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ВЛИЯНИЕ ОКСИДОВ МАГНИЯ И ЖЕЛЕЗА НА ПРОЦЕССЫ ФАЗООБРАЗОВАНИЯ И СПЕКАНИЯ АНОРТИТОВЫХ МАТЕРИАЛОВ НА ОСНОВЕ ПРИРОДНОГО СЫРЬЯ

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Керамические проппанты на основе силикатов и алюмосиликатов различной структуры используются при добыче углеводородов методом гидроразрыва пласта. Недостатком существующих проппантов является их высокая кажущаяся плотность. Перспективным материалом для получения проппантов является анортит $CaO·Al_2O_3·2SiO_2$, однако широкое применение анортитовой керамики в данной области ограничено вследствие недостаточной степени изученности системы MgO-CaO-$Fe_2O_3(FeO)$-Al_2O_3-SiO_2. В связи с этим, были исследованы физико-химические процессы, протекающие при обжиге смесей на основе каолина и мела с добавками оксида магния и оксида железа (III) для получения анортитовой керамики. Установлено, что введение оксида магния в количестве 5 – 10% в шихту для получения анортита позволяет получать керамику с нулевым водопоглощением при температуре обжига 1250 °С. Увеличение температуры обжига до 1300 °С приводит к пережогу керамики и уменьшению ее прочности. Оксид магния взаимодействует с каолином с образованием шпинели и форстерита. Наиболее высокая прочность при сжатии (350 – 390 МПа) достигается при введении в шихту 5% MgO. Структура керамики – микрозернистая с размером зерен менее 5 мкм. Оксид железа (III) в незначительной степени минерализует процесс синтеза анортита за счет участия в твердофазной реакции образования твердых растворов на основе геленита. При температуре обжига 1350 °С происходит интенсификация процесса спекания керамики за счет плавления частной эвтектики между анортитом и оксидом железа (III), что снижает водопоглощение керамики с содержанием 5 – 10% Fe_2O_3 в шихте до значений порядка 2 – 3%. Прочность такой керамики составляет 230 – 250 МПа.

Ключевые слова: анортит, керамика, каолин, оксид магния, оксид железа, спекание, пористость, прочность, проппанты

MAGNESIUM AND IRON OXIDES INFLUENCE ON SINTERING PROCESSES AND PHASE FORMATION OF ANORTHITE CERAMICS BASED ON NATURAL RAW MATERIALS

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Ceramic proppants based on silicates and aluminosilicates with various structures are used in the hydrocarbons mining with hydraulic fracturing method. The disadvantage of these known proppants is their high apparent density. Anorthite $CaO·Al_2O_3·2SiO_2$ is a prospective material for proppants production. However, its wide application in this field is restricted due to insufficient

knowledge of the MgO-CaO-Fe_2O_3(FeO)-Al_2O_3-SiO_2 system. Consequently, the physical and chemical processes in the mixes of kaolin and chalk with magnesium oxide and iron(III) oxide additives during firing for anorthite ceramics were studied. It was found that adding of 5 – 10% magnesium oxide in batch for anorthite synthesis leads to obtain ceramics with near-zero water absorption at 1250 °C. Increasing the firing temperature to 1300 °C leads to overfiring of the ceramic and a decrease in its strength. Magnesium oxide reacts with the kaolin to form spinel and forsterite. The highest compressive strength (350 – 390 MPa) is achieved for ceramics with 5% MgO in the batch. The ceramics has fine-grained structure with the grain sizes less than 5 μm. Iron(III) oxide is a weak mineralizer for anorthite synthesis, and its mineralizing effect occurs during the formation of gehlenite-based solid solutions. The sintering process of anorthite ceramics is intensified at 1350 °C due to the melting of the anorthite – iron(III) oxide eutectic. This leads to decrease the water absorption of ceramics with 5 – 10% Fe_2O_3 in batch to about 2 – 3%. The compressive strength of this ceramics is about 230 – 250 MPa.

