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Title of the project: PREPARATION AND CHRACTERIZAION OF NEW INORGANIC MATERIALS WITH SPECIFIC PROPERTIES

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Date:

Date:

Short description of the research activities

The aim of this study stay was to get acquainted with modern methods of the preparation and characterization of new inorganic materials with specific properties. Following materials were investigated in the frame of the project:

- Titania-ruthenia based materials and their precursors containing various amount of individual components as advanced inorganic materials with photocatalytic and photovoltaic properties.
- Yttria-stabilized zirconia (YSZ) type materials to be used as matrices for immobilization of radioactive high level waste containing transuranium (TRU) elements.

Precipitation / sol-gel techniques were used for the preparation of the titania-ruthenia based materials. The prepared materials were thermally treated in various gas environments.

YSZ based materials were prepared by mixing of YSZ powder (containing Zr : Y = 85.77 : 14.23 mol %) and Ce/Nd oxide powder in respective molar ratio in a ball mill. The samples were calcined at 1500 °C for 24 hours in a stream of air and crushed in a mortar. The ceramic samples were subjected to the leach test according to the Materials Characterization Center, USA (MCC-1) protocol [1]. The influence of hydrolytic corrosion to these matrices was investigated by emanation thermal analysis.

The instrumental methods such as electron microscopy, surface area determination by nitrogen sorption / desorption, thermogravimetry, differential thermal analysis, emanation thermal analysis, X-ray powder diffraction, mass spectroscopy were used during the investigation.

The mathematical models developed at NRI Řež under participation of Prof. I. N. Beckman, Moscow State University (actually the NATO research program fellow at NRI) were used for the evaluation of the emanation thermal analysis data and their comparison with the results of other methods of thermal analysis.

The measurements by traditional methods of thermal analysis (thermogravimetry, differential thermal analysis), X-ray diffraction measurements, electron microscopy measurements and surface area measurements were carried out in the collaboration with the Institute of Inorganic Chemistry AS ČR, Řež. The scientific level of the research work carried out at the NRI Řež was highly recognized by the international partners of NRI from Japan and Russia.

The results of investigation carried out during the study stay were presented in national and international meetings, namely:

- Topical meeting on emanation thermal analysis held in Řež on August 9. 10. 2000
- 2nd Czech-Japanese Workshop on workshop on advanced methods for characterization of inorganic materials held in Prague on September 8 9th.

The experience and know-how gained during the research project will be used in the further research and teaching work at Faculty of Science, University of Košice. The collaboration between the NRI Řež and University of Košice is planned for the next period in order to continue the started activities.

The description of the results obtained in the frame of this project and their detailed interpretation is given further in this report. The results of the research will be published in international journals. Therefore all the description given further should be considered as \underline{CONF} <u>IDENTIAL</u>.

Acknowledgement:

The financial support obtained in the frame of NATO Science Fellowships Programme is highly acknowledged by the developer as well as the host institution. This acknowledgement will be written in the scientific papers prepared for publication in international journals.

I. Information about the advanced materials investigated

I.1 Titania-ruthenia based materials

Interest concerning titania based materials has grown after 1972, when Honda and Fujishima published their discovery that water could be split upon illuminating on TiO_2 single crystal electrode to oxygen and hydrogen [1]. From this time the TiO_2 photocatalysis has been applied to a variety of problems.

The applications are based on well known band structure of semiconductors (TiO_2) , consisting of the valence band, VB, and the conduction band, CB (Fig. 1).



Fig. 1 Schematic illustration of a TiO₂ particle used as a redox photocatalyst [2].

When a photon with an energy of hv matches or exceeds the energy gap between filled and valance band – called bandgap energy, E_g – an electron e_{cb}^{-} is promoted from the valence band, VB, into the conduction band, CB, leaving a hole h_{vb}^+ behind. Created electrons in the conduction band and the holes in the valence band have a limited lifetime. In the absence of electron acceptors and donors on/or near the surface they usually recombine radiationlessly and dispate their energy into heat:

$$TiO_2 \xrightarrow{h\nu} TiO_2(\vec{e_{cb}} + h^+_{\nu b})$$
$$TiO_2(\vec{e_{cb}} + h^+_{\nu b}) \xrightarrow{h\nu} TiO_2 + heat$$

But, when surface adsorbed substrate is present, photogenerated conduction band electrons can be transferred to an acceptor molecule at the surface:

$$e_{cb} + A \rightarrow A^{\bullet}$$

Likevise, valence band holes, h^+_{vb} , can be filled by suitable electron donors:

$$h^+_{vb} + D \rightarrow D^{\dagger}$$

The radical ion A^{\cdot} and $D^{\cdot+}$ can participate in several pathways: (1) they may react chemically with themselves or other absorbates, (2) they may recombine by back electron transfer to form excited

state of one of the reactants or (3) they may diffuse from the semiconductor surface and participate in chemical reaction in the bulk of the solution. These different possibilities predetermine TiO_2 to be useful catalysator of many organic and inorganic reactions, induced by irradiation of TiO_2 particles. The reactions can be classified as involving oxidations and oxidative cleavages (e.g. gaseous anaerobic degradation of ethanol to acetaldehyde), reductions (e.g. acetylene reduction to ethylene and ethane), degradation of inorganic anionic pollutants (e.g. NO_3^- , or CN^- ions), geometric and valence isomerisations (e.g. isomerisation of quadricyclene to norbornadiene), substitutions (e.g. photofluorinations of olefins), condensations (e.g. generation of amino acids), polymerizations (e.g. formation of polystyrene from styrene).

Such reactions are applicable in variety of problems of environmental interest, water and air purification, especially in the elimination of toxic chemicals such as halogenated aliphatic and aromatic hydrocarbons from wastewater, soil lechates and groundwater. They can also be successfully used in odor control, destruction of bacteria and viruses, inactivation of cancer cells.

