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THERMAL ANALYSIS OF MECHANOCHEMICALLY ACTIVATED GLASS

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Thermal analysis (TG, DTG, DTA, DSC) has been used to study the influence of mechanochemical activation of glass making batch on its melting and obtained glass crystallization. It revealed, that long time (12 h) mechanical treatment accelerates the glass batch melting and also improving network homogeneity influence the internal structure of the obtained glass. Refinement of the glass, at the beginning reduces temperature and increases degree of crystallization as a result of nucleating action of the increasing surface area of grains. However long time activation lowers the crystallization ability of glass and increases crystallization temperature. This is attributed to the deformation of the structure surface layer and surface energy increase, hampering the crystals nuclei formation.

Keywords: *glass crystallization, glass mechanochemistry, glass melting*

Introduction

Mechanical treatment as a long lasting grinding or milling can initiate many chemical reactions of solid bodies and accelerate their progress. There are known cases in which the reactions induced by mechanical energy have a course different from that occurring under the influence of temperature. An example here are some reactions of minerals decomposition [1]. The object of study of mechanochemistry are the chemical processes induced by mechanical energy introduced into the system.

The chemical activation by long lasting dry grinding of material not only increases its reactivity by specific surface area increase but it also improves mutual contact of reactant grain and disturbs the surface layer structure. Mechanical energy input generate the local overheating of the reactant grains up to high temperatures. Results of the activation are dependent on the physical and chemical properties of grinded material and mechanical treatment procedure. These relations are not recognized enough.

The influence of the dry mechanical activation of glass raw materials batch on its melting, and activated glass powders crystallization are the subject of the paper.

In metallurgy the mechanical energy is used to obtain amorphous alloys (mechanical alloying) [2]. Up to now mechanochemistry has not yet found application in the processes of the production of inorganic glasses. Many of them are obtained from a mixture of the batch components, between which there may occur reactions, already at low temperatures.They can be intensified if the batch is subjected to mechanical treatment through long lasting refinement in appropriate milling installations, which is a method often used in mechanochemistry.

The silicate-phosphate glasses have been selected as the object of study of the application of mechanical activation in the process of the production of glasses and its crystallization. These glasses are of the special interest as well as of numerous investigations on account of their bioactivity and application in stomatology and surgery [3].

To obtain them the components of different chemical reactivity are used. These are usually Na_2CO_3, $CaCO_3$ and H_3PO_4, which react with each other very quickly, as well as the poorly reactive SiO_2 in the form of quartz sand. Quartz forms with the other components a homogeneous silicate-phosphate melt but not until the temperature is about 1000°C.

Earlier there are formed phosphates what is accompanied by volatilization of a part of P_2O_5, which causes changes in the chemical composition of the glass, difficult to control. Losses of P_2O_5, due to volatility may reach up to 30 mass%. It is expected that the mechanochemical treatment of the batch will reduce the temperature of the P_2O_5 and SiO_2 combining and formation of the silica-phosphate melt and thereby reduce the volatility of phosphorus.

Melted phosphates and silicates form with difficulty a homogeneous melt which may show the phenomenon of phase separation during its cooling. It can be expected that mechanochemical treatment of

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Table 1 Chemical composition of glasses/mass%

Component	Sample			
	S2	S4	46-1/F	I
SiO_2	45	34.7	34	34.5
CaO	24.5	24	47	40
P_2O_5	6	5.9	14	16.5
Na_2O	24.6	24	–	–
B_2O_3	–	11	–	–
MgO	–	–	5	8.5
CaF_2	–	–	0.5	0.5

the batch will increase the homogeneity of the newly forming glass.

On the other hand, the mechanical activation of the obtained glass will facilitate its crystallization by surface nucleation stimulation. Nuclei formation is an important process initiating crystallization of glass [4, 5].

The advantageous influence of mechanical activation has been observed in earlier investigations [6]. On the glass surface there are formed then centers of nucleation initiating crystallization.

