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APPLICATION POTENTIAL OF EMANATION THERMAL ANALYSIS

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The application potential of the emanation thermal analysis with respect to the actual needs of chemical technology and material science is given.

The emanation thermal analysis (ETA), considered as the less common method of thermal analysis, has been used in various fields of investigations [1]. This method is based on the measurement of inert gas release from solids previously labelled by the inert gases. The method has been advantageously used in the investigation of morphology and surface area changes during solid state processes, such as aging of precipitates, drying of geleous materials, thermal decomposition of minerals, hydration of hydraulic binders, in the solid state reactions which are of practical importance for chemical technology, environmental technology etc. The emanation thermal analysis enabled us to follow the morphology changes continuously in the respective conditions of solid state processes, i. e. in wet stage of samples when hydrating, during thermal treatment when being sintered.

By means of ETA such processes could be indicated which were not accompanied by mass changes, enthalpy changes, i. e. which are not revealed by thermogravimetry or DSC, respectively.

The determination of diffusion parameters or permeability of inert gases in polymers is one of the important way for characterization and the quality diagnostics of these materials. It has been possible by means of this method, (which is also called for isothermal measurements diffusion structure analysis) to reveal the local structure detects in polymer membranes and in thin films of organic and inorganic materials.

The suitable choice of the technique for inert gas incorporation into the solid samples is very important in this case. Inorganic materials can be suc-

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cessfully labelled by means of ion implantation, especially surface layers can be advantageously labelled when using a simple device by Jech [2]. The scheme of this device is given in Fig. 1, the introduction of the inert gases is very simple.

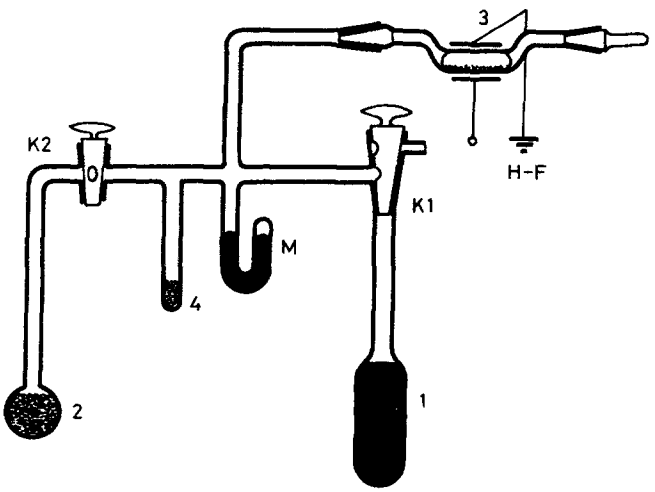

Fig. 1 The scheme of the apparatus for introducing a gas by ion bombardment in a high frequency discharge: 1 - adsorption pump, 2 - reservoir of the inert radioactive gas, 3 - sample cell, 4 - metallic calcium for inert gas purification, *K1* and *K2* - valves in glass apparatus, *M* - vacuometer, *H-F* - high frequency field generator

Inert gas incorporation into solid samples

The ion implantation is a general method for incorporation of inert gases into solids. Depending on the energy of ions various concentration profils of inert gas atoms in solid sample can be achieved. The simple way for labelling of surface layers using Jech device operates under voltage of 10 kV, producing low temperature discharge in the slightly evacuated cell in which the target material is situated.

The nuclear reactions, which give rise the inert gas nuclides e. g. the radioactive decay of radium according to the scheme $^{224}Ra \overset{\alpha}{\rightarrow} {}^{220}Rn$, can be also used for incorporation of the radon atoms formed by the decay into the solid. The parent radium atoms serve as an "recoiled ion microimplantator", producing radon atoms with the energy of 85 keV/atom. Radon atoms

penetrate into the solid samples several hundreds of nanometers, depending on the composition of the target materials (for example the penetration depths ^{220}Rn in MgO is R = 41.7 nm, in SiO_2 R = 65.4 nm, in Ba-stearate R = 94 nm and for comparison in air = $8.3 \cdot 10^4$ nm).

The parent radionuclide of ^{224}Ra can be adsorbed on the surface and deposited or used as an external source on a metal foil. The close contact of the external source to the sample to be labelled in vacuum ensured the sufficient path for ^{220}Rn atoms formed during α-decay of ^{224}Ra.

