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THEORY OF EMANATION THERMAL ANALYSIS. III. EXPERIMENTAL VERIFICATION OF THE MATHEMATICAL MODEL FOR INERT GAS RELEASE FROM POROUS SOLIDS

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ABSTRACT

The mathematical model for the inert gas release from porous solids has been experimentally verified. The structure relaxation and sintering of the following solids have been investigated by the emanation thermal analysis at constant heating rate: silica gel, thoria powder, ferric oxide powder of various thermal history, commercial ferric oxide powder (1360 WF, Bayer, F.R.G.) and pellets, uranium dioxide xerogel and aged xerogel. Experimental results of ETA are interpreted using results of surface area, porosity and dilatometry measurements.

INTRODUCTION

The gap existing in the theory of emanation thermal analysis, ETA [1,2], namely in the description of the thermal behavior of porous solids has been dealt with in the previous papers [2,3] of this series. To describe the properties of the real dispersed medium we have introduced the idea of the diffusion of radon atoms via a quasicontinuum and their escape via migration by their recoil path or other defects. It was proved by computer simulation [3] that this model is able to describe the behavior of the highly defect solids during non-isothermal heating. The aim of this paper is to verify experimentally the mathematical model for the inert gas release from porous solids in the investigations of porous xerogels and powders of ionic crystals.

For the description of the changes taking place during heating in a porous solid following parameters have been used [3]:

(1) the radius of pores, r_p and $r_{p,0}$;

(2) the number of pores, N_p, the kinetic constant, K_p, and the activation energy, E_p, of the sintering, and the activation energy, E_s, of the radon diffusion in the solid matrix.

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The defectivity (defect state) of a solid has been characterized by the parameter ϵ, expressing statistically the fraction of defects serving as high-mobility paths for inert gas escape from the defect solid.

The mean diffusion coefficient, D_d, for the quasicontinuum depends on ϵ and the temperature, as follows

$$D_d = d_0\epsilon \exp(-E_{dd}/RT)$$
$$= d_0\epsilon_0 \exp\left[-(E_{dd}/RT) - \frac{P_d}{\beta}\int_{T_0}^{T} \exp-(E_{rd}/R\tau)/d\tau\right] \tag{1}$$

where D_d is the mean diffusion coefficient of the quasicontinuum, d_d is an appropriate constant, ϵ_0 is the initial value of the parameter ϵ, E_{dd} is the mean activation energy of the diffusion jumps, P_d and E_{rd} are the constants of the kinetics of the annealing of defects, and β is the heating rate.

First-order kinetics for the annealing of the continuous defects is supposed.

It has been shown in the Part II of this series [3] that higher ϵ_0 values, as well as lower E_{dd} values, lead to higher values of the emanation rate from a solid, and to a higher slope of the low temperature part of the ETA curve. The form of the ETA curve in this temperature range is, however, also affected by the value of the activation energy, E_{rd}, of the restoration of the matrix [3].

The following examples of the experimental ETA curves demonstrate the possibility of application of the mathematical model [3] for inert gas release from porous solids and verify this model.

EXPERIMENTAL RESULTS

Silica gel

In Fig. 1, curve 1 is the ETA curve of the silica gel sample Pragosil ($S = 600$ m^2 g^{-1}, Nuclear Research Institute, Czechoslovakia) during heating in air at a constant heating rate (5 K min^{-1}).

The sample was prepared by a sol-gel method which ensured the spherical shape of the particles. The sample is X-ray amorphous. The mean particle size is 180–200 μm, the mean radius of pores is 10 nm. The sample was labeled by impregnation with an aqueous solution containing ^{228}Th and ^{224}Ra nuclides. The atoms of ^{220}Rn are formed according to the scheme: $^{228}\text{Th} \xrightarrow{\alpha} {}^{224}\text{Ra} \xrightarrow{\alpha} {}^{220}\text{Rn}$.

