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Initial sintering stage of thoria powder investigated by emanation thermal analysis

VLADIMÍR BALEK
Nuclear Research Institute, 250 68 Řež, Czechoslovakia

The initial stage of free sintering of thoria (ThO_2) has been investigated by means of emanation thermal analysis. Thoria powder (having surface area of 18 $m^2 g^{-1}$) was prepared from thorium oxalate (homogeneously labelled by ^{228}Th) by heating to 500° C. The release of ^{220}Rn was studied at various temperatures. The curves of radon diffusion release measured during isothermal heating of thoria powder at four temperatures (705, 735, 780 and 825° C) have been used for investigating the kinetics of the surface changes of thoria powder during the initial stage of sintering. The experimental data evaluated obey the kinetic law $\Delta E_p \sim S_{eff} = \text{const} \times t^n$, where E_p is the emanating power due to the diffusion of radon in intergranular space and open pores, S_{eff} is the effective surface area, t is time and n equals 0.64. The effective surface area S_{eff} has been proposed as a new parameter characterizing the active surface of powdered solid and its changes during sintering.

1. Introduction

Emanation thermal analysis (ETA), based on the measurement of the release of inert radioactive gases from samples previously labelled [1, 2], has been succesfully used for the determination of surface area changes [3, 7] and the study of thermal behaviours of ceramic powders in dynamic experimental conditions [8, 9]. The aim of this paper is the investigation of the initial sintering stage of thoria powder by measuring the release of radon (^{220}Rn) in the temperature range between 700 and 825° C.

Thoria is of considerable importance as material for electrotechnical ceramics, as a fertile material in nuclear energy application, a refractory material and a catalyst. It is moreover an advantageous material for this study as it is free from phase changes up to melting point.

2. Theoretical considerations

2.1. Release of radon from dispersed solids

The release of radon from a solid labelled by its parent nuclides is characterized by the emanating power, E, defined as the ratio of the rate of the radon release of the rate of radon formation from the parent isotope by the radioactive decay

$$^{228}\text{Th} \xrightarrow{\alpha} {}^{224}\text{Ra} \xrightarrow{\alpha} {}^{220}\text{Rn}.$$

The values of E are to be considered as composed of [2]

(a) a recoil part, E_r, due to the fact that every atom of radon gains, during its formation by decay of radium, an energy of 85 keV,

(b) a diffusion part, E_p, due to the diffusion in intergranular space and open pores of the dispersed solid and

(c) a diffusion part, E_d, due to the diffusion of radon in the solid matrix of the dispersed material.

The emanating power, E, can be expressed as the sum

$$E = E_r + E_p + E_d. \qquad (1)$$

Fig. 1 gives a scheme of the release mechanisms of radon from dispersed solid.

2.1.1. *Discussion of* E_r

The recoil part of the emanating power, E_r, for single cubic crystallites of thoria having an edge of $a > r_0$ can be expressed as [10, 11]

$$E_r = K_1 S_{eff}, \qquad (2)$$

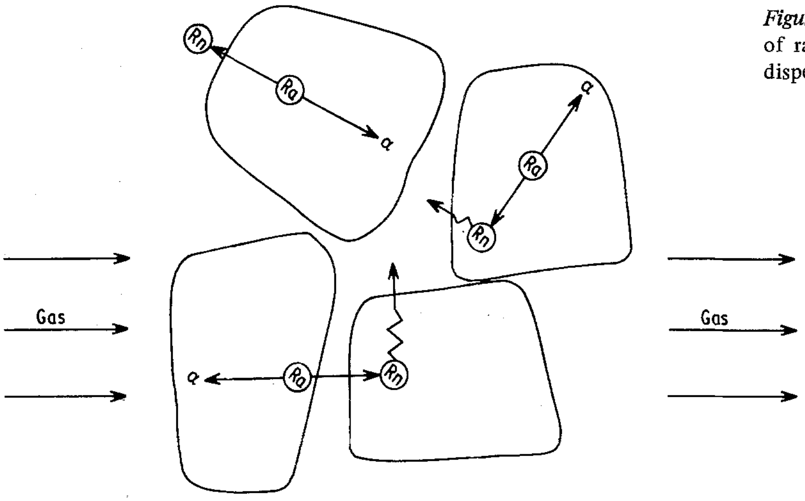

Figure 1 Scheme of the mechanisms of radon release from crystallites of dispersed solid.

where K_1, the temperature independent constant, equals $r_o\rho/4$, r_o is the path of the recoiled atoms in the solid, ρ is the density and S_{eff} is the effective surface area related to the mass of the sample. The path, r_o, of the recoiled atoms of radon (^{220}Rn) in thoria has been estimated as 40 nm (supposing the density of thoria to be 9.3 g cm^{-3}). For smaller single grains having an edge, $a < r_o$, Equation 2 is no longer valid. For thoria grain having an edge of $a = r_o$, the recoil release rate $E_r = 0.94$.

