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BASIC TECHNOLOGICAL FEATURES OF PRODUCTION AND PERFORMANCE EVALUATION OF PROPPANTS USED IN OIL AND GAS PRODUCTION BY HYDRAULIC FRACTURING

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The results of studies of the structure, phase composition, and mechanical and chemical properties of aluminosilicate, magnesia-quartz, and glass-ceramic proppants (RosProp, BorProp, ForeRCP, Wauli, etc.) are reported. It is shown that glass-ceramic proppants outperform ceramic analogs because a highly efficient method of dispersing a melt jet into droplets is used to spherize the particles and because of the structural features manifested in the formation of a homogeneous dense material represented by microcrystals with pyroxene composition.

Key words: proppants, hydraulic fracturing, ceramics, glass ceramics, chemical stability, sphericity, roundness.

Proppants (substances used to keep fractures open) are spherical granules used in oil and gas production by means of hydraulic fracturing of a formation in bedrock (HF). Hydraulic fracturing is a mechanical method of intensifying oil and gas production: fluid is pumped into the well at high velocities, causing fracturing of the bedrock formation and the formation of highly conductive fractures. To prevent their closure a proppant is fed into the well [1].

In accordance with GOST R 51761 and GOST R 54571, the main performance metrics of proppants include: sphericity, roundness, mechanical compression strength, particle size distribution, acid resistance, and density.

The mechanical compression strength is the most important property of proppants, making it possible to use them at great depths of oil and gas occurrence. Rounded quartz sand, whose strength does not exceed 42 MPa, can be used up to 2500 m. In the course of the development of hydraulic fracturing technology a need arose for proppants that can withstand high pressures. This is secured by using synthetic proppants, which are divided into proppants of medium and high strength in terms of mechanical strength in compression. Medium-strength proppants can withstand pressures up to 69 MPa, which corresponds to depth 3500 m. High-strength proppants, such as zirconium oxide, can withstand pressures up to 100 MPa, which allows them to be used at oil and gas depths > 3500 m [2, 3].

Granulometric composition, sphericity, and roundness of granules affect the packing density of proppants in a fracture and in consequence its filtration resistance and conductivity.

The density of proppants determines their transfer and arrangement along a fracture, hydraulic fracking being more efficient the lower the density.

Since acid-containing fluids are used in hydraulic fracturing, an important property of proppants is their acid resistance [4].

The fluids used in fracturing are classed as water- or oil-based polymer-containing fluids, multiphase and foamed fluids, emulsions, viscoelastic surfactant solutions, and acid systems. The choice of fluid for hydraulic fracturing is significantly influenced by the density of the proppant, to increase which requires the use of more highly viscous fluids, which complicates the implementation of hydraulic fracturing [4].

The most common synthetic proppants are aluminosilicate and magnesia-quartz proppants.

Proppants are produced by companies like Carbo Ceramics (USA), Norton-Alcoa Proppants (USA), Sintex (Brazil), Wauli (PRC), Borovichi Refractories Plant JSC (RF), Carbo Ceramics LLC (Eurasia) (RF), WellProp LLC (RF), and Fores (RF) LLC.

Aluminosilicate proppants are obtained mainly from refractory clays, kaolins and bauxites with prolonged firing at temperatures 1400 – 1600°C. To improve the physicochemical parameters of aluminosilicate proppants, the feedstock

