

Emanation thermal analysis and its application potential ^α

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Abstract

The principle of emanation thermal analysis, based on the measurement of inert gas released from solids, is given. The labelling techniques for sample preparation and the mechanisms of the inert gas release are discussed. The potential of emanation analysis in various fields is outlined.

INTRODUCTION

During the past two decades, the range of thermoanalytical methods has been increased to include emanation thermal analysis [1,2]. This method is still considered a less-common method of thermal analysis even though it has already been applied in various fields. Emanation thermal analysis (ETA) is based on the measurement of the inert gas released from solids, usually previously labelled by the inert gases. The atoms of the inert gases (neon, argon, krypton, xenon, radon) are used as trace indicators or a microprobe of the defect state of the solid and its changes. The inert gas atoms do not react with the solid matrix and their release is controlled primarily by diffusion. The processes which influence the inert gas diffusion in the solid matrix and pores or surface area of the sample can be revealed by this method. Minor effects in the solid unaccompanied by changes in sample mass or enthalpy, which cannot be investigated by thermogravimetry or DTA, respectively, can be investigated by ETA. The method can be used in the study of both crystalline and non-crystalline materials. The radioactive nuclides of inert gases are readily applicable because of their easy and sensitive detection in trace concentrations.

SAMPLE PREPARATION FOR ETA MEASUREMENTS

Most of the solids to be investigated by ETA do not naturally contain inert gas and it is necessary to label them with a trace amount of the inert

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gas. Various techniques can be used for the introduction of the inert gas atoms into the samples to be investigated.

Diffusion technique

This is based on the diffusion of the inert gas into solids at elevated temperatures and pressure of the gas. The substance to be labelled and the inert gas (usually labelled with radioactive nuclides, e.g. ^{85}Kr) are placed in a high-pressure vessel which is then closed and heated for several hours at the temperature of approximately $0.3\text{--}0.5 T_{\text{melt}}$ of the substance to be labelled, and finally quenched in liquid nitrogen. The amount of inert gas introduced into the sample depends on time, temperature and pressure, as given by the diffusion equation.

Physical vapour deposition (PVD)

This method is usually carried out in an inert gas (argon) atmosphere. The inert gas atoms are captured in the structure of the deposited substance. In this method, the thin films produced are automatically labelled by the inert gas, the release of which can be used for diagnostics of the film during its subsequent heating.

Implantation of accelerated ions of inert gases

This technique has also been used for labelling samples to be measured by ETA. The amount of inert gas introduced and its concentration profile depends on the energy of ion bombardment and the properties of the labelled matrix. A number of techniques can be used for inert gas ion bombardment [1]. A defined ion beam can be produced using a magnetic separator. A versatile low-cost technique for sample labelling was invented by Jech [3] (see also ref. 1) in which the ionisation and acceleration of ions takes place in a low-temperature plasma produced by a high-frequency discharge. The TESLA transformer for vacuum testing is used for the discharge production. The gas surrounding the sample at pressures of $0.01\text{--}0.1$ torr contains inert gas radioactive nuclides, e.g. ^{85}Kr or ^{222}Rn . Using ions with energy of 10 keV, surface layers of several nanometers thick can be labelled.

Inert gases produced from nuclear reactions

The recoil energy of nuclear reactions producing inert gases can be used for the implantation of gases into solid samples. Some of the nuclear reactions which have been used for the production of inert gas atoms and their introduction into solid samples are listed in Table 1.

TABLE 1

Nuclear reactions which can be used for production of inert gas atoms and their introduction into solid samples