The value of the emanation rate in any moment of the heating run is composed of several parts, corresponding to: (i) the radon release rate by recoil of ^{220}Rn; (ii) the indirect recoil of ^{220}Rn from the surface of the pores where ^{220}Rn has been introduced due to its direct recoil process; (iii) the diffusion of radon in the pores; and (iv) the diffusion of radon in the solid matrix. The radon diffusion in the solid matrix can be neglected at temperatures below 700 °C, i.e., below the temperature corresponding to 0.5 times the melting point of silica in the absolute temperature scale.

The value of E_{20} measured at room temperature reflects the high surface area of the sample. During linear heating, the emanation rate reflects the changes of the surface area and porosity due to the dehydration (ca. 100 °C) and escape of traces of volatile substances remaining in the sample after the gelation process (ca. 300–400 °C). In the region above 800 °C, an increase in the emanation rate is observed indicating the diffusion of radon in the matrix. The abrupt decrease of the emanation rate in the range 900–1050 °C is due to the structure relaxation of the amorphous silica, being accompanied by a decrease in porosity and surface area. The shrinkage of the sample was observed in this temperature range, though the spherical shape of the particles did not change. The subsequent increase in E at 1000 °C corresponds to the diffusion of Rn in the silica matrix.

The experimental ETA curve of silica gel (Fig. 1, curve 1) corresponds fairly well to the theoretical ETA curve (Fig. 1, curve 2) simulating the behavior of the porous solid with the following parameters (see ref. 3): radius of the pores, < 100 nm; indirect recoil parameters, $K_e = 0.01$ K s^{-1}, $E_e = 140$ kJ mol^{-1}; sintering parameters; $K_p = 10^{13}$ K s^{-1}, $E_p = 160$ kJ mol^{-1}; defect annealing parameters; $K_r = 10^{11}$ K s^{-1}, $E_{rd} = 160$ kJ mol^{-1}; parameters of radon diffusion in the solid matrix, $D_{s,0} = 1.0$, $E_s = 280$ kJ mol^{-1}.

The ETA results of the structural relaxation (sintering) of silica gel agree with the data of Lazarev et al. [4].

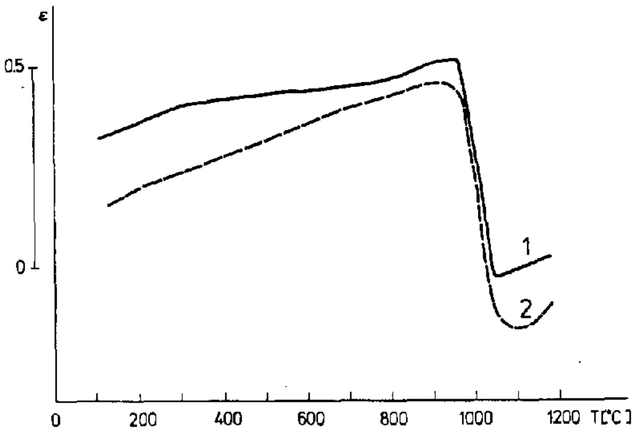

Fig. 1. Experimental (1) and theoretical (2) ETA curves of silica gel. The experimental curve of silica gel ($S = 600$ m^2 g^{-1}) was measured during heating in air at a heating rate of 5 K min^{-1}.

Thorium oxide powder

The thorium oxide powder studied is an example of a dispersed material with cubic grains ($S = 18$ m^2 g^{-1}). The sample was prepared by the decomposition of thorium oxalate at 480 ° C, homogeneously labeled by ^{228}Th and ^{224}Ra. The ETA curves of thorium oxide powder measured during heating in air at a constant rate of 10 K min^{-1} up to different temperatures are shown in Fig. 2. The values of E_{20} measured at room temperature mainly reflect the surface area and the morphology of the sample. As previously mentioned, the emanation rate E_{20} of this sample measured at room temperature is due to the direct and indirect recoil of Rn atoms and to the diffusion of Rn in the intergranular space.