Many of the reactions have already found interesting and important practical applications in production of goods for various fields of everyday life:

- self-sterilizing photocatalytic tiles
- self-cleaning building materials
- anti-fogging glasses
- photocatalytic air cleaners
- photocatalytic water purificators
- films for automobile side-view mirrors

As it can be seen, titanium oxide has a lot of applications, unfortunately there are some limitations defending its wider spreading out. The limitations concern the light usable in photocatalytic reaction of titanium dioxide. For photocatalysis only two (anatase, rutile) from three possible crystal forms (brookite is the third one in addition to two previously mentioned) are used. Anatase generally shows the highest photoactivity. Band gap energy between VB and CB for anatase-type titanium dioxide is 3.2 eV, which corresponds to UV light 388 nm. Band gap energy for the rutile-type is 3.0 eV corresponding to violet light (413 nm). So the light usable in the photocatalytic reaction of titanium dioxide is limited to that with the wavelengths lower than 420 nm. But for the effective practical photocatalytic utilization of the TiO₂ visible light would be more desirable.

One of the ways how to reach this requirement is addition of transition metals and metals oxides to titanium dioxide as "dopants", so the photochemical responsiveness of the material expands and material can make use of light in the visible region.

Mixed-phase Ti/Fe metal oxide colloids, containing from 10 to 50 atom. % Fe have been investigated from this point of view [3]. It was found, that iron-containing TiO₂ particles showed higher quantum yields than pure TiO₂ colloids. Fe(III) doping

of TiO_2 has been shown to increase the quantum efficiency for the photoreduction of N_2 [4] and to enhance photoreactivity for water cleavage [5].

 N_2 reduction was also studied by Cr(III)-doped TiO₂ [6]. The metal ions dopants are thought to inhibit the recombination of photogenerated charge carriers and thus to make them possible to reach the surface and react with an adsorbed substrate.

With the aim to develop the photocatalytic material usable in broader wavelength region, RuO_2 -doped titanium dioxide of the composition $(TiO_2)_x$ - $(RuO_2)_{1-x}$ (x=1, 0.9, 0.7, 0.5, 0.3, 0.1, 0) we have studied.

In the present study we have investigated processes taking place during thermal behavior of the prepared titania-ruthenia materials. This treatment of the materials in the inert gas, oxidation or reduction atmospheres can lead to the formation not only $(TiO_2)_x$ - $(RuO_2)_{1-x}$ materials but $TiO_2/RuO_2/Ru$ or TiO_2 -Ru based materials, with enhanced photoactivity due to formation of micro photoelectrochemical cells which principles are shown in Fig. 2



Fig. 2 TiO₂ powders with deposited (a) metal particles and (b) metal + metal oxide particles

For photocatalytic applications mainly "titania-rich" materials are interesting (x = 1, 0.9, 0.7), but "ruthenia-rich" phases (x \le 0.5) have also possible practical applications. Ruthenium oxide is a transition metal oxide with rutile-type structure possessing metal like conductivity. After heating with other rutile-type oxides it yields the conductive ruthenate ceramics, or conductive solid solutions. Ruthenium oxide electrodes are well known DSA (dimensionally stable electrodes) type electrodes used by chlorine-alkali chemistry as corrosion resistant, low overpotential electrodes for chlorine evolution [7]. The ruthenium-oxygen systems have also attracted attention as possible candidate material for very-large-scale integrated circuits metalization. Ru and/or RuO₂ electrodes can be used in construction of random-access memories (DRAM) for computers or thin film resistors used as temperature sensors [8]. The influence of Ti doping and thermal treatment on dielectric constant (ε_v) and resistivity is also interesting topic of scientist's attention.

I.2 Yttria-stabilized zirconia

[6]

Yttria-stabilized zirconia (YSZ) material has been proposed as a matrix for portioned TRU waste immobilization. YSZ has excellent phase stability and chemical durability. The cubic system (fluorite structure) of YSZ is much better in durability than the tetragonal and monoclinic systems [9].

It was found that in YSZ specimens containing up to 40 mol% Nd the fluorite phase was formed regardless the sintering atmosphere.

Yttria-stabilized zirconia forms solid solutions with tri- and/or tetra-valent TRU elements and can incorporate significant amounts of Pu and Np in its lattice. In addition, zirconia is well known as feasible resistant material to α -decay damage [10].

From the view of potential use of YSZ in TRU waste immobilization it is of interest to study the properties of YSZ and its alteration products after leaching.

In the present study the migration of radon in YSZ samples containing Ce and/or Nd admixtures (as Pu and/or Nd simultans) as well as the comparison of behaviour of YSZ samples before and after the leaching test is described.

II. Experimental

II.1 Preparation of titania-ruthenia based materials

Analytical grade TiCl₄ (Kanto chemicals) and RuCl₃ (Furuya metal) were used in synthesis.

Hydrous titania and ruthenia were prepared by very slow adding of a dilute alkaline solution ammonia (2M) into the 0.7M solution of $TiCl_4$ or $RuCl_3$ in 0.1M hydrochloric acid. Precipitated gels were filtered, washed several times to remove chlorine impurities and then partially dried at 120 °C for 10 hours in air.

The mixed hydrous titania-ruthenia based materials $(TiO_2)_x$ - $(RuO_2)_{1-x}$ •nH₂O (x=0.9, 0.7, 0.5, 0.3, 0.1) were prepared by similar procedure. 2M ammonia was slowly added to the solution containing TiCl₄ and RuCl₃ in respective molar ratios (Ti:Ru = 9:1; 7:3; 5:5; 3:7; 1:9). Precipitated gels were filtered, washed several times to remove chlorine impurities and then partially dried at 120 °C for 10 hours in air.