α -decay	$^{226}\text{Ra} \xrightarrow{\alpha} ^{222}\text{Rn}$ $^{228}\text{Th} \xrightarrow{\alpha} ^{224}\text{Ra} \xrightarrow{\alpha} ^{220}\text{Rn}$
β -decay	$^{83}\text{Se} \xrightarrow{-\beta} ^{83}\text{Br} \xrightarrow{-\beta} ^{83}\text{Kr}$ $^{133}\text{Te} \xrightarrow{-\beta} ^{133}\text{I} \xrightarrow{-\beta} ^{133}\text{Xe}$
(n, α)	$^{40}\text{Ca}(\text{n}, \alpha) ^{37}\text{Ar}$ $^{88}\text{Sr}(\text{n}, \alpha) ^{85\text{m}}\text{Kr}$ $^{136}\text{Ba}(\text{n}, \alpha) ^{133}\text{Xe}$
(n, p)	$^{39}\text{K}(\text{n}, \text{p}) ^{39}\text{Ar}$ $^{85}\text{Rb}(\text{n}, \text{p}) ^{85}\text{Kr}$ $^{133}\text{Cs}(\text{n}, \text{p}) ^{133\text{m}}\text{Xe}$
(n, γ) and β -decay	$^{37}\text{Cl}(\text{n}, \gamma) ^{38}\text{Cl} \xrightarrow{-\beta} ^{38}\text{Ar}$ $^{79}\text{Br}(\text{n}, \gamma) ^{80}\text{Br} \xrightarrow{-\beta} ^{80}\text{Kr}$ $^{127}\text{I}(\text{n}, \gamma) ^{128}\text{I} \xrightarrow{-\beta} ^{128}\text{Xe}$
Fission (n, f)	$^{238}\text{U}(\text{n}, \text{f}) \text{Xe, Kr, ...}$

Introduction of parent nuclides

In some cases, for example when carrying out longer lasting and/or high-temperature measurements of surface and morphology changes, it is necessary to introduce parent nuclides of the inert gas, e.g. radon, as a relatively permanent source of the labelled gas. Trace amounts of thorium ^{228}Th can be introduced into the sample by co-precipitation during the sample preparation from a solution or by adsorption on the surface of the sample. ^{220}Rn is formed by spontaneous alpha decay according to the scheme $^{228}\text{Th} \xrightarrow{\alpha} ^{224}\text{Ra} \xrightarrow{\alpha} ^{220}\text{Rn}$ and can be introduced into the solid owing to the recoil energy (85 keV per atom). The above nuclear reactions which give rise to the radon nuclides, have also been used for the incorporation of the inert gas into the solid sample. Radon atoms penetrate several tens of nanometers, depending on the composition of the target materials: for example, the penetration depth of ^{220}Rn in MgO is 41.7 nm; in SiO_2 , it is 65.4 nm. The parent isotopes of radon serve as "recoil ion implantators". See the scheme in Fig. 1.

TRAPPING AND RELEASE OF THE INERT GASES FROM SOLIDS

The solubility of inert gas atoms, such as xenon, krypton and radon, in inorganic solids is small. The inert gases are trapped at lattice defects such

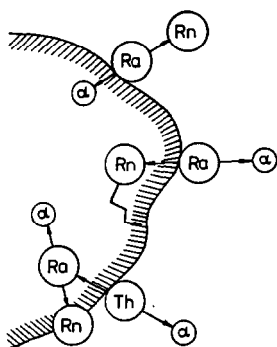


Fig. 1. Scheme of sample labelling by recoil ion implantation. Radionuclides ^{228}Th and ^{224}Ra were adsorbed on the surface and the inert gas ^{220}Rn was produced according to the reaction $^{228}\text{Th} \rightarrow ^{224}\text{Ra} \rightarrow ^{220}\text{Rn}$, and introduced by recoil energy (85 keV per atom) into depths of several tens of nanometers.

as vacancy clusters, grain boundaries and pores. The defects in the solids can serve both as traps and as diffusion paths for the inert gas. A survey of the influence of various factors on the migration of inert gases in solids is given in refs. 2 and 4.

In instances when the inert gas atoms are incorporated into the solids without their parent isotopes, diffusion in the matrix is the main mechanism for the gas release from solids. In instances when the parent nuclides of the inert gas are incorporated into the solid samples as a permanent source of the inert gas, the recoil mechanism of the inert gas release should be taken into account in addition to the diffusion. Recoil plays an especially important role in samples of large surface area and at temperatures where diffusion of the inert gas is negligible.

The theoretical concepts describing the release mechanisms consider separately the cases in which the inert gases are incorporated without and with their parent nuclides [2,4]. In the first approach, it is assumed that no structural or phase changes take place in the solid during heating in the considered temperature range.