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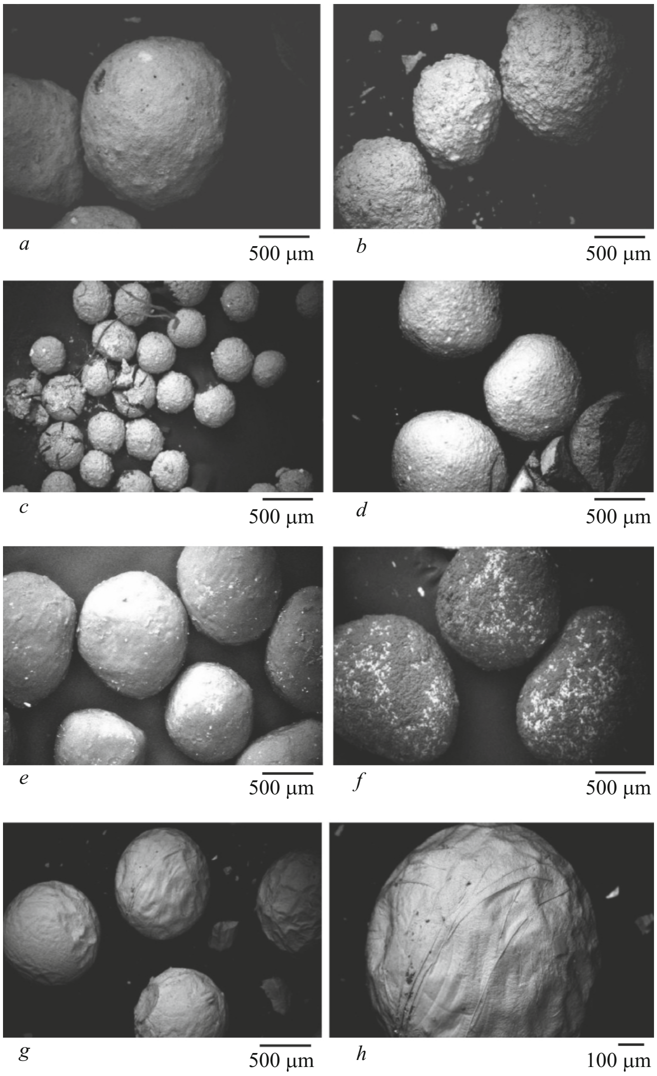

Fig. 1. Electron-microscopic images of proppants at magnifications ×40 and ×100: *a*) RosProp; *b*) BorProp; *c*) Wauli; *d*) ForeProp; *e*) ForeESP; *f*) ForeRCP; *g*, *h*) glass-ceramic proppants.

is fired beforehand at temperatures 900 – 1550°C. For higher completion of the sintering process, predominantly iron-containing sintering additives are introduced into the body. Formation of aluminosilicate proppants is conducted mainly in tower spray dryers and disk or drum granulators [5 – 7].

Magnesia-quartz proppants are obtained from talc, serpentinite, olivine and other magnesium-containing raw materials by double firing. During the first firing at temperatures 950 – 1200°C, all shrinkage processes take place in magnesium-containing raw materials. After heat treatment, quartz-feldspar or quartz sand is introduced into the magnesium-containing raw material for synthesis of clinoenstatite at the second firing stage at temperatures 1100 – 1350°C and reduction of the forsterite content, which reduces the performance of the proppant. The formation of magnesia-quartz proppants is conducted similarly to aluminosilicate proppants [8 – 14].

Glass-ceramics, which have superior characteristics, can be used as alternative materials for the production of proppants. The technological advantage of glass-ceramic proppants is the possibility of using petrurgic raw materials (basalts, diabases, granitoids, etc.) as raw materials, as well as waste from their extraction and processing [15 – 18].

Glass-ceramic proppants are obtained by dispersing a jet of melt into droplets, which in the course of flight acquire a spherical shape under the action of surface tension forces after which they undergo directed bulk crystallization [15 – 17].

A comparative analysis of the physicochemical properties of ceramic and glass-ceramic proppants was undertaken in the present work. A JSM-5610 LV scanning electron microscope with an EDX JED-2201 chemical analysis system (electron microscopy, chemical analysis), a Panalytical Empyrean DY1098 x-ray diffractometer (x-ray phase analysis), a Galdabini Quasar 100 universal electromechanical testing machine (strength characteristics), and automatic press for 1500 kN Matest C041N (strength characteristics) were used for the investigation. Electron microscopic images of proppants at ×40 and ×100 magnifications as well as the microstructure of ceramic and glass-ceramic proppants at ×500 and ×1000 magnifications are displayed in Figs. 1 and 2.

The standard technique employing the Crumbien–Schloss diagram was used to study the sphericity and roundness. A deviation from the spherical shape is defined as the ratio of the difference in the diameters of the perpendicular granules to the average diameter of the granule.

