Chemistry for Sustainable Development **14** (2006) 333–343

Mechanochemical Interaction of Calcium Carbonate with Diopside and Amorphous Silica

A. M. KALINKIN[1], A. A. POLITOV[2,3], E. V. KALINKINA[1], O. A. ZALKIND[1] and V. V. BOLDYREV[2,3]

[1]*Tananaev Institute of Chemistry and Technology of Rare Elements and Mineral Raw Materials,*
Ul. Fersmana 26a, Murmansk Region, Apatity 184209 (Russia)

[2]*Institute of Solid State Chemistry and Mechanochemistry, Siberian Branch of the Russian Academy of Sciences,*
Ul. Kutateladze 18, Novosibirsk 630128 (Russia)

[3]*Novosibirsk State University,*
Ul. Pirogova 2, Novosibirsk 630090 (Russia)

(Received January 31, 2006)

Abstract

Processes that occur during mechanochemical activation of the mixtures of diopside with calcite and amorphous silicon dioxide with calcite in a centrifugal planetary mill are investigated. According to the data of IR spectroscopy and XPA, with calcite content up to ~10 mass %, mechanochemical interaction of the mixture components results in the formation of a substance which is similar to carbonate-containing silicate glass. During mechanochemical activation of a mixture of amorphous silicon dioxide with calcite (at a molar ratio of 1 : 1) the degree of interaction between the components decreases substantially, the major part of input mechanical energy is consumed for the achievement of mechanochemical equilibrium between calcite and aragonite. Investigated processes were compared with the previously discovered mechanically induced absorption of carbon dioxide by calcium- and magnesium-containing silicates. The data on phase formation under heating of mechanochemically activated mixtures of silica with calcite are reported.

INTRODUCTION

Our attention to this subject is due to the following circumstances. First, the interaction of calcium carbonate with silica-containing components is the basis of synthesis of silicate minerals, in particular those incorporated in cement. Diopside is a widespread non-metal mineral in mining wastes; it is a potential raw material for obtaining binders [1]. It is known that the preliminary mechanical activation (MA) of the mixture allows one to reduce the temperature of silicate synthesis, decrease its duration and improve the binding properties of the formed compounds [2–4]. At the same time, the features of the mechanochemical interaction of $CaCO_3$ with silica and silicates have been investigated insufficiently thoroughly.

Second, prolonged pounding of stable calcium- and magnesium-containing minerals, such as diopside ($CaMgSi_2O_6$), okermanite ($Ca_2MgSi_2O_7$), *etc.*, in the air is accompanied by an unusual mechanochemical effect. It was discovered that silicates possess the ability to absorb selectively carbon dioxide from the atmosphere in amounts comparable with the calcium content of minerals [5, 6]. The absorbed CO_2 is present in ground minerals in the form of carbonate ions, which are mainly associated with calcium cations. According to the experimental data, including those obtained in controllable CO_2 atmosphere, the mass concentration of carbonate in the ground samples reaches ~50 mass %, calculated for $CaCO_3$. It was established that the discovered effect is due not to the surface chemisorption of carbon dioxide or to mechanochemical transformation of silicate into carbonate but to the previously unknown effect of concentrated insertion of CO_2 molecules into the silicate. Carbon dioxide is homogeneously dissolved at the molecular level in the structure of disordered silicate matrix without the formation of individual crystal carbonate phases. We assumed that the insertion of carbonate ions into the silicate matrix can occur not only during mechanically induced absorption of gaseous CO_2 by the mineral but also as a result of the joint mechanical treatment of silicate or silica with $CaCO_3$ (calcite). In the present investigation, we studied the processes that occur during the joint MA of calcite with the representative of the group of chain silicates – diopside, as well as with the reactive amorphous silica. For the mechanically activated mixture of calcite with amorphous silicon dioxide, the data on phase formation during annealing are also reported.

Mechanochemical activation of individual amorphous silica and calcite was studied in [4, 7–10]. According to [7], during MA of the KSK grade silica gel in a centrifugal planetary mill, after the initial grinding stage within 3 min mechanical treatment, dense aggregates of particles are formed; specific surface and porosity start to decrease rapidly with an increase in activation time. According to the data of [4], MA of hydrated amorphous silica results in its partial dehydration, which is accompanied by a sharp decrease in specific surface, while, to the contrary, MA of anhydrous amorphous silicon dioxide causes some increase in this parameter.

It was shown in [8] that calcite is transformed into aragonite during treatment in a vibratory mill. After prolonged grinding (for more than 100 h), mechanochemical equilibrium arises, that is, a steady state with the constant calcite to aragonite ratio (30 % calcite : 70 % aragonite) is realized, independently of which of these two modifications was taken as the initial one. To perform the calcite ® aragonite transformation, it is necessary to overcome a definite level of energy rating during treatment. In the case of the reverse process. this level increases, which correlates with the data on thermally stimulated phase transitions between these two minerals: the transition of calcite into aragonite as the more stable phase, according to the equilibrium $P–T$ conditions, can be carried out at a lower temperature than the reverse process [11]. Vibratory milling of calcite results in an increase in specific surface from 2 to 10 m^2/g during the first 30 min of grinding, and then it decreases gradually due to aggregation [8]. Mechanically induced phase transition calcite a aragonite is preceded by amorphization; some intermediate state is likely to be realized during it [9]. It was discovered that the size of steel balls can affect the direction of the polymorphous transition calcite a aragonite during MA in a centrifugal planetary mill [10]. Transformation of calcite into aragonite was observed during the treatment with the balls of small diameter (1 and 3 mm); after activation for 60 min, according to XPA data, the mixture was composed of 70 % aragonite and 30 % calcite. After the balls were replaced by larger ones (8 mm) and treatment duration was 20 min longer, the formed aragonite was fully transformed into calcite as a result of the reverse process. According to the proposed model [10], the transition calcitea aragonite, which is accompanied by an increase in density, can proceed through the stage of amorphization in the substance compression wave, while the reverse transformation takes place in rarefaction wave. Variation of ball size changes the treatment regime and created favourable conditions for either direct or reverse process.