When the inert gas has been incorporated into a solid without its parent nuclide(s), the inert gas can be released by diffusion processes which depend on the diffusion mechanisms. A number of equations have been proposed [2,5] to describe the temperature dependence of the inert gas release. Assuming that the release of the inert gas (introduced by, for example, ion bombardment) is a reaction of the first order, the rate of gas release can be expressed in differential form

$$-dN/dt = \nu N \exp(-\Delta H/RT) \quad (1)$$

where N is the number of atoms trapped per unit surface area, ν is a constant (the frequency of oscillation of atoms in the lattice is assumed to

equal 10^{-13} s^{-1}), ΔH is the activation enthalpy of the inert gas diffusion and R is the molar gas constant equal to $8.3143 \text{ J K}^{-1} \text{ mol}^{-1}$.

A linear rise of temperature ($T = T_0 + \beta t$) where β is the heating rate and ΔH is independent of N , is also assumed. By differentiating eqn. (1) and equating it to zero, the following expression for T_{max} is obtained [2,5]

$$\Delta H/RT_{\text{max}} = (\nu/\beta) \exp(-\Delta H/RT_{\text{max}});$$

$$\Delta H/T_{\text{max}} = \ln(\nu T_{\text{max}}/\beta) - 3.64 \quad (2)$$

The value of the activation enthalpy ΔH can be determined directly from the ΔH value found experimentally at the temperature of the maximum. The relationship between ΔH and T_{max} in the given temperature range is close to linear. Similar formulae have been derived [6] taking into account different gas distributions. The temperature dependences of the inert gas release rate generally exhibit peaks, the maxima of which (T_{max}) are governed mainly by the value of ΔH .

If the parent nuclide(s) of the inert gas have been incorporated into the solid, the inert gas is formed by radioactive decay of the parent nuclide. The gas atom may escape from the solid either by recoil energy ejection or by any one of several types of diffusion processes [7].

The release mechanisms of radon atoms formed in a solid grain by the decay of radium are shown schematically in Fig. 2. When the radium atom lies close to the surface of the grain of the solid, the recoil energy (85 keV per atom) that the radon atom gains during decay of the parent may be sufficient to eject the gas atom from the grain. Alternatively, the radon atom may escape by diffusion before it undergoes the decay.

Using the theories of both recoil and diffusion processes, the following expressions have been proposed for the release rate of the inert gas. The term emanating power E is usually used, being defined as the ratio of the rate of gas release to the rate of gas formation in the solid.

The term E_r of the emanating power attributable to recoil can be expressed as

$$E_r = K_1 S_1 \quad (3)$$

where K_1 is a temperature-independent constant, that depends on the path of the recoiled gas atoms in the solid, and S_1 is the external surface area of the sample. The path of recoiled atoms of radon has been estimated; for example, it is 40 nm in thoria. Expression (3) is valid for isolated grains of the solid that are larger than the path of the recoiled radon atoms. For finely dispersed solids, the constant K_1 depends on the dispersity and morphology of the sample.

The term E_p of the emanating power due to the inert gas diffusion in the intergranular space and open pores can be expressed as

$$E_p = K_2 S_2 \quad (4)$$

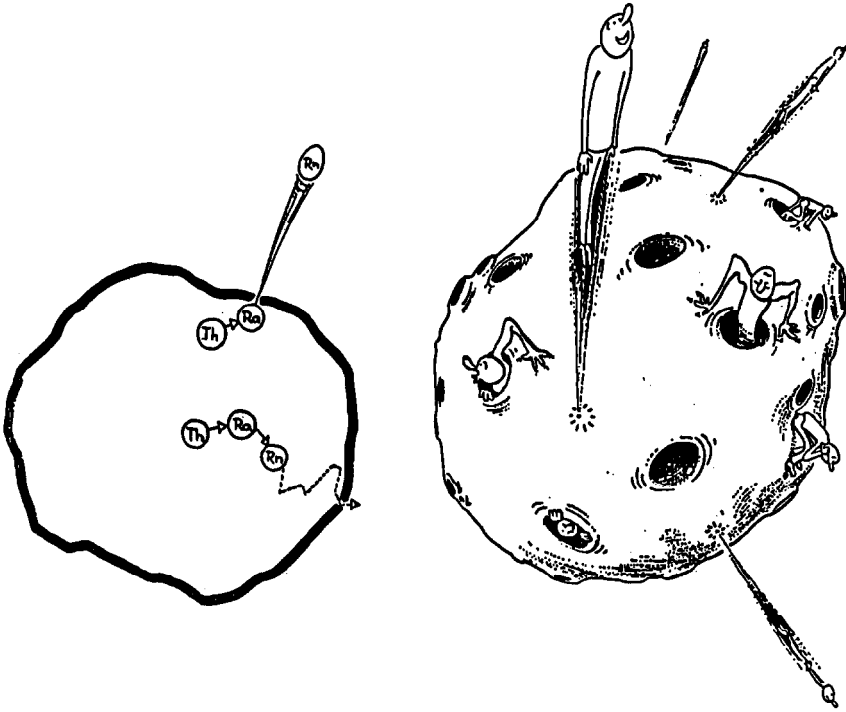


Fig. 2. Scheme of the release of radon from the sample by recoil and diffusion mechanisms.

