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Evolution of the porosity and characterization of alumina matrix proppants from bauxite, ball clay and natural manganese ore

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A series of alumina matrix proppants based on the composition of bauxite and ball clay were studied. In order to improve the sinterability and mechanical properties, natural manganese ore (NMO) was used as a doping additive. The phase formation was estimated by XRD, the crush strength under 52 MPa closing pressure was measured, and as well the densification process was evaluated by the apparent density, real density, pore size distribution and microstructure. The results show that NMO doping leads to achieving a good crush strength in a wide temperature range of 1150-1350 °C. Open porosity decreased significantly at a high temperature of 1350 °C by doping with NMO, whereas closed porosity increases because of the existence of a considerable Fe_2O_3 content and excessive grain growth. The proppant obtained with a high crush strength and low apparent density, prepared by doping with 5 wt.% NMO and sintering at 1350 °C is beneficial to its utilization in the petroleum or gas industries.

Keywords: Al₂O₃, Natural manganese ore, Porosity, Proppant.

Introduction

The proppants are solid particles with a certain roundness and sphericity, which are used in hydraulic fracturing operations in the petroleum or gas industries. The proppants must have the mechanical strength of supporting the hydraulically created fracture, which form channels of higher permeability than the reservoir rock. An alumina matrix proppant is usually applied due to its outstanding crush strength and low acid solubility in wells. For their large scale application in an oil field, low cost has to be regarded as a priority when the compositions of fracturing proppants are considered. The preparation of an alumina ceramic with excellent properties always is associated with increased cost on account of second phases [1-4]. Low-grade natural manganese ore (NMO) consisting of Mn, Fe, Si and Al oxides is available in China and has the virtue of low cost [5]. The addition of reagent grade Mn(CH₃COO)₂·H₂O has been reported to promote grain growth and densification [2, 6]. However, few studies have involved the effect of NMO on the sintering behavior and mechanical properties of alumina ceramics.

In this paper, raw bauxite was used as a substitute for industrial grade alumina to prepare an alumina matrix proppant. NMO is used as an additive to improve sinterability, to control the microstructure and promote the mechanical properties. It is difficult to prevent the development of porosity in a proppant during the pelletizing process and pressureless sintering. In ceramic materials, porosity is considered as a negative factor, which significantly reduces the mechanical properties. The main purpose of the present study was to investigate the influence of a NMO additive on the evolution of porosity, on microstructural improvement and the crush strength of alumina matrix proppant, and to discuss the densification mechanism by studying the apparent density, real density, grain size, pore size distribution and morphology, as well as to find an optimal NMO content and sintering temperature for a proppant.

Experimental Procedure

The initial composition called BC was obtained by mixing 95 wt.% bauxite and 5 wt.% ball clay. Doping 1, 3, 5 and 8 wt.% NMO in the BC composition respectively, were designated as samples BCN₁, BCN₃, BCN₅ and BCN₈. The chemical compositions of the raw materials are given in Table 1. This shows that the bauxite consists of a large amount of Al₂O₃, as well as small amounts of SiO₂ and TiO₂, which is used as a substitute for industrial grade alumina to reduce the production costs. Ball clay is mainly composed of SiO₂ and Al₂O₃, which makes contributions in workability, plasticity and strength to the green bodies. The NMO containing a large amount of MnO₂, SiO₂, Fe₂O₃ and Al₂O₃ was doped as a sintering additive in this investigation.

The processing scheme was adopted as follows: the mixed powers were first homogenized in a ball mill with a

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Component	Bauxite	Ball clay	NMO
Al ₂ O ₃	81.60	40.30	18.52
SiO_2	7.21	55.36	29.65
TiO ₂	3.96	1.20	0.37
Fe ₂ O ₃	0.65	1.51	12.49
MgO	0.61	0.26	1.23
CaO	0.47	0.28	0.40
SO_3	0.45	0.11	0.02
P_2O_5	0.26	0.06	0.74
ZrO_2	0.17	0.04	0.02
K ₂ O	0.07	0.72	1.74
MnO ₂	-	0.01	33.68
Others	4	0.15	1.14

Table 1. Composition (wt.%) of the raw materials

rotation rate of 300 rpm for 6h, dried at 105 °C followed by 50 μ m sieving and left in a granulator to form spherical green bodies 0.75-1.25 mm in diameter. Sintering was carried out at temperatures between 1150 and 1350 °C in air with a heating rate of 5 K·minute⁻¹ and a soaking time of 3 h.

