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Dedicated to Dr. Robert Mackenzie on the occasion of his 75th birthday

THERMAL BEHAVIOUR OF MECHANICALLY AMORPHIZED COLEMANITE

II. Internal structure reconstitution processes of ground colemanite

I. Waclawska

University of Mining and Metallurgy, 30–059 Cracow, Poland

Abstract

The effect of mechanical treatment on phase transitions of calcium borate-colemanite was studied. The decrease in the particle size of the original material and the increase in its internal structural disorder affect the thermal stability, characteristic temperatures and thermodynamic parameters of phase transitions such as structural relaxation and crystallization, occurring during the heating of this amorphous material. With increasing degree of amorphization of colemanite a change is observed in the structural mechanism of its crystallization.

Keywords: crystallization, glass transition effect, mechanical treatment, phase transition, structural relaxation

Introduction

The mechanical treatment of crystalline solids result in the reduction of the crystallites size and in an increase of their internal structural disorder. The consequence is the solid-state amorphization of the crystalline material.

In Part I of this paper the effect of mechanical treatment on the thermal decomposition of calcium borate-colemanite has been discussed in detail. The effect of prolonged grinding was interpreted in terms of the internal thermal dehydration and dehydroxylation of colemanite and changes in its structure accompanying this process. It has been found that mechanical treatment of colemanite causes most of the X-ray diffraction lines to reduce, but some become transformed into diffuse bands characteristic of an amorphous substance. With increasing time of milling the FTIR spectra of amorphized colemanite obtained by mechanical treatment from its crystalline form become similar to those of a glass of the same chemical composition. These phenomena are evidence that mechanical treatment causes gradual destruction of this mineral, mainly along its cleavage planes.

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The present paper provides information on the influence of mechanical treatment on the internal structure reconstitution processes and the accompanying effects of structural relaxation and recrystallization of colemanite.

These processes may be used to obtain precursors for vitreous and glass-ceramic materials of various relations between the crystalline phase and the amorphous matrix.

Experimental

Coarse, monocrystalline hydrated borate – colemanite $Ca_2B_6O_8(OH)_6 \cdot 2\ H_2O$ – was examined. The colemanite samples were subjected to dry grinding by vibration milling for periods ranging from 1 to 90 h.

To study the thermal stability of the mechanically amorphized colemanite, differential thermal analysis measurements were made with a Perkin-Elmer DTA-7 apparatus. A detailed description of the apparatus can be found in an earlier paper. The samples of 30 mg mass placed in platinum crucibles and in dry nitrogen atmosphere were first heated at a rate of 10°C min^{-1} up to 700°C, i.e. to a temperature ~50°C above the glass transition effect, where they were in both structural and thermal equilibrium. The samples were then cooled through T_g to 550°C at a constant cooling rate of 10°C min^{-1} and reheated at the same rate to 800°C. The glass transition temperature T_g was determined from the inflection point in the rapidly rising part of the enthalpy curve (Fig. 2) and the enthalpy values accompanying the glass transition were calculated using the 7 Series/Unix Thermal Analysis Software Library.

Results and discussion

Structure reconstitution processes of mechanically amorphized colemanite

Structural relaxation

It is known that during heating or cooling, glasses exhibit the structural strain relaxation phenomenon (glass transition effect). These strains are the consequence of the disordered arrangement of elements in the glass structure. Relaxation of stresses is connected with loosening of a part of the chemical bonds in the glass structure which is manifested by an endothermal reversible deflection in the DTA curves, illustrating jump-like changes in the specific heat (Δc_p).

Structural relaxation occurs also in thermally amorphized minerals which can assume a state of structural elasticity allowing the relaxation of internal strains [1]. The product of thermal dehydration and dehydroxylation of coarse-crystalline colemanite is an amorphous substance, which exhibits a reversible, endothermal glass transition effect at 650°C, confirming its vitreous nature. It is accompanied by a certain value of excess enthalpy, which does not disappear on reheating. This additional enthalpy is connected with the loosening of chemical bonds in the preserved elements of the primary structure of the mineral [2].