where K_2 is a constant that depends on temperature, and S_2 is the internal surface area of the sample.

The term E_s of the emanating power due to the inert gas diffusion in the solid matrix of the sample can be expressed as

$$E_s = K_3 \exp(-\Delta H/2RT) S_3 \quad (5)$$

where K_3 is a temperature-independent constant, ΔH is the activation enthalpy of inert gas diffusion in the solid matrix, R is the molar gas constant, T is the absolute temperature and S_3 is the area representing the sum of the cross sections of all diffusion paths, such as dislocations, grain boundaries, etc.

The total emanating power E can be obtained by summing these

$$E = E_r + E_p + E_s \quad (6)$$

MEASUREMENT OF INERT GAS RELEASE

The apparatus for emanation thermal analysis consists of several components designed to ensure the detection of inert gas, and to provide sample heating and temperature control. In addition, the instrument supplies the carrier gas with flow stabilisation, and measures the gas flow and complementary parameters.

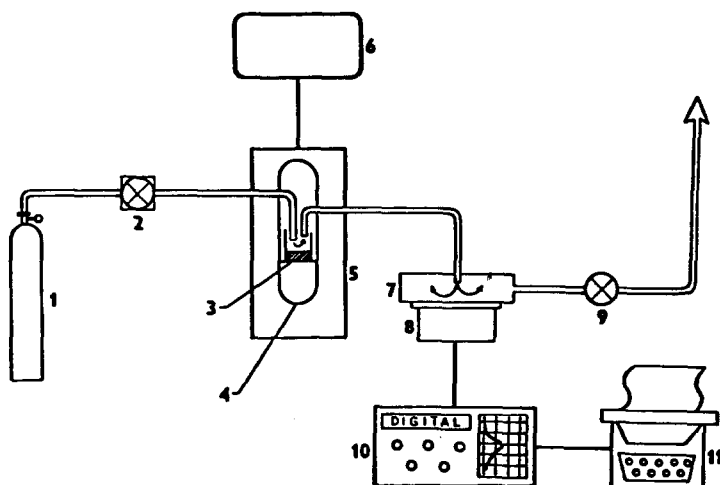


Fig. 3. Scheme of the apparatus for emanation thermal analysis: 1, gas supply; 2, gas flow stabiliser and flow rate meter; 3, labelled sample; 4, sample holder; 5, furnace; 6, temperature controller; 7, measuring chamber; 8, radioactivity detector; 9, flow rate meter; 10, counts meters; 11, data processor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

During an analysis, the carrier gas (air, nitrogen or another suitable gas) carries the inert gas released by the sample in the reaction vessels (situated in a furnace) into a detector for the inert gas. For example, to measure the α -activity of Rn, a scintillation counter, ionisation chamber or semiconductor detectors can be used. On the other hand, all β -activity measurements involving Kr, Xe and Ar are made by Geiger-Müller tubes. Gamma-active gases can be measured by a γ -spectrometer. The stable nuclides of inert gases are measured by a mass spectrometer.

To ensure optimum conditions for a direct comparison of ETA data with results obtained by other thermoanalytical methods, devices were constructed to provide simultaneous measurement of additional parameters [7]. Figure 3 shows the scheme of the ETA apparatus.

POTENTIAL OF THE ETA APPLICATION

The theoretical considerations summarised above indicate that emanation thermal analysis can be applied to the investigation of processes taking place in solids or on their surfaces. Any process in a solid or its phase boundary leading to a change in either the surface and/or changes in the inert gas diffusivity (permeability) becomes indirectly observable from the ETA measurements.

