. Experimental results

The TG-DSC results of coal gangue are shown in figure 1. Weight loss of the gangue mainly occurred from 350 to 900°C . A wide endothermic peak of the DSC curve was observed in the range of 200 to 400°C , which might have been caused by the loss of free and adsorbed water. With the increase in temperature, weight loss was 21.8%, and a valley appeared at approximately 510°C , which was caused by the combustion of residual coal in the gangue [12]. Weight loss between 890 to 1067°C was slight; however, abundant reactions and phase changes occurred. Metakaolinite decomposed into amorphous Al_2O_3 and SiO_2 at 976°C [13-14], after which, rod-like mullite ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$) appeared as the temperature increased [15]. Therefore, in our research, the samples were first heated to 300°C , at $5^\circ\text{C}/\text{min}$, and were held for 30 min to remove the water vapour, and were then heated to 650°C at

2°C/min and held for 30 min to eliminate the residual coal. Moreover, the sintering temperature was defined as higher than 1067°C to obtain a high-strength high-toughness mullite phase.

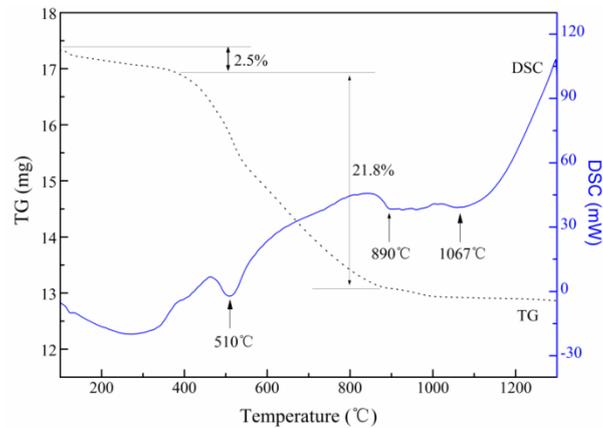


Figure 1. TG-DSC curves of coal gangue.

The sintering temperature has a great impact on the mechanical properties of ceramics [6,16]. The bending strength of ceramics sintered at different temperatures was shown in figure 2, which indicates that the highest bending strength of 85KPa was obtained at the sintering temperature of 1350°C. Figure 3 presented the bulk density and apparent porosity of ceramics sintered at different temperature. It indicated that that with the increase of sintering temperature, the apparent porosity decreased while bulk density increased, and then both of them remained steady when the temperature reached 1350°C (about 18% and 2.70 g/cm³, respectively).

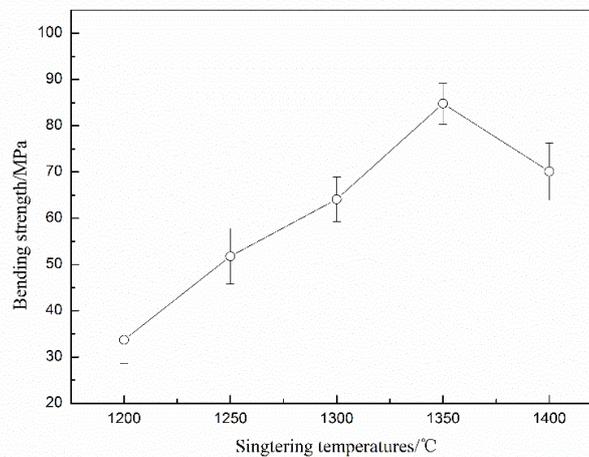


Figure 2. Bending strength of ceramics sintered at different temperatures

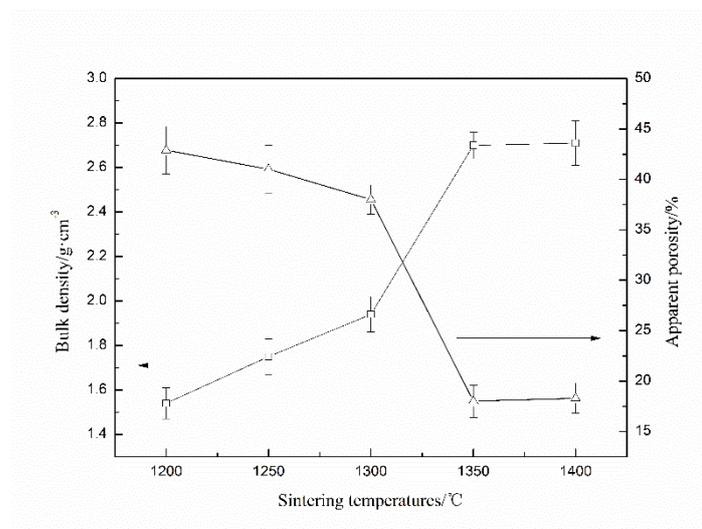


Figure 3. Bulk density and apparent porosity of ceramics sintered at different temperatures

Compared with the bauxite-sintered ceramics (as shown in Table 1), the samples obtained are low cost, and show a lower bulk density while similar bending strength and apparent porosity. Hereby, the gangue was very probably selected for the preparation of proppants that involved in the exploitation of coalbed methane. The low cost results mainly from the cheap starting materials of gangue and from the lower sintering temperatures.