For finely dispersed solids where isolated grains cannot be supposed, Equation 2 cannot be generally applied. In this case some recoiled atoms of radon escaping from the crystallite of thoria end in neighbouring crystallites (see Fig. 1) from which they can be consequently released by diffusion. The path of recoiled atoms of ^{220}Rn in air has been estimated as 8.3×10^{-3} cm (supposing the density of air to be 1.23×10^{-3} g cm^{-3}).

Consequently, the direct and indirect recoil of the atoms of radon should be taken into account when considering dispersed solids. The total recoil part, E_r, of the emanating power can be expressed by

$$E_r = E_{r,\mathrm{direct}} + E_{r,\mathrm{indirect}}. \qquad (3)$$

The release due to the indirect recoil is strongly affected by the dispersity and morphology of the powder. For a single crystallites of thoria, $E_{r,\mathrm{indirect}} = 0$ and $E_r = E_{r,\mathrm{direct}}$.

In the case of dispersed solid, the constant K_1 in Equation 2 depending on the dispersity and morphology of the sample. In this case radon atoms released by recoil from the crystallites move to the external surface of the sample by diffusion in intergranular space and in pores filled by air.

2.1.2. *Discussion of* E_p

The part of the emanating power, E_p, due to the diffusion of radon through intergranular space and open pores to the surface of a sample of dispersed solid can be expressed as

$$E_p = K_2 T^{1/4} S_{eff}, \qquad (4)$$

where K_2 is the temperature independent constant, T is the temperature and S_{eff} is as before.

2.1.3. *Discussion of* E_d

The part of the emanating power which is due to the radon diffusion in the solid matrix, E_d, can be expressed by [2]

$$E_d = K_3 \exp(-\Delta H/2RT), \qquad (5)$$

where $K_3 = (D_o/\lambda)^{1/2} S_{eff}\rho$, D_o being the pre-exponential factor of the expression for the temperature dependence of the radon diffusion coefficient in the solid and λ being the decay constant of radon. S_{eff} and ρ are as defined previously, ΔH is the activation energy of radon diffusion in the solid matrix, R is the gas constant and T is the absolute temperature.

2.2. Effective surface area, S_{eff}

The dependence of E on the surface area reflects the dispersity and morphology of the sample of dispersed solid. The quality of the surface is mainly reflected by the radon recoil release and by the release due to the radon diffusion in intergranular space and open pores. The term "effective surface area", S_{eff}, in Equations 2, 4 and 5 represents the active surface area taking part in the recoil and diffusion processes. S_{eff} can be expressed either in the conventional way (e.g. in m^2 g^{-1}) using a reference sample of the solid substance having a known values of S_{eff}, or in a relative way, assuming the S_{eff} of the reference sample to be equal to 1.

The behaviour of the samples of active powers during the initial stage of their sintering can be described by the surface area obtained from ETA measurements more conveniently than by the surface area measured for example by absorption methods. The latter reflects the state of the solid at liquid nitrogen temperature, which does not necessarily correspond to that at elevated temperatures.

2.3. Evaluation of the emanating power from ETA measurements at various temperatures

2.3.1. Room temperature

The values of emanating power measured at room temperature, E_{25}, are composed of a part E_r due to the radon recoil (which is temperature independent) and a part E_p due to the randon diffusion in the intergranular space and open pores (which depends on temperature). E_d, which corresponds to the radon diffusion in the solid matrix, is for most inorganic solids negligible at room temperature. Consequently, E_{25} for thoria powder can be expressed as

$$E_{25} = E_r + (E_p)_{25}. \qquad (6)$$

For single crystals of ionic solids, E_{25} can be supposed to be equal to E_r, as $(E_p)_{25}$ is negligible at room temperature.

2.3.2. Elevated temperatures

For E_r, E_p and E_d which compose the emanating power, E, measured at elevated temperatures, is given by

$$E_T = E_r + (E_p)_T + (E_d)_T, \qquad (7)$$

where E_T is the emanating power measured at the temperature, T. At temperatures lower than 30 to 50% of the melting point, T_m, (in the absolute temperature scale) the E_d part can be neglected.