ETA has been used in the study of such solid state processes as aging of precipitates or geleous materials, recrystallisation, annealing of structure defects and changes in the defect state of both crystalline and non-crystalline solids, sintering, phase changes, surface and morphology changes

accompanying thermal decomposition of solids, and chemical reactions in solids and on their surfaces, including solid–gas, solid–liquid and solid–solid interactions. Chemical reactions of practical importance for chemical technology, metallurgy and environmental technology as well as the technology of building materials, have also been studied by means of ETA.

The kinetics of surface area changes, mechanisms of defect annealing, pore sintering and the kinetics of morphology changes in general can be evaluated from ETA results in both isothermal and non-isothermal conditions.

The temperature intervals for surface and defect state changes, phase changes and chemical transformations have been determined, and new insights into the respective processes have been obtained using ETA experimental data. For example, the existence of metastable phases during the thermal decomposition of solids and changes in the concentration of structure defects in the pre-melting behaviour of crystalline solids were revealed by ETA.

The results of emanation thermal analysis are often compared with those obtained by other methods, such as surface area measurements, X-ray diffraction, DTA, thermogravimetry and dilatometry. The equipment for simultaneous measurements by ETA, DTA, TG, DTG or dilatometry available from Netzsch ensures the optimal conditions for direct comparison of the results.

In contrast to X-ray diffractometry, emanation thermal analysis makes it possible to investigate poorly crystalline or amorphous solids. In contrast to adsorption measurements for surface area determination, ETA permits a continuous investigation of the surface, even at elevated temperatures during heat treatment of solid samples or their hydration under wet conditions, without the necessity of interrupting the heat treatment or the hydration and cooling the sample to liquid nitrogen temperatures. For this reason, ETA may reflect the nature of the surface at elevated temperatures more accurately than adsorption measurements.

In contrast to DTA and thermogravimetry, emanation thermal analysis makes it possible to investigate processes that are not accompanied by thermal effects or mass changes. ETA permits the study of the sintering of powdered or gel samples, which would be difficult by means of dilatometry.

Moreover, by applying different radioactive labelling of either the surface alone or the volume of the grains, the processes taking place in the surface and in the bulk of the sample have been discerned by ETA. This is especially advantageous when studying the thermal behaviour of thin films or coatings on substrates. By labelling the thin film to a depth not exceeding its thickness, ETA gives information concerning the thin film alone, without the influence of the larger substrate. This is the advantage of ETA over X-ray investigations, when the thin film represents a negligible part of the sample. On the other hand, when the interaction of the thin film with the substrate

during heating is to be investigated, a deeper inert gas implantation can be used.

The high sensitivity of ETA to the chemical interactions between a solid surface labelled with the radioactive inert gas and aggressive agents has enabled us to reveal the very beginning of corrosion reactions. The durability of materials towards aggressive liquids and gases, as well as the effectiveness of preserving coatings, can be tested by means of ETA.

The possibility of thin-film labelling by inert gases during physical deposition (PVD) or chemical vapour deposition (CVD) on a substrate can be applied successfully for diagnostics of the thin layers immediately during their processing and thermal treatment.

In addition, ETA measurements make it possible to obtain direct information about the diffusion parameters of the inert gas in the solid. The diffusion coefficient D and the activation energy ΔH of the inert gas diffusion can be evaluated. The diffusion parameters of inert gases in inorganic and organic materials are important for characterisation of the transport properties of materials. The determination of inert gas permeability in polymers is an important way of testing the local structure and revealing irregularities in polymer membranes and composites.

Examples of the fields in which emanation thermal analysis has potential applications are given below.

IONIC CRYSTALS

Diagnostics of the defect state

Inert gas diffusion parameters evaluated from ETA measurements reflect the mobility of inert gases in the solids, which can be used to determine the state of the defects in the solids. Inert gas atoms incorporated into solids are situated on the natural and/or artificial defects produced, for example, by ion bombardment, neutron irradiation or mechanical treatment. The release of the inert gases on sample heating reflects the thermally stimulated processes, i.e. diffusion, annealing of defects, etc. It was shown that the mobility of inert gas atoms in the ionic crystals differs in various crystallographic directions, owing to the channelling effect. The mobility of the inert gases (the activation energy) can be used as a parameter characterising the defect state of an ionic crystal lattice and may cause the formation of the metamict phase. The annealing of the metamict phase is indicated by a sharp ETA peak. The activation energy of inert gas release and of recrystallisation of the metamict phase can be evaluated from the peak temperature. A number of alkali halides, alkali earth halides and oxides, have been investigated by ETA [8–10].

