Science of Sintering, **45** (2013) 273-279

doi: 10.2298/SOS1303273A

UDK 666.762.15;549.632

Role of Acid-Base Interactions in Synthesis of Cordierite from Talc and Sillimanite Group Minerals

E. G. Avvakumov[1], G. G. Lepezin[2], A. A. Gusev[1], O. B. Vinokourova[1]
[1] Institute of Solid State Chemistry and Mechanochemistry SB RAS, St. Kutateladze, 18, Novosibirsk, 630128, Russia
[2] Institute of Geology and Mineralogy SB RAS, Prospekt Akademika Koptyuga, 3, Novosibirsk, 630090, Russia

Abstract:
It has been found that the mechanical activation of mixtures of sillimanite group minerals with talc and silica additives in grinding-activating devices with periodic and flow action provides significant acceleration of their interaction with formation of cordierite at the subsequent high-temperature treatment. It is shown that the output of cordierite depends on nature of mineral: in mixture with a sillimanite it is considerably higher, than with an andalusite and kyanite, while the rate of mullitization of these minerals has opposite character. It means that the formation of mullite during heat treatment is not a limiting step in synthesis of cordierite. It is shown that the rate of reaction is determined by the difference in the acid-base properties of these minerals, which depend on the coordination of aluminum cations by oxygen ions, different for each of the modifications.
Keywords*: Cordierite, Synthesis, Sillimanite group minerals, Talc, Quartz, Mechanical activation, Heat treatment*

1. Introduction

Studying of synthesis, structural and chemical properties of the cordierites are being developed intensively with the aim of preparation on their base of materials with the predetermined properties distinguished by low coefficients of thermal expansion allowing using them in the various areas of technology.

The most complete summary of the methods for producing cordierite ($2MgO \cdot 2Al_2O_3 \cdot 5SiO_2$) and cordierite ceramics is given in [1]. Cordierite is synthesized by solid state reaction, crystallization from the melt, crystallization of glasses of appropriate compositions, gels calcination (sol-gel method), pyrolysis and combustion of mixtures and hydrothermal method.

Cordierite is prepared in industry usually by sintering of mixtures of talc ($3MgO \cdot 4SiO_2 \cdot H_2O$), kaolin ($Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$) and aluminum oxide Al_2O_3, at temperatures of 1400-1500 °C for 20-60 hours, in this way synthesized products contain cordierite and 20% of other phases including spinel, mullite, clinoenstatite that degrade performance properties of ceramics. For this reason, new methods are developed to bring down energy expenses and to improve quality of end products. They include a method of mechanical activation of mixtures with the subsequent heat treatment. Application of this method to the above mixture allowed to reduce the temperature, to increase the rate of formation of cordierite and to reduce

*) **Corresponding author**: avvakumov@solid.nsc.ru

quantity of by-products (undesirable and harmful) [1]. These data have been obtained with the use of laboratory planetary mills providing high-energy ball milling, but a large-scale implementation requires mills of continuous action. One version of a flow centrifugal mill proposed recently [2, 3, 13], was used along with a laboratory mill in this work.

Talc, kaolin and alumina are not the only materials for preparation of cordierite. It can be synthesized also from mixtures of other minerals. In particular, the sillimanite group minerals (andalusite, sillimanite, kyanite) can be used as alumosilicate raw materials.

Synthesis of cordierite from kyanite and talc has been realized in [4]. It is shown that the process passes through the stage of formation of mullite from kyanite and subsequent interaction with talc and quartz:

Stage 1: $3\,(Al_2O_3 \cdot SiO_2) = (3Al_2O_3 \cdot 2SiO_2) + SiO_2$

Stage 2: $2\,(3Al_2O_3 \cdot 2SiO_2) + 3\,SiO_2 + 2\,(3MgO \cdot 4\,SiO_2 \cdot H_2O) =$
$3\,(2MgO \cdot 2Al_2O_3 \cdot 5SiO_2) + 2\,H_2O$

It is possible that the interaction with andalusite and sillimanite occurs in a similar way, but we have not found the information concerning this question in the literature.

However, it is known that mullite’s formation from andalusite and sillimanite requires higher temperatures than that from kyanite. Temperature of decomposition of kyanite into mullite and quartz is 1340°C, same for andalusite and sillimanite is 1530°C and 1650°C respectively [5]. Therefore, synthesis of cordierite with the participation of andalusite and sillimanite, if a limiting stage is formation of mullite, should be much more difficult than with participation of kyanite.