II.2 Preparation of Yttria-stabilized zirconia

The YSZ powder (containing $Zr : Y = 85.77 : 14.23 \mod \%$) and Ce/Nd oxide powder in respective molar ratio were mixed in a ball mill, calcined at 1500 °C for 24 hours in a stream of air and crushed in a mortar. After this procedure the powder mixtures were palletized at 130 MPa and sintered under stream of air for 80 hours in an electric resistant furnace. Finally, the samples were crushed in mortar and powder adjusted 75 nm using a sieve. The YSZ samples of following composition were prepared and tested:

Sample 1: 100 mol % YSZ no Ce nor Nd admixtures

Sample 2: 51.85 mol % YSZ + 48.15 mol % Ce Sample 3: 80.62 mol % YSZ + 19.38 mol % Ce Sample 4: 90.64 mol % YSZ + 4.68 mol %Ce + 4.68 mol % Nd Sample 5: 71.53 mol % YSZ + 18.98 mol %Ce + 9.49 mol % Nd Sample 6: 51.84 mol % YSZ + 24.08 mol %Ce + 24.08 mol % Nd

The ceramics samples were subjected to the leach test according to the MCC-1 protocol [11]. The samples were denoted as *A* -before the leach test and B - leached samples.

II.3 Instrumentation

The emanation thermal analysis measurements were carried out using modified NETZSCH DTA-REM 404 equipment at the heating rate of 6K/min, in 50 ml/min of the carrier gas (argon, argon+H₂).

TG and DTA measurements were carried out using NETZSCH STA 404 Equipment, in an alumina crucible and heating rate of 6K/min.

XRD patterns were obtained by using a Siemens D500 diffractometer equipped with CuKa radiation.SEM micrographs were obtained with PHILIPS Equipment (Type XL 30CP).

III. Results

III.1 Titania-ruthenia based materials

The results concerning titania-ruthenia based materials are presented in two parts. First part describes the characterization of hydrous titania $TiO_2 \cdot nH_2O$ during heating in argon and argon containing 10% hydrogen, respectively. The second part contains the results of the study of $(TiO_2)_{x-1}$ (RuO₂)_{1-x} $\cdot nH_2O$ (x=0.9, 0.7) as precursors for titania-ruthenia materials.

III.1.1 Investigation of thermal behavior of TiO₂•nH₂O (n=0.58) during heating in argon and argon containing 10% hydrogen

(i) Thermal treatment in argon

TG/DTG and DTA results of the hydrated titanium dioxide prepared by the sol-gel technique are shown on Fig. 3. The sample was heated in argon up to $1100 \,^{\circ}$ C.



Fig. 3 Thermoanalytical characterization (curves TG and DTA) of TiO₂•0.58H₂O heated in argon (heating rate 6 K/min)

Initial sample, used for the thermal treatment was characterized by XRD as poorly crystallized anatase (see Fig. 4, curve a). According to TEM photographs (Fig. 5a) the sample consists of approximately 5 nm large grains forming agglomerates. BET surface area of the initial sample was 213 $m^2 \cdot g^{-1}$.

In the TG curve (see Fig. 3), continuous mass loss up to 800 °C was observed during the heating. This mass loss is due to the dehydration of the sample. The total observed mass loss is 11.5%, therefore for TiO₂•nH₂O n=0.58 mol H₂O.



Fig. 4 XRD patterns of TiO₂•0.58H₂O heated in Ar

The changes in the titania sample after the heating in argon to 300, 500, 800 and 1100 °C, respectively were characterized by XRD, BET and TEM measurements. In the sample heated to 300 °C no change in comparison with the initial sample was observed by XRD (see Fig. 4b). From the TEM micrographs we could see that the liberation of water took place (Fig. 5b). The surface area of the sample heated to 300 °C decreased to 148.4 $\text{m}^2 \cdot \text{g}^{-1}$.

The sample heated to 500 °C was characterized by narrower X-ray diffraction lines with higher intensity, indicating the formation of a better crystallized anatase. Growing of the grain size was detected in the sample heated to 500 °C on TEM micrographs, being accompanied by a decrease of the surface area to 89.7 m²•g⁻¹. After heating to 800 °C the formation of well-developed crystals was observed on TEM micrographs (Fig. 5d), the surface area continued to decrease to 41.6 m²•g⁻¹ until 800 °C. The narrow peaks of the XRD patterns (see Fig. 4d) are in agreement with this finding. This XRD pattern reflected also another important feature: the phase transition from anatase to rutile took place at this temperature and diffraction lines of both, rutile and anatase were present in the sample. From XRD

pattern in Fig. 5e it followed that in the sample heated to 1100 °C the phase transformation anataserutile was finished as only well-crystallized rutile was found in the sample (see Figs. 4e and 5e).



Fig. 5 TEM micrograps of TiO₂•0.58H₂O during heating in Ar

Emanation thermal analysis (ETA) was used in order to obtain additional information about the microstructure changes under *in-situ* conditions. The ETA was already advantageously used in the investigation of inorganic materials for this purpose [12].

The ETA results of hydrous titania of $TiO_2 \cdot 0.58H_2O$ are presented in Fig. 6 (curve 1). Two processes taking place during the heating from 20 - 1000 °C were distinguished. The first process was attributed to the microstructure changes accompanying the dehydration process (see the



enhanced radon release rate from 25 - 330 °C as a consequence of water liberation from the sample surface).

Fig. 6 Experimental ETA results (curve 1) compared with the results of the mathematical modeling (curves 2 - 8) of the radon release from TiO₂•0.58H₂O

The following decrease of radon release rate in the range 330 - 800 °C was attributed to the growth of primary anatase grains and consequent decreasing of the sample surface area. This finding is in accordance with TEM and surface area measurements described above.