The goal of the present work is to investigate the processes that occur during the mechanochemical activation of the mixtures of diopside ($CaMgSi_2O_6$) with $CaCO_3$ and of amorphous silicon dioxide with $CaCO_3$.

EXPERIMENTAL

The initial $CaMgSi_2O_6$ sample was a monomineral fraction (–0.125 mm) of diopside from the Kovdor deposit (the Kola peninsula). The concentration of impurity minerals in diopside (carbonates, mica) did not exceed 1 mass %. According to the data of chemical and atomic absorption analysis, the initial diopside is characterized by the following composition (mass %): SiO_2 49.70±0.08; CaO 24.50±0.05; MgO 16.10±0.05; Al_2O_3 1.34±0.05; FeO 2.88±0.05; TiO_2 0.48±0.05; Na_2O 0.43±0.05; K_2O 0.19±0.02; MnO 0.08±0.02. Calcium carbonate and amorphous $SiO_2 \times xH_2O$ (concentration of H_2O: 20.9 %) of "ch.d.a." reagent grade (analytically pure) were used in experiments. Anhydrous amorphous silica was obtained by annealing $SiO_2 \times xH_2O$ at 1000 °C for 20 h. The specific surface of the initial diopside, calcite, and anhydrous and hydrated silica was 0.18, 0.22, 14.8 and 250 m^2/g, respectively. Mechanochemical activation of the samples was carried out in AGO-2 planetary mill [12] with the centrifugal factor of 60*g*. The input energy for diopside + $CaCO_3$ and silica + $CaCO_3$ mixtures was 1.0 and 2.7 MJ/kg per 1 min of MA, respectively. Milling bodies were steel balls 5 and 8 mm in diameter. The ratio of ball mass to the sample mass was 10 for diopside + $CaCO_3$ mixture and 20 for silica + $CaCO_3$ mixture. In order to minimize milling of equipment, periodic forced mixing of the charge and preliminary lining of the cylinders and balls with the mixture to be ground was carried out [13]. X-ray phase analysis of the samples was carried out with DRON-2 diffractometer (CuK_α radiation). The IR spectra were recorded in KBr tablets with UR-20 spectrometer. Differential thermal analysis was carried out with NTR-70 and PRT-1000 instruments with Pt–Pt/Rh thermocouple. The TG curve was recorded with a torsion balance VT-1000. The presence of CO_2 in samples was determined using the volumetric method [14] with the help of AN-7529 analyser. A weighed portion of the sample was annealed in the furnace at 1200 °C; the evolved carbon dioxide was absorbed with titrated barium hydroxide solution. The amount of absorbed CO_2 was determined using the potentiometric method, specific surface of the samples was measured by means of thermal desorption of nitrogen using FlowSorb II 2300 set-up (Micrometrics).

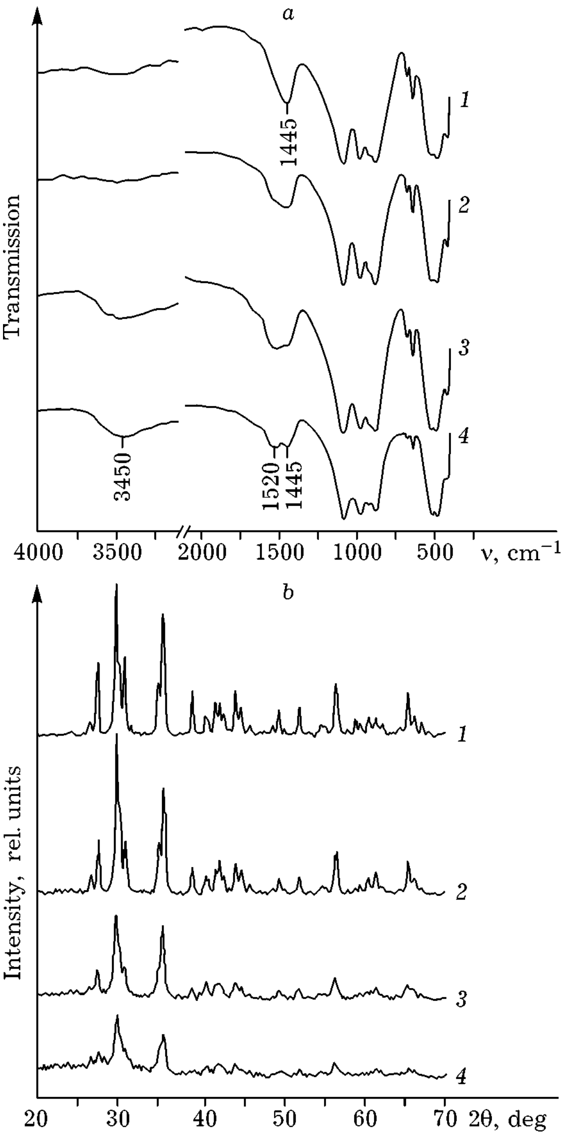

Fig. 1. IR spectra (*a*) and diffraction patterns (*b*) of the mixture of diopside with calcite: *1* – initial mixture, *2–4* – after MA for 3, 12 and 30 min, respectively. Concentration of calcite in the initial mixture is 5 mass %.

RESULTS AND DISCUSSION

MA of diopside + $CaCO_3$ mixture

The IR spectra and diffraction patterns of the initial and mechanically treated mixtures of diopside with calcite are shown in Fig. 1. The mass concentration of calcite in the initial mixture was 5 %, maximal time of treatment was 30 min, milling bodies were balls 8 mm in diameter. In the diffraction patterns of the initial mixture (see Fig. 1, *b*, curve *1*), only diopside is identified due to relatively low $CaCO_3$ content, as well as due to partial overlapping of calcite and diopside reflections. With an increase in MA time, a decrease in the intensity of diopside reflections and their broadening are observed (curves *2–4*).

