Feasible Recycling of Industrial Waste Coal Gangue for Preparation of Mullite Based Ceramic Proppant

Guomin Li1, a *, Haiqiang Ma1, b,Yuming Tian2, c, Kaiyue Wang1, d, Yi Zhou1, e, Yaqiao Wu1,f, Xinwei Zou1, g, Jianying Hao1, h, Pinbo Bai3, i

1 School of Materials Science and Engineering, Taiyuan University of Science and Technology, Taiyuan 030024, Shanxi, P. R. China
2 Shanxi engineering vocational college, Taiyuan 030009, Shanxi, P. R. China
3 Changqing Fracturing Proppant Co. Ltd, Yangquan 045000, Shanxi, P. R. China
E-mail: ligm@tyust.edu.cn

Abstract. Industrial waste coal gangue was successfully utilized to prepare the mullite-based ceramic proppants. The experiments involved the pelleting technology of proppant through intensive mixer and following the sintering process under different temperatures. The crystalline phase, microstructure, density and breakage ratio of the proppants were investigated. The results showed that with the increasing of sintering temperature, the crystalline phases were transformed to rod-like mullite, which formed the cross-linked structure, improving the densification of proppants. Consequently, the breakage ratio under the closure pressure of 35 MPa exhibited declining trend and reached the minimum value of 6.8% at 1450 °C. Owing to the easy preparation, feasible design, low cost and moderate breakage ratio, the mullite-based ceramic proppant prepared by coal gangue and bauxite is promising candidate for fracturing proppants in future applications.

1. Introduction
Proppant is a crucial material used in the hydraulic fracturing operations in the petroleum and gas industry, and its main role is to “prop open” rock cracks to effectively improve the production of oil and gas wells. [1, 2] Traditionally, the high grade bauxite is the main raw material of preparing mullite-corundum based proppants, possessing excellent performance including high strength and acid resistant. However, the high grade bauxite is facing over-exploitation and exhaustion with the increasing exploitation demand of oil and gas, which results in the skyrocketing of high grade bauxite and the higher cost of proppants in return. Therefore, it is essential to seek the alternatives for the resource of high grade bauxite.

Coal gangue is the by-product discharged in the process of coal mining and coal washing, which formed and coexisted with coal seam during the course of coal formation, containing some combustibles and abundant minerals. Long-term and continuous accumulation of coal gangue not only occupies a large amount of cropland but also causes serious damage to the ecological environment. [3, 4] With the development of circular economy, industrial wastes are known as the misplaced resources. Consequently, the disposal and utilization of coal gangue has become an urgent problem. Recently, the use of coal gangue as raw materials for the preparation of cement, refractory materials and ceramics has already made certain progress. [5–8]

Despite much attention being focused on the recycling and reusing of coal gangue, there are only a few reports on its use preparing proppant. The main chemical compositions of coal gangue used in our work are SiO₂ and Al₂O₃ (see table 1), which are essential elements for the mullite formation,
providing silicon source and aluminum source. Our previous study showed that coal gangue could be used as the additive to synthesize the ceramic proppant applied in coal bed methane (CBM) well. [9] In this work, the coal gangue was originally exploited as the main raw material to replace part of the Ill bauxite to prepare the proppants of CBM well by pelletization and sintering process under different temperatures. Crystalline phase evolution, microstructure, bulk density, apparent density and breakage ratio of the proppants sintered at different temperatures were investigated to evaluate the feasibility of preparation technology. In addition, the mullite-based ceramic proppants synthesized by coal gangue and bauxite exhibit excellent anti-crushing ability, showing great potential for CBM well exploitation as low coat and high-efficiency fracturing proppants.

2. Experimental section

2.1 Preparation of proppant

The industrial waste coal gangue and natural low-grade bauxite (from Yangquan area in Shanxi Province, China) were used as the raw materials, and their components are displayed in table 1. First, the coal gangue and bauxite were ground to the desired size using a planetary ball mill. Second, the coal gangue (50 wt%) and bauxite (50 wt%) were transferred into an intensive mixer (R02, Eirich Co. Ltd, Germany) to mix homogeneously and following the pelletization of spherical green bodies by adding appropriate water discontinuously. After drying, the dried green bodies were passed through a set of sieves of meshes (aperture size of 0.90 mm–0.45 mm). Finally, the as-made samples were sintered in a multi-function electric furnace at different temperatures for 2 h, at a heating rate of 5 °C·min⁻¹ under Air atmosphere and then were passed through a set of sieves of 20/40 meshes (aperture size of 0.85 mm–0.425 mm). The final products were labeled as CP1200, CP1250, CP1300, CP1350, CP1400 and CP1450, according to the sintering temperatures.

