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EFFECT OF GAS ENVIRONMENT ON TITANIA FILMS MICROSTRUCTURE CHARACTERIZED BY EMANATION THERMAL ANALYSIS

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Abstract

Emanation thermal analysis (ETA), based on the measurement of the release of radon previously incorporated into the sample, was used to characterize the differences in the thermal behavior porous titania film (thickness 200 nm),when heated in argon and in oxygen, respectively, in the range from 20 to 800°C. It was observed that the annealing of porosity and structure defects in the near surface layers of the porous titania film (anatase) was enhanced on heating in oxygen in comparison to the heating in argon. ETA results were compared with SEM micrographs and XRD patterns of the titania film samples heated to 500 and 800°C, respectively. A mathematical model was used for the evaluation of the temperature dependence of the titania films microstructure development.

Keywords: emanation thermal analysis, sol-gel, structure defects annealing, titania films

Introduction

Titania films have attracted great attention as chemical sensors [1], ceramic separation membranes [2, 3], electrodes [4,6] as well as photocatalysts [7-12]. When using sol-gel coating techniques for the preparation of titania films, the thermal treatment of the deposited films is necessary to remove solvents and organic molecules of the precursors, to anneal structure irregularities and to tailor the durable layers with requested properties. It was demonstrated [13] that porous titania films with anatase structure can be prepared by sol-gel coating technique and the subsequent heat treatment in oxygen at 500°C for 2 h. Several authors, e.g. [13, 14] observed that titania films deposited on silica glass plate preserved anatase structure after heating up to 800°C.

The purpose of this study is to characterize the thermal behavior of porous titania films under *in situ* conditions of heating up to 800°C in argon and oxygen, respectively, and to reveal differences in the annealing of porosity and near surface structure defects, serving as radon diffusion paths. Emanation thermal analysis (ETA) [15-17] was used to this aim. In our previous studies the ETA was already used to monitor the microstructure development of titania gel layers [18] as well as titania powders [19] during heating of their precursors in argon. A good agreement was found between ETA results, surface area measurements and microstructure characteristics obtained by TEM, SEM and XRD, respectively. The advantage of the ETA application consists in the possibility to characterise the microstructure changes under *in situ* conditions of the heating of the samples in selected gas environments and to bring about information about transport properties of the samples labeled with radon atoms.

Background of ETA applications

ETA is based on the measurement of radon release rate from samples previously lar belled by trace amounts of ^{228}Th and ^{224}Ra radionuclides. Atoms of radon, ^{220}Rn, are formed by the spontaneous α-decay of ^{228}Th and ^{224}Ra. ^{224}Ra and ^{220}Rn atoms are incorporated into the sample due to the recoil energy (85 keV atom^{-1}) which the atoms gained by the α-spontaneous decay. The penetration depths of the recoiled ^{224}Ra and ^{220}Rn atoms in inorganic solids are up to several tens of nanometers depending on chemical composition and density of the solids [15]. The mechanisms of radon release from labeled samples are (i) released due to the recoil energy of the radon atoms, (ii) diffusion in open pores, intergranular space or interface boundaries, respectively and (iii) radon diffusion in the matrix of the solids. The total measured radon release rate, E_{T0TAL} (also called emanating rate, E), can be written as

$$E_{TOTAL}(T)=E_R+E_D(T)\Psi(T) \quad (1)$$

The second term of the equation for E_{T0TAL} is a product of two functions: E_D characterizing the radon permeability along structure irregularities serving as diffusion paths, and $\Psi(T)$ is the function characterizing the decrease (or increase) of the number of the radon diffusion paths.