The IR spectrum of the initial mixture (see Fig. 1, *a*, curve *1*) contains three clearly exhibited bands in the region 1050–850 cm^{-1}, the so-called diopside-type bands which characterize the vibrations of silicon-oxygen tetrahedron in the crystal structure of the mineral [15]. Non-split band at 1445 cm^{-1} corresponds to n_3 degenerated asymmetric stretching vibrations of the carbonate group of calcite. As a result of MA, the intensity of diopside bands in the region 1050–850 and 700–600 cm^{-1} decreases (curves *2–4*), which confirms the XPA data on an increase in structural distortions. The appearance of the band related to the stretching vibrations of OH groups (3450 cm^{-1}) in the IR spectrum, as a result of MA, is the evidence of hydration resulting from the absorption of atmospheric moisture. Under mechanical action, the shape of the carbonate band at 1445 cm^{-1} changes noticeably. With an increase in MA time, the peak of CO_3^{2-} group broadens gradually and turns after grinding for 30 min into a double band with absorption maxima at 1445 and 1520 cm^{-1}. Splitting of this band provides evidence of a decrease in the symmetry of the carbonate group, which removes the degeneration of this vibration. A similar double carbonate peak is present in the IR spectra of diopside after its grinding in a mechanical mortar in the air and in AL-1000 activator in the atmosphere of CO_2 [5, 6].

Previously, on the basis of IR spectroscopic data, an analogy was drawn between the forms of occurrence of absorbed CO_2 in MA samples of diopside and in diopside (Ca + Mg) basalt glass obtained by rapid cooling of melts containing dissolved carbon dioxide [5, 6]. Dissolution of CO_2 in silicate mass (up to ~10 mass % CO_2) occurs at high temperature and pressure corresponding to the earth's magma: $t \sim 1500$ °C, $P \sim 1$ GPa. At carbon dioxide pressure below 0.1 GPa, its solubility in melts does not exceed 0.1 % [16, 17]. It should be noted that the IR spectra of carbonate minerals (calcite, dolomite) contains non-split single peak (~1450 cm^{-1}) corresponding to n_3 stretching vibration of non-distorted CO_3^{2-} group in which all the C–O bonds are equivalent [18]. If the oxygen atoms of carbonate group interact with the other atoms surrounding them (for example, those of the glass silicate matrix), C–O bonds become non-equivalent, and the symmetry of the carbonate group decreases, which results in splitting of n_3 band of the stretching vibrations of CO_3^{2-} group. As a result, a unique double band with the maxima at 1435 and 1515 cm^{-1} appears in the IR spectrum of the glass [16]. We assumed on the basis of these data that CO_2 absorbed in MA samples of diopside and other Ca-containing silicates is present in the same form, that is, as distorted carbonate groups inserted into the disordered glass matrix. It follows from the analysis of IR spectroscopic data shown in Fig. 1, *a* that in the case of MA of diopside with a small amount of calcite added, similarly to the mechanically stimulated interaction of $CaMgSi_2O_6$ with CO_2, the formation of a substance similar to carbonate silicate glass occurs.

The data obtained by the thermal analysis of the initial mixture of diopside with $CaCO_3$ and that treated mechanically for 30 min are shown in Fig. 2. On the DTA curve of the initial mixture (see Fig. 2, *a*), the endoeffect in the region 600–800 °C corresponds to calcite decomposition; in the same region, mass loss due to CO_2 removal is observed. For MA-mixture (see Fig. 2, *b*), the behaviour of the curves is quite different. Total mass loss increases to 7.1 % against 2.6 % for the initial mixture; the corresponding temperature range broadens substantially. In the region 200–500 °C, removal of water absorbed by the sample as a result of the contact with atmospheric moisture occurs. The temperature range of carbonate decomposition broadens in comparison with the initial mixture to 500–870 °C. According to analysis results, after MA for 30 min, the mass concentration of CO_2 in the sample increases from (2.5±0.2) to (3.7±0.3) %, which is likely to be due to sorption of atmospheric carbon dioxide by diopside. The DTA curve (see Fig. 2, *b*) exhibits an exoeffect at 730 °C corresponding to the annealing of defects and crystallization of diopside from the amorphous phase, which follows from the XPA data (not shown). It is necessary to note that crystallization of diopside is incomplete: the diffraction patterns of the sample after MA for 30 min and annealing for 15 min at 800 °C are similar to those of the sample after MA for 3 min. The endoeffect of CO_2 removal is not exhibited in DTA curve because it is superimposed on the exoeffect of diopside crystallization (see Fig. 2, *b*).

A decrease in the diameter of milling bodies to 5 mm had no noticeable effect on the results obtained. We carried out additional ex-

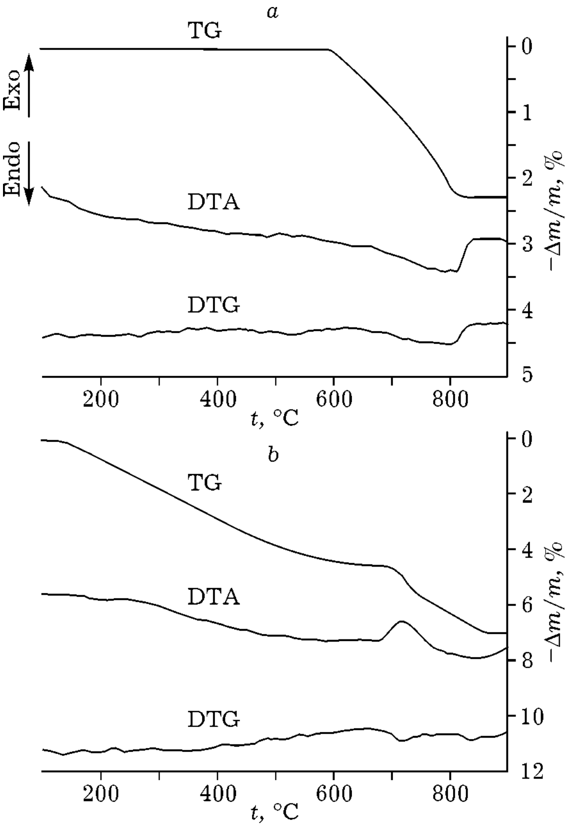

Fig. 2. Data of thermal analysis of a mixture of diopside with calcite: *a* – initial mixture, *b* – after MA for 30 min. Concentration of calcite in the initial mixture is 5 mass %.

periments on MA of a mixture of diopside with $CaCO_3$ in the same proportion but with the addition of a small amount (up to 5 % mass) of water. The degree of splitting of the carbonate band in the IR spectrum in the region 1520–1440 cm^{-1} (not shown) was somewhat smaller in the presence of water, in comparison with the dry MA fort he same treatment time. This is likely to be the evidence of a decrease in the degree of interaction of calcite and diopside. The specific surface of a mixture of diopside and calcite with 5 % H_2O after MA for 30 min was (8.1±0.3) m^2/g. For comparison, the specific surface of a similar mixture after MA without the addition of water is equal to (6.3±0.2) m^2/g.