In the case of long lasting investigations of the solid state processes, such as aging of geleous materials or treatment of the samples to high temperatures, when the inert gas incorporated into the solid by means of ion implantation or diffusion can be released, before the solid state process should be finished, it can be recommended to incorporate the parent radioisotope of the inert gas into the surface of the sample. In this case the parent radioisotope serves as the permanent source of the inert gas, for example radionuclide of thorium ^{228}Th (half life 1.9 years) gives rise to ^{224}Ra (3.4 days half life) and subsequently to the inert gas nuclide radon ^{220}Rn (half life 55 sec). The radionuclide ^{228}Th can be either deposited on the surface or incorporated into the sample by coprecipitation, melting etc. In Fig. 2 the scheme of the recoil incorporation of parent nuclides and inert gas nuclides into the surface layers of solid is demonstrated.

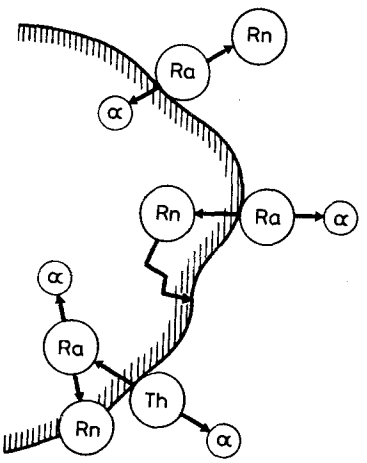

Fig. 2 The scheme of recoil incorporation of parent nuclides and inert gas nuclides into surface of solids

Mechanisms of inert gas release from solids [3]

Inert gas atoms incorporated into the solid sample can be released by following mechanisms:

- inert gas diffusion in the solid matrix (depending on temperature)
- inert gas diffusion in pores of dispersed or porous solids (depending on temperature)
- release of "hot" atoms of radon due to their recoil energy, (temperature independent)

The computer modelling of the inert gas release from solids possessing various properties (diffusion characteristics, surface area etc.) which was based on the physical model using above mentioned mechanisms described fairly well the experimental curves [4]. The mathematical models suggested by Flgge and Zimens [5], Balek and Kríz [6] and Beckman and Balek [7] enabled us to evaluate the experimental data of emanation thermal analysis. The quantitative parameters of inert gas diffusion or surface area changes, morphology changes have been used in the diagnostics of inorganic as well as polymer macromolecular materials.

Apparatus for emanation thermal analysis

Several equipments enabling the measurement of the inert gases released from solids have been used, depending mainly on the purpose of the measurement and on the inert gas used as the probe. In case that non-radioactive(stable) nuclides of inert gas atoms (helium, neon, argon, krypton, xenon) are used, the mass spectrometer is used for the detection of the gas. In the case when the radioactive nuclides of the inert gases already mentioned are used, (and for radon especially), radioactivity scintillation detectors should be employed for the inert gas detection. The ETA equipment can be coupled with the simultaneously performed equipments for DTA, TG and other traditional techniques of thermal analysis. The simultaneous equipment for all the mentioned thermal analysis techniques is commercially available from NETZSCH company, Selb, FRG. The simple device for emanation thermal analysis can be delivered by the Nuclear Research Institute, Rez, Czechoslovakia. The labelling apparatus for the introduction of inert gases into solid samples is also produced.

Examples of application

1. Characterization of structure defects mobility and their thermal stability

The inert gas atoms incorporated into solid samples are situated on the natural and/or artificial defects produced e.g. by ion bombardment, mechanical treatment, etc. The inert gas atoms are released on sample heating, due to the thermally stimulated processes, to the annealing of the defects, diffusion etc.

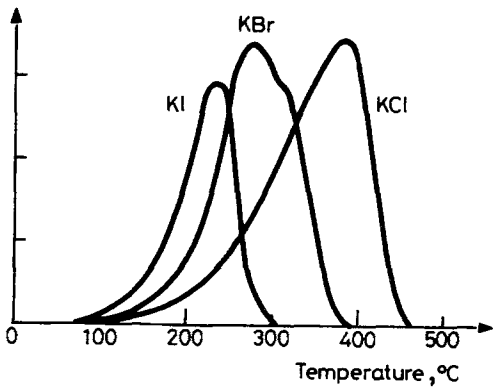

Fig. 3 Temperature dependence of the krypton release from KCl, KBr and KI single crystals, labelled by ion bombardement in a high frequency discharge

In Fig. 3 the temperature dependence of the ^{85}Kr release rate [8] from alkali halides, KCl, KBr and KI are demonstrated. The activation energies of the krypton diffusion can be evaluated from the peak temperature, which corresponds to 184, 160 and 147 kJ/mol, respectively. The mobility of the defects is characterized by the ETA curves of the irradiated samples. In Fig. 4 the ETA curve of the irradiated single crystal of corundum is represented. During the irradiation, the radiation defects are created including the formation of the metamict phase in the surface layers on the single crystal [9]. The annealing of the structure defects is indicated on the ETA curve. The recrystallization of the metamict phase takes place at 700-800°.