In the mathematical model used in this study for the evaluation of ETA results it was supposed that the temperature dependence of the radon release rate, $E_D(T)$, due to diffusion involves parameters which determine the radon diffusion, taking into account the average diffusion length of radon $L_D=(D/\lambda)^{1/2}$, where D is the radon diffusion coefficient and λ is the radon decay constant. In the evaluation of ETA results obtained in this study it was supposed that radon can migrate along several independent paths, such as micropores, intergranular space, as well as interface boundaries. We assumed that for ionic solids at the temperatures below 0.4 $T_{melting}$, the radon migration can proceed along non-equilibrium defects, such as micro-pores and near-surface structure defects, whereas equilibrium structure defects can serve as additional paths for radon diffusion above 0.6 $T_{melting}$ of the respective solids. Therefore, the mechanism of radon diffusion along two independent paths of the disordered heterogeneous solid was considered in the modeling. The following expression was used for the temperature dependence of the emanating rate E_D, due to diffusion

$$E_D=(3/y)(\coth y-\{1/y\}) \quad (2)$$

where $y(T)=(S/M)\rho/(D/\lambda)^{1/2}$.

S/M is the surface area of open pores, inter-granular space and of interfaces serving as radon diffusion paths, ρ is density of the sample, $(D/\lambda)^{1/2}$ is the average radon diffusion length. D is the radon diffusion coefficient and λ is the radon decay constant; $D=D_0\exp(-Q/RT)$, where D_0 is the factor depending on the number of diffusion paths and their availability for radon atoms migration, Q is activation energy of radon migration involving both the activation energy of the escape of radon atoms from the traps in the solid sample and that of the migration along diffusion paths in the solid.

In the case when the number of radon diffusion paths and/or surface area decreases on heating, the structural function $\Psi(T)$ has a descending character, whereas if the number of radon diffusion paths increases during sample heating, the structural function $\Psi(T)$ has an increasing character. Several expressions for $\Psi(T)$ functions were recently proposed by Beckman and Balek [20] for the description of changes of the structure defects amount in solids. The descending character of the $\Psi(R)$ function can be expressed by Eq. (3).

$$\Psi(T)=0.5\left[1+\operatorname{erf}\frac{1-\frac{T_m}{T}}{\frac{\Delta T\sqrt{2}}{T}}\right] \quad (3)$$

where erf is the sign for the integral Gauss function, T_m is the temperature of maximal rate of the annealing of the defects which serve as radon diffusion paths, ΔT is the temperature interval of the respective solid

state process.

In this study the annealing of the number of radon diffusion paths in titania films will be described by the $\Psi(T)$ function given in Eq. (3).

Experimental

Preparation of samples

Titania gel films were deposited on the silica glass plate by using the titanium oxide sol prepared as described in [13]. The gel was dipped onto a substrate on a spinner at 6000 rpm, and subsequently the sample was kept in air for 10 min and then heat-treated at 500°C for 2 h in oxygen. In the second step the additional gel amount was dipped onto the sample on the spinner at 3000 rpm, and finally, the sample was repeatedly heat-treated at 500°C for 2 h in oxygen. The total thickness of the titania films was 200 nm.

Labeling of the samples for ETA measurements

The samples for ETA measurements were labeled using adsorption of ^{228}Th and ^{224}Ra radionuclides from acetone solution. The specific activity of the sample was 10^5 Bq per gram. The labeled samples were stored at least three weeks prior to ETA measurements in dry conditions to allow the radioactive equilibrium between ^{228}Th and ^{224}Ra nuclides to be established. The recoil depths of ^{224}Ra and ^{220}Rn ions implanted by the recoil energy (85 keV/atom) into anatase were calculated by means of the TRIM code [21] as: 27 nm (straggling 6 nm) and 27 nm (straggling 6 nm), respectively. Therefore, we supposed that in anatase sample the maximal depth of the radon atoms penetration was 66 nm.

