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USE OF EMANATION THERMAL ANALYSIS IN THE STUDY OF THERMAL BEHAVIOUR OF INORGANIC MATERIALS

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Emanation thermal analysis [1, 2] (ETA) is based on the measurement of the inert gas release from samples previously labelled. The high detection sensitivity of radioactive nuclides used for the measurement makes it possible to use very low concentrations of the inert gases (10^{-14} at %) so that no influence of the inert gases on the properties of the solids can be supposed.

The inert gas can be incorporated into solid samples together with their parent nuclides, e.g. by coprecipitation during the sample preparation or by adsorption on the sample surface. In the latter case the inert gas atoms are incorporated into the surface layers of several tens of nanometers, due to the recoil energy (85keV/atom) which every ^{220}Rn atom gains in the moment of its formation by the ^{224}Ra decay, according to the scheme

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

The radioactive nuclid ^{228}Th serves as the permanent source (the half life = 1.9 y) of ^{220}Rn (the half life = 55 s).

The release rate E of radon atoms depends on surface area and the diffusion coefficient of radon in the solids investigated. The temperature dependence of the radon release rate for a single isolated grain of the solid in which no chemical nor phase transformations take place can be expressed in a simplified way by Eq. (1)

$$E = KS\rho\,[1 + D_0 \exp(-Q / 2RT)] \qquad (1)$$

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where K - is the constant independent on temperature, S - is surface area, ρ - is density, D_o - pre-exponential factor, Q - apparent activation energy of Rn diffusion, R - is gas constant, T - is temperature.

Experimental

The solid samples investigated were labelled by ^{228}Th and ^{224}Ra, representing a relative stable source of ^{220}Rn. By this way the labelling of samples enabled us to investigate the behaviours of solids upto the high temperatures in several heating and cooling runs without the necessity to re-label the sample. The parent nuclides of radon were co-precipitated or adsorbed at the sample.

The equipment for emanation thermal analysis permitted to measure the trace amount of inert gases, carried from the sample by the carrier gas (air, argon, etc.) into the radioactivity detector. The scheme of the ETA apparatus is given in Fig. 1. The ETA equipment [3] produced by Netzsch (Selb, FRG), gives the possibility of simultaneous measurements of several parameters during thermal treatment of sample (DTA, TG/DTG, detection of gaseous products of reaction, dilatometry etc.).

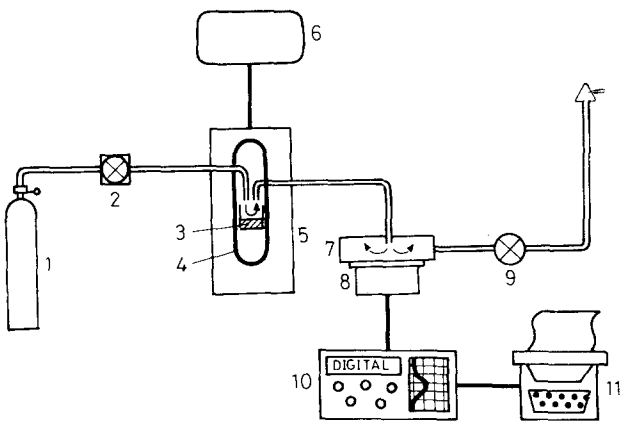

Fig. 1 Scheme of the apparatus for emanation thermal analysis 1 - gas supply, 2 - gas flow stabilizer and flow rate meter, 3 - labelled sample, 4 - sample holder, 5 - furnace, 6 - temperature controller, 7 - measuring chamber, 8 - radioactivity detector, 9 - flow rate meter, 10 - counts meter, 11 - data processor and printer (plotter)

Examples of the ETA application

Thermal decomposition of various iron(II)salts

In Fig. 2a-d the results of ETA, DTA and dilatometry are demonstrated, which were obtained during air heating of various iron salts (Mohr's salt, iron(II)sulphate, iron(II)oxalate and iron(II, III)hydroxocarbonate) at the constant heating rate 10 deg/min. The temperature intervals of the salts decomposition were determined from these results, the ETA giving the information on the morphology changes of the intermediate products [4] of thermal decomposition.

The differences in the morphology of the iron(III)oxide samples prepared by heating to 700, 900 and 1100° were tested [5] by the ETA during the subsequent heating of the samples at the heating rate 10 deg/min.

