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TRANSPORT PROPERTIES AND MICROSTRUCTURE CHANGES OF TALC CHARACTERIZED BY EMANATION THERMAL ANALYSIS

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Thermal behavior of talc samples (from locality Puebla de Lillo, Spain) were characterized by emanation thermal analysis (ETA), DTA and TG. The ETA, based on the measurement of radon release rate from samples, revealed a closing up of surface micro-cracks and annealing of microstructure irregularities of the talc samples on heating in the range 200–500°C.

For ground talc sample a crystallization of non-crystalline phase formed by grinding, into orthorhombic enstatite was characterized as a decrease of radon mobility in the range 785–825°C and by a DTA exothermal effect with the maximum at 830°C. ETA results characterized the microstructure development of the talc samples on heating and served to evaluate their radon mobility and transport properties on heating and cooling. Transport properties of the talc samples were evaluated by using ETA experimental data measured during heating to 600 and 1300°C, respectively, and subsequent cooling to room temperature.

Keywords: *DTA, emanation thermal analysis, microstructure changes, radon diffusion, talc, TG, thermal behavior, transport properties*

Introduction

Talc is used as raw material in many industrial applications [1, 2]. Grinding has been used to make suitable size of particles in order to control the reactivity of raw materials. It is known that dry grinding leads to random delamination of the silicate layers, to a strong structural alteration with important particle size reduction and to an increase in surface area [1–8]. In this paper the emanation thermal analysis (ETA) was used to characterize transport properties and microstructure changes of talc samples on heating and subsequent cooling to various temperatures. DTA and TG were used in order to support the interpretation of ETA results.

The ETA was already used in the investigations of the microstructure development of the natural and ion exchanged vermiculite, thermal behavior of ground vermiculite, thermal reactivity of ceramic clays, etc. [9–12].

Experimental

Samples and methods

Talc from Puebla de Lillo (Leon, Spain) [4] was studied. A vibratory mill (HERZOG, Type HSM 100) was used to produce the ground sample. Grinding time was 5 min.

Differential thermal analysis (DTA) and thermogravimetry (TG) measurements were performed in air at a heating rate 10°C min^{-1} by using Seiko TG/DTA 6300 equipment. The B.E.T. surface area was determined by using the results of N_2 adsorption obtained by equipment Micrometrics 2200 A Model, Norcross GA (USA).

ETA measurements were carried out on heating in air at a heating rate of 6 K min^{-1}, using a Netzsch ETA-DTA 404 instrument, type 404. The ETA [8–10] involves measurements of radon release rate from samples previously labelled by ^{220}Rn atoms. The ^{220}Rn atoms were incorporated into the sample to a maximum depth of 80 nm [13] due to recoil energy (85 keV $atom^{-1}$), which the atoms gained by the spontaneous α-decay. ETA has been already used to characterize microstructure changes in surface and subsurface of the samples during heating. Thus, an increase in the radon release rate, E, may characterize an increase of the surface area of the interfaces, whereas the decrease in E may reflect processes like closing up structure irregularities that serve as paths for radon migration, closing pores and/or a decrease in the surface area of the interfaces [14–16].

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Results and discussion

Thermal behaviour of natural and ground talc samples

Results of TG and DTA presented in Figs 1a and b characterized the thermal behavior of natural un-ground and ground talc samples, respectively. From the TG results of the ground talc sample (Fig. 1b) it followed that a mass loss took place in the range from 30 up to 150°C. Only a small mass loss was observed in this temperature range with the un-ground sample (Fig. 1a). These results are in agreement with particle size diminution and surface area evolution due to grinding of the sample and associated with the weekly bound OH groups on the broken edges of the ground talc particles [4]. From surface area measurements we observed that the surface area of natural talc before grinding was 3 m^2 g^{-1} and that it increased after grinding to 110 m^2 g^{-1}.

From Fig. 1a it followed that on further heating of the natural un-ground talc sample, a DTA endothermal effect was observed in the range of 960°C, due to the loss of structural water and accompanied by the formation of enstatite ($MgSiO_3$) and silica [4, 17, 18]. This was confirmed by the mass loss that took place with the natural un-ground talc sample in range 900–1050°C. It followed from Fig. 1b that the crystallization of non-crystalline phases, formed by grinding of the talc sample, into orthorhombic enstatite [17] was characterized by an exothermal effect at 830°C.