From the values of E measured at two different temperatures (e.g. at room temperature and the temperature, T) the values of ΔE_p can be obtained from

$$\Delta E_p = E_T - E_{25}. \qquad (8)$$

The values of ΔE_p can be advantageously employed in Equation 4 for the characterization of the changes of surface area, S_{eff}. The values of ΔE_p for thoria powder were obtained from Equation 8 using E_{25} and E_T (measured at temperatures of 705, 735, 780 and 825° C). This temperature range corresponds to 29 to 32% of the absolute melting temperature, T_m ($T_m = 3050°$ C for thoria). Consequently, the values of ΔE_p characterize the change of surface area taking place during the initial stage of thoria powder sintering.

3. Experimenal procedure

3.1. Preparation of ThO_2

Thorium oxide powder was prepared by heating thorium oxalate dihydrate in air for 3 hours at 430° C and subsequent heating for 1 h at 500° C. The initial thorium oxalate dihydrate was prepared by adding 1 M oxalic acid solution drop by drop to the 1 M thorium nitrate solution (containing trace amounts of ^{228}Th) under intensive stirring and heating to boiling point. After adding all the stoichiometric amount of oxalic acid, the precipitate was heated for 1 h, filtered, washed by warm water until oxalate ions were present in the filtrate, and dried at room temperature in air. The surface area of thorium oxide prepared was 18 m^2 g^{-1}. The specific activity of the samples was 2×10^5 sec^{-1} per gram of ThO_2.

3.2. ETA measurements

For the measurement of the release rate of radon (in counts per sec) the ETA apparatus described in [1, 12] has been used. The values of radioactivity of Rn released from the sample were divided by the values of the total radioactivity of the sample, the latter being proportional to the rate of radon formation from the parent nuclides. The values of the relative emanating power, E, obtained by this way are expressed in relative units (e.g. in %).

Before being used for ETA measurements the samples were stored for 1 month in order to establish the radioactive equilibrium between the parent (^{288}Th) and daughters (^{224}Ra and ^{220}Rn). For every measurement a fresh portion

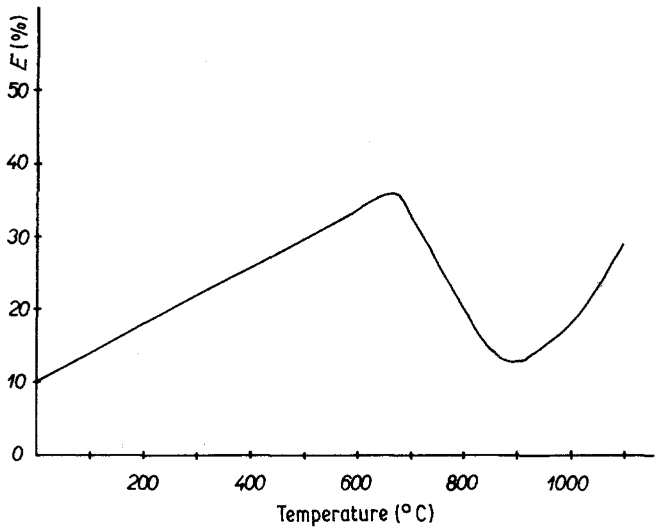

Figure 2 Temperature dependence of the emanating power, E, of thoria powder during heating in air at a heating rate of 10 K min^{-1}.

(20 to 30 mg) of the initial thoria powder was used, previously tempered to 165° C for 10 min.

The release rate of radon was measured (a) at room temperature, (b) during heating with linearly rising temperature of 10 K min^{-1}, and (c) during isothermal heating at temperatures of 705, 780 and 825° C.

For the isothermal ETA measurement the samples were inserted into the preheated furnace; the time necessary for the sample to reach the temperature of the furnace was 1 min. After heating for various times at a definite temperature the samples were quenched in air and the release rate of radon measured at 25° C.

3.3. Surface area determination

Surface area values of the quenched samples have been determined by the method based on the subsequent absorption–desorption of nitrogen [13, 14].

3.4. X-ray diffraction

X-ray diffraction patterns were obtained by use of a Micrometa (supplied by Chirana, ČSSR) using nickel-filtered Cu*Kα* radiation. Diffraction lines were read to an accuaracy of ± 0.05 %. From line broadening the size of grains, coherent with the X-rays, was estimated. The lattice parameters of the heat-treated thoria samples were evaluated by the Cohen method.