The crush strength was tested according to the standard of SY/T5108-1997 [7]. The crush strength of proppants was evaluated by the crush ratio. This could reach the standard in the case of a crush ratio with a value less than 10%. The proppants with size between 0.55-0.83 mm in diameter were tested under a stress of 52 MPa, where the stress was applied uniformly in one minute and held for another two minutes. The mass of proppants used in the test was W_{p} , and that of fractured particles sieved through an 0.45 mm screen was W_{f} . The crush ratio (*f*) was calculated using the formula:

$$f(\%) = \frac{W_f}{W_p} \times 100\% \tag{1}$$

The apparent density (ρ_A) of proppant was measured as follows: the pycnometer was first weighed (M_I), afterwards, proppants were put in it and weighed (M_3), distilled water was subsequently filled in and weighed accurately after pumping the air from the pores (M_4), lastly, the empty pycnometer full of distilled water was weighed (M_2), in addition, the density of distilled water was tested (ρ_L), The apparent density of proppant was calculated using the formula:

$$\rho_A(g/cm^3) = \frac{(M_3 - M_1)\rho_L}{(M_3 - M_1) - (M_4 - M_2)}$$
(2)

Open porosities ($P_{\rm O}$) were tested using a PoreMaster GT–60 mercury intrusion porosimeter (MIP). The real densities (ρ_R) were measured by a AccuPyc1330 pycnometer after the specimens had been crushed and milled to diameters less than 26 µm [8]. The closed porosity (P_C) and total porosity (P_T) was calculated using the following formulaes:

$$P_{\rm C} = 100(1 - \rho_A / \rho_R) \tag{3}$$

$$P_T = P_O + P_C \tag{4}$$

The chemical compositions of the raw materials were characterized using an ARL AdvantX X-ray fluorescence spectrometer (XRF). The crystalline phases of the sintered materials were identified using an ARL XTRA X-ray diffractometer (XRD). The microstructures of the sintered samples were observed using a JEOL JSM-5900 scanning electron microscope (SEM), equipped with an energy dispersive X-ray spectrometer (EDS). To prepare the samples for SEM observations, the samples were set in epoxy resin and finely polished using 20, 10, 5, 2.5 and 1 μ m diamond suspensions. Etching was required in order to distinguish alumina grains. Chemical etching was performed in a 40% HF solution for 10 minutes.

Results and Discussion

XRD patterns of sample BC and BCN₅ sintered in the range of 1150-1350 °C are shown in Fig. 1. It is clear that the main crystalline phases in the samples are Al₂O₃ and $3Al_2O_3 \cdot 2SiO_2$. At 1250 °C, the rutile derived from bauxite is identified in Fig.1(a). By contrast, aluminum titanate as a consequence of the reaction between rutile and alumina along with the disappearance of rutile peaks is identified in Fig.1(b). The intensity of mullite peaks increase with an increase of the temperature from 1250 °C to 1350 °C, as shown in Fig.1(a) and 1(b). This can be attributed to the formation of secondary mullite from the reaction of silica-



Fig. 1. XRD patterns of samples sintered at different temperatures for 3 h: (a) BC; (b) BCN₅. A- α -Al₂O₃; M- mullite; R- rutile; T- aluminum titanat.



Fig. 2. Crush ratio of samples sintered at different temperatures.

rich phases with alumina. The XRD analysis does not show the presence of any crystalline phase of Mn. In fact, the manganese displays a variable valency, so that a complex series of oxides may exist. Therefore different manganese cations with different valency states substitute on the aluminum cation sites, resulting in the formation of nonstoichiometric compounds in the alumina ceramic. This behavior is in agreement with the results reported in other studies [3, 9].

The crush ratio of proppants is illustrated in Fig. 2, which shows a similar reducing trend with an increase of the temperature, and exhibits their minimum values at 1350 °C. The sample BC only meets the demand at a temperature of 1350 °C, whereas sample BCN5 can achieve the specified value of crush strength (crush ratio less than 10%) in a wide temperature range of 1150-1350 °C, and thus it is prone to an optimal control of the sintering process. Compared with the sample BCN_5 , the crush strength of sample BCN_8 decreases slightly, which indicates that a suitable amount of NMO additive is beneficial to improve the crush strength of a proppant.

The apparent density of proppants as a function of sintering temperature is shown in Table 2. The results reveal that NMO promotes the apparent density at a low temperature (i.e. below 1250 °C). The apparent density of samples BC and BCN₅ is at its maximum at 1300 and 1200 °C, but decreases to 3.43 and 3.26 g/cm³ with further sintering at 1350 °C. Fig. 3 shows the effect of the incorporation of NMO on apparent density and closed porosity of proppants at a high temperature of 1350 °C. The closed porosity increases, while the apparent density reduces with an increase of the NMO content. The contrast in cross section microstructures of samples BC and BCN5 are shown in Fig. 4. There is a matrix containing a large number of connected, small size and irregular shape pores within the sample BC. However, the microstructural analysis of sample BCN₅ shows isolated, large size and approximately spherically-shaped pores. The enhancement of closed porosity and large pore size in the sample BCN₅ can be

Table 2. Apparent density of proppants obtained Apparent density/g·cm Sample 1150 °C 1200 °C 1250 °C 1350 °C 1300 °C 3.37 BC 3.33 3.40 3.46 3.43 BCN₁ 3.34 3.39 3.43 3.46 3.42 BCN₃ 3.40 3.43 3.37 3.45 3.46 3.29 BCN₅ 3.45 3.46 3.46 3.26 BCN₈ 3.39 3.43 3.45 3.28 3.24



Fig. 3. The effect of NMO content on apparent density and closed porosity of proppants sintered at 1350 °C.