Figures 2a and b depict the ETA results used to characterize the thermal behaviour of the natural talc mineral before and after grinding. The ETA results are presented in Fig. 2 as temperature dependences of the radon released rate, $E(T)$, as experimental data (points) and as model curves (lines) obtained by fitting the ETA experimental data [16]. The ETA results brought about new information about the thermal behavior of the talc samples. The increase in radon release rate, $E(T)$, observed in the range 30–250°C is in agreement with delamination of the silicate layers, a structural alteration with important particle size reduction and an increase in surface area of the talc mineral. It was assumed that the increase of the radon release rate, $E(T)$, in the range 30–250°C was due to radon diffusion along micro-cracks and micro-pores that served as radon diffusion paths. A 'single jump' random diffusion mechanism was supposed to take place in this temperature range in the sample labeled by radon to the depth of 80 nm [13]. The decrease of the radon release rate, $E(T)$, in the range 250–450°C indicated a closing up the micro-cracks that served as paths for radon migration. No changes in the $E(T)$ were observed in the temperature range 600–800°C, consequently, no micro-

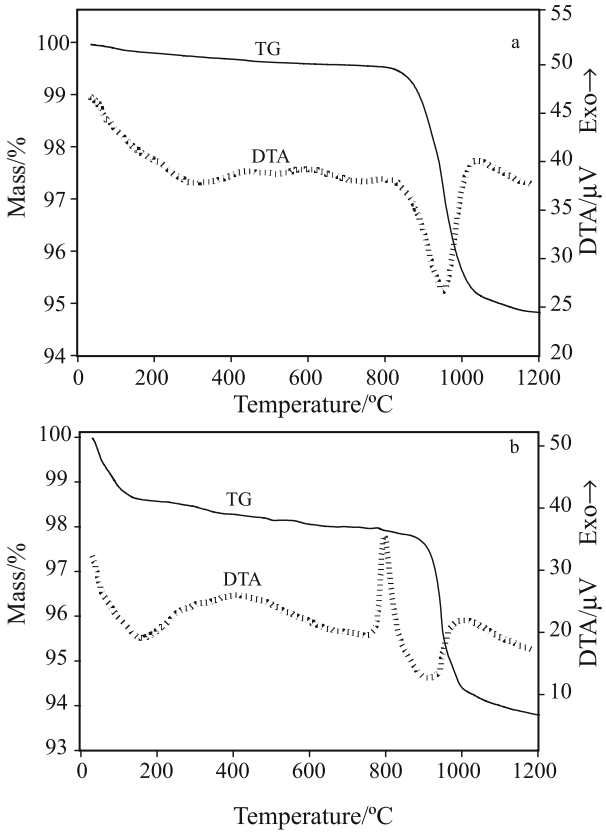

Fig. 1 Results of DTA and TG of talc samples a – un-ground and b – ground sample

structure changes were supposed in this range. However, on heating in the range of 785–870°C an abrupt decrease of $E(T)$ was observed in Fig. 2b with the ground sample, ascribed to the crystallization of non-crystalline phase into orthorhombic enstatite [4, 17]. On the contrary, no decrease of the radon release rate, $E(T)$, was observed for the un-ground talc sample at this temperature range (Fig. 2a). This is in agreement with the DTA data (Fig. 1a).

The increase of the radon release rate, $E(T)$, observed on heating above 870°C (Figs 2a, b) for both un-ground and ground talc samples, respectively, was ascribed to the enhanced mobility of radon in bulk of the samples. The loss of structural water from the talc samples took place in this temperature range as observed by TG (Figs 1a, b). However, the increase of radon release rate, $E(T)$, observed on heating of the sample in the temperature range above 1000°C differed for un-ground and ground talc sample (Fig. 2), corresponding to the structure development of the respective samples. Hence, the ETA made it possible to characterize differences in the transport properties during thermal treatment of the ground and un-ground samples, respectively. The ETA experimental data were used to calculate the radon mobility on heating in both un-ground and ground talc samples.