MA of the mixture silica + $CaCO_3$

The mixture SiO_2 + $CaCO_3$ was subjected to mechanochemical activation with the molar ratios SiO_2 : calcite equal to 19 : 1 and 1 : 1; the mixture $SiO_2 \times xH_2O$ + $CaCO_3$ was treated at a molar ratio equal to 1 : 1. Balls 5 mm in diameter were used as milling bodies. According to the data of IR spectroscopy (not shown), the processes that take place during the joint MA of anhydrous amorphous silica and calcite at the molar ratio of 19 : 1 (corresponding to 8 mass % $CaCO_3$ in the mixture) are similar to those described above for a mixture of diopside and calcite. The non-split band of stretching vibrations of CO_3^{2-} group in the initial mixture gradually gets broader and after MA for 10 min turns into a double peak with the maxima at 1440 and 1515 cm^{-1}.

The diffraction patterns of SiO_2 + $CaCO_3$ mixture with the molar ratio of 1 : 1 after MA for 10, 90 and 120 min are shown in Fig. 3. One can see that the intensity of calcite reflections decreases gradually with an increase in MA time; at the same time, mechanically induced phase transition of calcite into aragonite occurs. After MA for 120 min, aragonite becomes the prevailing phase (see Fig. 3, curve *3*). The IR spectra of the samples of SiO_2 + $CaCO_3$ mixture with the molar ratio of 1 : 1 exhibits changed during MA that correspond to the phase transition calcite ® aragonite: the calcite band at 1445 cm^{-1} shifts to shorter wavelengths, while the band at 880 cm^{-1} shifts to

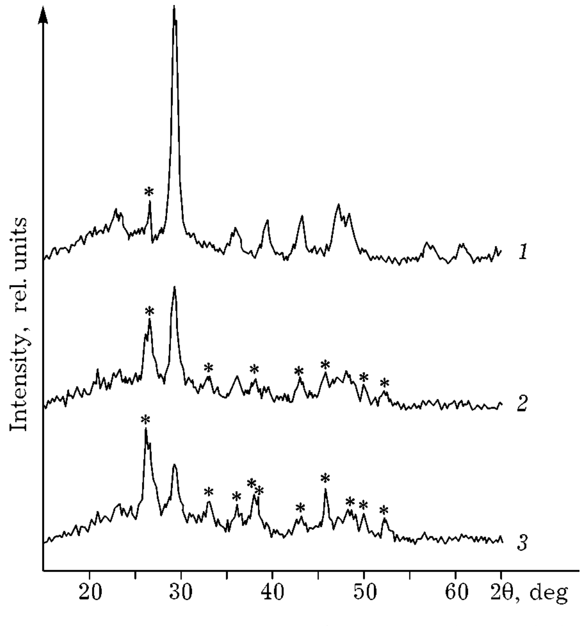

Fig. 3. Diffraction patterns of the mixture SiO_2 + $CaCO_3$ with the molar ratio 1 : 1 after MA for 10 (*1*), 90 (*2*), and 120 min (*3*). The erflections related to aragonite are marked with an asterisk.

longer wavelengths (Fig. 4, *a*, curve *1*). The band of the stretching vibrations of CO_3^{2-} group in the region of 1500 cm^{-1} broadens as a result of MA, but no splitting occurs. According to the results of analysis of SiO_2 + $CaCO_3$ mixture after MA for 120 min, in comparison with the initial mixture, CO_2 content decreases by the amount corresponding to the decomposition of ~ 10 % of carbonate. The specific surface of this MA sample is about two times as large as that of the initial mixture and makes 12.9 m^2/g. The main contribution into an increase in the specific surface is made by dispersing of amorphous SiO_2 [4], the major part of which is likely not interacting with $CaCO_3$.