3.5. Electron micrographs

Electron micrographs of thoria samples were obtained by use of a Transition Electron Microscope (supplied by Tesla, ČSSR), having a magnification of 6150×.

4. Results and discussion

4.1. ETA measurements at linear rise of temperature

The ETA curve obtained during heating of thoria powder in air from 25 to 1,000° C at a rate of 10 K min^{-1} is shown in Fig. 2. The increase of the emanating power, E, in the temperature interval between 25 and 660° C is supposedly due to the radon release from irregularities of the surface layers, from open pores and from the intergranular space of thoria powder. The surface area diminishes during this heating from 18 to 15 m^2 g^{-1}. In the range between 650 and 900° C the decrease of E indicates the annealing of the surface and grain boundary defects in the sample, diminishment of open porosity and surface area. The transmission electron micrographs in Fig. 3 demonstrate the changes in the shape of crystallites of thoria powder during this heat-treatment.

The surface area changes during this heating from 15 m^2 g^{-1} (600° C) to 4.2 m^2 g^{-1} (735° C) and 2.4 m^2 g^{-1} (1100° C). The exponential increase of E in the range above 900° C is due to radon diffusion in the solid matrix of thoria. This explanation has been moreover confirmed by X-ray diffraction patterns. The sizes of grains estimated by X-ray diffraction are: 40 nm for thoria before the thermal treatment and 60 nm and 90 nm for thoria treated to 705 and 825° C, respectively. The smaller the grain size estimated, the greater the concentration of grain boundary and other non-

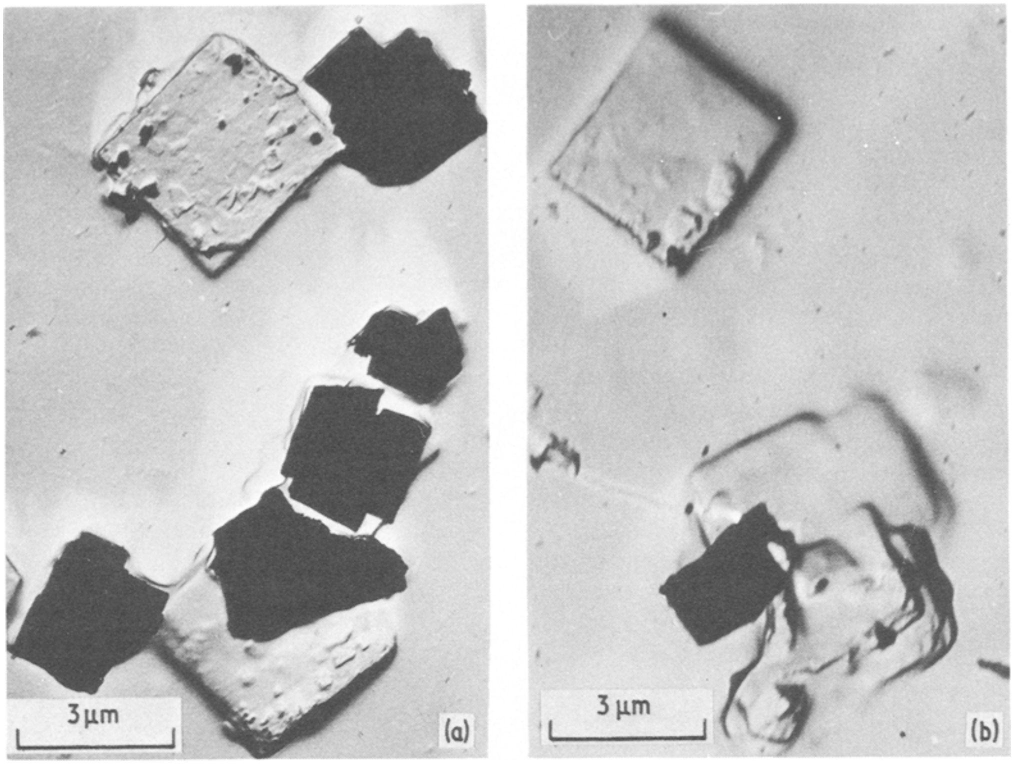

Figure 3 Transmission electron micrographs of thoria powder samples heated for 5 minutes at (a) 705, (b) 780 and (c) 825° C. The black blocks correspond to the crystallites extracted into the replica.

equilibrium defects in the sample that can be supposed. According to this, during the initial stage of sintering in the temperature range used, the concentration of the non-equilibrium defects in thoria decreases with the temperature of heat-treatment.