Comparison of the defect state of iron(III)oxides prepared from various salts

The influence of the thermal and chemical history on the active state of powdered iron(III) oxide can be estimated from apparent activation energy of radon diffusion determined from the experimental ETA results, obtained during heating or cooling of the sample. In the temperature range below 0.5 melting point in the absolute scale the apparent activation energy of radon diffusion reflects the topochemical defects remaining in the structure of iron(III)oxide after the decomposition of the iron salts used for the preparation of oxide samples. Hüttig [6] and Hedvall [7] called this phenomenon the structure memory of solids.

Figure 3 shows the dependences $\log(E - E_{20})$ *vs.* $1/T$ for iron(III)oxide samples prepared by heating various iron salts to 1100°. The values of the apparent activation energy of radon diffusion Q were evaluated from the slopes of the curves in Fig. 3 in the temperature range 600-800°. The following values q were found: 46, 79, 117 and 126 kcal/mol for iron(III) oxides prepared by heating Mohr's salt, iron(II)sulphate, iron(II,III)hydrocarbonate and iron(II)oxalate, resp. The highest value corresponds to the sample ex-oxalate, indicating the highest defect state.

Characterization of oxide ceramics intermediate products

The ETA application is especially advantageous in cases of investigation of geleous and poorly crystallized materials where traditional methods of materials' diagnostics, such as X-ray diffraction, do not give satisfactory results.

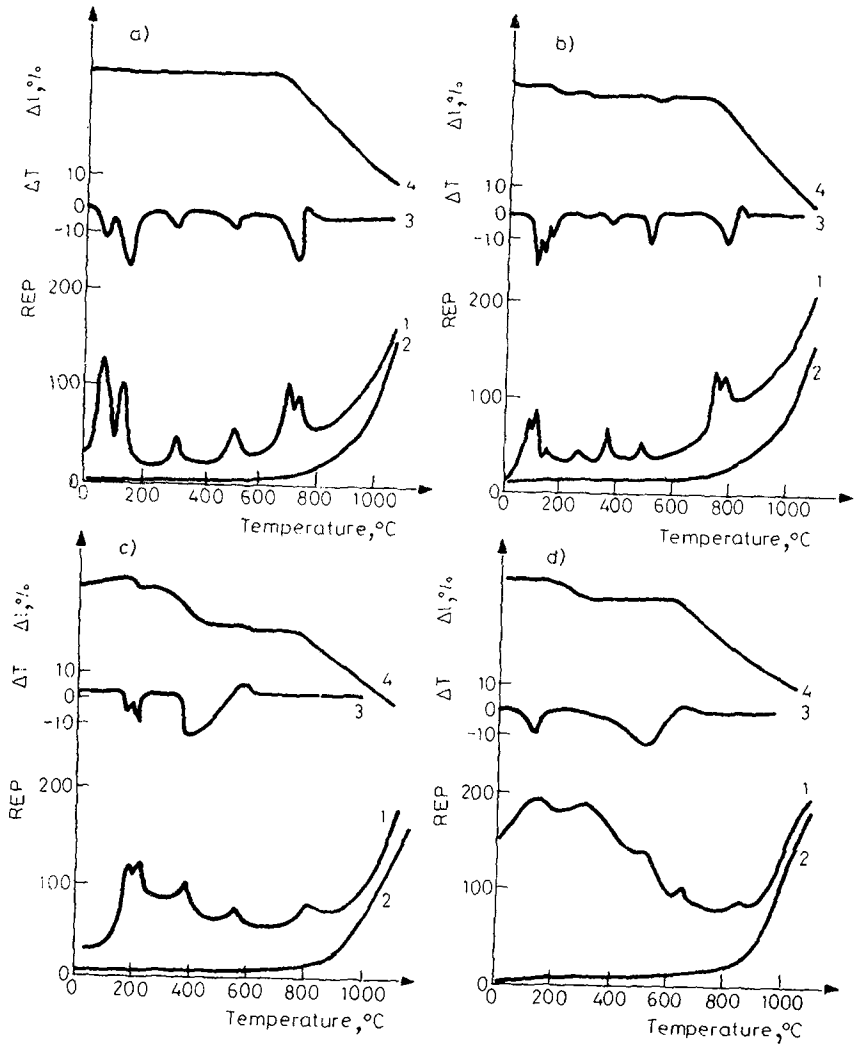

Fig. 2 ETA (curve 1), DTA (curve 3) and dilatometry (curve 4) of various iron (II) salts measured during heating in air at the heating rate 10 deg/min; curve 2 is the ETA curve of the sample during second run heating, no changes were observed on the DTA and dilatometry curves during second run heating. a) iron (II) sulphate heptahydrate, b) Mohr's salt, c) iron(II) oxalate dihydrate, d) iron (II, III) hydroxocarbonate

The voluminous precipitates and geleous inorganic materials are characterized by the high permeability of inert gas (radon). In Fig. 4 the changes of the radon release rate (ETA curve) and the dilatometry measurement

results are compared for urania xerogel droplets, prepared by sol-gel technique. In the temperature range 750-950° the decrease of the emanation rate indicates the recrystallization of urania xerogel, whereas no change on the dilatometry curve was observed. By further heating above 1000°, when the shrinkage of the sample takes place, the radon release is at first enhanced, (due to the radon diffusion release) and further it drops (when the densified structure hinders the radon release [8].