Experimental

The object of investigations were glasses from the system SiO_2–P_2O_5–CaO–Na_2O and SiO_2–P_2O_5–CaO–MgO (Table 1). The composition of the glass S-2 was close to that of the first known bioactive glass, elaborated by Hench [7]. It is distinguished by great biological activity, but its mechanical strength is poor. The glass S-4 contains an addition of B_2O_3 to increase its chemical and mechanical resistance. However, at the same time, its bioactivity becomes reduced. Glasses 46-1/F and I are used to produce glass-ceramic materials containing apatite and wollastonite. The presence of these crystal phases increases the mechanical strength of the material while its bioactivity is retained. Mg and F increase the ability to crystallize and they also have an advantageous influence on the adhesion of the material to the osseous tissue in a living body.

Standard glass raw materials were used for the synthesis of glasses. The batch prepared from chemical grade purity were mixed and divided into two parts: soft and reactive compounds (Na_2CO_3, $CaCO_3$, $MgCO_3$, H_3BO_3, CaF_2 and H_3PO_4 98 vol% solution) and hard resistant quartz sand (99.50% SiO_2). The first part was ground for 1 h , the second one was activated by grinding for 12 h. Both parts were mixed and milling again for homogenization. Sample mixed 1 h for homogenization (sample 1 h) and containing 12 h activated sand and mixed (sample 12 h) were studied and their properties compared to determine the activation effect. Mechanical activation and mixing was carried out in Planetary Mono Mill Pulverisette 6 (Fritsch), equipment commonly used in mechanochemical experiments.

The prepared batches were subjected to thermal investigations (TG, DTG, DTA) by mean of Derivatograph C. The volume of a weighed portion was 80 mg, the heating rate was 10 K min^{-1} in air atmosphere. The batches were melted in a laboratory electric furnace at the temperature 1400°C and kept at this temperature for about 2 h. The obtained glass was grinded into the following fractions: 0.3–0.1, 0.1–0.045 and <0.045 mm. All glasses were subjected to thermal analysis (volume of a weighed portion was 60 mg, the heating rate was 10 K min^{-1}, in air atmosphere) to determine their crystallization. Identification of crystal phases appearing in the course of heating of glass samples obtained from mechanical activated batches was carried out by X-ray diffraction analysis (XRD) , X Pert Philips diffractometer, using CuK_α radiation.

Results and discussion

Melting of the activated glass batch

The effect of mechanical activation on the reactions in the glass batches during their heat treatment is shown by the curves of the thermal analysis.

The batch for sodium–calcium glass S-2 (6 mass% of P_2O_5) homogenized for 1 h shows the endothermic peak induced by the release of water present in the raw materials. At 195°C the endothermic effect of the beginning of H_3PO_4 decomposition can be observed, accompanied by gradually removal of water. Quartz becomes reacted in a rather small degree; at 580°C there the endothermic peak of its polymorphic transition is still visible. At about 700°C there begins the endothermic decomposition of calcium and sodium carbonates, accelerated by their reaction with quartz and formation of sodium and calcium silicates which form an eutectic melt. Rest of the sodium carbonate reacts now with silicates and undergoes decomposition at about 882°C (endothermic peak) (Fig. 1).

12 h long activation of the batch diminishes by 50°C the temperature of the decomposition of carbonates and the formation of silicate melt (peak at 756°C) and to 807°C – the reactions of Na_2CO_3 decomposition.

Introduction of 11 mass% of B_2O_3 lowers the beginning of the decomposition of carbonates and formation of the melt to 685°C. The temperature of the final stage of Na_2CO_3 decomposition becomes slightly changed to 895°C. 12 h long activation causes the occurrence of the endothermic peak within

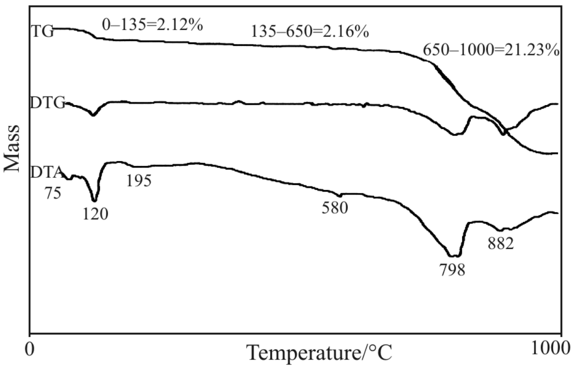

Fig. 1 Thermal analysis of S-2 batch homogenized 1 h

the range 460–560°C induced by the reaction of quartz with H_3BO_3, combined with its decomposition. There are formed low-melting silicates the presence of which lowers, the temperature of the reaction of the decomposition of carbonates and formation of silicate-borate-phosphate melt.