Key words: anorthite, ceramics, kaolin, magnesium oxide, iron oxide, sintering, porosity, strength, proppants

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INTRODUCTION

Ceramics proppants are spherical granules used in oil and gas mining through the hydraulic fracturing method. The proppants with the highest compressive strength are produced from mixtures of refractory clays, kaolin, and bauxites, which form mullite ($3Al_2O_3{\cdot}2SiO_2$) and corundum (α-Al_2O_3) in different ratios during firing. These proppants have a high apparent density (3.3-3.9 g/cm^3) and require high sintering temperatures about 1400-1600 °C [1]. The high density of proppants poses difficulties in oil and gas mining as it necessitates increasing the density of the transport liquid by adding various reagents, including acids. This leads to increased mining costs and higher quality requirements for oil and gas mining equipment. Consequently, there is currently extensive research being conducted on new materials for ceramic proppants with lower apparent densities [2].

The apparent density of proppants can be decreased to 2.5-2.7 g/cm^3, and sintering temperatures could be reduced to 1300-1350 °C by reducing Al_2O_3-containing components in the batch. This, along with the use of sintering additives, allows for the production of mullite and silica-mullite ceramics [3, 4]. Proppants with density 1.8-2.0 g/cm^3 and lower could be produced from the mixtures of red clays with low-melting nature raw materials [5]. However, these types of proppants contain a glassy phase that decreases their density but also reduces their compressive strength. As a result, these proppants cannot be used in deep occurrence hydrocarbon resources deposits.

Another method to reducing the density of proppants is through the synthesis of ceramics containing low-density crystalline phases, such as cordierite ($2MgO{\cdot}2Al_2O_3{\cdot}5SiO_2$) with a density of 2.60 g/cm^3. However, cordierite proppants exhibit low compressive strength [6, 7]. To solve this problem, cordierite-mullite composite ceramics have been synthesized [8], which possess higher strength. In addition, it should be noted that these composite ceramics require a higher sintering temperature (1350-1400 °C).

Anorthite ceramics are a promising alternative to cordierite ceramics. Anorthite ($CaO{\cdot}Al_2O_3{\cdot}2SiO_2$) has a density of 2.76 g/cm^3, and anorthite-based materials can be easily synthesized from stoichiometry mixtures of kaolin and refractory clays with CaO-containing constituents such as calcite, gypsum, limestone, etc., by firing at temperature ranging from 1100 to 1250 °C [9-13]. The addition of glass-forming components containing B_2O_3 or Na_2O to the batches in amounts of 8-10% leads to a decrease the closed porosity of anorthite ceramics [13-15].

There are active efforts underway to mine refractory clays and kaolin in the Russian Federation. Additionally, numerous studies have been conducted on local clay raw materials for their potential applications in various fields of science and technology [16]. However, using high-quality raw materials for the production of anorthite proppants is considered impractical due to limited mineral reserves. Currently, research in the field of proppants is focused on ceramic materials made from unconventional raw materials, including industrial waste [1, 7]. This approach allows for cost reduction in production and minimize the amount of waste that can not be effectively utilized through chemical methods [17].

Anorthite building and houseware ceramics can be obtained using red clays and waste materials, from metallurgical and energy industries, such as ash, slag and sludge [18-22]. These raw materials together form a $MgO\text{-}CaO\text{-}Al_2O_3\text{-}Fe_2O_3(FeO)\text{-}SiO_2$ system. Despite extensive research in this field, there is a lack of a systematic approach to studying this system, making it difficult to design and predict the properties of anorthite ceramics. In particular, the effects of magnesium and iron oxides on the physical and chemical processes during the synthesis and sintering of anorthite ceramics based on clays have not been well investigated.

MATERIALS AND METHODS

A model batch for anorthite synthesis was prepared by mixing enriched Kyshtym kaolin (KAH-1) and chalk (MTD-2, GOST 17498-72) in accordance with the stoichiometry of reaction (1).

$$\begin{aligned} &Al_2O_3{\cdot}2SiO_2{\cdot}2H_2O + CaCO_3 = \\ &= CaO{\cdot}Al_2O_3{\cdot}2SiO_2 + 2H_2O + CO_2. \qquad (1) \end{aligned}$$

Iron(III) oxide for ferrites (quality A according to TU 6-09-563-85) and heat-treated magnesium hydrocarbonate (analytical grade according to GOST 6419-78) were used as additives.