The second process starts at the temperature 800 °C and it is evoked by anatase-rutile phase transition. In the temperature range 800 - 950 °C the increase of emanation release rate is visible as the result of higher structural disorder during phase transition. Above 950 °C decrease of E reflects formation of well crystallized material.

The experimental ETA results were evaluated using mathematical model, which we have already successfully used in the description of ETA curves of other systems [13]. The principles of the mathematical modeling are described below. The modeling of the ETA curve enabled us to obtain kinetic parameters characterizing the radon diffusion from the sample. The model ETA curve (see curve 2 in Fig. 6) is expressed as a sum of two processes, taking place simultaneously. The overall value of radon release rate probability E(T) can be therefore expressed as $E(T) = E_1(T) + E_2(T)$. In the construction of the overall model ETA curve (curve 2 in Fig. 6) the following theoretical dependences were considered:

$$E_i(T)=A_i \bullet D_i(T) \bullet S_i(T)$$
 i=1, 2;

 A_i is a constant, T is temperature, $S_i(T)$ is an integral Gauss function expressing changes of the surface area upon heating as an S-like curve

$$S_i(T) = 1 - 0.5[1 + erf(z)]$$
 where
 $erf(z) = (2/\pi^{1/2}) \int_{0}^{z} exp(-z^2) dz$

 $z = \frac{T - T_{mi}}{\sigma_i \cdot 2^{1/2}}$, $\sigma_i = \frac{\Delta T_i}{3}$, T_{mi} is the temperature corresponding to the maximal rate of the S_i(T)

change, ΔT_{ι} is width of the temperature range in which $S_i(T)$ takes place. Function $D_i(T)$ reflects temperature dependence of radon diffusion considering Arhenius law

$$D_i(T) = D_{i0} * exp(-Q_i/RT)$$
 i=1,2

In this function, Q_i is the activation energy of radon diffusion in the respective solid phase; D_{i0} - is the pre-exponential factor characterizing the respective lattice property.

The temperature dependences of the diffusion component $D_1(T)$ and $D_2(T)$ used in the modeling of $E_1(T)$ and $E_2(T)$ are demonstrated as curves 3 and 4, respectively. Curves 5 and 6 in Fig. 6 are derivatives of S-like shape functions describing the change of surface area of the sample on heating in the temperature intervals where the respective solid-state processes take place. The resulting model dependences of $E_1(T)$ and $E_2(T)$ are represented in Fig. 6 as curves 7 and 8. These curves were obtained as the product of diffusion component (see curves 3 and 4, resp.) and respective functions $S_i(T)$ describing the change of surface area on heating.

Model curve 7 in Fig. 6 reflects the process of radon release during the dehydration of the sample. As it can be seen from the Table 1, the maximal radon release rate of this process corresponds to the temperature T_m =413 °C. The activation energy Q of the radon release from the sample during dehydration was determined as Q=7.2 kJ•mol⁻¹.

Fig. 7 shows the shape of S(T) function, describing the change of the surface area of the sample resulting from dehydration, in comparison with experimentally found surface area values calculated by BET method. It follows that a good agreement between experimental and theoretical results was obtained.

The ETA model curve 8 (see Fig. 6) characterizes the phase transition anatase-rutile. As it can be seen from the Table 1, temperature of the maximal radon release obtained by modeling was $T_m=964$ °C, and width of this effect was 134 °C (see Fig. 6, curve 7). The value of the activation energy of the radon diffusion corresponding to the anatase-rutile transition was calculated to be Q=588 kJ•mol⁻¹, which is considerably higher than for the dehydration process (7.2 kJ•mol⁻¹).

E(T)=E1(T)+E2(T)	А	Q[kJ/mol]	T_m / C	$\Delta T / C$	
E1	$2.*10^{-10}$	7.2	413	785	
E2	3.8*10 ¹⁴	588	964	134	

Table 1. The values of activation energy Q of radon migration in the near surface layers calculated using the proposed mathematical model.



Fig. 7 Values of BET surface area obtained experimentally (dots) for samples heated to various temperatures compared to "ETA surface area values" (full line) determined from the theoretical curves.

It is to point out, how this mathematical model agrees with the experimental data. In Fig. 8 the results of mathematical modelling of radon behaviour in thermally treated sample are compared with the XRD patterns of the intermediate products of the thermal treatment. From Fig. 8, we can suppose that the anatase-rutile transition can start in the conditions used in this work already after 700 °C and be over at 1100 °C. The XRD patterns of the intermediates heated to 500 °C confirmed the presence only anatase, whereas at the temperature 800 °C both anatase and rutile were detected. Finally, at 1100 °C when ETA model curve shows that the phase transition was over, the only rutile was detected.



Fig. 8 Thermal behavior of from TiO₂•0.58H₂O characterized by ETA model curves and XRD patterns of intermediate products of heating.

(ii) Thermal treatment in argon containing 10% of hydrogen

The initial sample was heated in Ar/H_2 reducing atmosphere. TG and DTA curves of this process are in Fig. 9. The mass loss, observed on TG curve is a little higher in comparison to the mass loss in inert gas (argon) argon atmosphere. This difference in the mass loss observed during heating in the two different gaseous media was probably due to the loss of oxygen, creating non-stochiometric defects on heating in the reducing gaseous medium (under presence of hydrogen).

The interesting information is available from DTA curve. The exothermic peak corresponding to the anatase-rutile phase transition, observed on the DTA curve during heating in argon at 1000 °C, was shifted to 900 °C when sample was heated in Ar/H_2 .