The lattice parameter of thoria powder before the thermal treatment (i.e. heated at 500° C for 1 h) was estimated to be 0.5603 ± 0.072 nm, the lattice parameters of thoria treated at 705° C for 5 min and 825° C for 30 min were 0.5580 ± 0.0006 nm and 0.5599 ± 0.0005 nm, respectively. The latter value agrees well with tabular value for artificial thoria single crystal equalling 0.5599 nm.

4.2. ETA measurements at room temperature

The emanating power, E_{25}, measured at room temperature can be used for the direct investigation of the surface area of dispersed solids. However,

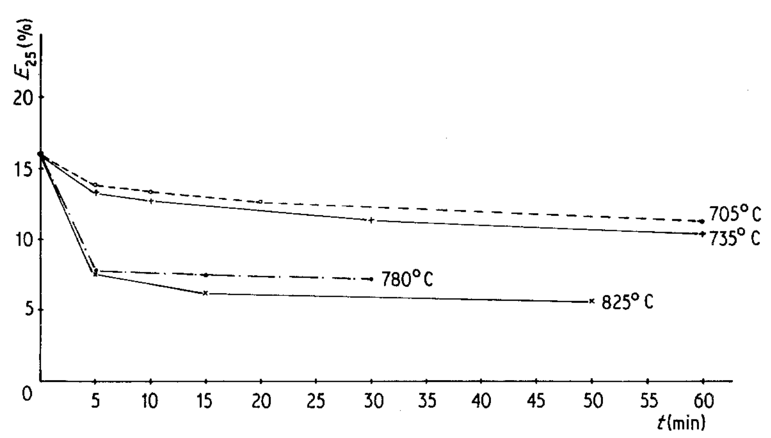

Figure 4 The values of E_{25} measured at room temperature for thoria powder samples treated at 705, 735, 780 and 825° C for various time intervals.

the validity of Equation 2 should be verified for every series of investigated solids of the given history.

Zhabrova and Shibanova [5] experimentally found the proportionality between E_{25} values and surface area, S_{ads}, when thoria powders of surface areas of between 10.0 and 300.0 $m^2 g^{-1}$ were studied. No simple relationship between E_{25} and S_{ads} was found by Skladzien [15] for thoria powders with a surface area of between 0.1 and 1.0 $m^2 g^{-1}$.

The values of E_{25} for thoria powder samples measured in this work are represented in Fig. 4. We have verified the linear dependence of E_{25} values and S_{ads} values for the samples of thoria powder prepared by the heating at temperatures from 500 and 1100° C. The linear dependence $E_{25} = K_1 S_{ads}$ has been found (see Fig. 5) in two ranges of surface area values: between 2.4 and 5.5 $m^2 g^{-1}$ and 14 and 18 $m^2 g^{-1}$. The constant, K_1, of the two regions differs: in the region of the higher S_{ads} values, representing the very beginning of the initial sintering stage, $K_1 = 1.92 \pm 0.1$; in the region of lowered surface area, $K_1 = 0.88 \pm 0.3$.

Consequently, the values of emanating power, E_{25}, measured at room temperature cannot be simply used for the assesment of the surface area changes of the thoria powder samples of the given thermal history. We have therefore proposed another way to this aim using the values of emanating power, E_T, measured at elevated temperatures.

4.3. ETA isothermal measurements at elevated temperatures

ETA curves obtained during isothermal measurements of thoria powder at 705, 735, 780 and 825° C, in air, are shown in Fig. 6. From E_T values measured at the respective temperatures and E_{25} values measured at room temperature the values of ΔE_p have been calculated using Equation 8.

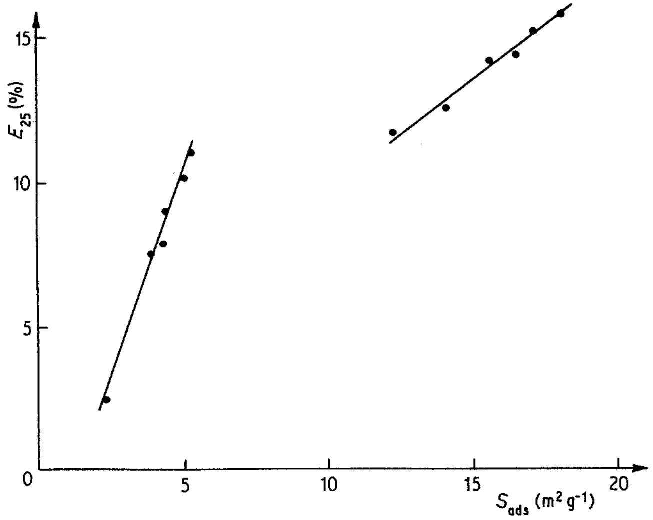

Figure 5 The dependence between the values of E_{25} and surface area, S_{ads}, for thoria samples with various thermal histories.