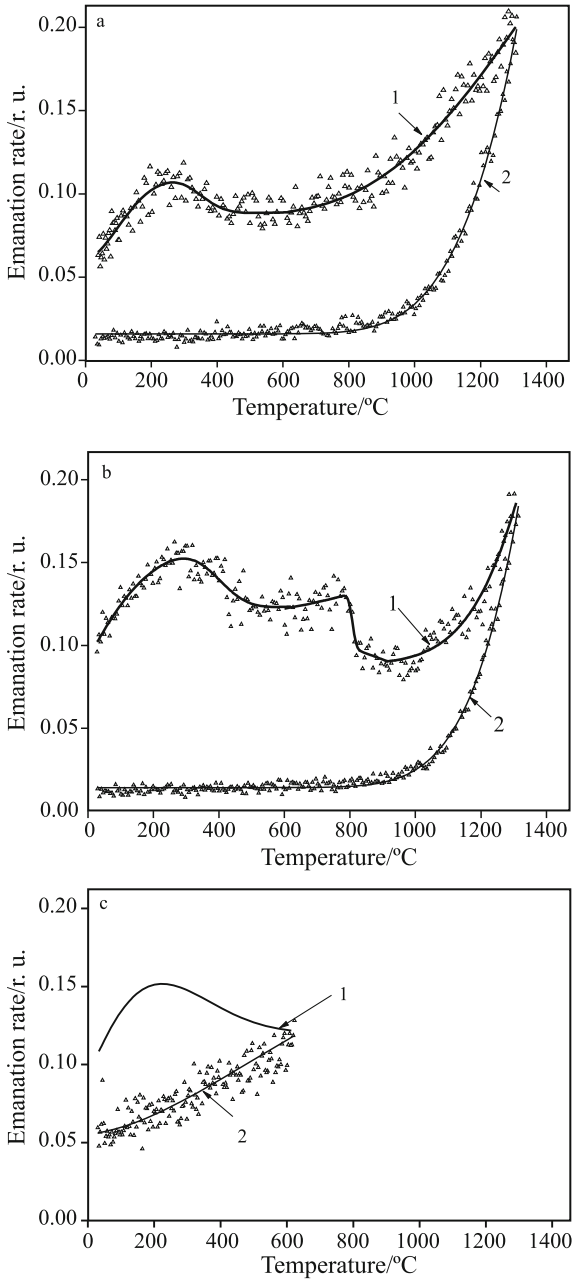

Fig. 2 Emanation thermal analysis (ETA) results of talc samples measured during 1 – heating and 2 – subsequent cooling in air: Temperature dependences of the radon release rate, $E(T)$ in the form of · · · – experimental data and as — – model curves obtained by fitting with the experimental data: a – unground sample heating to 1300°C, b – ground sample heating to 1300°C, c – ground sample heating to 600°C

Transport properties of the talc samples

Transport properties of the talc samples were calculated from the ETA results (Fig. 2) by using the radon mobility measured in the temperature intervals 20–400 and 900–1250°C, respectively.

Temperature dependences of radon release rate, $E(T)$, measured by ETA were used in the evaluation of transport properties of samples by using a mathematical model described in [19]. Several diffusion mechanisms were supposed for radon release from the labelled samples depending on the temperature range considered. On heating of the talc sample in a temperature range up to about 250°C the diffusion in open pores was supposed. It was assumed that radon migration along inter-granular space or interface boundaries and the bulk diffusion in the matrix took place at more elevated temperatures. Changes in the temperature dependences of the radon release rate, $E(T)$, can be expressed [19] as

$$E(T)=E_D(T)\Psi(T) \quad (1)$$

where $E_D(T)$ is characterizing the radon mobility along structure irregularities that served as radon diffusion paths, and $\Psi(T)$ is describing changes in the number of the radon diffusion paths. Temperature dependences of the radon release rate, $E(T)$, obtained by ETA were used for the evaluation of transport properties (radon mobility) characterization.