4

NMO content/ wt.%

6

8

attributed to the existence of Fe₂O₃ in the composition. Oxygen will be produced at an elevated temperature, either with the occurrence of Schottky defects or Frenkel defects as described in equations (5) and (6). The oxygen is enwrapped by a liquid phase to form closed pores within the compact [10].

Schottky reaction:

3.20

0

2

$$3O_o^x + 2Fe_{Al}^x = 2Fe_{Al}^{'} + V_o^{''} + 1/2O_2$$
(5)

Frenkel reaction:

$$3O_o^x + 2Al_{Al}^x + 6Fe_{Al}^x = 6Fe_{Al}^x + 2Al_i^x + 3/2O_2$$
(6)

Beyond that, the presence of large size grains also induces an increase of closed porosity. As seen from Fig. 5, the microstructural analysis of sample BC shows irregular and angular grains with an average size of 2-3 µm. Sample BCN₅ presents an outstanding modification of grain size and morphology. A matrix of coarse grains with an average size of 5-10 µm surrounded by small grains with faceto-face contact is exhibited in Fig. 5(b). The EDS analysis that was carried out on a large size grain in polished and acid etched sample BCN5 is shown in Fig. 6. This indicates that Mn is well distributed throughout the grains. Therefore, it may be concluded that Mn cations substitute the Al sites, resulting in rapid diffusion within single grains during the sintering process. The process of excessive grain growth is enhanced as a result of the fast diffusion paths formed. Grain growth occurs with the dissolution of smaller grains during the liquid phase sintering. Thus, the small grains disappear along with the formation of some pores [11].



Fig. 4. Micrographs on polished surfaces of samples sintered at 1350 °C: (a) BC; (b) BCN₅.



Fig. 5. Micrographs on etched surfaces of samples sintered at 1350 °C: (a) BC; (b) BCN₅.



Fig. 6. EDS spectrum of a large size grain in sample BCN $_5$ sintered at 1350 °C.

Open porosity evolution of sample BC and BCN₅ during the sintering process is shown in Fig. 7. The pore size distribution of sintered samples displays a sharp peak at 0.5-1 µm. The open porosity decreases gradually with an increase of the temperature. The values for sample BC sintered at 1150, 1250 and 1350 °C are 35.63, 32.46 and 14.79%, and those for sample BCN₅ are 24.25, 18.80 and 5.29%, respectively. This implied that NMO has a positive effect on the decrease of open porosity. During liquid phase sintering, the wetting liquid will attempt to pull the particles together to minimize their respective free energy. But there is insufficient liquid phase to fill all the pores in sample BC, resulting in the formation of an amount of open pores in the sintered body. However, the liquid phase content is increased due to the dissolution of SiO₂, Fe₂O₃, and CaO introduced from the NMO, which is able to improve the densification through the fast liquid diffusion path and the capillary driving force [12-14]. The open, closed and total porosities of samples sintered at 1350 °C, together with the crush ratios are summarized in Table 3. The trend of the crush ratio varying with the NMO content is in accord with that of the total porosity. Sample BCN5 sintered at 1350 °C is not provided with a high crush strength but a low apparent density, which is prevailing in the petroleum or gas industry, by virtue of its prior strength and low settlement rate in a fluid [15, 16].

Conclusions

The results highlight that low-cost alumina matrix proppants with a high crush strength may be prepared by doping NMO into bauxite and ball clay. With an increase of the NMO content, the open porosity decreases and the crush strength is enhanced evidently, while the apparent density is reduced along with the formation of large quantities of closed porosity at a high sintering temperature. The larger the amount of NMO, the higher is the number of closed pores at a temperature of 1 350°C. This is related to the existence of Fe₂O₃ and grain growth behavior as a result of the addition of NMO. The 5 wt.% NMO-doped alumina matrix proppant is characterized by a low apparent



Fig. 7. Size distribution of pores in sintered samples: (a) BC; (b) BCN_5 .

Table 3. Open, closed and total porosities and crush ratio of proppants sintered at 1350 $^{\rm o}{\rm C}$

Sample	Open porosity/%	Closed porosity/%	Total porosity/%	Crush ratio/%
BC	14.79	4.56	19.35	6.30
BCN ₁	12.30	4.80	17.10	4.00
BCN ₃	9.24	6.19	15.43	2.80
BCN5	5.29	8.82	14.11	2.00
BCN ₈	5.10	9.46	14.56	2.60

density but superior crush resistance, which makes it favorable for utilization in the petroleum or gas industries.

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