ETA measurements

The labeled anhydrous porous titania film sample deposited on the silica glass (size 3x4 mm) was placed in a furnace (Fig. 3 [17]) and heated in the temperature range 20-800°C at the rate of 6°C min^{-1} in the flow of argon or oxygen, respectively. The constant flow of the gas (flow rate 50 mL min^{-1}) took the radon released from the sample into the measuring chamber of radon radioactivity. The resulting ETA curve is presented as a temperature dependence of the radon release rate E (in relative units); $E=A_\alpha/A_{\text{total}}$, where A_α is α-radioactivity of radon released in unit time from the labeled sample, and A_{tolal} is the total γ-radioactivity of the labeled sample. A_{total} is proportional to the rate of radon formation in the sample. Semiconductor and NaI (Tl) detectors were used for the α- and γ-radioactivity measurements, respectively.

Other characterization techniques

SEM micrographs were obtained by HITACHI Equipment (Type S-5000) operating at 10 kV; extracting voltage was 3.0 kV, beam intensity was 10 μA. XRD patterns were obtained by using RIGAKU X-ray diffractometer RINT 2000 equipped with an apparatus for thin film analysis at the fixed incident angle 1.2°.

Results and discussion

From XRD patterns and SEM micrographs (Figs 1 and 2, respectively) it followed that titania film heated at 500°C/2 h in oxygen (used as starting materials in this study) was porous, of anatase structure, and contained microcracks on the surface. From Fig. 1 it followed that after the subsequent heat-treatment to 800°C in argon or oxygen, respectively, the samples preserved anatase structure. The increase of the grain size in the sample heated to 800°C/5 h in nitrogen was observed by SEM (Fig. 2). Therefore, we assumed that the amount of structure irregularities decreased in this sample as compared to the initial titania films

heated at 500°C/2 h in oxygen. Figure 3 shows the differences in the thermal behavior of titania films revealed by ETA during heating in argon (curve 1) or oxygen (curve 2), respectively. We assumed that the increase of the radon release rate, *E,* observed in the temperature range 50-250°C in both curves 1 and 2 (Fig. 3) was due to the radon diffusion along structure irregularities in surface and very near surface layers of the samples. The random 'single jump' diffusion mechanism of radon was supposed to control the release or radon in this temperature range. The slopes of the respective ETA curves slightly differed in this temperature range. The reduced slope of the increase of radon release rate, *E,* observed during the sample heating in oxygen (curve 2, Fig. 3) as compared to the sample heating in argon (curve 1, Fig. 3) reflected the decreased amount of the surface and near surface structure irregularities. We therefore assumed that the heat treatment in oxygen was in favor of the annealing of structure irregularities in the titania film near surface layers. The decrease of the radon release rate, *E,* observed in curves 1 and 2 (Fig. 3) in the ranges of 250-800 and 250-550°C, respectively was ascribed to the annealing of the structure irregularities and porosity in the titania films in the respective gas environment. This is in agreement with the results by Hirashima and Kusaka [14] who investigated by means of elipsometry the thickness of sol-gel made titania films after their heating in air to selected temperatures up to 800°C. The decrease of the film thickness with the heating temperature and the corresponding increase of the density of titania films was attributed to sintering. In this respect, ETA results (Fig. 3) characterized the annealing of structure irregularities and porosity and monitored the sintering process of the titania films. SEM micrographs (Fig. 2) confirmed this interpretation of ETA results.

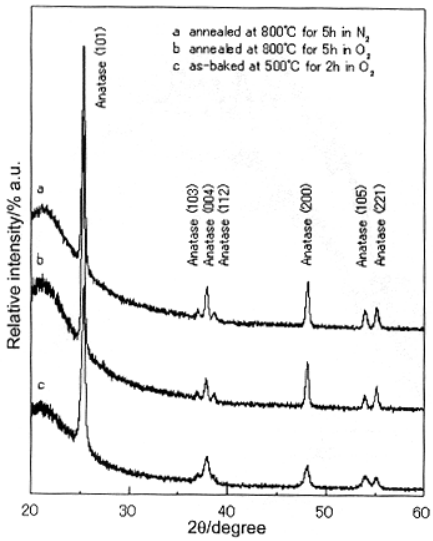

Fig. 1 XRD patterns of titania films samples a - sample annealed at 800°C/5 h in nitrogen; b - sample annealed at 800°C/5 h in oxygen; c - initial sample heated at 500°C/2 h in oxygen. (CuK_α radiation at the fixed incident angle 1.2° was used)