METALS AND SEMICONDUCTORS

Determination of transport properties and the defect state

The difference in the mobility of neon, argon, krypton and xenon ions in a tungsten single crystal have been demonstrated experimentally [11] (Fig. 4). The diffusion of radon in various metals, including Mo, W and Fe, measured at elevated temperatures led to the determination of the temperature of lattice loosening [12] — the Tamman temperature. Diffusion data give information on the interaction of the gas with lattice defects, its precipitation into gas-filled bubbles, and also the chemical and structural changes of the investigated metals and semiconductors. Results for Si, Ge, GaAs and SiC are given in ref. 13.

CERAMICS

Thermal decomposition of raw materials

The determination of the temperature intervals for surface area and morphology changes accompanying the thermal decomposition of minerals, raw materials and intermediate products have been studied. The kinetics of these changes have been evaluated and their mechanisms, based on the comparison of ETA results with those of other methods (DTA, TG, X-ray patterns, surface area, etc.) have been determined [4,14,15].

Assessment of active (non-equilibrium) state of thermally decomposed powders

From the ETA curves measured during the cooling of heat-treated materials, the active state of the powders (the non-equilibrium defect state) can be assessed. The values of the activation energy ΔH of radon diffusion in samples labelled by radon parent nuclides, ^{228}Th , were used as a parameter characterising differences in the defect (active) state of iron(III) oxide samples prepared by heat-treatment of various iron salts [14,16–18].

Testing reactivity of powders

The temperature of the ETA effect corresponding to the solid state reaction is the parameter applied for testing the ability of ceramic powders to react in a mixture [19]. The reactivities of iron(III) oxide samples of different thermal and chemical histories towards zinc oxide (labelled with ^{228}Th) have been compared with surface area measurements [20] (Fig. 5). It has been demonstrated that the ETA curves reflect the reactivity in a more objective way than the surface area determined by adsorption measurement [21]. Using this measurement, the reactivities of titania samples in the

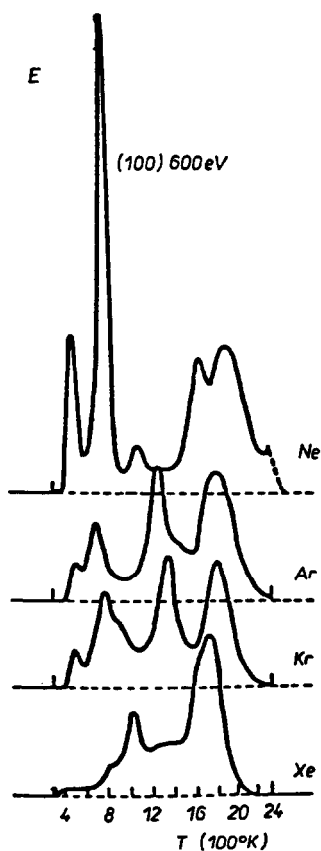


Fig. 4. Temperature dependence of Ne, Ar, Kr and Xe release from tungsten single crystal [11]. The inert gases were incorporated by ion bombardment at the energy of 600 V in the crystallographic direction (100).

mixture with BaCO_3 [22] and of zirconia samples in the mixtures with SiO_2 [23] have been determined.

Determination of sinterability

The use of ETA makes it possible to reveal the changes taking place during heating of active powders, including annealing of surface and structural defects, and to evaluate the kinetics of early-stage sintering (e.g. the early sintering study of ThO_2 by means of ETA is demonstrated in Fig. 6 [24]). The ETA heating curves reflect any change in surface area and morphology. From the ETA cooling curves, the defect state of the sample after the preceding heat-treatment can be assessed [25].