In this paper, we study the influence of mechanical activation in the grinding devices and subsequent high-temperature processing on the rate of synthesis of cordierite from mixtures of talc with sillimanite group minerals with a view to identifying the factors that determine the synthesis of cordierite.

2. Experimental

The experiments were carried out on a mixture of talc, quartz and one of sillimanite group minerals. The impurity of the components in raw products consist primarily of iron, the total content of impurities in them does not exceed 1% by mass (table 1).Mechanical activation was carried out in planetary mill AGO-2 (acceleration of 40 g) with steel vials and steel balls of 8 mm in diameter [6] as well as in flow centrifugal mill of continuous action [2, 3, 13]. In the case of AGO-2, ball mass to sample mass ratio was 20:1, the activation time was varied from 5 to 15 minutes. Passing the mixture through a flow centrifugal disc mills produced 35 kg / h. The integral intensity of 100% of the reflex of cordierite (with the interplane distance 0,862 nm (2θ=10.74) in X-ray diffraction patterns was used for the quantitative determination of the content of cordierite, which is present in the products of calcination.

3. Results and discussion

Sillimanite group minerals have the general formula $A1_2SiO_5$ (wt% $A1_2O_3$ = 62.9; SiO_2 = 37.1), but belong to different polymorphic modifications, their stability in the field of pressure-temperature (PT) the coordinates are shown in Fig. 1 [9, 12]. The stability field of magnesium cordierite is shown here also [10]. The presented data show that the cordierite in equilibrium with kyanite can co-exist only at high pressures and in a very narrow field, while with andalusite and sillimanite, it has a wide area of overlap. It would be possible to assume that formation of cordierite with participation of kyanite should be much faster and at lower temperatures than with participation of andalusite or sillimanite, but our experiments have shown that this is not so.

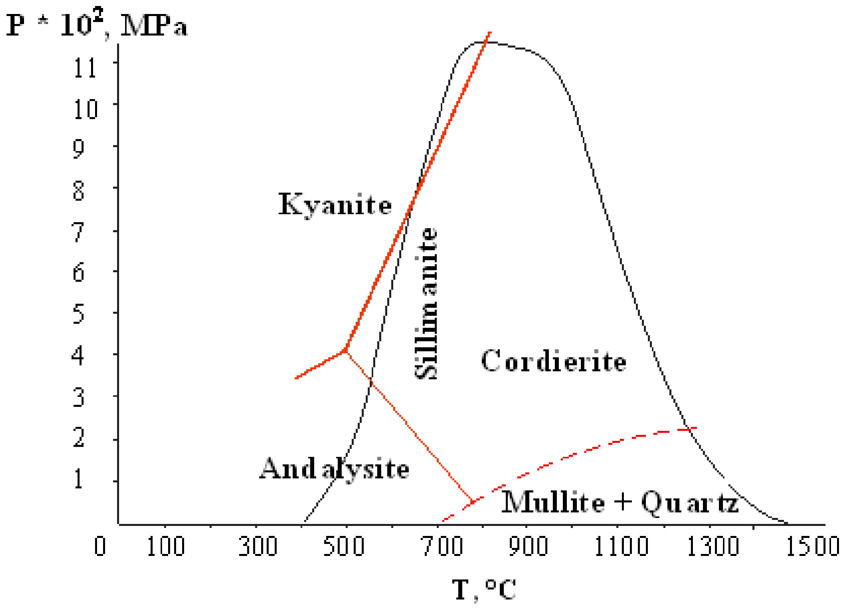

Fig.1. The situation in PT coordinates of the triple point (andalusite, sillimanite, kyanite), and the stability field of magnesium cordierite.

Kinetics of mullitization of kyanite, depending on the temperature and conditions of mechanical activation is studied in [8] where it is shown that the activation energy is the same for nonactivated and activated state and is equal to 630 ± 10 kJ / mol. The differences concern to the frequency factors. According to the PT diagram, kyanite at heating first should be transformed to sillimanite and then to mullite. However, such a transition is not fixed in our experiments because of the great similarity in structures and in the diffraction patterns of mullite and sillimanite, as well as a large degree of amorphization of kyanite as a result of mechanical activation.