The proppants RosProp, BorProp and Wauli are aluminosilicate proppants. They are characterized by a distorted spheroidal shape with deviations from sphere of 4, 25, and 11% for RosProp, BorProp and Wauli, respectively.

Needle-shaped crystals with a cross-sectional size of 1 – 4 μm and 25 – 60 μm in a longitudinal section are present in RosProp proppants. Moreover, these proppants contain flaky crystals of various sizes. Needle and flaky crystals are randomly arranged. X-ray phase analysis (Fig. 3*a*) showed that RosProp proppants are 80% mullite and 20% corundum.

The BorProp proppants are characterized by a fine-crystalline granular structure with a significant number of pores with diameters 1 to 20 μm. Similarly to RosProp, BorProp proppants contain two main phases — mullite and corundum, but their corundum content is about 40%, which explains the relatively higher characteristics of the material (Table 1).

Similarly to BorProp, the Wauli proppants are characterized by a fine-crystalline granular structure and the presence of corundum and mullite as the main phases but at the same time relatively better physicochemical characteristics, which can be explained by a denser structure, the absence of pores, and a significantly higher corundum content (up to 90%).

Oxides of iron, titanium, chromium, and manganese are present in the chemical composition of aluminosilicate

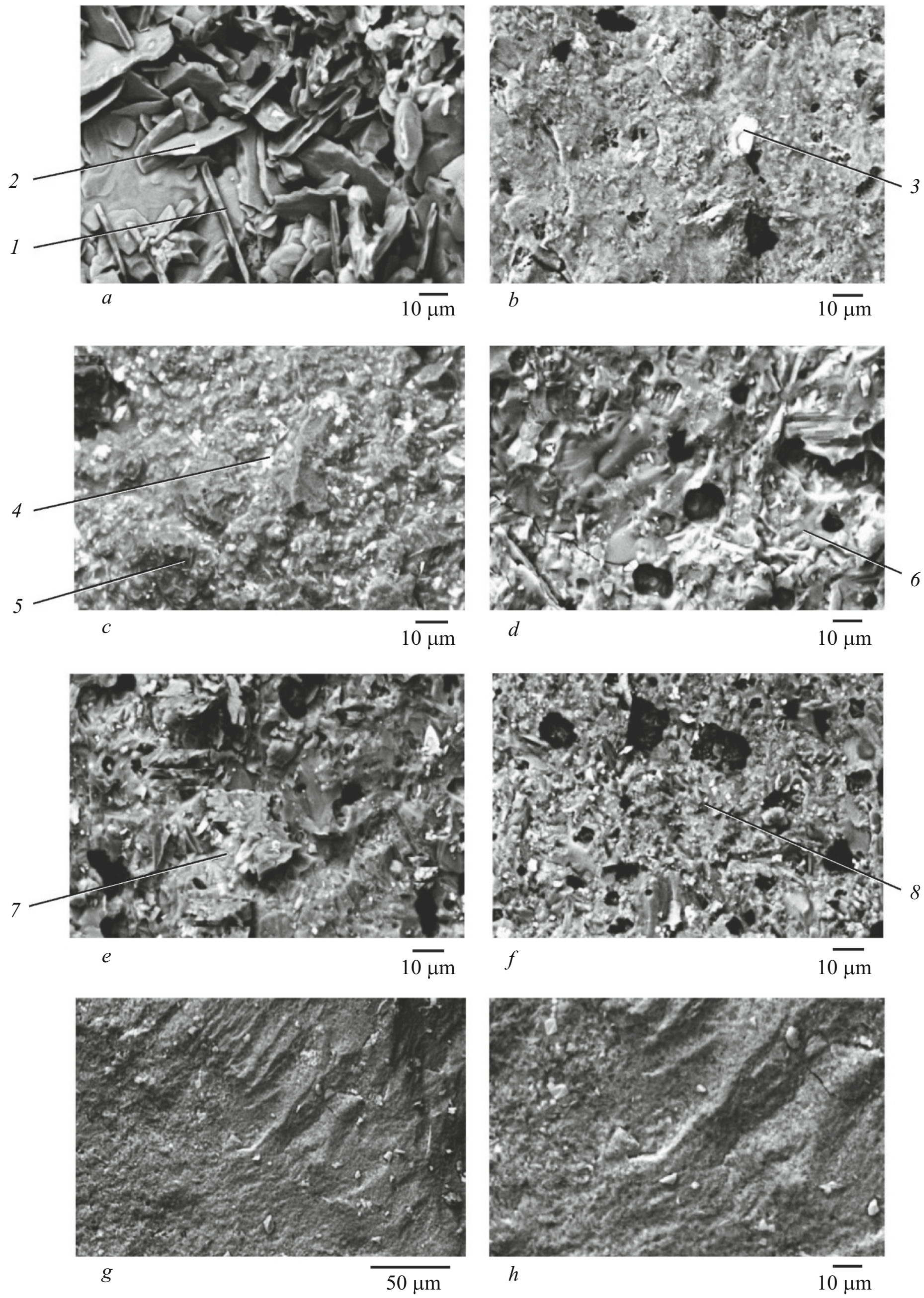

Fig. 2. Microstructure of proppants at magnifications ×500 and ×1000: *a*) RosProp; *b*) BorProp; *c*) Wauli; *d*) ForeProp; *e*) ForeESP; *f*) ForeRCP; *g*, *h*) glass-ceramic proppants; *1 – 8*) areas of chemical probe analysis.