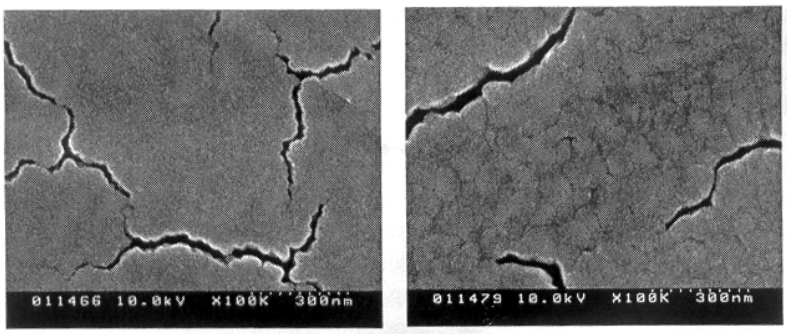

Fig. 2 SEM micrographs of titania films a - heated to 500°C/2 h in oxygen and b - subsequently heated at 800°C/5 h in nitrogen

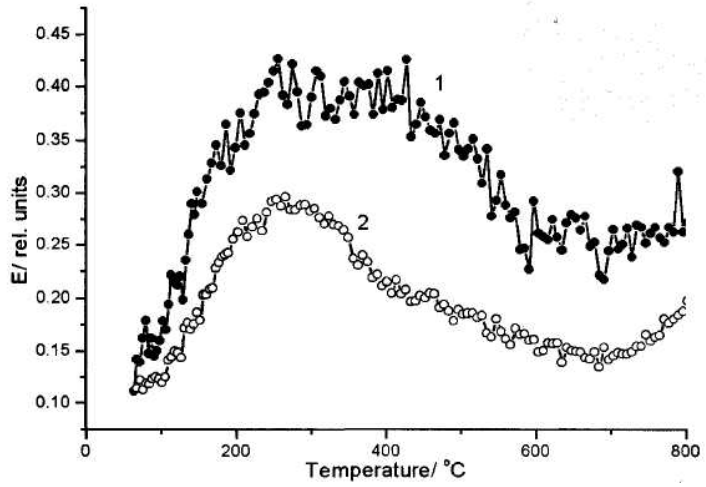

Fig. 3 The ETA results of titania film measured on heating in argon (curve 1) and oxygen (curve 2)

From ETA results in Fig. 3 it followed that the annealing of the porosity and near surface irregularities of the titania films was enhanced during heating in oxygen in comparison to the heating in argon, respectively. This is probably due to the stoichiometric reconstruction [22] of the titania surface on heating in oxygen. Nevertheless, this assumption has to be confirmed in our next study. In this study we found an agreement of ETA results and XRD patterns (Fig. 1) which indicated that the intensity of the diffraction lines increased after subsequent heating of the samples to 800°C/5 h both in nitrogen or oxygen, respectively. Moreover, the growth of anatase grains was observed by SEM (Fig. 2b). Similarly, Negishi and Takeuchi [23] observed the grain growth in the sol-gel prepared porous titania thin films heated to 800°C.