During the heating of the sample up to 1000 ° C, the annealing of the surface defects and irregularities of the surface, and first stage of sintering take place. The ETA curve 2 in Fig. 2 describes the behavior of thoria powder after heating to 500 ° C in air. The surface area of this sample is smaller (12.1 m^2 g^{-1}) than that of the initial sample (18 m^2 g^{-1}) which is reflected by the decreased E_{20} value. The change in the slope of curves 1 and 2 indicates the change in the morphology of the thoria samples which took place during heating up to 500 ° C in air. In the temperature range 660–850 ° C a decrease in the emanation rate was observed, indicating the initial stage of sintering. The surface area decrease in this temperature interval corresponds to $S = 4.2$ m^2 g^{-1}. The subsequent increase in the emanation rate above 900 ° C is due to the diffusion of radon in the thoria matrix.

In Fig. 2, curve 3, the behavior of thoria heated to 1000 ° C in air is described. The considerably lowered E_{20} value reflects the decrease in the surface area of the sample after heating to 1000 ° C ($S = 2.4$ m^2 g^{-1}). The change in the slopes of the ETA curves 2 and 3 (Fig. 2) in the lower

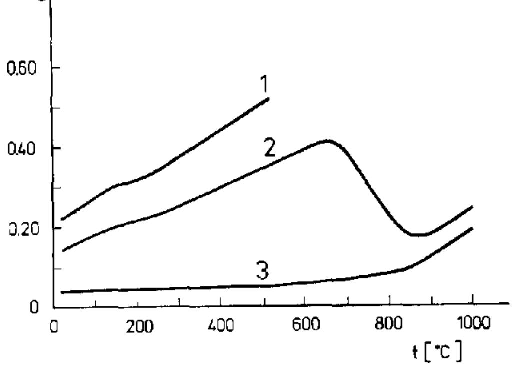

Fig. 2. ETA curves of thorium oxide (ex-oxalate) during heating in air at a heating rate of 5 K min^{-1}: (1) initial sample ($S = 18$ m^2 g^{-1}); (2) sample preheated to 500 ° C ($S = 12.1$ m^2 g^{-1}); (3) sample preheated to 1000 ° C ($S = 2.4$ m^2 g^{-1}).

temperature range, indicates the changes in the morphology of the thoria sample during the stepwise heating of thoria up to 1000 °C. The lower part of curve 3 (Fig. 2) indicates that the surface irregularities were fully annealed. The increase in E above 800 °C reflects radon diffusion in the thoria matrix.

On comparing curves 1–3 of Fig. 2, the characteristics of thoria powder can be seen. These characteristics are in good agreement with surface area measurements and the direct microscopic study of the morphology of the sample [5].

At the same time it should be pointed out that these ETA curves of thoria correlate well with the theoretical curve computed on the basis of the theoretical model of inert gas release from porous solids [3]. The changes in the surface area and morphology can be described by the parameter introduced by Kříž and Balek [3] for the characterization of the defectivity of a disperse (porous) sample.

Ferric oxide powder

In Fig. 3 the ETA curves of ferric oxide samples prepared by the thermal decomposition of basic iron (II, III) carbonate and the subsequent heating to 700 (1), 900 (2) and 1100 °C (3), are demonstrated.

The samples differ in their surface areas: the respective values of the surface area are: 53.1 $m^2 g^{-1}$ (1); 2.4 $m^2 g^{-1}$ (2); and 1.1 $m^2 g^{-1}$ (3). The differences in the surface areas is reflected in curves 1–3 (Fig. 3) by the values of the emanation rate, E_{20}, measured at room temperature.