Batches were prepared by mixing the components with distilled water in a planetary mono mill Pulverisette 6 (Fritsch, Germany). Specimens with a cylindrical form (7×7 mm) were obtained using the cold uniaxial pressing method. A water solution of polyvinyl alcohol (5%) was used as a binder. The specimens were sintered at temperature ranging from 1200 to 1350 °C in an electric furnace. The porosity of materials were estimated by water absorption in accordance with GOST 7025-91. The compressive strength of specimens was examined using a hydraulic press PGM-100MG4 (Stroypribor, Russia). X-ray diffraction analysis was conducted using a DRON-3M diffractometer (Bourevestnik, Russia), and scanning electron microscopy was performed using a JSM 6000 microscope (Jeol, Japan).

RESULTS AND DISCUSSION

Anorthite ceramics sintering was intensified by the addition of MgO, as shown in Fig. 1. The water absorption of pure anorthite ceramics without additives after firing at 1200-1300 °C is 30-32%. The porosity of ceramics sintered at 1200 °C decreases with increasing MgO content. Adding 2.5% MgO to batch allows for a reduction in water absorption to 9-12%. Ceramics with 5-10% MgO have near-zero water absorption after firing at 1250-1300 °C.

Negative values of linear shrinkage are due to the expansion of materials during the thermal dissociation of calcium carbonate and kaolinite to calcium oxide (CaO) and metakaolinite ($Al_2O_3{\cdot}2SiO_2$) respectively, in the temperature range of 650-900 °C. For ceramics with 5-10% MgO in the batch, shrinkage is increased 12.5-15.0% with the firing temperature increasing from 1200 to 1250 °C, due to densification during sintering. However, there is a decrease in shrinkage values by 2-3% for ceramics with 5-10% MgO after firing at 1300 °C, which is attributed to overfiring of the ceramics. Water absorption of overfired ceramics does not increase.

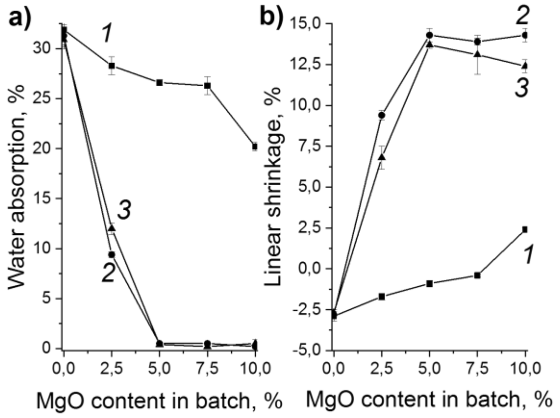

Fig. 1. Water absorption (a) and linear shrinkage (b) of anorthite ceramics with varying MgO content in the batch after firing at temperatures: 1 – 1200 °C; 2 – 1250 °C; 3 – 1300 °C

Рис. 1. Зависимость водопоглощения (а) и линейной усадки (b) анортитовой керамики в зависимости от содержания MgO в исходной шихте при температуре обжига: 1 – 1200 °С; 2 – 1250 °С; 3 – 1300 °С

The phase composition of ceramics (Fig. 2) is represented by anorthite ($CaAl_2Si_2O_8$), spinel ($MgAl_2O_4$) and forsterite (Mg_2SiO_4). The formation of spinel and forsterite is due to the solid-state reaction between metakaolinite and MgO according to reaction (2).

$$Al_2O_3{\cdot}2SiO_2 + 5MgO = MgAl_2O_4 + 2Mg_2SiO_4. \quad (2)$$

Spinel and forsterite possesses the simplest crystal structures in the $MgO\text{-}Al_2O_3\text{-}SiO_2$ system, which explains their primary formation in the ceramics.