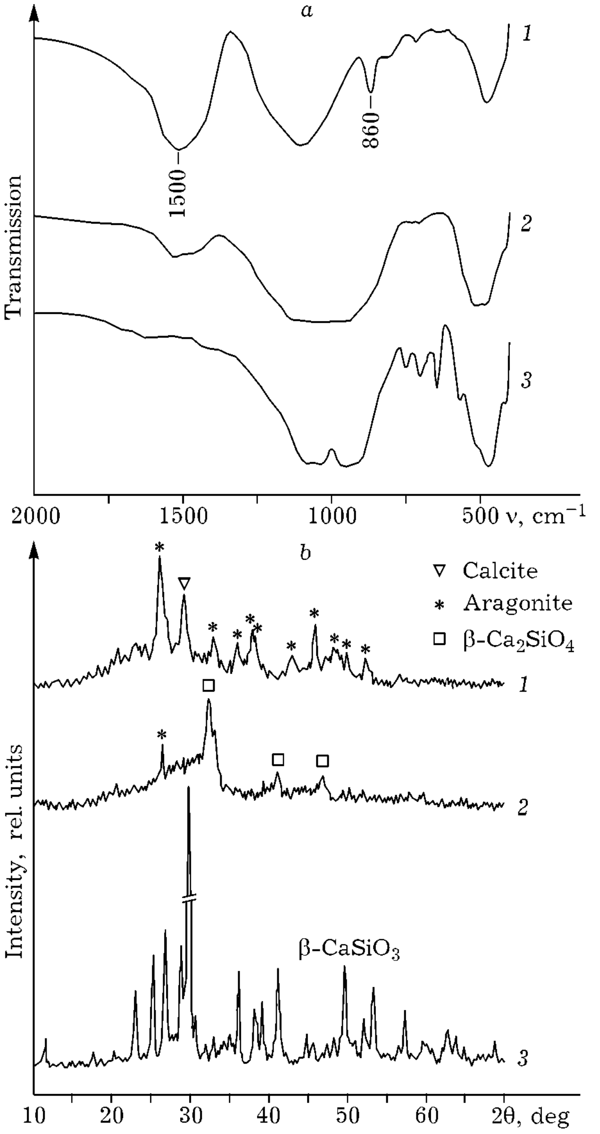

Fig. 4. IR spectra (*a*) and diffraction patterns (*b*) of the mixture SiO_2 + $CaCO_3$ with the molar ratio 1 : 1 after MA for 120 min without heating (*1*) and after heating to 780 (*2*) and 880 °C (*3*).

Interesting structural changes are observed during the annealing of the mixture SiO_2 + $CaCO_3$ with the molar ratio 1 : 1 after MA for 120 min. According to the data of thermal analysis (Fig. 5), decomposition of carbonate proceeds within temperature range 500–850 °C. According to the data of XPA (not shown), the ratio calcite : aragonite gradually changes in favour of the former on heating; after heating to 500 °C, calcite becomes the prevailing phase. A similar process takes place during the annealing of a mixture of calcite and aragonite obtained as a result of MA of calcite in a centrifugal planetary mill [10].

In order to reveal the nature of the exoeffect at 830 °C (see Fig. 5), we recorded the IR spectra and diffraction patterns of the mixtures heated to 780 and 880 °C and kept for 15 min at these temperatures. A sharp decrease in the intensity of the band of CO_3^{2-} group in the region of 1500 cm^{-1} is the evidence of the decomposition of the major part of carbonate at 780 °C (see Fig. 4, *a*, curve *2*), which agrees with the thermogravimetric data (see Fig. 5). At the same time, the reflections of b-Ca_2SiO_4 (larnite) appear in the diffraction patterns, though no complete crystallization of this dicalcium silicate occurs (see Fig. 4, *b*, curve *2*). Under heating to 880 °C (see Fig. 4, *b*, curve *3*), b-$CaSiO_3$ (wollastonite) is formed. So, the exothermal peak

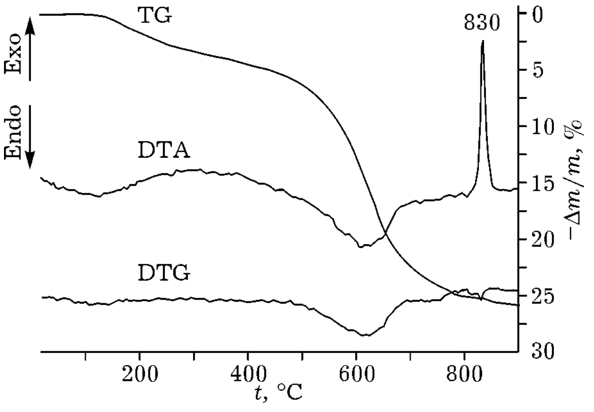

Fig. 5. Data of thermogravimetric analysis of SiO_2 + $CaCO_3$ mixture with the molar ratio 1 : 1 after MA for 120 min.

at 830 °C corresponds to the crystallization of wollastonite. In the initial mixture, wollastonite is formed at 1100–1200 °C. It should be noted that a similar exo peak but somewhat shifted to higher temperature (860 °C) is present in the DTA curves of the samples of $SiO_2 + CaCO_3$ mixture as early as after MA for 3 min. The diffraction patterns of this mixture annealed at 900 °C (not shown) after MA for 3 min contain the reflections of b-$CaSiO_3$ and b-Ca_2SiO_4; the content of these two silicates is approximately the same, according to XPA data. With an increase in MA time, the presecne of larnite in the annealed mixture gradually decreases; after MA for 10 min, after annealing at 900 °C for 2 h, only the reflections of wollastonite are present in the diffraction patterns.

In $SiO_2 + CaCO_3$ mixture with the molar ratio of 1 : 1, replacement of anhydrous amorphous silica with hydrated one has no effect on the character of the described processes, according to the data of XPA, IR spectroscopy and thermal analysis (not shown). It should be noted that in the case of MA of a mixture of calcite with $SiO_2 \times xH_2O$ for 120 min the exoeffect of b-$CaSiO_3$ formation somewhat shifts to higher temperatures (850 °C) in comparison with a similar sample containing anhydrous SiO_2 (see Fig. 5). The specific surface of the sample $SiO_2 \times xH_2O + CaCO_3$ after MA for 120 min is 18.9 m^2/g, that is, 7 times smaller than that for the initial mixture, which agrees with a sharp decrease in S_{sp} during MA of individual hydrated amorphous silica [4].

Mechanochemical activation of the mixtures of amorphous anhydrous silica and calcite at the molar ratio corresponding to the formation of $2CaO \times SiO_2$ and $3CaO \times SiO_2$ was studied in [2]. The process was carried out in a planetary mill EI-2X150 with quartz balls 5–6 mm in diameter in the cylinders with quartz lining; the centrifugal factor was 40*g*, maximal treatment time was 60 min. The authors of [2] observed a decrease in intensity and broadening of the reflections of calcite with an increase in MA time; according to XPA data, no formation of aragonite was observed. No splitting of the carbonate band at 1450 cm^{-1} in the IR spectra occurred under MA. According to thermogravimetric data, MA of mixtures was accompanied by partial (up to ~10 %) mechanolysis of carbonate. The derivatograms of MA mixtures clearly exhibited an exothermal peak in the region 380–430 °C corresponding to the annealing of defects and crystallization of amorphous $CaCO_3$. In our experiments, we did not observe any similar exoeffect (see Fig. 5); the start of thermal dissociation of carbonate shifted after MA towards lower temperatures (500 °C). The difference between our data on phase formation during MA of a mixture of calcite and silica and the data on thermal analysis of activated samples, against the results obtained in [2], is likely to be due to different MA conditions, first of all with higher energy input in our experiments, and also with the different components ratio of the mixtures.

