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Toughening effect of mullite whisker within low-density ceramic proppants

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Abstract

Main crystal phases of low-density ceramic proppants prepared by bauxite and feldspar are granular corundum and whisker-shaped mullite. Mullite whiskers are interlocked with one another and piled up inside the pores. High aspect ratio of mullite whiskers inside the pores can greatly enhance the fracture toughness. The dominant toughening mechanism for the proppants is attributed to crack bifurcation and deflection and pulling out and bridging effect of mullite whiskers.

Keywords

ceramics, sintering, mullite whisker, toughening mechanism, crack bifurcation and deflection

Introduction

Ceramic proppants are crucial materials added in the hydraulic fracturing process to increase the conductivity of natural oil and gas wells and coalbed methane wells.[1,2] Currently, low-density high-strength ceramic proppants have been considered ideal fracturing materials[3] due to many advantages of being difficult to precipitate and easy to pump and low requirement of fracturing fluid viscosity. However, it is almost impossible to acquire both low density and high strength without additives. It has been reported that additives such as titanium dioxide, chromic oxide, and lanthanum oxide can improve the strength of proppants, but inevitably increase the manufacturing costs.[4] In addition, Liu et al.[5] reported many proppants were often performed at excessively high temperatures between 1300°C and 1600°C. Therefore, the research work should be focused on improving the fracture resistance of ceramic proppants. Meanwhile, low cost and low sintering temperature also need to be considered in the structural design of ceramic proppants.

Most ceramic proppants are alumina-based, using kaolin and bauxitic clays as the raw materials.[6] The phases of ceramic proppants mainly consist of corundum and mullite. Mullite is an outstanding phase with excellent properties, such as low thermal expansion coefficient, high creep resistance, good chemical and thermal stability, with retention of mechanical properties to elevated temperature and stability in oxidative atmospheres.[7] Above all, mullite whisker is an effective reinforcement for composite materials because of whisker toughening.[8]

Ceramic proppants can fracture when the stress reaches or exceeds a certain value. Previous studies have shown that the fracture of ceramic proppants was transgranular fracture rather than intergranular fracture.[4] In addition, there was a very interesting phenomenon that the breakage resistance of the proppants sharply increased with the slow increase of sintering temperature. This may be related to the toughening of mullite whiskers. To clarify this phenomenon in detail, the microstructure of ceramic proppants was systematically studied.

In the present work, second-grade bauxite and fluxing agent feldspar were used to prepare ceramic proppants at 1240°C. The toughening effect of mullite whisker within the proppants was explored from the microstructure.

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Table 1. Chemical compositions of the raw materials (wt%).

	Al_2O_3	SiO_2	Fe_2O_3	TiO_2	CaO	MgO	K_2O	Na_2O	LOI
Bauxite	60	13.8	6.5	2.4	0.3				17
Feldspar	9.08	46.73	0.82	1.04	9.29	4.47	4.91	3.06	20.6

Al_2O_3: aluminum oxide; SiO_2: silicon dioxide; Fe_2O_3: iron oxide; TiO_2: titanium dioxide; CaO: calcium oxide; MgO: magnesium oxide; K_2O: potassium oxide; Na_2O: sodium oxide; LOI: loss on ignition.

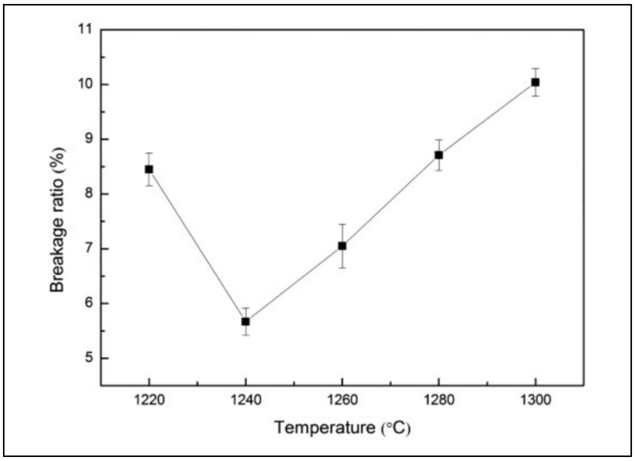

Figure 1. Breakage ratios of the prepared proppants.