proppants (Table 2); they act as mineralizers in these ceramics. Iron Fe^{3+} belongs to the additives that activate the sintering process but slow down the recrystallization process due to the formation of solid solutions with a wide isomorphism of cations, which prevent the growth of corundum crystals. Titanium, chromium and manganese oxides act as mineralizers that accelerate recrystallization and activate the sintering process due to the formation of solid solutions with sintered material with various types of point defects, which accelerate the diffusion of the slowest ion [19].

The chemical composition of ceramic proppants, determined using a JSM-5610 LV scanning electron microscope with an EDX JED-2201 chemical analysis system, at the points indicated in Fig. 2 is given in Table 2.

ForeProp, ForeESP and ForeRCP are magnesia-quartz proppants. Similarly to aluminosilicate proppants, magnesia-quartz proppants are characterized by a distorted spheroidal shape, and the deviation from the ideal spherical shape ranges from 5 to 25%.

TABLE 1. Main Performance Metrics of the Studied Proppants

Metric	Proppant/country of origin								
	RosProp[1]/ RF	BorProp[1]/ RF	Wauli[1]/ CPR	ForeProp[2]/ RF	ForeESP[2]/ RF	ForeRCP[2]/ RF	Glass-ceramic[4]/RB	Carbo Ceramics[3]/USA	Sintex[3]/ Brazil
Fraction	20/40	18/20	40/70	16/20	16/30	12/18	20/30	All fractions	
Sphericity, arb. units	0.9	0.7 – 0.9	0.9	0.9	0.7 – 0.9	0.7 – 0.9	0.97	0.9	
Roundness, arb. units	0.7 – 0.9	0.7 – 0.9	0.7 – 0.9	0.7 – 0.9	0.7 – 0.9	0.7 – 0.9	0.97	0.9	
Bulk density, kg/m^3	1900	1560	1650	1590	1670	1500	1680	–	1500 – 2100
Resistance to crushing at pressure 51.7 MPa, % of destroyed granules	4.47	2.56	1.17	3.72	1.63	0.39	0.30	Dependant on fraction and proppant type	
Solubility, %:								–	
HCl	0.12	0.05	0.47	0.97	0.05	0.61	0.8		–
HCl + HF	7.25	7.92	7.54	8.83	9.12	9.76	2.0		5 – 6
Loss on ignition, %	–	–	–	–	2.95	2.12	–	In the presence of polymer coating	

Notes:

[1] The studies complied with GOST R 51761.

[2] The studies complied with GOST R 51761.

[3] The manufacturer's declared data are presented.

[4] Designed and produced in the glass and fibrous materials industry laboratory.