The ETA curves measured during heating of the samples in air at a constant heating rate of 10 K min^{-1} describe the behavior of the samples

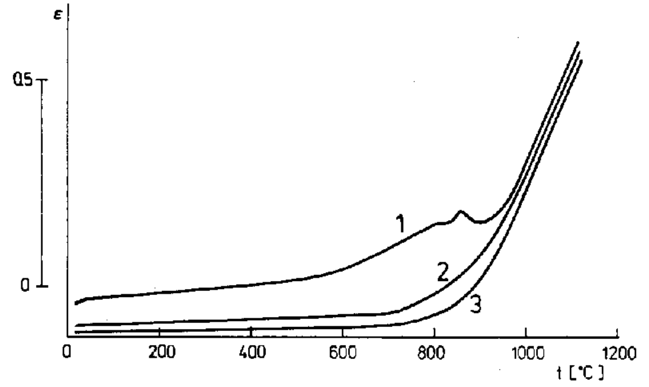

Fig. 3. ETA curves of ferric oxide powders (ex-basic iron (II, III) carbonate) during heating in air at a heating rate of 5 K min^{-1}: (1) sample preheated to 700 °C for 2 h ($S = 53.1$ $m^2 g^{-1}$); (2) sample preheated to 900 °C for 2 h ($S = 2.4$ $m^2 g^{-1}$); (3) sample preheated to 1100 °C for 2 h ($S = 1.1$ $m^2 g^{-1}$).

during the thermal treatment. The differences in the slopes of the ETA curves in the low-temperature range characterize the difference in the morphology of the samples. The effect observed on ETA curve 1 (Fig. 3) at temperatures of 830–860 °C corresponds to the initial stage of sintering of the particles, the subsequent increase in the emanation rate is due to the diffusion of radon in the ferric oxide matrix. The mentioned effect was not observed on curves 2 and 3 (Fig. 3) which supports this assumption.

By comparing the ETA curve of thorium oxide powder and ferric oxide powder we can see that the sintering process is indicated on the ETA curves at different temperature intervals, depending on the activation energy, E_p values, of the sintering process. It has to be mentioned here that the temperature dependence of the emanation rate, its decrease and subsequent exponential increase all depend on the relationship of E_p to E_s. With the increasing difference $(E_s - E_p)$, the respective effect on the ETA curve becomes more pronounced.

The role of the difference $(E_s - E_p)$ on the general shape of the ETA curve in the high-temperature region has been confirmed experimentally. The behavior of ferric oxide samples (Bayer, AG, F.R.G., type 1360 WF, $S = 10.7$ m^2 g^{-1}), as powder and pellets pressed at 375 MPa cm^{-2}, are compared in Fig. 4. The ETA results of the powder and pellet forms are shown together with the dilatometric curve of the pellet, which coincides well with the respective ETA curve.

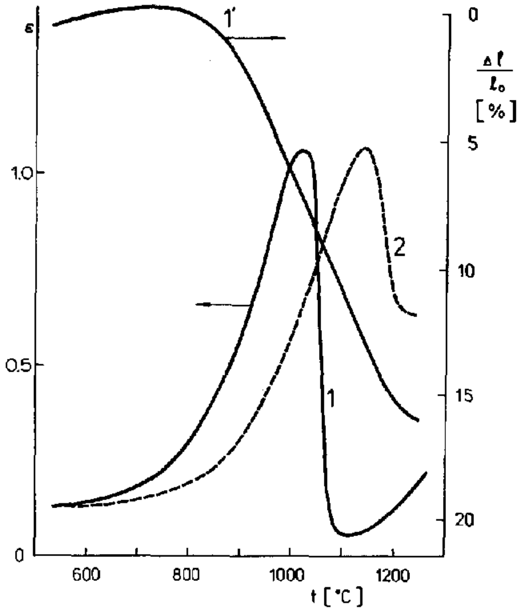

Fig. 4. ETA and dilatometric curves of commercial ferric oxide samples (Bayer, F.R.G., type 1360 WF) measured during heating in air at a constant heating rate of 5 K min^{-1}; (1) ETA curve of the pellet prepared from the powder with a pressure of 375 MPa cm^{-2}; (2) ETA curve of the powdered ferric oxide sample; (1') dilatometric curve of the ferric oxide pellet.