The batch for (Ca, Mg) silica-phosphate glass (46-1/F) shows the peak of water release from the phosphoric acid at 157 and 188°C; at 570°C the peak for quartz can be observed, and from 640°C there begins the two-stage reaction of the decomposition of carbonates, combined with their reaction with silica and phosphates formation the effect of which is the formation of an eutectic melt.

12 h long activation intensifies the reactions occurring between the batch components (Fig. 2). There appear reactions between the phosphoric acid and the other components of the batch. At 386°C there takes place the reaction of the synthesis of magnesium phosphate. At 574°C there appears the endothermic peak accompanied by the loss of mass. This is indication of the reaction of the formation of calcium silicates, accelerated by the presence of phosphates; this reaction is not visible in a non-activated batch. The thermal effect of the final reaction of decomposition becomes a single one and it is shifted to 795°C. In the activated batch it is preceded by a slowly proceeding decomposition, evidenced by a gradual loss of mass (TG curve, Fig. 2) which begins already at 170°C.

As a consequence, the decomposition peak at 795°C is accompanied by 18.56% loss of mass, while in the non-activated batch it was greater (23–53%). This illustrates the increasing chemical interaction between the components, induced by activation which brings the reduction of the temperature of reaction in which they participate. Intensity of components interaction at the low temperature range accompanied by loss of mass increases as well.

The thermal analysis curves show that mechanical activation increases the intensity of the interactions between the batch components. The effect is the increased degree of the advancement of reaction. The thermal effects of the reaction which are not intensive enough to be visible on the thermal analysis curves of a standard batch appear on the curves of an activated batch, and their temperature becomes reduced. At the temperature of polymorphic transformation silica reacts with the other components. The reaction is facilitated by the disorder of the quartz structure being the consequence of this transformation enhanced by mechanical activation.

The influence of activation becomes especially significant when into the batch composition there are introduced components of high reactivity such as H_3BO_3 and H_3PO_4. This effect is confirmed by the reduction of the softening temperature of the activated batch.

Crystallization of the glasses

Thermal analysis of glasses melted from mechanically activated batches has revealed essential differences in the crystallization temperature (T_c) (Fig. 3) as compare with not-activated. It becomes reduced by 20–30°C, while the two-stage crystallization becomes single-stage crystallization the temperature of which

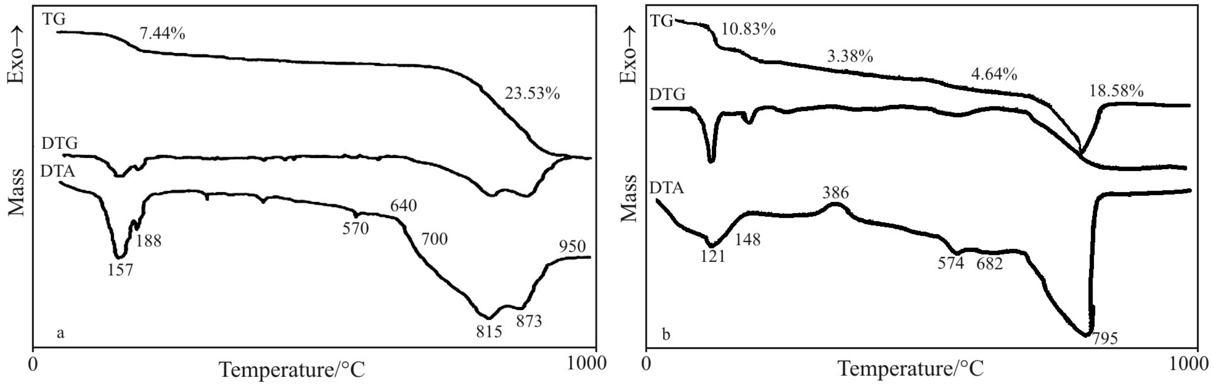

Fig. 2 Thermal analysis of 46-1/F batch after activated: a – 1 h and b – 12 h

Table 2 Phase composition of crystallized glasses obtained from batches mechanical activated by 1 and 12 h