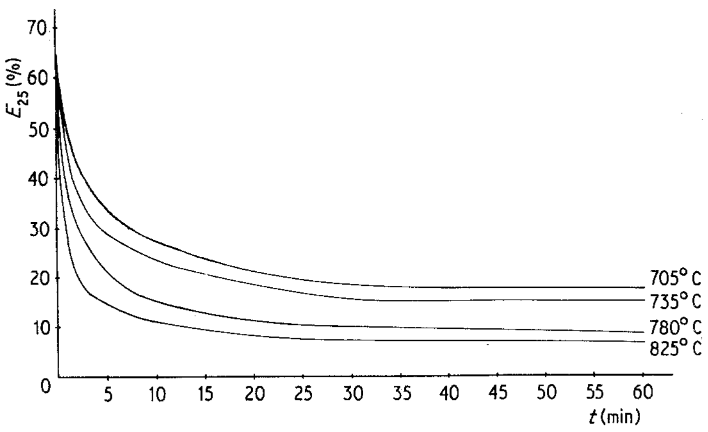

Figure 6 The emanating power, E, for thoria powder measured at 705, 735, 780 and 825° C in isothermal conditions.

As has already been stated, the E_p values obtained from ETA isothermal curves can be used as the measure of the surface area, S_{eff} (see Fig. 4). The time dependence of ΔE_p is demonstrated in Fig. 7.

According to Equation 4 we can replace ΔE_p by S_{eff}, in the linear dependence, giving

$$\log S_{eff} = n \log t + c/K_2 \quad (9)$$

and consequently

$$S_{eff} = \text{const} \times t^n, \quad (10)$$

where const $= c/K_2$, t is time, n is the constant characterizing the solid-state process of the sintering initial stage, $n = 0.64$, in this case and S_{eff} is the effective surface area of the powder.

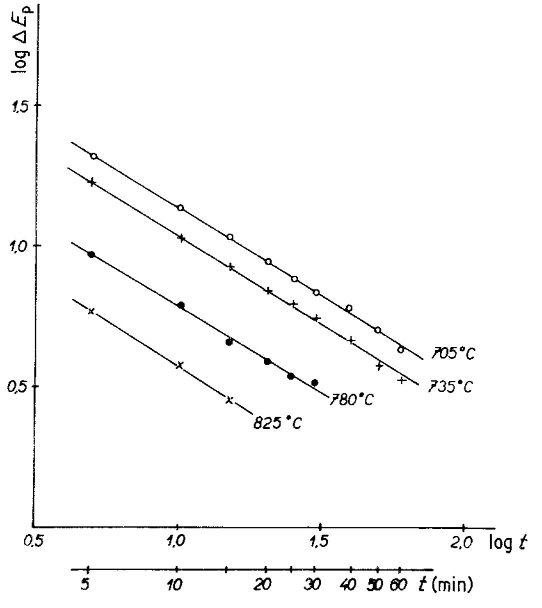

Figure 7 The dependence of log (ΔE_p) on log t for thoria powder treated at various temperatures (as in Fig. 6).

The character of the linear dependence between log S_{eff} and log t (see Fig. 7) in the temperature range between 705 and 825° C signifies that the initial stage of sintering of thoria in this temperature range is controlled by a single mechanism.

5. Conclusion

Emanation thermal analysis has been shown as a suitable method for investigating the initial stage of sintering of thoria powder. The evaluation of the emanating power, E, from ETA measurements at elevated temperatures means that information can be obtained about the changes in the active surface area which controls the initial sintering stage of thoria. The effective surface area, S_{eff}, elevaluated from ETA measurements has been proposed as a new parameter characterizing the active surface of a dispersed solid and its changes during sintering.

The advantage of the application of ETA to the study of initial sintering stages of dispersed solids consists not only in the possibility of gaining more objective characteristics of the active surface area changes but also in the possibility of investigating the surface of solids directly during heat-treatment, without the necessity to interrupt the heating and quench the sample, as needed for surface area measurement by common, e.g. adsorption, methods.

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