PROCESSING OF CERAMIC MATERIALS

Morphology changes in bulk ceramics and thin films

The changes in morphology taking place during aging, drying, calcination and firing of feed or intermediate geleous materials can be successfully

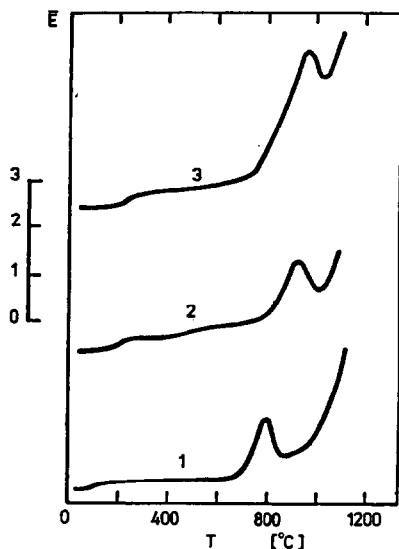


Fig. 5. The ETA curves of stoichiometric mixtures of $\text{ZnO} + \text{Fe}_2\text{O}_3$ obtained during heating in air at the linear heating rate of 5 K min^{-1} . The ZnO (equal in all three samples and labelled with ^{228}Th) served as the reference component for comparing the reactivities of three Fe_2O_3 haematite samples prepared by heating iron(III) carbonate to 700°C (curve 1), 900°C (curve 2) and 1100°C .

investigated by ETA. The method was used for quality testing of intermediate geleous products of urania, titania, silica, zirconia, etc. [26–29]. Thin ceramic films can also be investigated. ETA is sensitive to the morphology changes caused by deviations of technological conditions [30]; therefore it has been recommended as the control method for quality testing intermediate products of sol–gel processed ceramics in bulk and thin films. The morphology changes of TaSi_2 thin layers (transition from a very disordered state to a crystalline one) were revealed by the measurement of argon release which was included in the structure defects of the thin film prepared by sputtering [31] (Fig. 7).

Morphology changes during intercalation of molecules into host materials

The inclusion of various molecules into selected materials and minerals (so-called intercalation) is accompanied by microstructural changes. With ETA, these microstructure changes can be followed continuously [32].

Durability of ceramics

Testing the degradation durability of ceramic materials can be achieved by ETA. The initiation of the oxidation or reduction of ceramics (carbides,

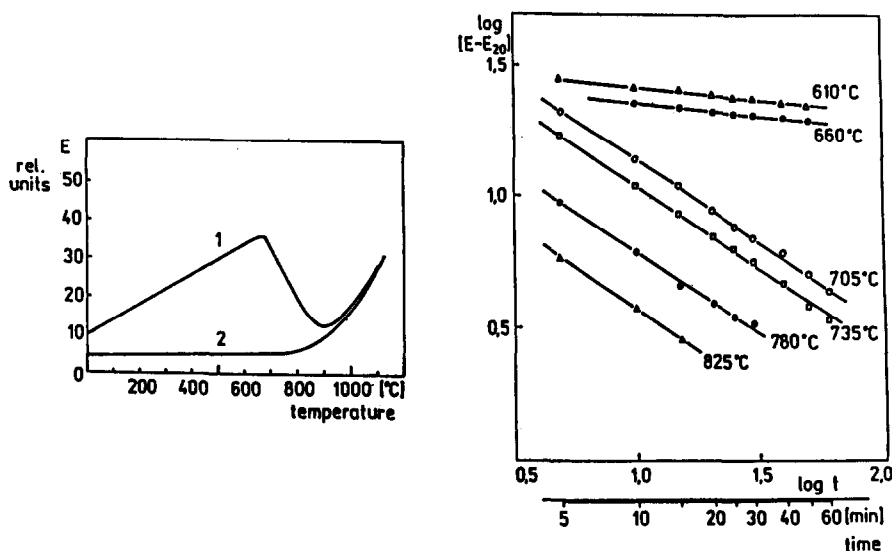


Fig. 6. ETA curves of ThO_2 powdered sample labeled with ^{228}Th , obtained during heating in air under the following conditions. Left, linear heating rate of 5 K min^{-1} up to 1100°C (curve 1, first heating run; curve 2, second heating run); and right, isothermal heating in the range $610\text{--}825^\circ\text{C}$. The formal kinetics of the surface defects annealing taking place at these temperatures was evaluated from the ETA results: $E = \text{const. time}^{0.64}$.

nitrides, etc.) has been indicated as an enhanced release rate of inert gas from the samples. ETA was used for testing the durability of Y-Ba-Cu-O superconducting ceramics towards humidity in the air [33].