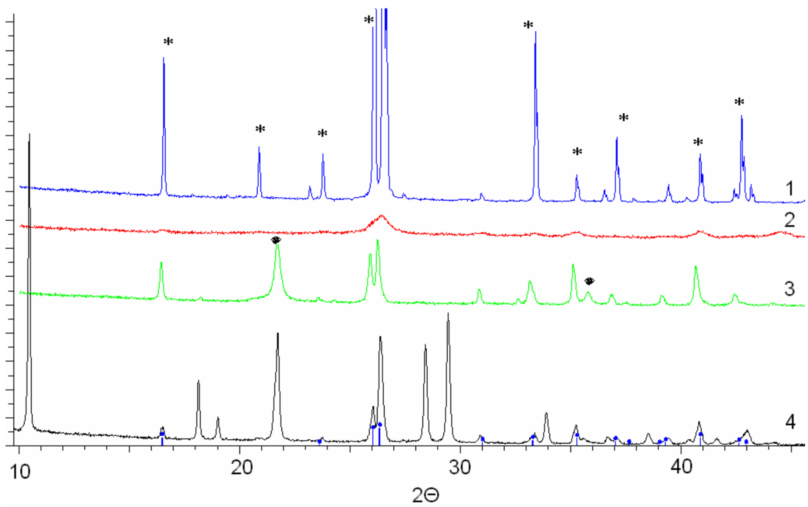

Fig.2. Diffraction patterns of sillimanite and kordierite. 1- initial sample, 2 - activated for 10 min., 3 - activated for 10 minutes and heated at 1300 ° C for 3 hours. 4 - activated and heat-treated mixture of sillimanite with talc and quartz at 1300°C for 3 hours. Arrows on a curve 4 mark the reflexes related to mullite.

Fig. 2 shows the XRD data for the initial, mechanically activated and thermally treated sillimanite (curves 1, 2 and 3, respectively). X-ray -amorphous phase (curve 2) is observed as a result of mechanical activation of sillimanite (as well as kyanite or andalusite). The subsequent heating leads to millite crystallization (curve 3). The appearance of two peaks at 22 and 36 degrees (curve 3) belonging to kristaballite phase can serve as the indicator of this process because diffraction patterns of mullite and sillimanite are similar. Mechanical activation of the mixture of sillimanite with talc for 10 minutes with subsequent heat treatment at 1300 ° C for 3 hours produced cordierite and mullite in a small quantity (curve 4, the peaks related to mullite are marked by arrows).

Cordierite is also formed in mixtures of kyanite or andalusite with talc after a joint mechanical activation and heat treatment at 1300 ° C for 3 hours.

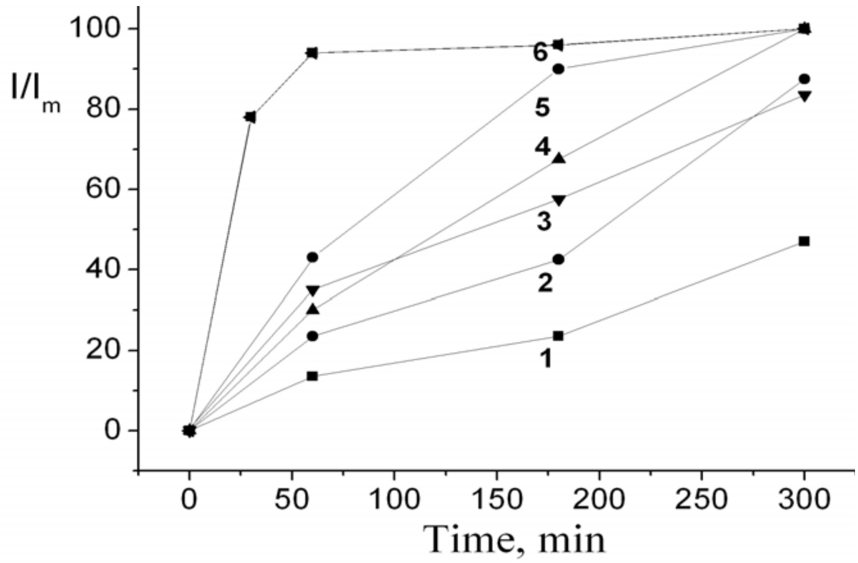

Fig. 3. The relative intensity of 100% of the basic reflex of cordierite (d = 0,862 nm) depending on the time of thermal treatment at T = 1300 ° C of mixtures of talc, quartz and minerals sillimanite group: 1-mixture without mechanical activation, 2 - mixture with kyanite activated for 5 minutes in AGO-2, 3 - after passing the mixture in a single flow centrifugal disk mill, 4 - mixture with kyanite activated for 10 minutes in AGO-2 5 - same with andalusite, 6 - same with sillimanite.