Experimental

Second-grade bauxite (<65 wt%) and feldspar were used as raw materials, and the compositions are presented in Table 1. Bauxite of 85 wt% and feldspar of 15 wt% were first mixed homogeneously in a strong mixing machine (R02; Eirich Co. Ltd, Germany) and then spherical green bodies formed with the addition of water. The formed green bodies were dried at 100°C for 2 h in a drying box and subsequently passed through a set of sieves of 20/40 meshes (aperture size of 0.85–0.43 mm). Then, the 20/40 mesh green particles were put in a high-temperature box-type sintering furnace and sintered at different temperatures (1220°C, 1240°C, 1260°C, 1280°C, and 1300°C) in air atmosphere for 2 h at a heating rate of 5°C min^{-1}, followed by furnace cooling. Finally, the cooled proppants were passed through the sieves of 20/40 meshes.

The phase compositions of the proppants were identified by powder X-ray diffraction (XRD; X'Pert PRO; Philips Co. Ltd, Holland) utilizing nickel-filtered copper K_α radiation with a scanning speed of 0.02° $step^{-1}$. The microstructure was examined by a field-emission scanning electron microscope (SEM; S-4800; Hitachi, Japan).

Results and discussion

The breakage ratio of the proppants under 52 MPa closed pressure is shown in Figure 1. As shown in Figure 1, the breakage ratio of the proppants first decreases and then increases with the increase of sintering temperature. The breakage ratio of ceramic proppants is minimum value (5.67%) as the sintering temperature is up to 1240°C. As the sintering temperature rises above 1240°C, the increase of breakage ratio may be related to pores. To further research the reason why the proppants have good crushing resistance, the microstructure of the proppants sintered at 1240°C was analyzed.

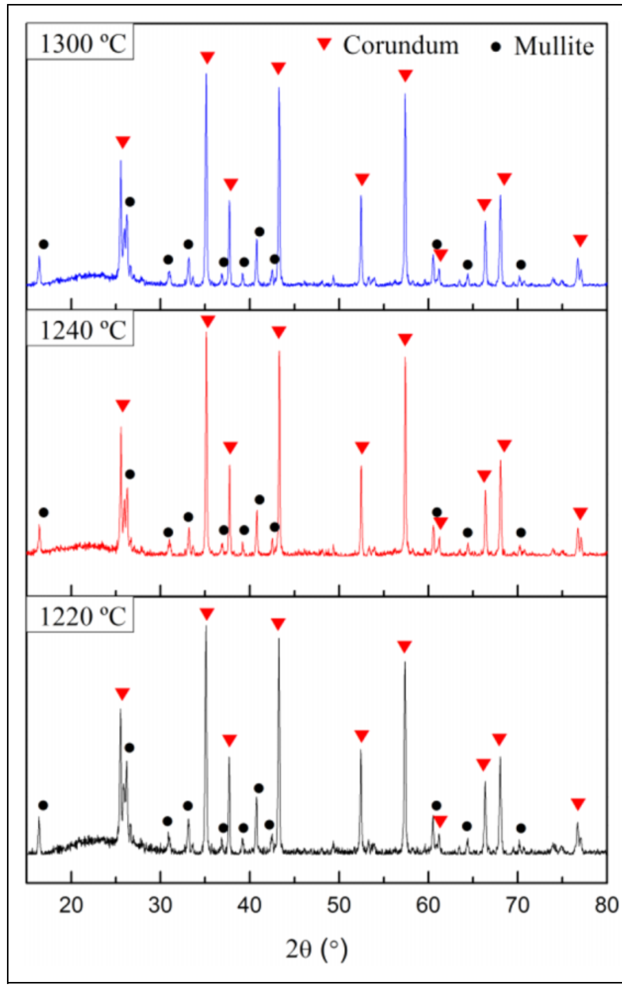

Figure 2. XRD patterns of the prepared proppants. XRD: X-ray diffraction.