Figure 1 shows the DSC curve of coarse-crystalline calcium borate-colemanite. It can be seen from the curve that during the heating of this substance typical glass

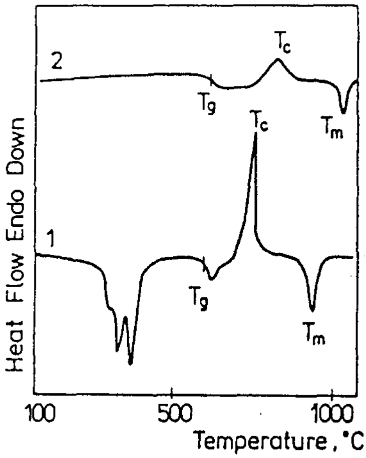

Fig. 1 DSC curves of: 1 - colemanite, 2 - $2CaO \cdot 3B_2O_3$ glass

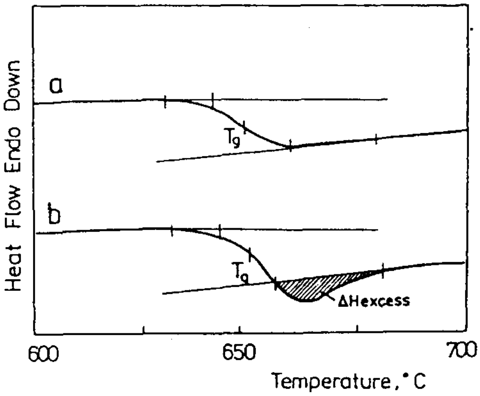

Fig. 2 DSC curve of structural relaxation of: a - $2CaO \cdot 3B_2O_3$ glass, b - colemanite

crystalline transformations take place: the glass transition effect (T_g), crystallization (T_c) and melting (T_m).

The effect of the grinding time on the thermal properties (such as T_g), the jump-like changes of the specific heat Δc_p and excess enthalpy accompanying the glass transition ΔH_{excess}), derived from the DTA experiments for colemanite samples are shown in Table 1.

In the early stage of colemanite grinding the temperatures of structural relaxation and the accompanying values of Δc_p remained practically unchanged while the values of excess enthalpy accompanying the glass transition effect distinctly decreased.

The increasing degree of the primary colemanite structural disorder is responsible for the decreasing values of excess enthalpy which, in turn, is responsible for the loosening of chemical bonds in the preserved structural elements of colemanite.

Table 1 Effect of grinding time on structural relaxation of amorphized colemanite derived from DSC

Grinding time/h	T_g/°C	Δc_p/J g^{-1} °C^{-1}	ΔH_{excess}/J g^{-1}
0	653.4	0.453	2.301
1	653.2	0.456	1.997
2	652.0	0.419	1.935
4	655.7	0.446	1.706
5	654.6	0.625	1.937
6	655.7	0.587	1.754
8	655.0	0.496	1.723
10	654.3	0.603	1.599
19	651.9	0.669	1.482
24	651.7	0.634	1.425
40	651.5	0.574	1.328
75	651.7	0.570	1.318
90	650.4	0.550	1.021

Somewhat higher temperatures (T_g) accompanying the glass transition effect may be an indication that the rearrangement of the structure of colemanite caused by the early stage of grinding and the obtained type of its disorder differ from the type of disorder specific for glasses.

Long grinding time causes the amount of preserved elements of the primary structure to decrease while the bonds of the remaining elements become weaker and weaker and during heating they undergo deeper rearrangement (higher Δc_p values), which makes structural relaxation easier and to appear at lower temperatures. Lower temperature is sufficient for attaining the viscosity of $10^{13.6}$dPas specific for the glass transition effect, when the structure contains smaller and weaker preserved elements.

Crystallization

The crystallization of the amorphous colemanite proceeds in one stage. The product of crystallization of vitrified colemanite is calcium triborate $2CaO{\cdot}3B_2O_3$ of a ring structure like its crystalline precursor. This kind of crystallization takes place when the chemical composition of the amorphous precursor is similar to that of the crystalline phase formed from it.

The effect of the grinding time on the crystallization properties (such as T_{onset} temperature, width of the crystallization peak L, enthalpy of crystallization ΔH_c and the thermal stability parameter $\Delta T = T_{onset} - T_g$) derived from DSC experiments for colemanite samples is shown in Fig. 3 and in Table 2.