On the basis of changes in the shape of absorption band of the stretching vibrations of CO_3^{2-} group in the IR spectra and the XPA data (see Fig. 1), it may be assumed the joint MA of diopside or silica with calcite in the case of the low content of the latter (up to ~10 mass %) the carbonate is almost completely inserted into the disordered silicate matrix. In this connection, it is interesting to stress that during the annealing of MA mixture of diopside with $CaCO_3$ the maximum of exoeffect of diopside crystallization corresponds to the sharpest decrease in sample mass due to the removal of CO_2 (see Fig. 2, *b*). In other words, the recovery of the crystal structure of the mineral occurs simultaneously with the decomposition of carbonate, This is an indirect evidence in favour of the assumption that carbonate is present in MA mixture not as a separate phase but is inserted into the disordered lattice of the mineral. During annealing of MA mixture, in addition to diopside crystallization, the formation of a small amount of okermanite $Ca_2MgSi_2O_7$ is possible as a result of the interaction of CaO with $CaMgSi_2O_6$, though the reflections of okermanite are not observed in the corresponding diffraction patterns (not shown).

In the investigation of processes involved in CO_2 absorption by silicates, a correlation between the degree of carbonization of the mineral under grinding and changes in Gibbs energy of the reactions of carbonate formation from silicates was discovered [19]. For example, for diopside and wollastonite, these reactions per 1 mol of CO_2 are represented as

$$1/2CaMgSi_2O_6(\text{diopside}) + CO_2 = 1/2CaCO_3(\text{calcite}) + 1/2MgCO_3(\text{magnesite}) + SiO_2(\text{a-quartz}) \quad (1)$$

$$CaSiO_3(\text{wollastonite}) + CO_2 = CaCO_3 + SiO_2 \quad (2)$$

The values of $\Delta_r G^o_{298.15}$ calculated according to the data of [20] correspond to reactions (1) and (2): $-(18.3\pm5.4)$ and $-(41.1\pm4.6)$ kJ/mol, respectively. It should be noted that these reactions are a simplified scheme of mechanically induced absorption of CO_2 by silicates, since even in the case of limiting saturation of MA similate samples with carbon dioxide, when the concentration of carbonate in them calculated for $CaCO_3$ reached 50 mass %, the reflections of crystal carbonates were not observed in the diffraction patterns. The probability of the formation of amorphous $CaCO_3$ is low because this compound is unstable and gets transformed into calcite with time. According to XPA data, in our experiments, storage of MA silicate samples with high carbonate content does not result in the formation of crystal carbonate phases, at least within several years. So, the interaction of calcium and magnesium silicates with CO_2 under standard conditions resulting in the formation of carbonates and silica is a thermodynamically permitted process which can be used, with some approximation, to estimate the degree of mechanically induced carbonisation of silicates: under identical conditions, this degree is higher for more negative value of $\Delta_r G^o_{298.15}$) for reactions like (1) and (2). Under the standard conditions, the following reaction is also possible:

$$Ca_2MgSi_2O_7(\text{okermanite}) + CO_2 = CaMgSi_2O_6 + CaCO_3 \quad (3)$$

because the corresponding Gibbs energy value is $\Delta_r G^o_{298.15} = -(82.7\pm5.6)$ kJ/mol. Taking into account this value, we may conclude that mechanically induced interaction of diopside $CaMgSi_2O_6$ with calcite resulting in the formation of amorphous carbonate-containing silicate is much less energy-profitable than the formation of the same substance from $Ca_2MgSi_2O_7$ and CO_2. Similarly, on the basis of $\Delta_r G^o_{298.15}$ value for reaction (2), one may conclude that the mechanochemical interaction of calcite with SiO_2 is less energy-profitable than absorption of carbon dioxide during the mechanical treatment of $CaSiO_3$. Nevertheless, the above-reported experimental data provide evidence that at least in the case of a small fraction of calcite in mixture with diopxide or with SiO_2 one can obtain the same state of carbonized silicate by two ways: as a result of mechanochemical interaction either between the initial compounds of reactions (2) and (3) or between the products of the same reactions. In this connection, some questions arise. What is the mechanism of the interaction of diopside (silica) with small amounts of calcite? What is the difference of this process from mechanically induced absorption of CO_2 by silicates? May one speak of the achievement of mechanochemical equilibrium in this case?

We stressed previously [6, 19] that the absorption of carbon dioxide molecules by calcium and magnesium silicates during MA is connected either with tribosorption [11] or mechanosorption processes [21]. Distortions of silicate structure, rupture of Ca–O–Si and Mg–O–Si bonds and the formation active centres on the freshly formed surfaces create favourable conditions for an increase in adsorption of gas molecules and their subsequent transport not only along micro cracks but also directly inside the particles along the appearing structural defects. Numerous data provide evidence that among these defects a special role is played by plastic deformations arising under the action of shear strain. It is known that plastic deformations provide the necessary mobility of components in mechanochemical synthesis, promote process completeness [11, 12, 21]. Two circumstances are to be mentioned. First, CO_2 molecules absorbed by silicate chemically interact with it forming CO_3^{2-} ions, mainly associated with calcium cations. Second, as we have already indicated, the degree of carbon dioxide absorption by silicate reaches the values comparable with the concentration of divalent cations, that is, formally corresponds to the mechanochemical transformation of silicates into carbonates. At the initial stage of MA, carbon dioxide molecules due to their high mobility rather quickly penetrate into the external layers of the silicate; naturally, after chemical binding they sharply lose their mobility. Diffusion hindrance for the penetration of CO_2 molecules into deeper-lying layers arise; the rate of gas absorption should decrease noticeably. Our previous kinetic experiments on MA of diopside in controllable CO_2 atmosphere confirm this assumption. At the first stage of MA, the rate of carbon dioxide absorption by diopside has the first order with respect to CO_2 pressure, then sorption processes becomes slower [6].