| Raw materials      | Al₂O₃ | SiO₂ | Fe₂O₃ | TiO₂ | CaO | L.O.I |
|--------------------|-------|------|-------|------|-----|-------|
| Bauxite            | 62.3  | 12.4 | 5.0   | 2.8  | 0.5 | 17.0  |
| Coal gangue        | 27.4  | 30.7 | 8.1   | 2.7  | 0.3 | 30.8  |

2.2 Characterization of proppant

The bulk density, apparent density and breakage ratio under 35 MPa pressure were determined by the Chinese Petroleum and Gas Industry Standard (SY/T 5108–2014). Apparent density was measured based on the Archimedes' principle. Breakage ratio was determined by the following formula: $\eta = m_1/m_0 \times 100\%$, where $m_1$ is the weight of the crushed specimens after testing and $m_0$ is the weight of the specimens before testing. The composition and phase purity of the as-synthesized samples were analyzed by an X’Pert PRO diffractometer with Cu-Kα radiation ($\lambda=1.5406$ Å), in scan steps of 0.02° in a 2θ range from 10° to 90°. The microscopic morphology and structures of the samples were observed on a field emission scanning electron microscope (FESEM, S-4800).

3. Results and discussion

3.1 Crystalline phase evolution in proppants

Figure 1 shows the XRD patterns of a series of proppants treated at different temperatures. The detailed Crystalline-phase evolution of the proppant is summarized in table 2. When the sintering temperature is below 1350 °C, the main diffraction peaks of CP1200, CP1250 and CP1300 can be indexed as mullite and SiO₂, there is some Al₂O₃ coexisted as well. By calculating the ratio of Al₂O₃ to SiO₂ in our work, it is evident that the SiO₂ is sufficient. Whereas the sintering temperature is not high enough that there are still SiO₂ and Al₂O₃ coexisted. As the temperature increases to 1350 °C, the diffraction peaks of Al₂O₃ gradually disappear, the main phase composition of proppants is mullite, and there are several weak diffraction peaks that can be indexed as the crystalline planes of quartz.
With further increasing temperature, the phase composition for CP1400 and CP1450 is stable and not changed any more, implying that the reaction was completed.

![X-ray diffraction patterns](image)

**Figure 1.** X-ray diffraction patterns of the proppants sintered at different temperatures, where CP1200 to CP1450 mean that the samples were sintered at temperatures from 1200 °C to 1450 °C.

**Table 2.** Crystalline phase, density and breakage ratio (35 MPa) of proppants

| Crystalline phase       | Bulk density (g·cm⁻³) | Apparent density (g·cm⁻³) | Breakage ratio (%) |
|-------------------------|-----------------------|----------------------------|--------------------|
| CP1200 mullite/quartz/corundum | 1.23                  | 2.64                       | 12.9               |
| CP1250 mullite/quartz/corundum | 1.26                  | 2.67                       | 10.5               |
| CP1300 mullite/quartz/corundum | 1.28                  | 2.71                       | 9.9                |
| CP1350 mullite/quartz     | 1.30                  | 2.73                       | 9.7                |
| CP1400 mullite/quartz     | 1.36                  | 2.81                       | 9.3                |
| CP1450 mullite/quartz     | 1.54                  | 2.85                       | 6.8                |

3.2 Morphology characterization of the proppants

To observe the detailed microscopic structures, SEM images provide some insights into the morphology and structure of the samples, and the representative images of cross-sections of the proppants sintered at different temperatures are shown in figure 2. As can be seen from figure 2a and b, the samples of CP1200 and CP1250 exhibit loose and flake-like structure. With the increase of sintering temperature, the needle-shaped mullite crystals (see figure 2c) come into being and begin to grow larger. For the CP1350 sample, the boundaries between the acicular mullite crystals become unclear, which may result from the formation of glass phase. Furthermore, the morphology of the products change remarkably when the sintering temperature increases to 1350–1450 °C, as seen in figure 2d–f, the acicular mullite crystals grow further and are transformed into rod-like mullite, which forms the cross-linked and dense structure. During the fracture process, this unique structure can restrain the growth of internal micro-cracks due to the fiber-reinforced effect, just like the role played by steel rebar in the reinforced concrete structure. Based on the above analysis, the crystal phase evolution in proppant during the sintering process may undergo the following reactions.[10–13]