The pressing of the ferric oxide powder results in a decrease in the E_p (or log K_p) value of the sintering kinetics. The temperature of the break of the ETA curve due to the sintering is lowered by 155 °C for the pellet when compared to that of the ferric oxide powder.

At the same time, the decrease in the emanation rate due to the sintering of ferric oxide is much more pronounced with the pellet than with the powder.

Fresh and aged xerogel of uranium dioxide

The differences in the ETA curves of freshly prepared uranyl gel and the uranyl gel aged for 30 days in humid conditions are shown in Fig. 5. Both samples were prepared by a sol-gel technique [6]; the initial xerogel is characterized by the mean particle size of 180–200 μm, and by the most probable pore size of 0.7–0.9 nm; it is amorphous. The aged xerogel has the crystalline structure of uranyl dioxide, as was proved by the X-ray patterns.

During the heating of both samples in argon $+5\%$ H_2, the decomposition of the residual gelation additives takes place below 600 °C. This process is indicated by the effects on the DTA, TG and ETA curves [7]. Above 600 °C, no changes in the DTA and TG curves were observed, the ETA curves of the samples differ, however, due to the character of the structure and morphology of urania, as shown in Fig. 5.

The relative high emanation rate at 600 °C of sample 1 (fresh xerogel) reflects the amorphous character of the sample; the lower emanation rate of sample 2 (aged xerogel) reflects the crystalline state of the sample. The decrease in the emanation rate of sample 1 in the temperature range 980–1100 °C indicates a decrease in the surface area and porosity of the sample. On the other hand, the sintering of the crystalline sample (curve 2)

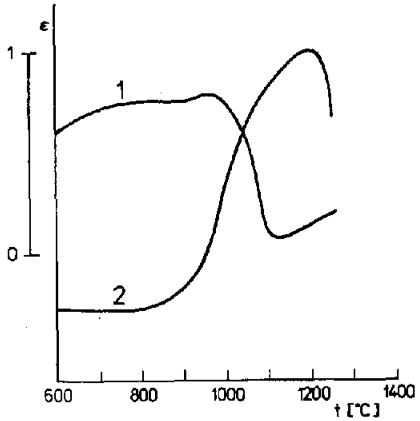

Fig. 5. ETA curves of the fresh xerogel (1) and aged xerogel (2) of uranium dioxide measured during heating in argon $+5\%$ H_2 at a heating rate of 5 K min^{-1}.

starts at much higher temperatures (above 1200 °C), comparable to those at the beginning of the sintering of urania powder prepared by common methods [8].

It should be noted once again that the differences in ETA curves 1 and 2 (Fig. 5) are caused by the different behavior of the amorphous and crystalline uranium dioxide samples, and by the different values of the activation energy, E_p, of sintering.

CONCLUSION

The mathematical model for the inert gas release from porous solid has been experimentally verified for porous and powder solids, labeled by the ^{228}Th and ^{224}Ra nuclides.

The sensitivity of the ETA curves to changes in the surface area and porosity (especially in the range of micropores, the size of which is comparable to the size of radon atoms) was demonstrated experimentally for samples of silica gel and fresh and aged xerogel of uranium dioxide. The abrupt decrease in the emanation rate of the samples corresponding to the structure relaxation (sintering) can be explained by our theoretical model.

It has been demonstrated that the differences in the surface area and morphology of the finely dispersed powders strongly affect the shape of the ETA curve in the low-temperature range. The slope of this part of the curve can be used for the characterization of the dispersed powders of ionic crystals (thorium oxide, ferric oxide) as well as of porous samples (silica gel, fresh xerogel of uranium dioxide).

The parameter ϵ_0, introduced into the model for the characterization of the defect state of the porous solids, can also be used for the characterization of the defect state of finely dispersed powders.

The dependence of the shape of the ETA curve in the high temperature section on E_p (i.e., log K_p) and on the difference $(E_s - E_p)$ was demonstrated experimentally using samples of ferric oxide and uranium dioxide xerogel.

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