Following equations were used to evaluate ETA data. In the modeling the radon release rate due to diffusion was expressed as

$$E_D(T)=A[F(T_0)-F(T)] \quad (2)$$

where

$$F(T)=\frac{1}{k_{D_0}\exp\left(-\frac{Q_D}{RT}\right)+\lambda_{Rn}},$$

$$A=\lambda_{Ra}C_{Ra}=2.2035\cdot10^{-6}\ [s^{-1}]$$

where C_{Ra} is the equilibrium concentration of ^{224}Ra, the decay constant of ^{220}Rn $\lambda_{Rn}=1.2464\cdot10^{-2}$ [s^{-1}], T_0 is the initial temperature of heating, k_D is the rate constant of radon diffusion, depending on temperature according to Arrhenius relationship,

$$k_D=k_{D_0}\exp(-Q_D/RT) \quad (3)$$

where Q_D is activation energy of radon desorption (diffusion), the molar gas constant

$$R=8.314\ \text{J mol}^{-1}\ \text{K}^{-1}$$

The parameters characterizing the radon mobility (values of activation energy of radon diffusion Q_D and constant k_0) for the talc samples were determined by using Eq. (3) and are summarized in Table 1.

Transport properties of the un-ground and ground talc samples were characterized in the temperature range 20–400°C by the values of activation energy Q_D=21±3 and 5±0.4 kJ mol^{-1} and values of k_0=6.8 and 0.1 s^{-1}, respectively (Table 1). Hence, the grinding enhanced the radon mobility in surface and

Table 1 Transport properties of talc samples determined by radon diffusion

	Sample treatment and maximum heating temperature	Measured on heating				Measured on cooling			
		20–400°C		900–1250°C		600–50°C		1250–50°C	
		Q_D/ kJ mol^{-1}	k_0/s^{-1}	Q_D/ kJ mol^{-1}	k_0/s^{-1}	Q_D/ kJ mol^{-1}	k_0/s^{-1}	Q_D/ kJ mol^{-1}	k_0/s^{-1}
1	Un-ground/1300°C	21±3	6.8	68±4	0.7	–	–	127±7	10
2	Ground/600°C	5±0.4	0.1	–	–	14±3	6.5	–	–
3	Ground/1300°C	5±0.4	0.1	232±9	$5.8\cdot10^5$	–	–	151±8	96

subsurface of the talc samples in this temperature range due to radon diffusion along micro-cracks and micro-pores.

In the temperature range of 900–1250°C following values of activation energy of radon diffusion were determined for the un-ground and ground talc samples: Q_D=68±4 and 232±9 kJ mol^{-1} and values k_0=0.7 and $5.8\cdot10^5$ s^{-1}, respectively.

These values of activation energy Q_D of radon migration by bulk diffusion mechanism characterized differences in transport properties of the un-ground and ground talc samples. In the un-ground talc heated to 870°C the radon mobility was higher (the value of Q_D=68±4 kJ mol^{-1}) as compared to the ground talc sample (Q_D=232±9 kJ mol^{-1}) heated to the same temperature of 870°C. This is in agreement with our observations obtained by thermal analysis and other methods in our previous studies [9, 20].

The decrease of the radon release rate, $E(T)$, observed by ETA (curve 1, Fig. 2) on heating in temperature range up to 450°C was ascribed to the annealing of structure irregularities that served as radon diffusion paths, whereas the decrease the emanation rate $E(T)$ in the temperature range 800–870°C corresponded to the crystallization of non-crystalline phase into orthorhombic enstatite.

The ETA results measured on talc samples during heating and cooling (Fig. 2 as curve 2) were used to characterize the transport properties of the talc samples pre-heated to 1300 and 600 °C, respectively. Radon diffusion characteristics, namely the values of the activation energy Q_D and of the constant k_0, for the respective natural un-ground and ground talc samples heat treated to 1300°C are presented in Table 1. The values of activation energy Q_D and constant k_0 for the natural un-ground and ground talc samples preheated to 1300°C are: Q_D=127±7 and 151±8 kJ mol^{-1} and values k_0=10 and 96 s^{-1}, respectively.

Consequently, it was assumed that the transport properties of the samples prepared by the heat treatment to 1300°C are slightly higher for the sample prepared from the natural un-ground talc in comparison to the sample prepared from the ground talc sample. This confirmed the assumption that grinding facilitated the formation of high temperature phases [17, 18].

Moreover, it was of interest to compare the transport properties of the intermediate products of talc based model ceramics samples prepared by heat treatment to 600 and to 1300°C, respectively. The radon diffusion characteristics of the ground talc sample heated to 600°C were calculated by using ETA experimental data in Fig. 2c, curve 2 and are summarized in Table 1.