The ETA can be used for the assessment of the thermal stability of the structure of special materials in thin films with highly conductive properties, anticorrosive properties, etc. The ETA curve of argon released from $TaSi_2$ sputtered as a thin film of the thickness of 2500 Å is represented [10] in Fig. 5. Argon atoms are included in the structure defects of the thin film, as

remained from the surrounded gas medium during sputtering. The peak on the ETA curve indicates the change of the morphology of the sample, which is caused by the crystallization of the thin film. The peak at higher temperature preveals the tenacity with which argon atoms are held in the thin film.

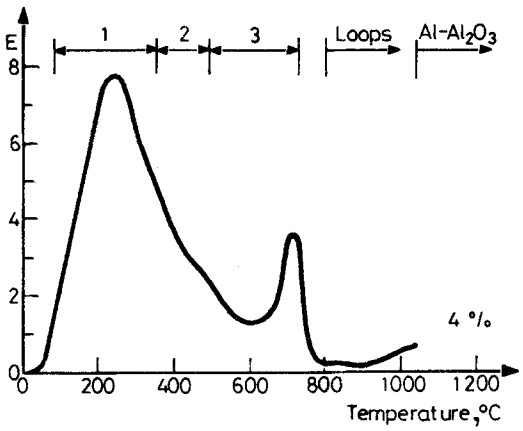

Fig. 4 Temperature dependence of the 85-krypton release from corundum crystals labelled by ion bombardement

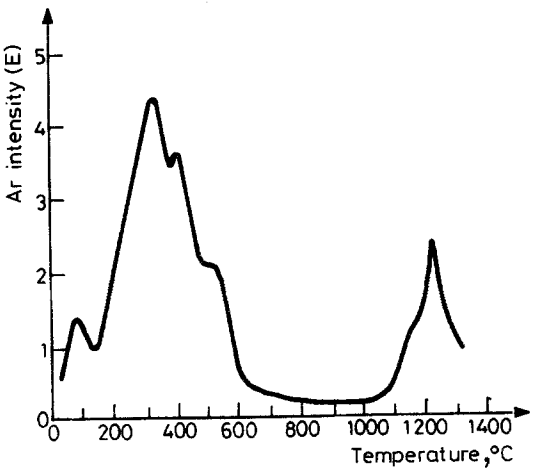

Fig. 5 The temperature dependence of argon release from $TaSi_2$ thin film during heating at the rate of 10 deg/min

Another example of the ETA application represents the annealing of the mechanically created defects in solid, which enhance the reactivity and sinterability. The characterization of the thermal behaviour of zinc ferrite, mechanically treated in a mill is demonstrated by the ETA curve and DSC curve in Fig. 6. The ETA indicates annealing of the surface defects at about 100° as well as the annealing of the metamict state created by milling, at about 400°. The decrease of the radon release rate at 700° can be ascribed to the enhanced sintering of the sample. As it follows from the DSC curve in Fig. 6, the annealing of the mechanically induced defects is accompanied by the exothermic effect. The ETA curves enabled us to investigate the early stage of sintering of ceramic powders, when the annealing of surface irregularities takes place.

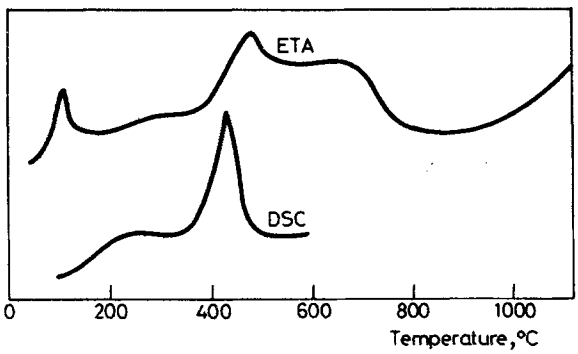

Fig. 6 ETA and DSC curves of zinc ferrite powder mechanically treated and labelled by means of the adsorption of ^{228}Th on the sample surface, heating rate 5 deg/min

2. *Characterization of the material prepared by sol-gel technique*

The sol-gel technique has been applied for preparation of the intermediate product in the manufacture of hightech. ceramics. The technological sol-gel process consists in gelation, gel washing, drying and its calcination, all of these steps significantly influence the quality of the intermediate and the final products. The emanation thermal analysis, being sensitive to the morphology changes in solids, especially precipitates and gels, has been used for the assessment of thermal behaviour of intermediate products of materials, such as uranyl gels, SiO_2-gels, TiO_2-gels, geleous materials for preparation of oxide glasses. [11]. In Fig. 7 the differences in the thermal behaviours of uranyl gels during heating in argon + 5 % H_2 are

demonstrated, the uranyl gels [11] being washed by ammonia solution for different time: 0.5 hour (curve 2), 3 hours (curve 3) and 9 hours (curve 1). The ETA enabled us to demonstrate the morphology changes of the solids directly in the conditions of the heat treatment, thus this method has been proved to be suitable for investigation of the aging of geleous materials, drying and sintering.