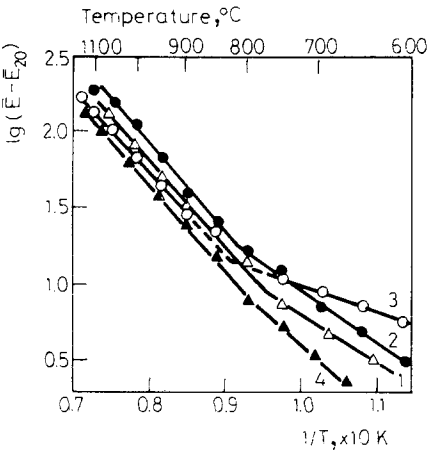

Fig. 3 The dependences $\log(E-E_{20})$ *vs.* $1/T$ for iron(III)oxides prepared by heating various iron salts to 1100°C in air: curve 1 - iron(II, III)hydroxocarbonate, curve 2 - iron(II)sulphate, curve 3 - Mohr's salt, curve 4 - iron(II)ocalate

Various urania xerogels prepared under different conditions (gelation additive concentration, washing, drying, aging, etc.) were characterized by means of ETA. The radon diffusion probe indicates sensitively the changes of the morphology of xerogel samples, which gives the possibility to reveal even very fine changes of materials caused by variation of technological conditions in the preparation of urania.

The ETA was applied for characterization of intermediate products of rutile prepared by calcination of ilmenite hydrolysate. The minor impurities present in the feed hydrolysate have to be washed out or suppressed by the suitable admixtures before calcination. The ETA curves in Ref. 9 represent the characterization of three samples of ilmenite hydrolysate treated in different ways (washing, aiming to remove the residual sulphate ions and adding various cations). It is obvious that the diminishing sulphate anions

content leads to the decrease of the anatas recrystallization temperature from 600 to 400°, the admixture of 0.5% ZnO leads [9] to the enhances formation of rutil at temperatures above 900°. The ETA enabled us to characterize solid state processes taking place during calcination of the hydrolysate and moreover to characterize the defect state of rutil prepared by the calcination.

Recently, the emanation thermal analysis was used for checking the preparation of Y $Ba_2Cu_3O_{7-x}$ superconducting ceramics [10] and for characterization of the transport properties of the ceramic materials during heat treatment in various atmospheres. The application of the emanation thermal analysis to the study of ceramic materials with "tailored" properties enabled us to reveal fine changes in the microstructure of the ceramic materials, which are responsible for their properties. This method was found advantageous also for evaluating the hydration of cements and Portland Clinker minerals. The application makes it possible to investigate in situ the microstructure changes during cement hydration without the necessity to interrupt the hydration process.

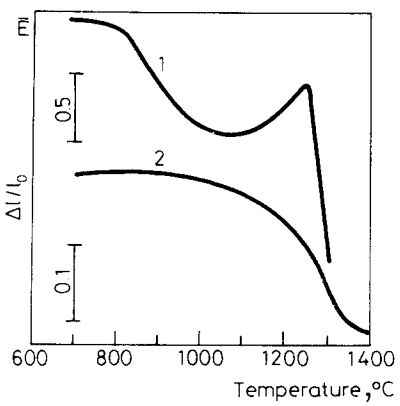

Fig. 4 The ETA curve (1) and dilatometry curve (2) of urania xerogel droplet measured during heating in argon + 5%H_2 at the heating rate 5 deg/min

It can be recommended for the evaluation of the structure defect state and its changes, for testing sinterability and reactivity of ceramic powders as well as for evaluation the durability of materials towards temperature and aggressive media [11, 12].

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Zusammenfassung – Emanations - Thermoanalyse [1, 2] (ETA) basiert auf der Messung von freigesetztem inerten Gas aus zufor markierten Proben. Die große Nachweisempfindlichkeit der bei der Messung verwendeten radioaktiven Nuklide ermöglicht die Anwendung sehr niedriger konzentrationen (10^{-14} Atom%) für das inerte Gas. Somit kann angenommen werden, daß die Eigenscahften des Feststoffes durch das inerte Gas nicht beeinflußt werden.