The results of ETA (Fig. 10) reflected the microstructure changes corresponding the dehydration and phase transition of anatase-rutile. The model ETA curve is also presented in Fig. 10 demonstrating a good agreement of the mathematical model proposed for this system with the experimental ETA data. The results of mathematical modeling are summarized in Table 2 and Fig. 10. The mathematical model used as well as the meaning of curves 1, 2...8 is the same as in Fig. 6.

Fig. 9 Thermoanalytical characterization (curves TG and DTA) of TiO₂•0.58H₂O heated in Ar/H₂



(heating rate 6 K/min)

When comparing both ETA model curves, process of dehydration takes place in the atmosphere of Ar/H_2 in broader temperature range in comparison to Ar, agreeing with TG results. While during heating in argon the mass loss observed at the TG curve was over at 800 °C, during heating in Ar/H_2 the mass loss continued up to 1100 °C. The activation energy values calculated for

radon diffusion from the ETA model curves in the reducing atmosphere and argon were found similar, being Q=10 kJ/mol and 7.2 kJ/mol, respectively.

E(T)=E1(T)+E2(T)	А	Q[kJ/mol]	T _m /°C	$\Delta T / C$	
E1	2*10 ⁻⁹	10	336	853	
E2	6*10 ⁻³	176	771	124	

Table 2. The values of activation energy of radon migration in the near surface layers calculated using the proposed mathematical model.



Fig. 10 Experimental ETA results (curve 1) compared with the results of the mathematical modeling (curves 2-8) of the radon release from TiO₂•0.58H₂O

The process of anatase-rutile phase transition is described by the ETA model curve (Fig. 10, curve 8). From Tables 1 and 2 it follows that the phase transition is characterized by the similar width of the process during heating in both, argon and argon/hydrogen ($\Delta T=134$ °C and 124°C, resp.). However the temperature of the maximum T_m was shifted in the case of heating in argon/hydrogen by 193 °C to lower temperature in comparison to the heating in argon. The value of the activation energy of radon diffusion corresponding to the anatase-rutile transition in argon/hydrogen was determined from the mathematical model as Q= 176 kJ/mol, whereas during heating in argon Q= 588 kJ/mol.

Fig. 11 summarizes the model ETA curves comparing directly the non-isothermal kinetics of these processes taking place during heating in Ar and Ar/H₂ respectively. From the figure can be seen broader interval of dehydration as well as lower temperature of phase transition in Ar/H₂.



Fig. 11 Comparison of ETA model curves describing the dehydration and phase transition of TiO₂•0.58 H₂O during heating in argon (full lines) and argon/hydrogen (dotted lines). *III.1.2 Thermal annealing of advanced titania-ruthenia materials*

(i) Thermal behavior in argon

Fig. 12 shows the thermoanalytical curves (TG, DTA) during heating of $(TiO_2)_{0.7}$ - $(RuO_2)_{0.3}$ •nH₂O and $(TiO_2)_{0.9}$ - $(RuO_2)_{0.1}$ •nH₂O in argon. The mass loss due to the dehydration was observed on heating up to 450 °C in both samples. From the total mass loss 23,95% it was concluded that the sample $(TiO_2)_{0.9}$ - $(RuO_2)_{0.1}$ •nH₂O contained 1.5 mol H₂O. For the system $(TiO_2)_{0.7}$ - $(RuO_2)_{0.3}$ •nH₂O the mass loss 18,74% corresponded to the liberation of 1.2 mol H₂O. From Fig. 12 it followed that the dehydration of $(TiO_2)_{0.7}$ - $(RuO_2)_{0.3}$ •nH₂O was accompanied by simultaneous crystallization of the sample. This crystallization was reflected by DTA as an exothermic effect with maximum at 500 °C. For $(TiO_2)_{0.9}$ - $(RuO_2)_{0.1}$ •nH₂O this exothermal effect was not observed on DTA on heating up to 600 °C.

It is to point out, how this mathematical model agrees with the experimental data. In Fig. 8 the results of mathematical modelling of radon behaviour in thermally treated sample are compared with the XRD patterns of the intermediate products of the thermal treatment. From Fig. 8, we can suppose that the anatase-rutile transition can start in the conditions used in this work already after 700 °C and be over at 1100 °C. The XRD patterns of the intermediates heated to 500 °C confirmed the presence only anatase, whereas at the temperature 800 °C both anatase and rutile were detected. Finally, at 1100 °C when ETA model curve shows that the phase transition was over, the only rutile was detected.

Fig. 8 Thermal behavior of from TiO₂•0.58H₂O characterized by ETA model curves and XRD patterns of intermediate products of heating.

(ii) Thermal treatment in argon containing 10% of hydrogen



The initial sample was heated in Ar/H_2 reducing atmosphere. TG and DTA curves of this process are in Fig. 9. The mass loss, observed on TG curve is a little higher in comparison to the mass loss in inert gas (argon) argon atmosphere. This difference in the mass loss observed during heating in the two different gaseous media was probably due to the loss of oxygen, creating non-stochiometric defects on heating in the reducing gaseous medium (under presence of hydrogen).

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(heating rate 6 K/min)

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Table 2. The values of activation energy of radon migration in the near surface layers calculated using the proposed mathematical model.

E(T)=E1(T)+E2(T) A		Q[kJ/mol]	T_m / C	$\Delta T/^{o}C$	
E1	2*10-9	10	336	853	
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Fig. 10 Experimental ETA results (curve 1) compared with the results of the mathematical modeling (curves 2-8) of the radon release from TiO₂•0.58H₂O

The process of anatase-rutile phase transition is described by the ETA model curve (Fig. 10, curve 8). From Tables 1 and 2 it follows that the phase transition is characterized by the similar width of the process during heating in both, argon and argon/hydrogen ($\Delta T=134$ °C and 124°C, resp.). However the temperature of the maximum T_m was shifted in the case of heating in argon/hydrogen by 193 °C to lower temperature in comparison to the heating in argon. The value of the activation energy of radon diffusion corresponding to the anatase-rutile transition in argon/hydrogen was determined from the mathematical model as Q= 176 kJ/mol, whereas during heating in argon Q= 588 kJ/mol.