For MA of a mixture of diopside (or silica) with calcite, the probability of the direct insertion of calcium carbonate into the silicate matrix, that is, mixing of the components at the molecular or cluster level, is low. One of the reasons confirming this assumption is the above-mentioned thermodynamic factor; its important role in the processes of deformation mixing was considered in review [22]. In addition, the IR spectroscopic data provide evidence that for the MA of calcite + silica mixture with the molar ratio of 1 : 1 even for a long time in AGO-2 no splitting of the carbonate peak in the region of 1500 cm^{-1} is observed (see Fig. 4, *a*, curve *1*). In other words, transformations of the initial mixture into a carbonate-containing glassy substance are not observed, unlike for the transformations during mechanically induced interaction of silicates with CO_2 or with a small amount of calcite. Speaking of the similarity of carbonate-containing glasses and carbonised mechanically activated silicates, one should keep in mind the following circumstances. The dissolution of CO_2 in silicate melts with the achievement of the saturated state occurs under the conditions close to the equilibrium. Carbonate-containing glass obtained by quenching inherit the structure and composition of these melts. Mechanically induced absorption of carbon dioxide by calcium and magnesium silicates is an extremely non-equilibrium process, though the degree of carbonisation (CO_2 content of the samples) also tends to some limiting value which depends on the composition of silicates and on MA conditions. The common features of glass and mechanically activated silicate samples are: 1) the absence of long-range order; 2) nearly identical short-range order, at least with respect to carbonate ions, as follows from the IR spectroscopic data. Along with this, comparing the structure and properties of glass and amorphous MA samples, one should keep in mind highly dispersed state and essential macroheterogeneity of the latter samples [23].

It is known that the MA of calcite is accompanied by reversible mechanolysis, that is, mechanochemical decomposition to form CaO and CO_2 [24, 25]. As we have indicated above, the results of analysis of CO_2 content point to the decomposition of carbonate also in our experiments on the MA of SiO_2 + $CaCO_3$ mixture. This means that some amount of free CaO is present in the system during MA. According to the data of MA of a mixture of CaO with SiO_2 taken in the molar ratio of 1 : 1 in a centrifugal planetary mill, calcium oxide gets bound into silicate to a definite extent. With a decrease in CaO content of the mixture and with an increase in energy input for MA, the fraction of bound calcium oxide should increase. In case of MA with small calcite content, at first the major part of it is likely to decompose; the formed CaO is bound to form silicate. Then the silicate absorbs CO_2 from the mill cylinder volume according to the previously investigated processes [5, 6]. In case of the high calcite content in mixture with silica, the degree of mechanolysis of $CaCO_3$ decreases substantially; the fraction of calcium oxide bound into silicate is insignificant even after treatment for a long time. With an increase in the calcite content of the mixture, the partial pressure of CO_2 in the cylinder will increase due to mechanolysis, therefore, the degree of mechanochemical decomposition of carbonate will decrease. Complete binding of calcium into silicate is likely to be prevented also by diffusion hindrance. As a result, the n_3 band of the stretching vibrations of carbonate group in the region of 1500 cm^{-1} remains non-split in the IR spectrum (see Fig. 4, *a*, curve *1*). As we have already shown above, changes in the shape of this band during MA correspond to amorphization and mechanically induced calcite ® aragonite transition. In this connection, it is interesting to note that the ratio calcite : aragonite in SiO_2 + $CaCO_3$ mixture after MA for 120 min, calculated on the basis of the integral width of the bands that are most intensive for these compounds, is equal to 2 : 3, which is close to the value (30 % calcite + 70 % aragonite) obtained for the treatment of calcite for 100–240 h in a vibratory mill [8] or for 60 min in a planetary mill with steel balls 1 mm in diameter [10].

Considering the possibility to achieve the mechanochemical equilibrium during MA of a mixture of silica and calcite or calcium silicate in the presence of CO_2, it is necessary to stress the following. Strictly speaking, to answer this question, it is necessary to carry out investigation within a broad composition range of the system $CaO-SiO_2-CO_2$ varying the energy input of MA. However, on the basis of the data obtained, it may be concluded that, under the conditions of our experiments with MA of silica or diopside with small amounts of calcite added, the same carbonate-containing X-ray amorphous phase is formed (through the stage of $CaCO_3$ mechanolysis and chemical interaction of CaO with SiO_2) as that formed in mechanochemically induced absorption of carbon dioxide by calcium silicates. With an increase in the fraction of calcite in SiO_2 + $CaCO_3$ mixture, mechanochemical equilibrium calcite a aragonite is established; the major part of mechanical energy input is consumed for the achievement of this equilibrium. Unlike for the mechanically activated mixture with a small $CaCO_3$ content, in this case silica and carbonate (calcite + aragonite) are present mainly as finely dispersed chemically unreacted components.

As we mentioned above, during the mechanochemical activation of Ca-containing silicates with CO_2, the concentration of carbonate ions in MA samples reaches the values which are formally equivalent to the transformation of silicate into carbonate. It mechanochemical synthesis of carbonate indeed took place in this process as the major phase but not as insertions at the molecular level into the silicate matrix, then, according to the results obtained, one might expect on the basis of XPA data that the mechanochemical equilibrium calcite ® aragonite would be established. Actually, this is not observed because the corresponding samples are fully X-ray amorphous in the limit.

It was shown in [4] that the important role in the mechanochemical synthesis of calcium silicates is played by the form in which the initial components are present: hydrated or anhydrous. Mechanochemical activation of the mixture $SiO_2 \times xH_2O$ + $Ca(OH)_2$ with the component molar ratio 1 : 1 in a centrifugal planetary mill for 30 min promotes a more complete synthesis of b-$CaSiO_3$ in comparison with the corresponding anhydrous oxides. Comparing our results with the data obtained in [4] one should note that the phase formation observed under heating of mechanically activated SiO_2 + $CaCO_3$ and $SiO_2 \times xH_2O$ + $Ca(OH)_2$ mixtures is similar in character. In both cases, the DTA curves exhibit a clear exo effect at 830–850 °C corresponding to wollastonite crystallization; the final product of heating to 900 °C is single-phase b-$CaSiO_3$ in both cases. For comparison, annealing of mechanically activated SiO_2 + CaO mixture at 900 °C leads to the formation of $Ca_3Si_2O_7$, a part of silica remains unreacted. By adding water in the amount of 2–5 % to the mixture SiO_2 + CaO, one can somewhat increase the degree of mechanochemical interaction between the components [4].