From Table 1 it is obvious that the ground talc heat treated to 600°C has a considerably higher mobility for radon (radon diffusion activation energy Q_D=14±3 kJ mol^{-1}) in comparison with the sample prepared by heat treatment to 1300°C (radon diffusion activation energy Q_D=151±8 kJ mol^{-1}).

This is in agreement with the results of other methods demonstrating that the microstructure of the samples heated to temperatures 600 and 1300°C differed.

Figure 3 depicts the results of the temperature dependences of the function $\Psi(T)$ calculated from the ETA experimental data presented in Fig. 2. The an-

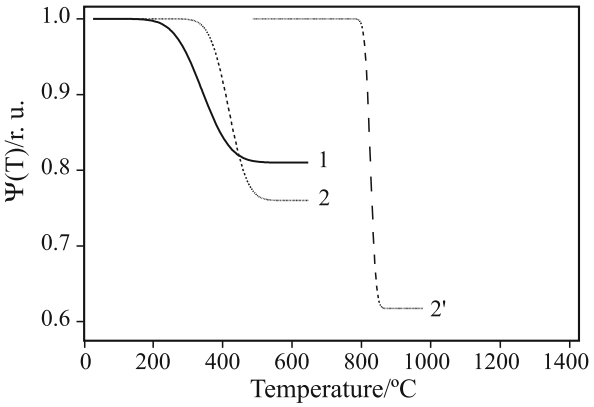

Fig. 3 Temperature dependences of $\Psi(T)$ function obtained by evaluation of ETA results. Curves 1 and 2 correspond to annealing of surface cracks and subsurface structure irregularities that served as radon diffusion paths on heating the unground and ground talc samples in the range 200–550°C. Curve 2′ corresponds to a decrease of radon mobility due to crystallization of non-crystalline phase into orthorhombic enstatite on heating the ground talc sample in the range 785–865°C

Table 2 Decrease of radon mobility due to annealing of microstructure irregularities of talc samples

Sample	Annealing of radon diffusion paths on heating up to 550°C				Crystallization of non-crystalline phase and formation of enstatite			
	T_{onset}/°C	T_{final}/°C	T_{max}/°C	$\Delta\Psi_1$/%	T_{onset}/°	T_{final}/°C	T_{max}/°C	$\Delta\Psi_2$/%
Un-ground	190	490	342	19	–	–	–	–
Ground	280	550	418	24	785	865	825	49

nealing of surface cracks and structure irregularities that served as radon diffusion paths was characterized by a decrease of the radon release rate on talc samples heating in the temperature range up to 400°C. Microstructure changes corresponding to the crystallization of the non-crystalline phase into orthorhombic enstatite were characterized with the ground talc sample by a decrease of radon release rate $E(T)$ in the range from 785 to 870°C.

By this way the ETA results brought about additional information about changes in the transport properties of talc samples on heating. By using this approach it was possible to determine the intensity of the radon mobility changes influenced by the processes in the mentioned temperature ranges.

Table 2 presents temperature intervals and maximum rate of the annealing of structure irregularities that served as radon diffusion paths (determined by temperatures T_{onset}, T_{final} and T_m) for the talc samples investigated. It followed from Fig. 3 and Table 2 that for the ground talc sample the onset of the annealing of surface cracks and subsurface structure irregularities was shifted to higher temperatures and the intensity of the annealing was enhanced by 26% (Fig. 3, curves 1 and 2).

From Fig. 3, curves 2 and 2′, and Table 2 it followed that the annealing of surface cracks and structure irregularities in the range 250–450°C represented a less intense decrease of the radon mobility of the talc sample as compared to the crystallization of non-crystalline phase into orthorhombic enstatite, observed with the ground talc in the range 785–865°C. It should be mentioned that with the un-ground sample, no decrease of E was observed above 800°C.

Conclusions

ETA results characterized the microstructure development of the talc samples on heating and served to evaluate their transport properties on heating and cooling by using the radon mobility. Annealing microstructure irregularities of talc samples on heating in the range 200–500°C was characterized as a decrease of radon release rate. For the ground talc sample a crystallization of non-crystalline phase, formed by grinding, into orthorhombic enstatite was characterized as by a decrease of radon mobility in the range 785–825°C, that was accompanied by a DTA exothermal effect in the range of 830°C. Transport properties of the talc samples heat treated to 600 and 1300°C, respectively were assessed by using radon mobility parameters.

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