Fig. 11 summarizes the model ETA curves comparing directly the non-isothermal kinetics of these processes taking place during heating in Ar and Ar/H_2 respectively. From the figure can be seen broader interval of dehydration as well as lower temperature of phase transition in Ar/H_2 .



Fig. 11 Comparison of ETA model curves describing the dehydration and phase transition of TiO₂•0.58 H₂O during heating in argon (full lines) and argon/hydrogen (dotted lines). *III.1.2 Thermal annealing of advanced titania-ruthenia materials*

(i) Thermal behavior in argon

Fig. 12 shows the thermoanalytical curves (TG, DTA) during heating of $(TiO_2)_{0.7}$ - $(RuO_2)_{0.3}$ •nH₂O and $(TiO_2)_{0.9}$ - $(RuO_2)_{0.1}$ •nH₂O in argon. The mass loss due to the dehydration was observed on heating up to 450 °C in both samples. From the total mass loss 23,95% it was concluded that the sample $(TiO_2)_{0.9}$ - $(RuO_2)_{0.1}$ •nH₂O contained 1.5 mol H₂O. For the system $(TiO_2)_{0.7}$ - $(RuO_2)_{0.3}$ •nH₂O the mass loss 18,74% corresponded to the liberation of 1.2 mol H₂O. From Fig. 12 it followed that the dehydration of $(TiO_2)_{0.7}$ - $(RuO_2)_{0.3}$ •nH₂O was accompanied by simultaneous crystallization of the sample. This crystallization was reflected by DTA as an exothermic effect with maximum at 500 °C. For $(TiO_2)_{0.9}$ - $(RuO_2)_{0.1}$ •nH₂O this exothermal effect was not observed on DTA on heating up to 600 °C.



Fig. 12 Thermoanalytical characterization (curves TG and DTA) of $(TiO_2)_x$ - $(RuO_2)_1$. _x•nH₂O heated in argon (heating rate 6 K/min). Solid curves: x = 0.9, dashed curves: x = 0.7.

To get supplementary information on the thermal behavior of the titaniaruthenia samples we used emanation thermal analysis (ETA). Fig. 13 and 14 presents experimental ETA curves of the samples $(TiO_2)_{0.9}$ - $(RuO_2)_{0.1}$ •nH₂O and $(TiO_2)_{0.7}$ - $(RuO_2)_{0.3}$ •nH₂O, respectively. From ETA results of $(TiO_2)_{0.9}$ - $(RuO_2)_{0.1}$ •nH₂O it followed that the increase of radon release rate E (see Fig. 13 curve 1) due to the sample dehydration was observed in the range 50 – 240 °C. We suppose that during the release of water from surface and intergranular space the diffusion diffusion of radon from the sample was enhanced. On further heating we supposed that the annealing of the irregularities of near surface layers and surface roughness led to the decrease of sample surface i.e. decrease of the area available for the radon diffusion. This process was reflected by ETA as a decrease of the radon release rate E. The decrease of E continued up to 580 °C for the sample (TiO₂)_{0.9}-(RuO₂)_{0.1}•nH₂O.



Fig. 12 Thermoanalytical characterization (curves TG and DTA) of $(TiO_2)_x$ - $(RuO_2)_1$. x•nH₂O heated in argon (heating rate 6 K/min). Solid curves: x = 0.9, dashed curves: x = 0.7.

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$$E_i(T) = A_i \bullet D_i(T) \bullet S_i(T) \qquad i=1, 2;$$

 A_i is a constant, T is temperature, $S_i(T)$ is an integral Gauss function expressing changes of the surface area upon heating as an S-like curve

$$S_i(T) = 1 - 0.5[1 + erf(z)]$$
 where
 $erf(z) = (2/\pi^{1/2}) \int_0^z exp(-z^2) dz$

 $z = \frac{T - T_{mi}}{\sigma_i \cdot 2^{1/2}}$, $\sigma_i = \frac{\Delta T_i}{3}$, T_{mi} is the temperature corresponding to the maximal rate of the S(T)

change, ΔT_{ι} is width of the temperature range in which $S_i(T)$ takes place. Function $D_i(T)$ reflects temperature dependence of radon diffusion considering Arhenius law

$$D_i(T) = D_{i0} * exp(-Q_i/RT)$$
 i=1,2,3

In this function, Q_i is the activation energy of radon diffusion in the respective solid phase; D_{i0} - is the pre-exponential factor characterizing the respective lattice property.

The model ETA curve for the sample $(TiO_2)_{0.7}$ - $(RuO_2)_{0.2}$ •nH₂O (see curve 2 in Fig. 14) is expressed as a sum of two simultaneous processes. For modeling this ETA curve the same model was used as for the modeling of the hydrous titania (see III.1.1).

The temperature dependences of the diffusion component $D_1(T)$ and $D_2(T)$ used in the modeling of $E_1(T)$ and $E_2(T)$ are demonstrated in Figs. 13 and 14 as curves 3 and 4, respectively. Curve 5 in Fig. 13 represents the temperature dependence $D_3(T)$. Curves 6 and 7 in Figs. 13 and 14 are derivatives of S-like shape functions describing the change of surface area of the sample on heating in the temperature intervals where the respective solid state processes take place. The dependences of $E_1(T)$ and $E_2(T)$ resulting from the modeling are represented as curves 8 and 9 in Fig. 13 and as curves 7 and 8 in Fig. 14, respectively. The curves were obtained as the product of diffusion component (see curve 3 and curve 4, resp.) and respective functions $S_i(T)$ describing the change of surface area on heating.