TABLE 2. Chemical Composition of Proppants

Proppant	Control area (see Fig. 2)	Oxide weight content, %								
		SiO_2	Al_2O_3	MgO	CaO	$K_2O + Na_2O$	Fe_2O_3	TiO_2	Cr_2O_3	MnO
RosProp	1	18.2	65.3	–	1.5	–	10.6	4.4	–	–
	2	5.5	71.2	–	7.0	–	13.4	1.8	0.8	0.3
BorProp	3	27.4	59.2	–	1.7	–	7.8	2.9	1.0	–
Wauli	4	11.6	88.4	–	–	–	–	–	–	–
	5	12.6	69.7	–	0.7	0.5	8.3	5.2	–	3.0
ForeProp	6	59.6	6.7	22.8	1.3	0.5	9.1	–	–	–
ForeESP	7	60.6	3.4	24.6	0.9	0.6	9.9	–	–	–
ForeRCP	8	57.6	3.7	23.3	1.4	0.5	13.2	–	–	–
Glass-ceramic	–	43.9	13.3	6.3	12.7	5.4	15.4	1.5	1.5	–

All magnesia-quartz proppants are characterized by a loose granular structure with a different number of pores ranging in size from 1 to 20 μm.

X-ray phase analysis (Fig. 3*b* and *c*) showed that enstatite and protoenstatite are present in magnesia-quartz proppants as the main phases and anorthite and forsterite as secondary phases, and the forsterite phase is absent in the ForeProp proppants while the protoenstatite phase is absent in the proppants ForeRCP. Protoenstatite is a high-temperature modification of enstatite that on cooling passes into clinoenstatite, which can cause the material to crack as a result of volumetric changes. With rapid cooling of the material this polymorphic transformation does not occur, which determines the presence of protoenstatite in the studied proppants. However, during the operation of proppants, due to the effect of high pressures, the transition of protoenstatite to clinoenstatite is possible, which can degrade the operational properties of the material. Forsterite is an undesirable phase in magnesia-quartz proppants, because it significantly reduces the mechanical strength of the material.