\[
3\text{Al}_2\text{O}_3 + 3\text{SiO}_2 \rightarrow 3\text{Al}_2\text{O}_3\cdot2\text{SiO}_2 (\text{Mullite embryo}) + \text{SiO}_2 (\text{Amorphous}) \quad (1100~\text{°C}~\text{to}~1150~\text{°C})
\]
\[
3\text{Al}_2\text{O}_3\cdot2\text{SiO}_2 (\text{Mullite embryo}) \rightarrow 3\text{Al}_2\text{O}_3\cdot2\text{SiO}_2 (\text{Acicular mullite}) \quad (1150~\text{°C}~\text{to}~1200~\text{°C})
\]
\[
3\text{Al}_2\text{O}_3\cdot2\text{SiO}_2 (\text{Acicular mullite}) \rightarrow 3\text{Al}_2\text{O}_3\cdot2\text{SiO}_2 (\text{Rodlike mullite}) \quad (1200~\text{°C}~\text{to}~1300~\text{°C})
\]
\[
\text{SiO}_2 (\text{Amorphous}) \rightarrow \text{SiO}_2 (\text{Quartz embryo}) \rightarrow \text{SiO}_2 (\text{Quartz cube}) \quad (1150~\text{°C}~\text{to}~1300~\text{°C})
\]
Figure 2. SEM images of cross sections of (a) CP1200, (b) CP1250, (c) CP1300, (d) CP1350, (e) CP1400 and (f) CP1450.

3.3 Density and breakage ratio
Density and breakage ratio values for the proppants are collected in table 2. Density is an important performance metric of any proppants. Variation of apparent density and bulk density with sintering temperature is shown in figure 3, from which it can be observed that the values of apparent density and bulk density incline to increase with increasing temperature. This is in agreement with the variation of breakage ratio, as shown in the inset in figure 3, which exhibits a decreasing trend with the increase of sintering temperature. Combining these results with figure 2, we know that the sintering process of proppants is actual a densification process accompanied by the elimination of pores and the formation of glass phase, because the glass phase can improve the arrangements of the rod-like mullite grains and decrease the grain boundary between the pores and gaps. This results in the increase of density and decrease of breakage ratio with the increasing of temperature. In addition, the appropriate amount of pores in proppants is beneficial to prevent the main crack from further growth and propagation in the process of fracture. The breakage ratio values of CP1300, CP1350, CP1400 and CP1450 under 35 MPa are less than 10%, meeting the standard as required by SY/T 5108–2014.

Figure 3. Bulk density, apparent density and breakage ratio (inset) under 35 MPa of proppants sintered at different temperatures.
Compared with the current products, our proppant exhibits low cost and high performance. Moreover, the roundness and sphericity of the proppants in our work all exceed 0.9, meeting the industrial standards. This further confirms the high efficiency of pelletizing technology using the intensive mixer.

4. Conclusion
The mullite-based ceramic proppants were successfully synthesized through pelletizing technology and subsequent sintering process, replacing 50 wt% bauxite by industrial waste coal gangue. Moreover, the density and breakage ratio of as-prepared products could meet the requirements of SY/T5108-2014 when the sintering temperature reached 1300 °C. This study showed that the design of replacing part of bauxite by coal gangue is feasible. The mullite-based ceramic proppants prepared by coal gangue and bauxite are promising fracturing proppants that can be mass produced and are commercially feasible for use in future applications. Furthermore, this facile synthesis strategy may open up a new avenue for the utilization of coal gangue in proppants preparation.

5. References
[1] Ma X X, Tian Y M, Zhou Y, Wang K Y, Chai Y S and Li Z G 2016 Mater. Lett. 180 127
[2] Zhao J Z, Liu Z L and Li Y M 2015 Mater. Lett. 152 72
[3] Li C, Wan J H, Sun H H and Li L T 2010 J. Hazard. Mater. 179 515
[4] Wang S B, Luo K L, Wang X and Sun Y 2016 Environ. Pollut. 209 107
[5] Cong X Y, Lu S, Yao Y and Wang Z 2016 Mater. Design. 97 155
[6] Gardner L J, Bernal S A, Walling S A, Corkhill C L, Provis J L and Hyatt N C 2015 Cem. Concr. Res. 74 78
[7] Ji H P, Fang M H, Huang Z H, Chen K, Xu Y G, Liu Y G and Huang J T 2013 Ceram. Int. 39 6841
[8] Xu H L, Song W J, Cao W B, Shao G, Lu H X, Yang D Y, Chen D L and Zhang R 2016 J. Mater. Cycles. Waste. Manag.19 1270
[9] Wang T H, Tian Y M, Zhou Y, Chai Y S, Li Z G and Bai P B 2016 J. Chin. Ceram. Soc. 35 848
[10] Chen C Y, Lan G S and Tuan W H 2000 J. Eur. Ceram. Soc. 20 2519
[11] Li N, Zhang X Y, Qu Y N, Xu J, Ma N, Gan K, Huo W L and Yang J L 2016 J. Eur. Ceram. Soc. 6 2807
[12] Schneider H, Schreuer J and Hildmann B 2008 J. Eur. Ceram. Soc. 28 329
[13] Zhu Z W, Wei Z L, Shen J X, Zhu L, Xu L, Zhang Y F, Wang S and Liu T 2017 Ceram. Int. 43 2871

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