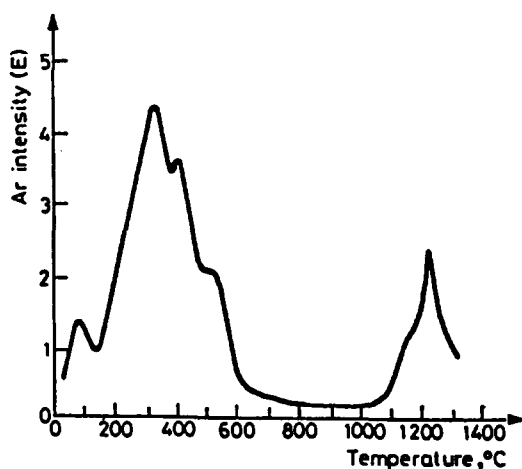


Fig. 7. Temperature dependence of argon release rate from 250 nm thick TaSi_2 thin film deposited by sputtering in argon atmosphere (argon atoms were captured during the sputtering process in the thin film defects).

BUILDING MATERIALS

Studying cement hydration

The application of ETA in this case is based on the fact that the surface area of Portland cement hydration products is much higher than that of initial clinker minerals [34]. Because of this, the initiation of hydration is indicated on the ETA isothermal curve as an increase in the radon release rate. The effects of admixtures and of elevated temperature were studied by means of this method; the morphology changes of the hydration products were followed continuously without interrupting the hydration process. The method was advantageously applied in the study of cementation of industrial waste products and in the study of chemical interactions of fly ashes with lime and slags [35].

Determining chemical resistance

The time dependence of the radon release rate can be used as a rapid method for assessment of the chemical resistance of hardened cement paste (concrete) towards liquid or gaseous aggressive media. The chemical interactions of the previously labelled sample surface are indicated as an enhanced radon release rate [36]. In this way, the chemical resistance of calcite (marble) towards ppm sulphur dioxide concentrations in humid air has been determined [37].

CHARACTERISATION OF GLASSES

Mobility of inert gases in glasses

The temperature dependence of helium and neon mobility in various glasses and glass-ceramics has been studied [38]. ETA was used to study the thermal behaviour of chalcogenide [39] and silica glasses [40]. The method made it possible to determine the temperatures of onset of the matrix changes connected with T_g transformation, crystallisation and melting. The kinetics of the crystallisation of oxide glasses was investigated by ETA. The method was used as the test method for model experiments in the vitrification of radioactive and industrial wastes [41].

The chemical resistance of glasses

The release of radioactive inert gases has been used as a very sensitive indicator of the chemical interaction of acid or alkaline solutions with the glass surface [42].

STUDY OF CATALYSIS

ETA has been used to study the preparation of catalysts and test their properties [43–46]. Catalytic reactions taking place on the solid surface are usually accompanied by inert gas release from the active sites responsible for the catalytic reactions. ETA has also been applied for studying the thermal behaviour of catalysts during their regeneration.

STUDY OF ORGANIC AND COMPLEX COMPOUNDS

The diffusion properties of organic compounds, as well as those of complex compounds with organic ligands, change when the phase or isophase changes or thermal decomposition takes place [47]. The ETA curves of Ba salts of phthalic, isophthalic and terephthalic acids [48] showed differences for those compounds exhibiting positional isomerism. A progressively increasing emanation release rate for Ba salts of long-chain monocarboxylic fatty acids has been reported [49].

Coals

ETA has been used as a fingerprint technique for investigating structural alterations in coals. The radon release rate changes reflect development in the microstructure of coals [50]. The diffusion characteristics (activation energy of radon diffusion and diffusion coefficient) have been evaluated for two types of British bitumenous coals as well as for charcoal [51].

Polymers and plastics

Inert gas mobility in polymers and plastics is an important parameter of the materials, as it depends on the crystallinity [52]. Inert gas mobility has been studied for polyethylene and polypropylene as a function of radiation treatment [53]. It was found that the irradiation of polyethylene with high doses (2000 MRad) resulted in a decrease in the radon diffusion coefficient with increasing doses. The diffusion (permeability) of inert gases in polymers is used as a parameter for predicting the operating performance of polymer separation membranes [54], and the properties of composites, construction materials, etc. Using ETA and autoradiographic detection, local structure defects in polymer membranes can be revealed [55].

CONCLUSION

Emanation thermal analysis has been applied to the study of a variety of materials. It is expected that new challenges in material science and in environmental science and technology will lead to new applications which should enlarge the application potential of this method even more.

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