The parameters used in the modeling are summarized in Table 3. The maximal radon release rate of the dehydration process in $(TiO_2)_{0.9}$ - $(RuO_2)_{0.1}$ •nH₂O corresponds to the temperature $T_m=275$ °C and in $(TiO_2)_{0.7}$ - $(RuO_2)_{0.3}$ •nH₂O to $T_m=279$ °C. The activation energy of the radon release during dehydration of $(TiO_2)_{0.9}$ - $(RuO_2)_{0.1}$ •nH₂O was determined as Q=11.56 kJ•mol⁻¹ and for the sample $(TiO_2)_{0.7}$ - $(RuO_2)_{0.3}$ •nH₂O as Q=13.7 kJ•mol⁻¹.

System	Model	А	Q[kJ/mol]	T_m / C	$\Delta T / C$
(TiO ₂) _{0.7} -(RuO ₂) _{0.3} •nH ₂ O	E = E1 + E2				
	E1	1.3*10 ⁻⁸	13.7	279	378
	E2	8.54	163.2	489	91
(TiO ₂) _{0.9} -(RuO ₂) _{0.1} •nH ₂ O	$\mathbf{E} = \mathbf{E}1 + \mathbf{E}2 + \mathbf{D}$				
	E1	$1.47*10^{-8}$	11.56	275	459
	E2	123.62	203.2	678	214
	D	0.013	177.6		

Table 3. The values of activation energy Q of radon migration in the near surface layers calculated using the proposed mathematical model.

From the E(T) dependences (Fig. 13 curve 9 and Fig. 14 curve 8) obtained by the modelling of the transition from the amorphous to crystalline phases it followed that for the sample $(TiO_2)_{0.9}$ - $(RuO_2)_{0.1}$ •nH₂O was T_m =678 °C and for the sample $(TiO_2)_{0.7}$ - $(RuO_2)_{0.3}$ •nH₂O was T_m =489 °C. The values of the activation energy Q of the radon diffusion corresponding to the phase transition were determined as follows (see Table 3) Q=203.2 kJ•mol⁻¹ for the sample $(TiO_2)_{0.9}$ - $(RuO_2)_{0.1}$ •nH₂O and Q=163.2 kJ•mol⁻¹ for the sample $(TiO_2)_{0.9}$ - $(RuO_2)_{0.1}$ •nH₂O.

Fig. 15 summarizes the model E(T) dependences comparing directly the non-isothermal kinetics of the dehydration and crystallization for the samples $(TiO_2)_{0.9}$ - $(RuO_2)_{0.1}$ •nH₂O (full line) and $(TiO_2)_{0.7}$ - $(RuO_2)_{0.3}$ •nH₂O (dashed line). As it is obvious from Fig. 15 there exists an influence of the ruthenium content on the position and width of the curves describing dehydration and crystallization of the samples, respectively. The temperatures corresponding to the maximal radon release rate E during dehydration are similar for both samples, however the dehydration of $(TiO_2)_{0.9}$ - $(RuO_2)_{0.1}$ •nH₂O takes place in the broader temperature range. More important differences could be observed for the crystallization process. The lower the titanium content in the compounds was, the lower temperature of the crystallization effect was observed.

Interesting correlations were obtained when comparing E(T) dependences obtained by the mathematical modelling for the sample $(TiO_2)_{0.9}$ - $(RuO_2)_{0.1}$ •nH₂O and the experimental results of X-ray powder diffraction and, transmition electron



spectroscopy.

Fig. 15 Comparison of E(T) dependences obtained by modelling for $(TiO_2)_{0.9}$ - $(RuO_2)_{0.1} \cdot nH_2O$ (full lines) and $(TiO_2)_{0.7} \cdot (RuO_2)_{0.3} \cdot nH_2O$ (dotted lines), respectively.



Fig. 16 TEM micrographs of $(TiO_2)_{0.9}$ - $(RuO_2)_{0.1}$ •nH₂O samples heated to various temperature in argon: a) initial sample; b) heated to 400 °C; c) sample heated to 600 °C.

TEM micrographs and XRD patterns of $(TiO_2)_{0.9}$ - $(RuO_2)_{0.1}$ •nH₂O heated to different temperatures are presented in Fig. 16 and 17, resp. As it follows from Fig. 16 the grain size did not change when the sample was heated to 400 °C. XRD patterns of the initial samples and heated to 400 °C revealed poorly crystalline character of both samples. However, the grain size of the samples heated to 600 °C increased (see Fig. 16) and the sample became crystalline. Anatase and rutile phases of titania and ruthenium oxide were identified by XRD in the sample (Fig. 17). From E(T) dependence (see Fig. 13, curve 8) it followed that crystallization onset temperature



(400 °C) well agreed with the results of TEM and XRD.

Fig. 17 XRD patterns of $(TiO_2)_{0.9}$ - $(RuO_2)_{0.1}$ •nH₂O heated in argon to different temperatures (1) room temperature, (2) 400 °C and (3) 600 °C

(ii) Thermal treatment in reducing gas environment (argon + $10\% H_2$)

It was shown above that during heating in argon up to 600 °C the dehydration of hydrous titania-ruthenia samples takes place. In order to asses the stability of the anhydrous titania-ruthenia samples in reducing gas environment the samples were reheated in argon containing 10% hydrogen. The results of TG and DTA obtained during reheating of anhydrous titania-ruthenia samples in argon / 10% hydrogen are presented in Fig. 18.