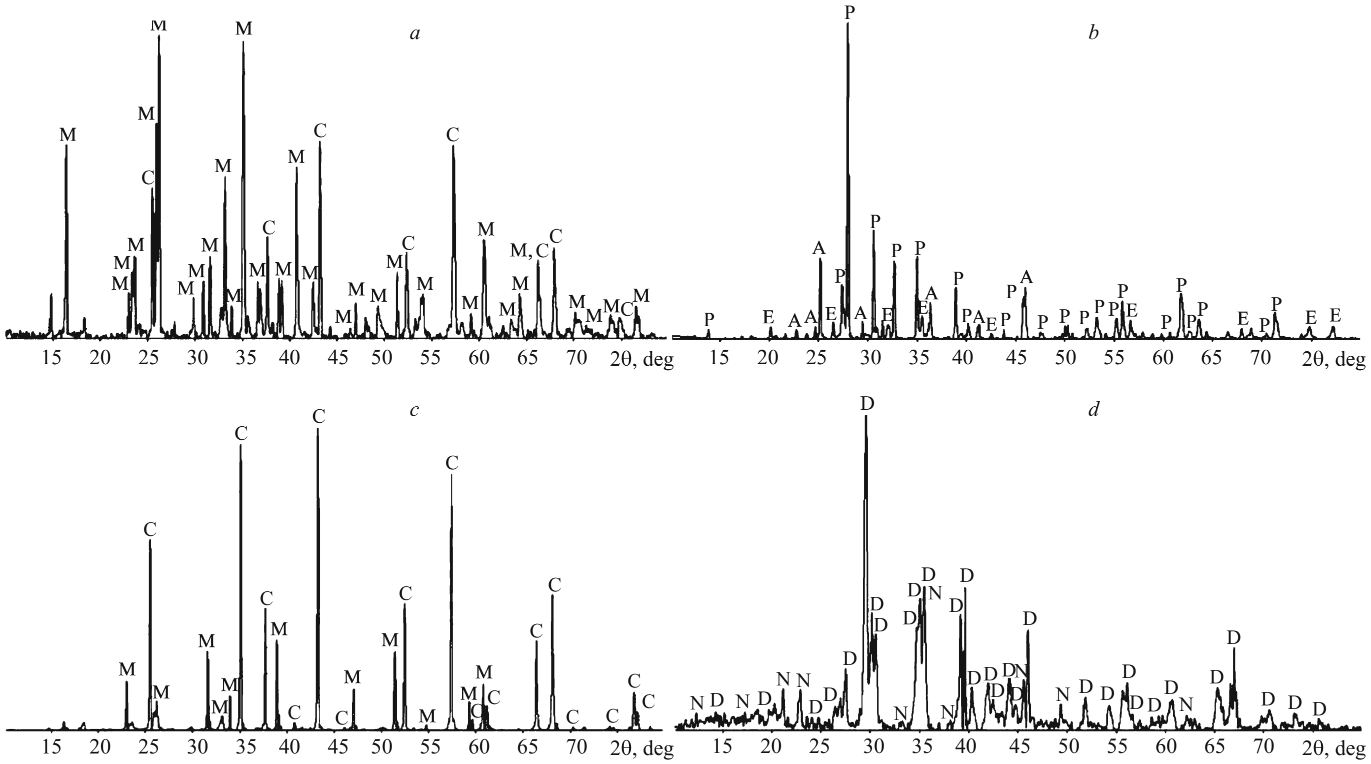

Fig. 3. Diffraction patterns of ceramic and glass-ceramic proppants: *a*) RosProp; *b*) ForeProp; *c*) Wauli; *d*) glass-ceramic; M) mullite; C) corundum; E) enstatite; P) protoenstatite; A) anorthite; F) forsterite; N) nepheline; D) augite.

Glass-ceramic proppants are characterized by a dense cryptocrystalline structure and a relatively small deviation from the spherical shape — up to 2%.

The main crystalline phase (Fig. 3*d*) in glass-ceramic proppants is a pyroxene solid solution of the augite type (Ca, Mg, Fe^{2+}) (Mg, Fe^{2+}, Al, Fe^{3+}) [$(Si, Al)_2O_6$], which is responsible for the high performance metrics of this glass-ceramic. Nephelin is a secondary phase, which actively crystallizes at a significant content of Na_2O in the presence of MgO.

The results for the mechanical strength in compression of magnesia-quartz ceramics and glass-ceramics are presented in Fig. 4. The studies were performed at constant loading rate 1 kN/min on cubic samples with dimensions 10 × 10 × 10 mm.

The values of the mechanical strength in compression for magnesia-quartz ceramics are at the level 200 MPa, while for non-crystallized glasses this value is higher and amounts to 360 MPa. After directed bulk crystallization of glasses at 850°C in 30 min the strength of the samples was 530 MPa, which is due to the formation of a fine-crystalline defect-free structure and a pyroxene solid solution of the augite type. Moreover, in terms of mechanical strength the obtained glass-ceramic is at the level of corundum ceramics, the mechanical strength of which reaches 500 MPa [20].

Glass-ceramic proppants surpass their ceramic counterparts in terms of the performance metrics. High metrics for the sphericity and roundness of glass-ceramic proppants are secured by using for spherization of particles the highly efficient method of dispersing a melt jet into droplets that acquire a spherical shape due to the action of surface tension forces. The formation of a pyroxene solid solution of the augite type during crystallization, which has a dense, fine-crystalline defect-free structure, provides high resistance to crushing and acids, which are the properties that determine the possibility of using materials as proppants.

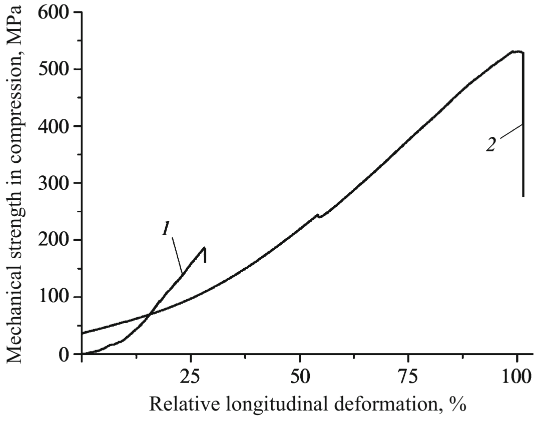

Fig. 4. Mechanical strength of magnesia-quartz ceramics and glass-ceramics: *1*) magnesia-quartz ceramics; *2*) glass-ceramic.

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