No. of glass	Temperature/°C	Crystallizing phases			
S2(1)	730	$Na_2Ca(Si_3O_8)$	$Na_2Ca_2(SiO_3)_3$		
S2(12)	719	$Na_2Ca(Si_3O_8)$	$Na_2Ca_2(SiO_3)_3$		–
S4(1)	625	$Na_2Ca_3(Si_6O_{16})$	–	–	–
S4(12)	680	$Na_2Ca_3(Si_6O_{16})$	–	–	–
46-1/F(1)	917	$Ca_5F(PO_4)_3$	$Ca_2Mg(Si_2O_7)$	$CaSiO_3$	–
46-1/F(12)	939	$Ca_5F(PO_4)_3$	$Ca_2Mg(Si_2O_6)$	–	–
I(1)	883	$Ca_5F(PO_4)_3$	$Ca_2Mg(Si_2O_6)$	$MgSiO_3$	$Mg_2(Si_2O_6)$
I(12)	913	$CaMg(Si_2O_7)$	$CaSiO_3$	$MgSiO_3$	–

lies in the middle between the temperature of the first and the second peak of two-stage crystallization.

Crystallizing compounds has been identified using Philips X Pert High Score computer programme. Activation can change type of the newly forming phases (Table 2). It is characteristic for phospho-silicate glasses (samples 46-1/F and I). Structural network of these glasses is composed of silicate and phosphate domains. Deep mechanical treatment can reduce its internal nonhomogeneity and number of crystallizing compounds diminishes (Table 2).

Worthy of note is the change of the glass transformation temperature (T_g). This is visible especially in the case of glasses containing B_2O_3 and increased amount of P_2O_5. Then there takes place its distinct reduction. It means that the mechanical activation of the batch influences the internal structure of the glass formed of it. The obtained results indicate that this refers in particular to glasses containing a considerable amount of the added glass network forming components B_2O_3 and P_2O_5. Thus it can be assumed that there takes place the increase in the homogeneity of the glass network both with respect to the distribution of the chemical compounds in it as well as its arrangement.

The influence of mechanical activation and refinement on the phase transitions in glasses was investigated. The thermal analysis of glasses is usually carried out on samples with the grain size 0.3–0.1 mm