Figure 2 displays XRD patterns of the proppants sintered at 1220°C, 1240°C, and 1300°C. From the patterns, the main diffraction peaks can be indexed to corundum (aluminum oxide (Al_2O_3); JCPDS: 10-0173) and mullite ($Al_6Si_2O_{13}$; JCPDS: 15-0776), and their diffraction peaks

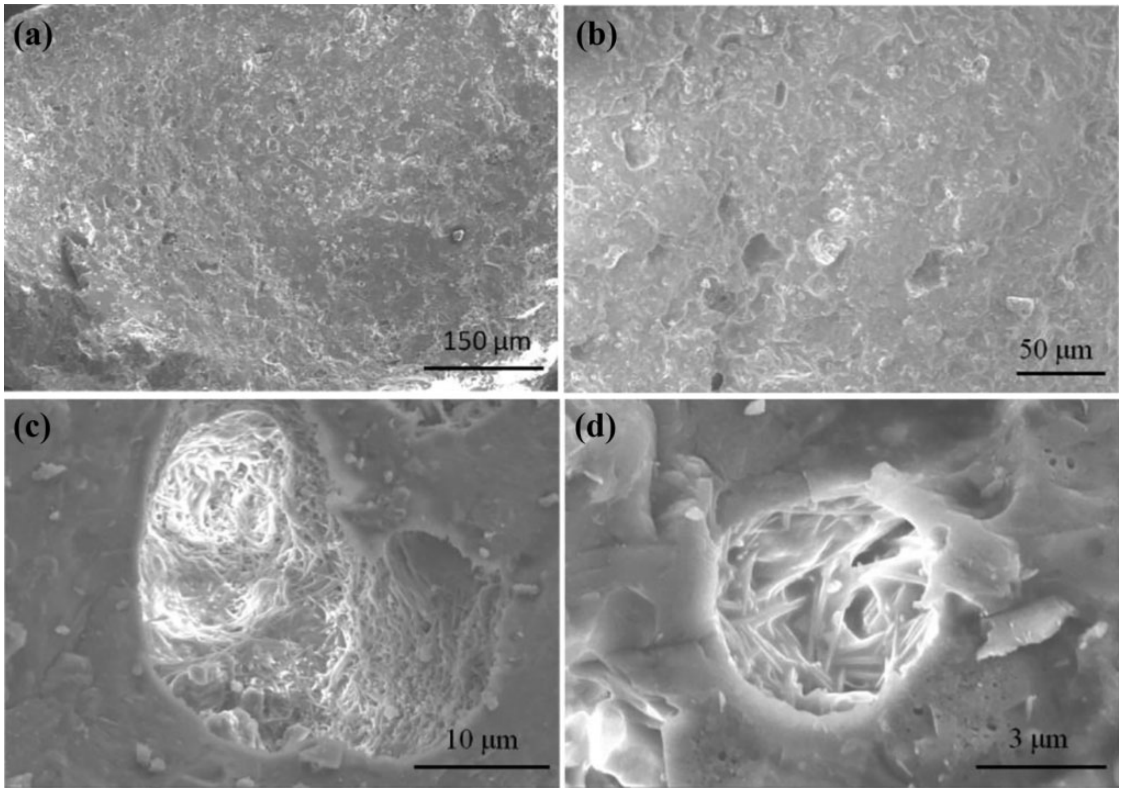

Figure 3. (a to d) SEM images of the proppants sintered at 1240°C (a: ×180, b: ×400, c: ×3000, d: ×10,000). SEM: scanning electron microscope.

are sharp, indicating corundum and mullite possess better crystallinity. It is obvious that the XRD patterns of the proppants sintered at different temperatures are very similar, and there is not much difference in the intensity of diffraction peaks. This shows that lower temperature has not much influence on the phase composition of the proppants. The crystal structure of corundum is trigonal with lattice constants $a = 4.758$ Å, $b = 4.758$ Å, $c = 12.991$ Å, while that of mullite is orthorhombic with $a = 7.546$ Å, $b = 7.690$ Å, $c = 2.884$ Å. There is no evidence of either Al_2O_3 or quartz phases. This indicates that feldspar can favor the formation of mullite crystals and promote the sintering process at low temperature.