Table 1. Comparison of two kinds of proppant ceramics

Raw materials	Sintering temperature[°C]	Bending strength[MPa]	Bulk density [g.cm ⁻³]	Apparent porosity
Bauxite	>1450	96	3.8	15%
Gangue	1250	85	2.7	18%

Figure 4. shows the XRD patterns of the ceramics sintered at different temperatures. At 1200°C, the proppants had a few peaks corresponding to the quartz phase (SiO₂) and mullite crystals (3Al₂O₃·2SiO₂); with the increase of sintering temperature, the peaks at 25.7° and 26.0° associated with the mullite crystals were generally enhanced and sharper, whereas the quartz-related peak located at 21.8° weakened.

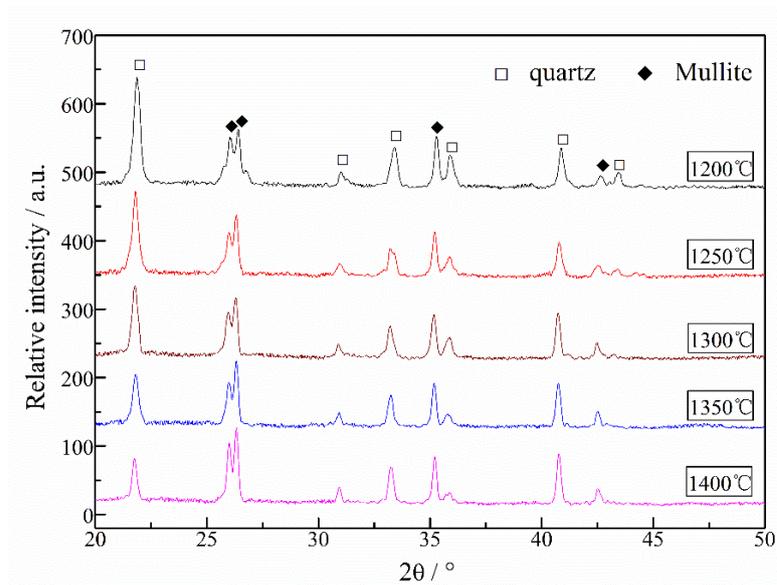


Figure 4. XRD patterns of ceramics at different sintering temperatures

Figure 5. shows SEM photos of fractured ceramics sintered at different temperatures. With the increase in sintering temperature, the porosity of ceramics decreases drastically. When the temperature reaches 1350°C, the bond bridge between crystal phase and glass phase becomes obviously improved and smooth.

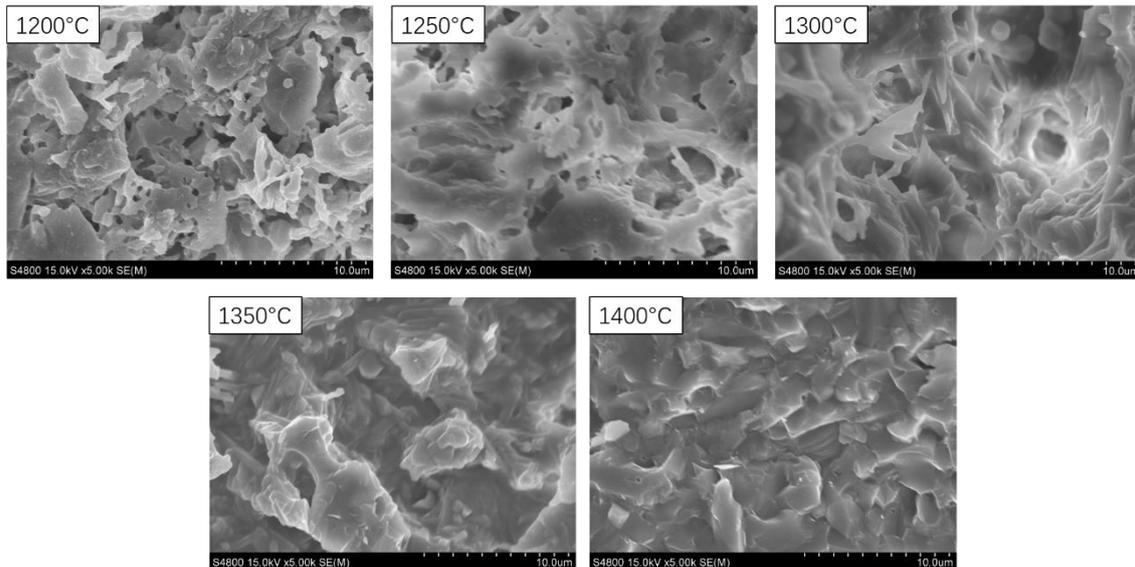


Figure 5. SEM images of the fractured ceramics at different sintering temperatures.