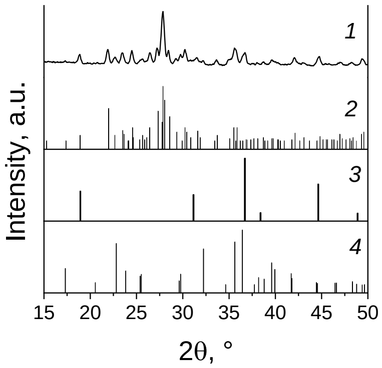

Fig. 2. XRD patterns of ceramics (1) with 10% MgO in batch after firing at 1300 °C and reference patterns of (2) $CaAl_2Si_2O_8$ (PDF # 12-0301), spinel (3) $MgAl_2O_4$ (PDF # 75-1798) and forsterite (4) Mg_2SiO_4 (PDF # 71-1081)
Рис. 2. Рентгеновская дифрактограмма керамики (1) с содержанием 10% MgO в шихте после обжига при 1300 °С и штрих-диаграммы эталонов анортита (2) $CaAl_2Si_2O_8$ (PDF № 12-0301), шпинели (3) $MgAl_2O_4$ (PDF № 75-1798) и форстерита (4) Mg_2SiO_4 (PDF № 71-1081)

Anorthite is a tectosilicate and has a more complex crystal structure compared to spinel and forsterite. According to [12, 13] the process of anorthite synthesis includes intermediate stages involving the formation of gehlenite ($2CaO{\cdot}Al_2O_3{\cdot}SiO_2$) and calcium orthosilicate ($2CaO{\cdot}SiO_2$). However, after firing at 1200 °C, anorthite is the only compound from the $CaO\text{-}Al_2O_3\text{-}SiO_2$ system present in the studied materials.

There is a deficiency of SiO_2 and Al_2O_3 relative to the stoichiometry of anorthite in ceramics due to the formation of by-products in the form of spinel and forsterite. Therefore, the composition of the materials in the $CaO\text{-}Al_2O_3\text{-}SiO_2$ diagram changes from pure anorthite point to points within an elementary triangle «anorthite-gehlenite-wollastonite». Within this triangle, there is low-temperature eutectic with a melting point of 1265 °C. Along with a small amount of impurities in kaolin, it provides the formation a melt at 1250 °C, which enhances the sintering of ceramics.

The calculated amount of liquid phase at eutectic melting point increases from 6.2 to 15.3% by mass as the MgO content in the batch increasing from 2.5 to 10.0%. For ceramics with 2.5% MgO in the batch, there is approximately 11-12% of liquid phase at 1300 °C, which is insufficient for liquid-phase sintering. This is evident in the higher porosity and lower fire shrinkage of these materials compared to ceramics with a higher MgO content. The compressive strength of ceramics with 2.5% MgO in the batch after firing at 1250-1300 °C is 160-200 MPa.

Ceramics with 7.5 and 10.0% MgO in the batch have 27 and 32% of the calculated amount of melt, respectively, at 1300 °C. This results in the formation of a significant amount of a glassy phase, which decreases the compressive strength from 340-390 MPa (1250 °C) to 120-290 MPa (1300 °C).

The highest strength characteristics are achieved for ceramics with 5% MgO in the batch, which exhibits a compressive strength of 380-390 MPa after firing at 1250 °C and 410-420 MPa after firing at 1300 °C. This is most likely attributed to the formation of an optimal amount of silicate melt (20-25%) during the sintering process. The ceramics demonstrate closed porosity with pore sizes ranging from 10 to 50 μm and fine-grain microstructure with grain sizes less than 5 μm (Fig. 3). The ceramics structure consists of sintered crystalline intergrowth of short-prismatic grains, strongly bonded to each other through interlayers of the glassy phase, which contributes to its high strength properties.

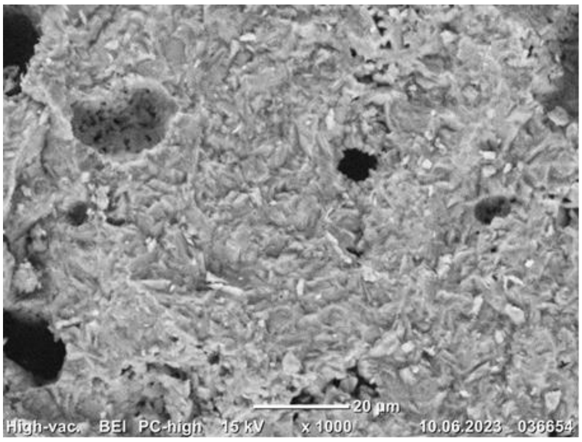

Fig. 3. Micrographs of fracture surface of anorthite ceramics with 5% MgO in the batch after firing at 1300 °C
Рис. 3. Микрофотография скола анортитовой керамики с содержанием 5% MgO в шихте после обжига при 1300 °С