Figure 3 presents low-magnification SEM images of the cross section of proppants sintered at 1240°C. It can be seen from Figure 3(a) and (b) that the proppants exhibit a fully glazed surface, and a few amounts of irregular small pores exist. Compared with the literature,[4] the fracture surfaces of the proppants look more ceramized and dense, which is mainly related to fluxing agent (feldspar). The melting point of feldspar is relatively low (about 1100°C),[9] and it melts over a range of temperature. This greatly facilitates the melting or decomposition of bauxite through appropriate mixing. In the present work, feldspar is used as a fluxing agent to form glassy phase at low temperature, especially as a source of alkali and alumina of glaze. From Figure 3(a), the glassy phase, resulted from the melting of feldspar, can encapsulate the precipitated crystals to produce glazed compacts owing to high viscosity of feldspar. In Figure 3(b), it is obvious that some small pores are connected by diffusion, and some small pores are still isolated. The size of the pores is about between 1 μm and 25 μm. The pores can result in the decrease of the density of proppants. Figure 3(c) and (d) presents high-magnification SEM images of the pores. Obviously a larger number of mullite whiskers are interlocked with one another and piled up inside the pores. It is well-known that pores are often areas of stress concentration. However, high aspect ratio of the mullite whiskers inside the pores can greatly enhance the fracture toughness.

Figure 4 shows SEM images of crack propagation in the proppants. It can be seen that cracks will appear when enough stress is applied to the proppants. In Figure 4(a) and (b), cracks appear in the stress concentration zone marked A under the action of external stress. And once a crack occurs, it will continue to extend forward owing to high fracture energy. As is shown in Figure 4(a), cracks initiate where stress is concentrated, and the initial cracks are wider. The cracks can bifurcate at the place marked B due to the resistance of mullite whiskers as they propagate forward. Crack bifurcation disperses the energy of the main cracks to a certain extent, which reduces the fracture energy