4. Discussion

The main crystalline phases of proppant ceramics sintered at 1200°C with coal gangue as the raw material are the mullite and quartz (see in figure 4). However, only the flake-like structures were observed in the 1200°C SEM photographs, and no regular geometric crystals appeared. When the temperature raised up to 1250°C, the materials began to melt and generally form amorphous glass phase (liquid phase). With the increase of liquid content, the speeds of diffusion and flow-mass transfer increased, and the liquid filled the gap among the particles, whereas, the particles flowed in the liquid phase, and the rearrangement occurred among the particles, and hereby, the porosity of

ceramics was greatly reduced. The diffraction peak of quartz phase went weaker as the temperature increased, which indicated that the quartz and other oxides formed into the amorphous state.

Although the XRD results showed the existence of mullite crystals below 1250°C, it was not observed in the SEM photograph until 1300°C. According to the TGA-DSC results, the mullite embryo formed below 1100°C. The presence of liquid phase facilitates the formation of acicular mullite. As the temperature increase up to 1300°C, These mullite crystal grows in size within the liquid phase through a dissolution and reprecipitation process from small-scale (fine acicular-like) shapes to thicker, large-scale, rod-like shapes. The viscous flow mechanism of liquid phase promoted the intense arrangement of the rod-like mullite grains [17] and the decrease of grain boundary between pores and gaps, which can lead to the densification of ceramic. Porosity can greatly determine the strength of the ceramics, and the source of cracks usually started at position of the pores [18], so, the stress at the pores of ceramics was larger than other parts of matrix. Glass phase can flow to the crack, the crack are thus covered with glassy phase. More glassy phase is consumed by alumina to form mullite at higher temperature and enhanced the strength of ceramics. Moreover, just as we know that the fiber-toughening effects improved the toughness and the strength of ceramics, the rod-like mullite also hindered the growth of internal micro-cracks.

5. Conclusions

In this work, the low-cost proppant ceramics sintered at 1350°C presented the best performance with a bending strength of 85MPa, an apparent porosity of 18% and a bulk density of 2.70g / cm³, which were very close to these of the bauxite-sintered, and thus the gangue were very probably selected for the proppants preparation in the exploitation of coalbed methane. During the sintering process, the oxides in the raw materials melted into amorphous liquid phase, and the diffusion mass transfer accelerated, promoted the growth of mullite embryo, the arrangement of the rod-like mullite grains.

6. References

- [1] Zhao X, Jian B, Xu Q, Liu J, Zhao Y and Duan P 2000 *Petroleum scienc.* 43 89-96.
- [2] Zou C 2013 *Unconventional Petroleum Geology.* 111–147.
- [3] Xu Z, Liu Q, Zheng Q, Cheng H and Wu Y 2016 *J. geochem explor.* 165 94-101.
- [4] Lu S, Cheng Y and Qin L 2015 *J china u min techno.* 25 819-825.
- [5] Song, D, Liu, Z, Wang, E, Qiu L, Gao Q and Xu, Z 2015 *Int rock mech min.* 78, 230-239.
- [6] Zhao J Z, Liu Z L and Li Y M 2015 *Mater. Lett.* 152 74.
- [7] Dong Z, Xia J, Fan C and Cao J 2015 *Constr build mater.* 100 63-69.
- [8] Zhao P F, Tian Y M and Liu A 2015 *China ' s Refractories.* 24 36-41.
- [9] Ma X X, Tian Y M, Zhou Y, Wang K Y, Chai Y S and Li Z G 2016 *Mater. Lett.* 180 127
- [10] Zhang D, Fan G, Ma L and Wang X 2011 *Int j coal geol.* 86 190-196.
- [11] Gu M, Dao E and K Mohanty 2015 *Fuel.* 150 191-201.
- [12] Yang N and Yue W 2000 *The Handbook of Inorganic Metalloid Materials Atlas* (Wuhan: Wuhan University of Technology Press)
- [13] Kakali G, Perraki T, Tsivilis S and Badogiannis E 2001 *Appl clay sci.* 20 73-80.
- [14] Xie Z and Xi Y 2001 *Cement concrete res.* 31 1245–49.
- [15] Wang C L, Ni W, Zhang Q S, Wang S, Gai G S and Wang W K 2016 *Constr build mater.* 104 109-115.
- [16] Liu Z L, Zhao J Z and Li Y M 2016 *Mater. Lett.* 171 302.
- [17] Chen C Y, Lan G S and Tuan W H 2000 *Jeur ceram soc.* 20 2519-2525.
- [18] Kong X C, Tian Y M, Chai Y S, Zhao P F, Wang K Y and Li Z G 2015 *Ceram. Int.* 4294–4300

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