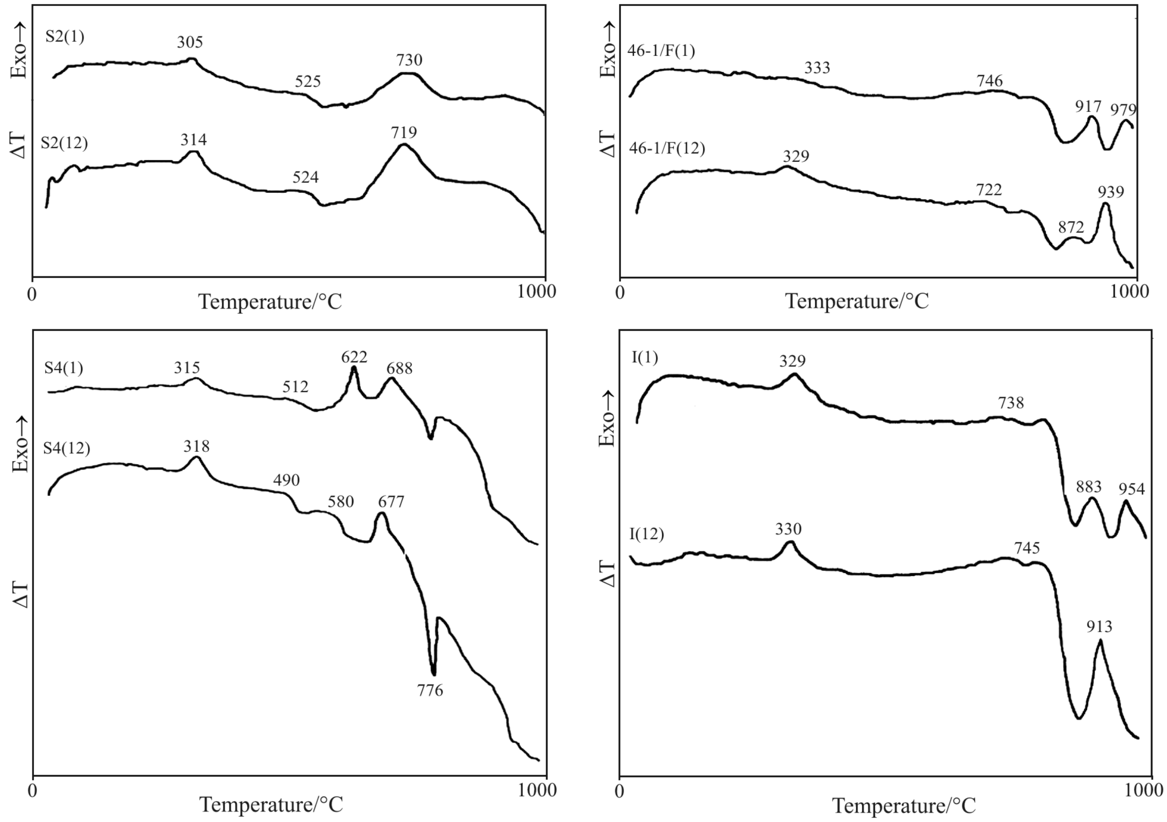

Fig. 3 DTA curves of glasses activated mechanochemically for 1 and 12 h

milled for 1 h. Thermal analyses of a sample of such grain size and of finer fractions: 0.1–0.045 mm and <0.045 mm were carried out. The fraction <0.045 mm was additionally mechanically activated for 4 or 24 h.

DTA curves of the glass fraction S-2 have shown that the degree of refinement has no influence on the T_g temperature of the glass (T_g 736°C). On the other hand, refinement below 0.045 mm increases the T_c temperature up to 739°C, and additional milling for 4 h increases T_c to 745°C. The crystallization peak area is decreasing in parallel respectively. A similar phenomenon is observed for the glass 46-1/F. The T_g value remains constant within the limit of the measurement error. On the other hand, the T_c temperature decreases at first from 886 to 871°C, and then increases with refinement up to 909°C (fraction <0.045 mm), and after additional milling it drops to 864°C. There appears then the second degree of crystallization with T_c equal to 992°C. The surface of the crystallization peak area in this case increases from 87.1 to 191°C, after 24 h activation it falls down to 83.4°C.

From the presented results of investigations it can be concluded that refinement to the grain size 0.045 mm increases the ability for crystallization, most probably as the result of the increase of the specific surface which has a nucleating effect as it is widely accepted. Further refinement causes the reduction of the ability to crystallize. It may be connected with the increase of the surface energy and internal structure of glass modification under the influence of milling, which hampers nuclei formation.

Conclusions

Thermal analysis revealed that mechanochemical activation allows to increase the interaction between the components of the batch and thereby to increase the intensity of reactions in the batch preceding its melting. This contributes to the reduction of the temperature of the formation of the glassy phase.

Mechanochemical activation of batches containing besides SiO_2 another network forming component, such as B_2O_3 or P_2O_5, is responsible for the fact that the newly forming two-component network is chemically and structurally more homogeneous. The result of this are the differences in the temperature and the course of crystallization between the glass melted from the traditional batch and that activated mechanically.

Activation of the traditionally melted glasses through their refinement has shown that at first it causes the reduction of the crystallization temperature but the increases degree of crystallization measured as the exothermal DTA peak area. The common opinion is that this is connected with the nucleating action of the external surface of the glass of which increases with its refinement. Results presented here indicate that it is accompanied by the internal structure modification influence. It has been noticed that refinement of the examined glasses below 0.045 mm has as its result the increase of the temperature of crystallization and lowering of the degree of crystallization. This can be attributed to deformation of structure of the surface layer and surface energy increase, which as a result hampers the nuclei formation, thereby shifting the maximum of the crystallization rate to higher temperatures and diminishing the crystallization ability of glass.

Acknowledgements

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