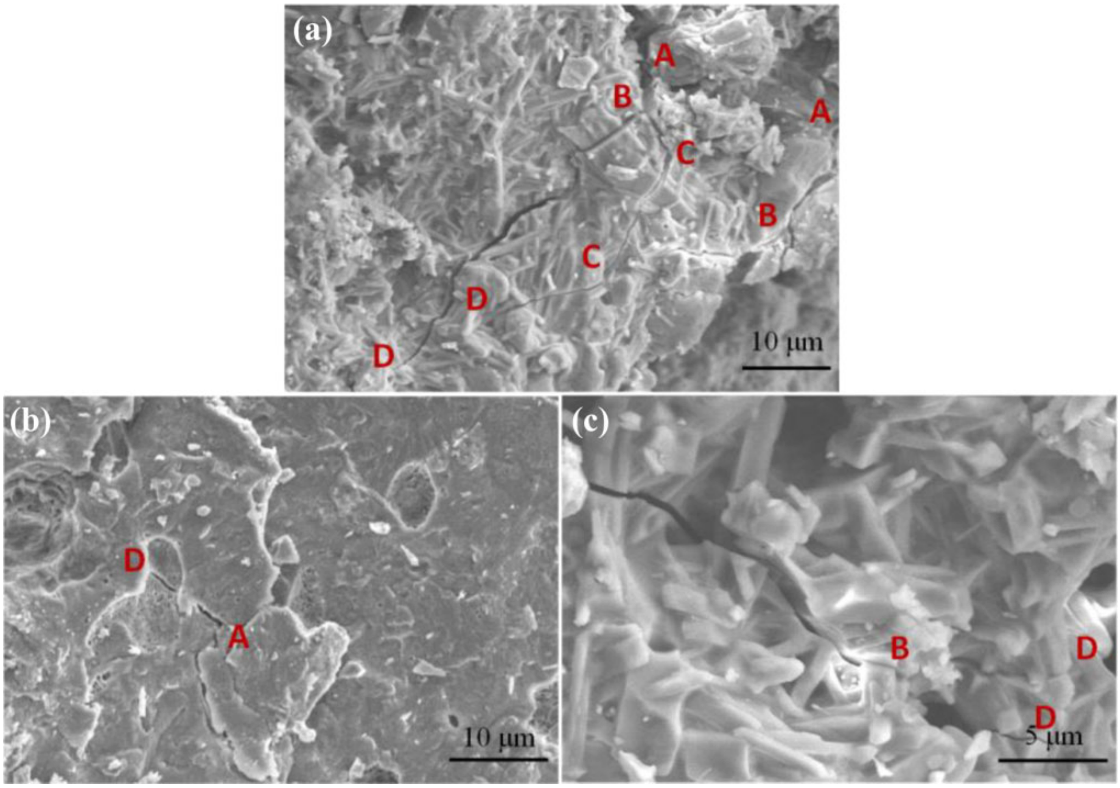

Figure 4. (a to c) SEM images of crack propagation in the proppants. SEM: scanning electron microscope.

and narrows the cracks. It is obvious that the sum of energy after crack bifurcation is lower than that before crack bifurcation. This indicates that the bifurcation of the crack can obviously consume the energy of the main crack. When the cracks with low energy resulted from the bifurcation continue to propagate forward, crack deflection occurs at the place marked C because of the resistance of mullite whiskers, resulting in slower propagating rate of the crack. In addition, the energy of crack decreases gradually. And every crack deflection consumes energy. It is obvious that many mullite whiskers undergo transgranular fracture, which retards the crack propagation by a kind of crack-closing mechanism. The pulling out or bridging effect of whiskers during fracture process makes the increase of energy dissipate as the proppants contain a certain aspect ratio of mullite whiskers. The cracks terminate at point D, thereby increasing the fracture toughness of the proppants.

In Figure 4(b), obviously, the point D at which the crack terminates is exactly inside the pore. This also confirms that the mullite whiskers in the pores have played a great role to withstand the crack propagation. Generally speaking, pores are often the source of fracture. However, when the crack extends to the pore in Figure 4(b), a large number of mullite whiskers in the pore prevent the crack from continuing to propagate forward, which prevents the proppants from breaking along the pore and improves the fracture toughness of the proppants. The toughening effect of mullite whiskers staggered in the pore is the same as that of Figure 4(a). Figure 4(c) is high-magnification SEM image of the development of crack. It is clear that the crack also bifurcates at point B rather than breaks through pore when it meets a small pore. Energy decreases after crack bifurcation. Then the bifurcated cracks terminate at point D very quickly owing to the pulling out or bridging effect of whiskers. This shows that the crack does not propagate across the pore but bifurcates along the surfaces of the pore. In short, the dominant toughening mechanism for the proppants is attributed to crack bifurcation and deflection and pulling out or bridging effect of mullite whiskers.

Conclusions

Low-density ceramic proppants were successfully fabricated at 1240°C by bauxite and feldspar. XRD pattern and SEM images suggest that the proppants are composed of granular corundum and whisker-shaped mullite. The addition of fluxing agent feldspar makes the proppants possess fully glazed surface. In addition, a few amounts of irregular small pores exist, and there are a larger number of mullite whiskers with high aspect ratio piled up together inside the pores, greatly enhancing the fracture toughness. Revealed by the fracture surface of the proppants, crack bifurcation and deflection disperse the energy of the main crack, and the pulling out and bridging effects of mullite whiskers retard the crack propagation.

Declaration of conflicting interests

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