Iron(III) oxide does not significant influence on the sintering of anorthite ceramics (Fig. 4). The water absorption of the ceramics after firing in the temperature range 1200-1300 °C is approximately 22-30%. A slight decrease in porosity is observed with an increase of Fe_2O_3 content for materials obtained at 1200-1300 °C. Anorthite ceramics with 5-10% Fe_2O_3 in the batch exhibit a water absorption of about 2-3% after firing at 1350 °C. The linear firing shrinkage of these materials is 11-12%. As mentioned earlier, the negative shrinkage of ceramics obtained at 1200-1300 °C is due to the expansion of materials during the decomposition of calcium carbonate and kaolinite.

The low-temperature eutectics with melting points approximately 1190-1200 °C are found in the $CaO\text{-}Fe_2O_3\text{-}SiO_2$ system. However, they are part of pseudobinary systems between calcium silicates and calcium ferrites. Therefore, their presence in the considered materials is unlikely because calcium ferrites are not observed in ceramics during the sintering temperature range (1200 – 1350 °C). The high porosity of ceramics obtained after firing at 1200-1300 °C also confirms the absence of melting during sintering in this temperature range.

The ceramics contain anorthite and hematite (α-Fe_2O_3), as shown in Fig. 5. According to [23] iron(III) oxide and kaolinite do not react with each other during heat treatment of their mixes in an air atmosphere.

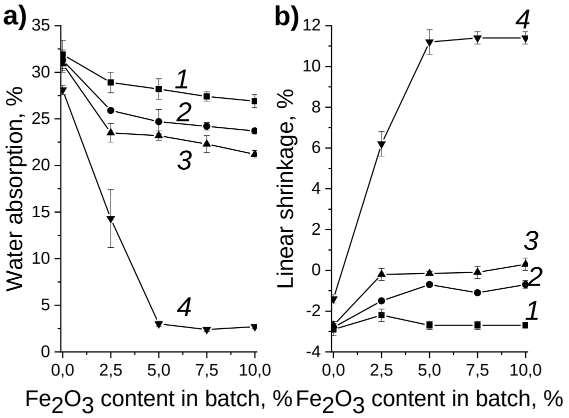

Fig. 4. Water absorption (a) and linear shrinkage (b) of anorthite ceramics with varying Fe_2O_3 content in the batch after firing at temperatures: 1 – 1200 °C; 2 – 1250 °C; 3 – 1300 °C; 4 – 1400 °C

Рис. 4. Зависимость водопоглощения (a) и линейной усадки (b) анортитовой керамики в зависимости от содержания Fe_2O_3 в исходной шихте при температуре обжига: 1 – 1200 °C; 2 – 1250 °C; 3 – 1300 °C; 4 – 1400 °C

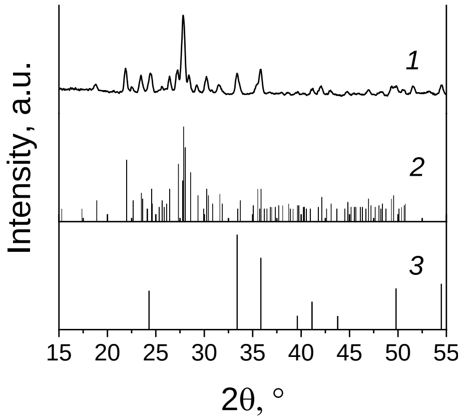

Fig. 5. XRD patterns of ceramics (1) with 10% Fe_2O_3 in batch after firing at 1350 °C and reference patterns of (2) $CaAl_2Si_2O_8$ (PDF # 12-0301) and hematite (3) α-Fe_2O_3 (PDF # 84-0310)

Рис. 5. Рентгеновская дифрактограмма керамики (1) с содержанием 10% Fe_2O_3 в шихте после обжига при 1350 °C и штрих-диаграммы эталонов анортита (2) $CaAl_2Si_2O_8$ (PDF № 12-0301) и гематита (2) α-Fe_2O_3 (PDF № 84-0310)

According to [23], solid-state reaction for synthesizing calcium ferrite from corresponding oxides begins at temperatures 950-1000 °C. However, experimental data suggest that in mixtures of kaolin, chalk and iron(III) oxide, the primary process during firing is the reaction between calcium carbonate and metakaolinite, resulting in the formation of anorthite precursors, such as gehlenite and calcium orthosilicate, followed by the direct formation of anorthite. Iron oxide in small concentrations can act as mineralizer of anorthite formation [25]. This explains the lower water absorption of Fe_2O_3-containing anorthite ceramics compared to pure anorthite ceramics.