At the early stage of grinding the crystallization temperature of colemanite decreases. The crystallization peak becomes narrower and elongated; at the same time

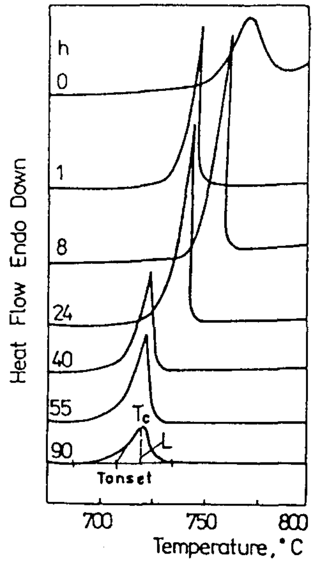

Fig. 3 DSC curves of crystallization of original and ground colemanite

the degree of recrystallization of ground colemanite increases (higher values of crystallization enthalpy). Lower values of the thermal stability parameter indicate greater tendency of the ground substance for devitrification. Such a behaviour of colemanite ground for 1–2 h is probably due to its rapidly increasing specific surface which promotes nucleation during the crystallization process.

Table 2 Effect of grinding time on crystallization of amorphized colemanite derived from DSC

Grinding time/h	T_{onset}/ °C	T_c/ °C	$W = T_{onset} - T_c$ °C	$\Delta T = T_{onset} - T_g$/ °C	L/ mW	ΔH_c/ J g^{-1}
0	755.9	771.4	15.5	102.9	31.9	96.1
1	740.3	748.2	7.9	87.9	142.5	144.7
2	745.0	754.7	9.7	92.8	194.0	200.0
4	749.3	758.0	8.7	93.8	162.7	240.2
5	754.5	763.4	8.9	99.8	149.0	214.6
6	745.9	755.0	9.1	90.7	174.6	237.8
8	752.1	762.2	10.1	97.6	191.7	217.8
10	741.3	751.6	10.3	87.6	219.1	237.1
19	738.3	748.3	10.0	86.6	179.0	179.0
24	736.6	746.3	9.7	86.5	170.3	201.6
40	716.6	725.1	8.5	65.7	83.6	148.5
55	711.9	722.2	10.3	58.4	73.5	141.2
60	707.6	720.3	12.7	57.2	31.8	100.6

With increasing grinding time of the mineral one can observe still a high degree of its recrystallization, although the crystallization temperature and width of the crystallization peak slightly increase. This may be due to an agglomeration of colemanite grains.

Long time grinding considerably lowers the thermal stability of an amorphous material. The crystallization of calcium triborate takes place at much lower temperatures, but its rate is much lower. This is evidenced by the shape of the crystallization peak which becomes less sharp. Simultaneously, the values of the crystallization enthalpy are diminishing, indicating the decrease of the degree of recrystallization of the ground material.

It has been found [1, 3] that the crystallization of thermally amorphized coarse-crystalline colemanite proceeds according to a diffusionless mechanism. The crystalline phase is formed through reorientation and topological adjustment of the elements of the amorphous structure like in displacive, polymorphic transformations.

Long time mechanical treatment of colemanite, while destructing its structural bonds, causes its amorphization degree to increase. Both the amount and the size of the preserved elements of the primary crystalline structure of colemanite decrease. Since they are the potential nuclei from which the structure of crystalline $2CaO{\cdot}3B_2O_3$ is formed, with a decrease in their amount, crystallization proceeds slowly, although it begins at a lower temperature.

It is probable that the degree of amorphization caused by long time grinding is so high that the recrystallization proceeds by way of diffusional displacements of the components at longer distances, which is a slow process. It begins at a lower temperature because single atoms change positions. Diffusion proceeds in aggregates of micro-powders. Their structure becomes similar to that of a glass, thus a short-range ordering takes place in it, being limited to single coordination polyhedra.

Conclusions

The decreasing particle size and the increasing degree of randomness of the internal structure of mechanically amorphized colemanite affect the thermal stability, characteristic temperatures and thermodynamic parameters of phase transition such as structural relaxation and crystallization occurring during the heating of this amorphous material.

The increasing randomness of the primary structure of colemanite causes an increase in its elasticity and homogeneity which enables easier relaxation of the internal stresses. The increase of the structural disorder of colemanite is also responsible for a systematic decrease of the values of excess enthalpy which accompanies structural relaxation in amorphized colemanite.

The large specific surface of colemanite which is distinctly increasing at the early stage of grinding, causes a reduction in its thermal stability and a simultaneous acceleration of its recrystallization.

The increase in the degree of structural disorder of the mineral progressing with long time grinding causes a decrease in the thermal stability, but recrystallization becomes more difficult. The degree of amorphization of colemanite, increasing under the influence of long time grinding, induces a change in the mechanism of its recrystallization leading to a transition from diffusionless to diffusive transformation.

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