Fig. 3 presents data describing the output of cordierite from mixtures of talc with each of the three minerals, activated and heat-treated under the same conditions. The effect of duration of activation in a laboratory mill and a single pass through the flow mill on the yield of cordierite has been investigated for a mixture of talc with a kyanite. The output of cordierite increases with increasing time of mechanical activation. The comparative analysis of the results shows that the most efficiently process of cordierite formation occurs in mixtures of talc with sillimanite, then with andalusite, and the least effectively with kyanite. The difference is very significant and the yield of cordierite formed from a mixture with sillimanite after 1 hour of heat treatment is almost 3 times greater than with kyanite. Andalusite takes an intermediate place.

If the reaction was associated with the appearance of mullite as an intermediate product, the situation should be reversed. As mentioned above, the temperature of mullitization for kyanite is the lowest among these minerals. We believe that the rate of reaction is determined by other factors, in particular, by structural and chemical properties of minerals of sillimanite group.

It is known that a change in coordination of cations by oxygen anions, changes the acid-base properties of compounds. Thus, as a rule silicium ion Si^{4+} in acidic silica has a tetrahedral environment, but it has octahedral environment in stishovite mineral, and compared with the original silica stishovite have more basic properties. For this reason, stishovite can coexist with such bases as FeO and NiO, which react with silica forming silicates. The change in the coordination of Al^{3+} in the aluminum compounds from 4 to 5 and 6 leads to a significant increase of their basic properties also.

In the lattice of kyanite, all aluminum ions have a coordination number of 6. The octahedra AlO_6 with SiO_4 tetrahedra interspersed between them are assembled in a chains. In andalusite, a half of Al ions has a coordination number of 5 while in sillimanite - of 4. Chains of AlO_6 - octahedra linked to SiO_4 - tetrahedrons in kyanite, andalusite and sillimanite are not just a chain of AlO6-octahedra, but double tape of AlO_4 and SiO_4 - tetrahedrons [10]. Thus, with transition from kyanite up to sillimanite the acidic properties of the mineral become stronger. Talc ($Mg_3(OH)_2Si_4O10$) has basic properties. In accordance with the mechanism of acid-base interactions sillimanite has to be most effective in reaction with talc, less effective should be andalusite and kyanite should be minimally active, what is observed experimentally.

Fig. 4 shows the diffraction pattern of the product obtained by heat treatment at 1300°C for 3 hours of a mixture of kyanite with talc and quartz previously activated for 10 minutes in the mill AGO-2. In comparison with the diffraction pattern shown in Fig. 2, the reflections belonging to mullite are very high, indicating a high concentration of mullite in the mixture.

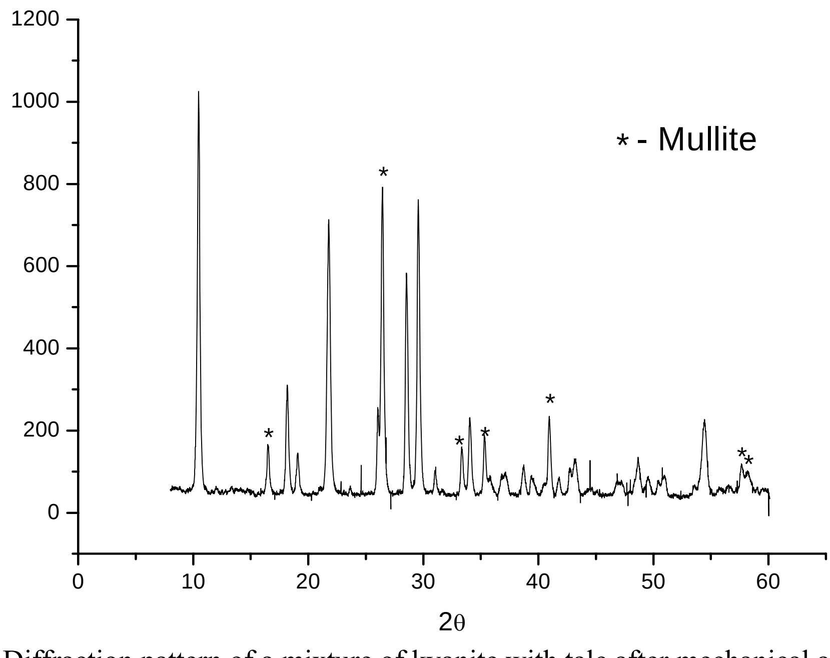

Fig.4. Diffraction pattern of a mixture of kyanite with talc after mechanical activation and heat treatment at 1300°C for 3 hours. The reflexes marked by asterisk relate to mullite, the others belong to cordierite.