3. Reactivity testing of Portland cement clinker and clinker minerals

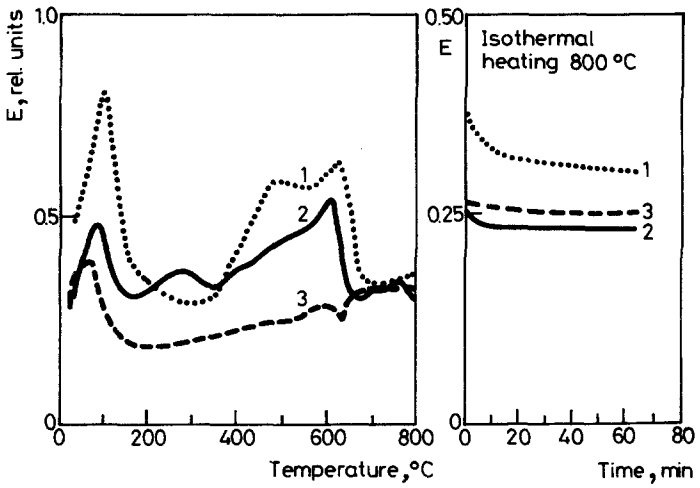

Fig. 7 ETA curves of 3 samples of ammonium diuranate gels as the intermediate products for manufacture of urania oxide. Heating rate 5 deg/min in argon : 5 % H_2. The samples differed in the washing time: curve 1 - 9 hours, curve 2 - 0.5 hours, curve 3 - 3 hours

The reactivity of Portland cement clinker has been tested by many methods, the ETA enabling us to reveal the very beginning hydration reaction. The cement hydration [12] is accompanied by the increased of the surface area, which is indicated by the increase of the radon release rate. In Fig. 8 the ETA curve measured during Portland cement hydration in the water suspension is demonstrated, as compared with the results of DSC and penetration resistance. It can be concluded that the results of ETA reflected the morphology changes during cement hydration. By means of ETA the investigation of the treatment and solidification of industrial waste. The interaction of the cement with slag and fly ashes in the water suspension can be investigated by means of ETA.

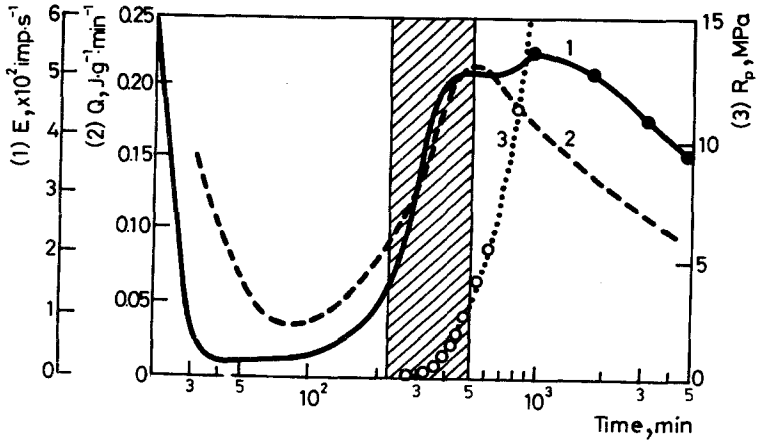

Fig. 8 Results of ETA (curve 1), DSC (curve 2), and penetration resistance (curve 3) during hydration at 20°C of Portland cement PC-400 Lochkov, water/cement = 0.3

It is to be mentioned that by means of ETA durability of concrete and other building materials has been tested in a very rapid way. The effectivity of various additions for increasing the durability of building materials has been tested by means of this method.

Conclusions

The emanation thermal analysis has been recently used in a number of important branches of chemical technology, environmental technology and material science. It is to expect that the application potential will be further enlarged, e.g. the application of the ETA in polymer science, in the characterization of coals [13], in the study of the permeability of building materials [14] with regard to radon as a dangerous agent for health in flats.

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Zusammenfassung — Im Hinblick auf die praktischen Erfordernisse der chemischen Verfahrenstechnik und Materialkunde werden die Anwendungsmöglichkeiten der Emanationsthermoanalyse beschrieben.