The effect of Fe_2O_3 in the considered materials appears to involve the formation of solid solutions with melilite structure based on gehlenite, as shown in scheme of reaction (3). It should be noted that there is unlimited solubility in the binary $Ca_2Al_2SiO_7$-$Ca_2AlFeSiO_7$ system.

$$Al_2O_3{\cdot}2SiO_2 + xFe_2O_3 + 4CaO \rightarrow 2CaO{\cdot}(Al,Fe)_2O_3{\cdot}SiO_2 + 2CaO{\cdot}SiO_2. \qquad (3)$$

In accordance with [26], the ternary system «anorthite-silica-hematite» there exhibits an eutectic with a melting point of approximately 1340-1360 °C. This phenomenon can explain the decrease in water absorption of Fe_2O_3–anorthite after firing at 1350 °C. However, the «anorthite-hematite» side of this ternary system has not been extensively studied, making it difficult to calculate the amount of melt in ceramics during firing and estimate the optimal sintering temperature.

The material structure (Fig. 6) contains numerous relatively small closed pores with sizes ranging from 5 to 20 μm. The ceramics exhibit anorthite grains with sizes less than 3 μm, as well as coarses (5-7 μm) grains of hematite.

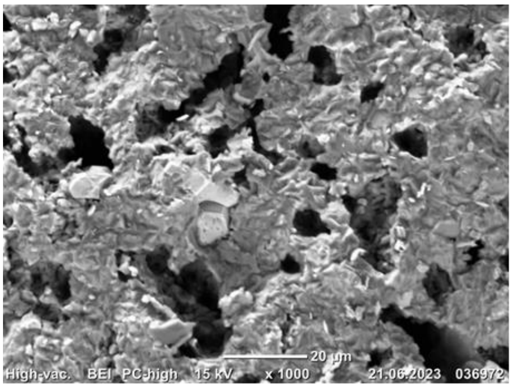

Fig. 6. Micrographs of fracture surface of anorthite ceramics with 10% Fe_2O_3 in the batch after firing at 1350 °C

Рис. 6. Микрофотография скола анортитовой керамики с содержанием 10% Fe_2O_3 в шихте после обжига при 1350 °C

The compressive strength of Fe_2O_3-doped anorthite ceramics obtained at 1200-1300 °C is 80-90 MPa. The reduction in ceramics porosity after increasing the firing temperature to 1350 °C leads to an improvement in strength of ceramics to 230-250 MPa to materials with 5-10% Fe_2O_3 in the batch.

CONCLUSIONS

The interaction between magnesium oxide and kaolinite in the batch for anorthite ceramics results in spinel and forsterite formations. This leads to a change the $CaO:Al_2O_3:SiO_2$ ratio from stoichiometric of pure anorthite to an increase in the CaO content in the $CaO-Al_2O_3-SiO_2$ system. As a result, there is 10-25% eutectic melt at 1250 °C during the sintering of anorthite ceramics with 5-10% MgO in the batch. This allows for the production of densely sintered ceramics with a fine-grain structure and high mechanical properties (340-390 MPa).

Iron(III) oxide is a weak mineralizer in the anorthite synthesis process and does not significantly influence sintering process of anorthite ceramics in the temperature range of 1200-1300 °C. Increasing the sintering temperature of anorthite ceramics with 5-10% Fe_2O_3 in the batch to 1350 °C allows for the production of materials with a water absorption 2-3% due to the melting of the $CaAl_2Si_2O_8-Fe_2O_3$ eutectic.

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The authors declare the absence a conflict of interest warranting disclosure in this article.

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