The interaction of silica and calcium oxide (hydroxide), which was investigated in [4] relates to the acid-base type. The processes investigated by us are closer in character to substitution reactions; the limiting stage is likely to be mechanolysis of $CaCO_3$. The data obtained are insufficient for definite conclusions on the mechanism of water effect to be drawn. Water added to diopside + $CaCO_3$ mixture seems to have a negative effect on $CaCO_3$ decomposition. At the same time, water that is to be evolved during dehydration of $SiO_2 \times xH_2O$ during MA of $SiO_2 \times xH_2O$ + $CaCO_3$ mixture has no noticeable effect (in comparison with anhydroux mixture) either on the transformation of calcite into aragonite or on phase formation during the annealing of mechanically activated mixture.

CONCLUSIONS

1. It is shown on the basis of the analysis of changes in the shape of the band related to the stretching vibrations of CO_3^{2-} group in the IR spectra and the data of XPA that the joint MA of diopside or silica with calcite in the case of small content of the latter (up to ~10 mass %), similarly to mechanically induced interaction of calcium- and magnesium-containing silicates with CO_2, results in the formation of a substance which is similar to carbonate-containing silicate glass. An intermediate stage in this case in calcite decomposition to form calcium oxide and CO_2.

The formed CO_2 reacts with the silica-containing component to form silicate, which absorbs carbon dioxide, according to the processes investigated previously.

2. MA of SiO_2 + $CaCO_3$ mixture with the molar ratio of 1 : 1, no splitting of the carbonate peak at 1500 cm^{-1} is observed in the IR spectra even after MA for a long time (120 min), that is, no transformation of the initial mixture into a carbonate-containing glassy substance occurs. The major part of input energy is consumed in this case for the achievement of the mechanochemical equilibrium calcite ® aragonite. Replacement of anhydrous amorphous silica by hydrated silica has no effect on the character of mechanochemical processes.

3. Phase formation under heating of mechanically activated mixtures of silica with calcite with a molar ratio of 1 : 1 is similar to the previously investigated mechanochemical interaction of $SiO_2 \times xH_2O$ with $Ca(OH)_2$. The final product of heating of mechanically activated mixtures to 900 °C in both cases is crystal b-$CaSiO_3$ (wollastonite).

REFERENCES

1 V. N. Makarov, Ekologicheskiye problemy khraneniya i utilizatsii gornopromyshlennykh otkhodov, part 1, Apatity, 1998.

2 A. T. Logvinenko, M. A. Savinkina, *Izv. SO AN SSSR. Ser. Khim. Nauk*, 7, 3 (1979) 60.

3 A. T. Logvinenko, M. A. Savinkina, M. I. Tatarintseva, *Ibid.*, 2, 1 (1973) 128.

4 N. V. Kosova, E. T. Devyatkina, E. G. Avvakumov, *Sib. Khim. Zh.*, 2 (1992) 135.

5 E. V. Kalinkina, A. M. Kalinkin, W. Forsling, V. N. Makarov, *Int. J. Miner. Process.*, 61 (2001) 273.

6 A. M. Kalinkin, A. A. Politov, V. V. Boldyrev *et al., Neorg. Mat.*, 38 (2002) 215.

7 D. P. Klevtsov, V. B. Fenelonov, V. Yu. Gavrilov *et al.*, *Kolloid. Zh.*, 51 (1989) 278.

8 R. Schrader, B. Hoffmann, *Z. anorg. allg. Chem.*, 369 (1969) 41.

9 Y. Iguchi, M. Senna, *Powder Technol.*, 43 (1985) 155.

10 M. V. Chaikina, Mekhanokhimiya prirodnykh i sinteticheskikh apatitov, Izd-vo SO RAN, Novosibirsk, 2002.

11 G. Heinike, Tribochemistry, Akademie-Verlag, Berlin, 1984.

12 E. G. Avvakumov, Mekhanicheskiye metody aktivatsii khimicheskikh protsessov, Nauka, Novosibirsk, 1986.

13 Inventor's certificate 1375328 USSR, 1988.

14 A. M. Dymov, Tekhnicheskiy analiz, Metallurgiya, Moscow, 1964.

15 M. S. Rutstein, W. B. White, *Amer. Miner.*, 56 (1971) 877.

16 G. Fine, E. Stolper, *Earth and Planetary Sci. Lett.*, 76 (1985/86) 263.

17 J. G. Blank, R. A. Brooker, in M. R. Carrol, J. R. Holloway (Eds.), Volatiles in Magmas, vol. 30, Mineralogical Society of America, Washington, DC, 1994, p. 157.

18 K. Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination Compounds, John Wiley & Sons, New York, 1997.

19 A. M. Kalinkin, E. V. Klinkina, T. N. Vasilieva, *Kolloid. Zh.*, 66 (2004) 190.

20 Termicheskiye konstanty veshchestv (Handbook), in V. P. Glushko (Ed.), VINITI, Moscow, 1968–1979.

21 G. S. Khodakov, *Kolloid. Zh.*, 56 (1994) 113.

22 P. Yu. Butyagin, Mekhanokhimicheskiy sintez v neorganicheskoy khimii, Nauka, Novosibirsk, 1991, p. 32.

23 Yu. T. Pavlyukhin, Ya. Ya. Medikov, V. V. Boldyrev, *Izv. SO AN SSSR. Ser. Khim. Nauk*, 12, 5 (1983) 46.

24 H. Grohn, R. Paudert, H. I. Bisinger, *Z. Chem.*, 2 (1962) 88.

25 V. I. Molchanov, V. I. Gordeeva, T. A. Korneva *et al.*, Mekhanikhimicheskiye yavleniya pri sverkhtonkom izmel'chenii, Nauka, Novosibirsk, 1971, p. 155.