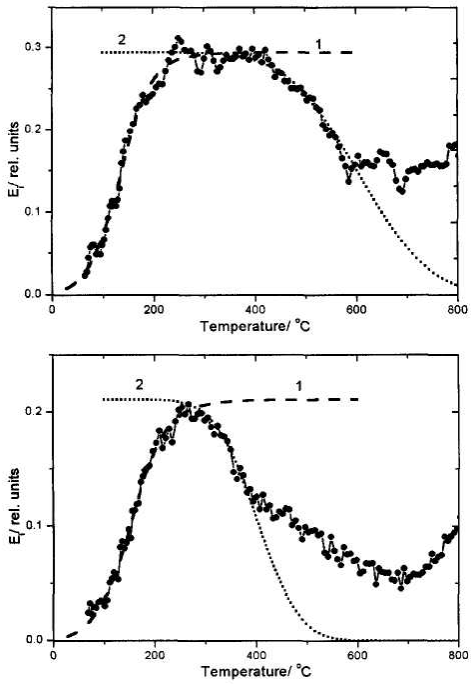

Fig. 4 Comparison of experimental ETA results with the model curves characterizing temperature dependencies of the annealing of near surface structure irregularities of the titania films on heating in argon (Fig. 4a) and in oxygen (Fig. 4b) Experimental results (radon release rate *E)* are represented as dots, curves 1 correspond to the temperature dependencies of radon release obtained by the modeling. Curves 2 correspond to the temperature dependencies of the decrease of the amount of structure defects, serving as radon diffusion paths

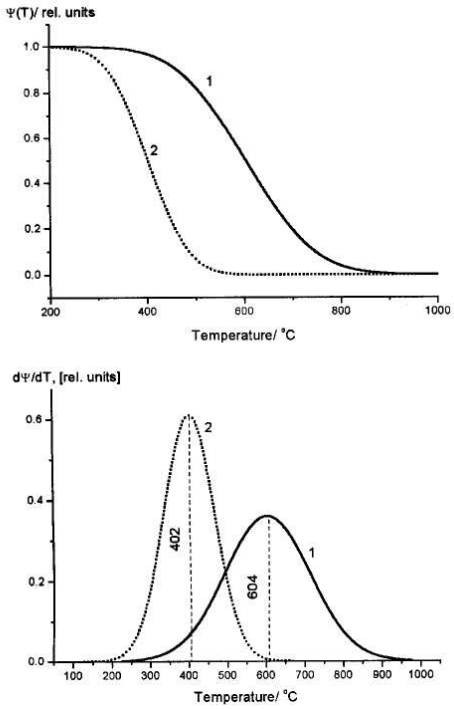

Fig. 5 Temperature dependencies of the functions Ψ(*T*) and dΨ/d*T,* characterizing the annealing of structure irregularities in the near surface layers of titania films during heating in argon and oxygen, respectively: a - as integral functions; b - as first derivative functions

ETA results were evaluated by means of the mathematical model, supposing that pores and near surface structure defects served as paths for radon diffusion. Temperature dependencies of radon release rate, E_D due to diffusion were calculated by using Eq. (2). Temperature dependencies of Ψ(*T*) functions, characterizing the decrease of the amount of the structure defects, were calculated by using Eq. (3). The results of the mathematical modeling were compared to the experimental ETA results. A good agreement of the results can be observed in Figs 4a, b. Figures 5a, b present the temperature dependencies of the functions Ψ(*T*) and dΨ /d*T*, which characterize the thermal behavior of the titania films during heating in the respective gas environment. From Fig. 5b it followed that maximal rates of the annealing of structure irregularities in titania films heated in argon and oxygen were reached at the temperatures of 604 and 402°C, respectively.

We would like to point out that the designed mathematical model [20] was used for the first time in this paper in the evaluation of ETA results which characterized the thermal behavior of porous thin films. The model will be used in the next papers for the description of thermal behavior of other solids, characterized by means of ETA.

Conclusions

It was demonstrated that the gas environment (argon, oxygen) used for the heat treatment of the porous titania films can significantly influence the development of their microstructure. ETA results measured under *in situ* heating conditions characterized differences in the annealing of near surface structure irregularities, serving as radon diffusion paths in titania films. The used mathematical model was found suitable for the evaluation of ETA results. SEM micrographs confirmed both the results of modeling and ETA measurements.

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