The formation of cordierite in a mixture of kyanite, talc and mullite can be the basis for mullite-cordierite ceramic composite consisting of chemically compatible components which inherits beneficial properties of cordierite (low coefficient of thermal expansion) and mullite (high temperature of melting and mechanical strength) and has a high sintering ability and crack resistance [11].

4. Conclusions

Thus, as a result of the study it has been found that the mechanical activation of mixtures of minerals of sillimanite group minerals with talc and silica additives in grinding-activating devices with periodic and continuous flow action provides a significant acceleration of their interaction with the formation of cordierite at the subsequent high-temperature treatment. It is shown that, with other things being equal, the output of cordierite depends on the nature of minerals. It is considerably higher in mixture with sillimanite, than with andalusite and kyanite, while the rate of mullitization of these minerals has opposite character. This brings us to the conclusion that the formation of mullite under heat treatment is not a limiting step in the synthesis of cordierite. The reaction rate is determined by the acid-base properties of these minerals, which depend on the coordination environment of aluminum cations, different for each of the modifications.

The centrifugal disc flow mill [2, 3, 13] can be used for practical implementation. This type of mills can provide the required level of activation of silimanite minerals in mixture with talc and silica for the synthesis of cordierite.

A positive aspect of these experiments is the fact that it is not need to use extremely pure minerals of silimanite groupe for synthesis of cordierites mass. The purity of second or third grade with quartz content of 10-15mas.% is enough for this purpose, which will inevitably decrease the cost of the final product.

5. References

1. E.G. Avvakumov, A.A. Gusev. Cordierite-perspective ceramic material, Publishing House of SB RAS, Novosibirsk, 1999 (in Russian).
2. E.G Avvakumov, Pat.55644 RF. Centrifugal mill continuous type, Bull. Inventions. № 24 (2006).
3 E.G.Avvakumov, A.M. Kalinkin, E.V. Kalinkina, Chemical Technology, 9 (2008) 590 (in Russian).
4. G.A.Lebedeva, I.S. Inina. Refractories and Technical Ceramics, 9 (2005) 42. (in Russian).
5 H.Schneider, K.Okada, J. Pask . Mullite and Mullite Ceramics. John Wiley & Sons. New York. 1994, p.112-114.
6 E.G Avvakumov, A.R Potkin, O.I . Samarin. Pat.975068 RF. Planetary Mill. Bull. Inventions № 43 (1982).
7 M.J. Holdaway, American Journal of Sciences, 271 (1971) 97.
8 G.G. Lepezin, E.G. Avvakumov, Y. V. Seretkin, O.B. Vinokurova, Chemistry for Sustainable Development, 20 (2012)339.
9 A.A. Yearlings, Journal of Inorganic Chemistry, 38 (1993) 1468.
10 H.Schneider, J.Schreuer, B.Hildmann, J. of European Ceram. Soc., 28 (2008) 329.
11 B.H. Mussler, M.W. Shafer, Bull. of American Ceramic Soc., 5 (1984) 705.
12 Mineralogical society of America. Reviews in mineralogy. The Al_2SiO_5 polymorphs. 22 (1990) 406.
13 G.R Karagedov, E.G. Avvakumov, Sci. Sint., 42 (2010) 239.

Садржај: *Утврђено је да механичка активација смеша силиманитне групе материјала са адитивима талка и силицијума у млиновима утиче на значајно убрзавање њихове међусобне интеракције и настајања кордијерита током даљег температурног*

третмана. Показано је да добијени кордијерит зависи од природе минерала: више кордијерита се добија из смеше са силиманитом него из смеша са андалузитом и кијанитом, док удео мулитне фазе има супротан карактер. То значи да формирање мулита током температурног третмана није лимитирајући фактор у синтези кордијерита. Утврђено је да је брзина реакције условљена разликом кисело-базних својстава минерала. Свостава зависе од односа катјона алуминијума и анјона кисеоника, који је различит за све модификације.
Кључне речи: *кордијерит, синтеза, силиманитна група минерала, талк, кварц, механичка активација, топлотни третман*