From the results obtained in this study it follows that the titania-ruthenia based materials $(TiO_2)_{0.9}$ - $(RuO_2)_{0.1}$ and $(TiO_2)_{0.7}$ - $(RuO_2)_{0.3}$ are more stable against reduction



in comparison to their ruthenia-titania samples of "mirror composition", i.e. $(RuO_2)_{0.9}$ - $(TiO_2)_{0.1}$ and $(RuO_2)_{0.7}$ - $(TiO_2)_{0.3}$, which we have studied elsewhere [14]. As it can be seen from TG curve in Fig. 18 the sample lost only 28.44 % of the theoretical value of mass loss corresponding to the total transformation of RuO₂ to Ru. Consequently we can describe the sample obtained by heating in argon/ hydrogen up to 600 °C as TiO₂/RuO₂/Ru. For comparison, in the sample (RuO₂)_{0.9}- $(TiO_2)_{0.1}$ the reduction of RuO₂ to Ru reduction took place in the extend of 67% of calculated value [14].

Fig. 18 Thermoanalytical characterization (curves TG and DTA) of anhydrous $(TiO_2)_x$ -(RuO₂)_{1-x} reheated in argon + 10% hydrogen after previous heating in argon to 600 °C (heating rate 6 K/min). Full lines corresponds to titania-ruthenia x = 0.9, dashed lines corresponds to titania-ruthenia x = 0.7.

For the sample $(TiO_2)_{0.7}$ - $(RuO_2)_{0.3}$ the mass loss on measured on heating in argon / hydrogen up to the temperature 500 °C was 86.64% of the theoretical value of mass loss corresponding to the total transformation of RuO₂ to Ru. Therefore the chemical composition of the sample obtained after heating in these conditions can be written as TiO₂/RuO₂/Ru. In is to point out that the chemical composition of the sample (RuO₂)_{0.7}-(TiO₂)_{0.3} treated on heating in the same conditions to 500 °C was TiO₂/Ru, i.e. transition of RuO₂ to Ru was complete.

From the XRD patterns of $(TiO_2)_{0.9}$ - $(RuO_2)_{0.1}$ (see Fig. 19) it followed that phases of anatase, rutile and ruthenium dioxide were identified in the sample after heating in argon to 600 °C. When this sample was reheated in argon / hydrogen to 600 °C only single anatase phase was identified. The content of Ru metal as minor component was not identified by XRD patterns as to the sensitivity limit of the equipment.



Fig. 19 XRD patterns of $(TiO_2)_{0.9}$ - $(RuO_2)_{0.1}$ •nH₂O (a) after heating in argon to 600 °C and (b) after reheating in argon + 10% hydrogen.

The ETA results (see Fig. 20) enabled us to determine the temperature (200 °C) of the onset of the loosening of the sample structure due to the formation of

ruthenium metal. Moreover, the slope of the temperature dependence of radon release rate observed during thermal treatment in the argon + 10% hydrogen corresponded to the intensity of the enhanced radon release, reflecting the intensity of the microstructure changes.

In agreement with our hypothesis, the intensity of the microstructure changes due to the formation of metal ruthenium in the titania-ruthenia sample was considerably higher in the temperature range 200 - 250 °C than in the range 20 - 200 °C. In addition we can state that on further heating in the range 250 °C – 500 °C where the release of oxygen from the sample continued (see dashed line in Fig. 18), the slope of the E(T) function was lowered indicating the formation of less dispersed (more compacted) sample with the increasing content of ruthenium metal. Taking into account that sample was only partially reduced to the temperature 250 °C, the ETA curves above 250 °C characterize the stable TiO₂/RuO₂/Ru material with constant porosity and surface area.



Fig. 20 ETA heating curve of $(TiO_2)_{0.7}$ - $(RuO_2)_{0.3}$ reheated in argon + 10% hydrogen after previous heating in argon to 600 °C (heating rate 6 K/min).

III.2 Yttria-stabilized zirconia

Yttria – stabilized zirconia has been proposed as a matrix for partitioned TRU waste. It was already found that YSZ specimens containing Nd up to 40 mol % formed after sintering only a fluorite phase regardless the sintering atmosphere. For Ce – doped ceramics up to 48 mol % the fluorite phase has been formed on heating in air. It was of interest to characterize migration of radon in the YSZ samples containing Ce and/or Nd admixtures and to compare the mobility of Rn in the respective YSZ samples before and after the leaching test.

The ETA measurements were performed under *in-situ* conditions of heating and subsequent cooling in air of the constant heating rate of 6 K/min in the temperature range 20-1300 °C.

The results are presented as temperature dependences of radon release rate normalized to the activity of radon parent radionuclides used for the labeling of samples. ETA results demonstrated that in the YSZ ceramic without admixtures of Ce of Nd (samples 1A and 1B) differences in Rn mobility before and after leaching of the samples were observed. The Rn mobility was enhanced after leaching in the hydrothermal conditions.

In order to characterize the amount of the defects serving as channels for the migration of radon atoms in the ceramic matrix, we calculated the value of the integral limited by the temperature dependencies of the radon release rate measured during the heating and subsequent cooling, respectively. The value of the integral can be expressed as follows:

$$\xi(T) = \int_{T_1}^{T_2} E(T')_{heating} dT - \int_{T_1}^{T_2} E(T)_{cooling} dT$$

On the other hand, the value of the activation energy Q of radon mobility can characterize the availability of the defects.

The above mentioned parameters, namely the activation energy Q and the integral ξ were used for the characterization of the investigated YSZ simulated waste forms. The values calculated from the REM results are summarized in Table 4.

Sample				لاح	Q [kJ•mol ⁻¹]	Temperature range for
No. Composition [mol %]			%]			Q determination
	YSZ	Ce	Nd			
1A	100	0	0	6.3002	197.6 7.9	1280 – 1080 °C 670 – 100 °C
1B				3.8129	175.5 10.7	1300 – 1070 °C 675 – 260 °C
2A	51.85	48.15	0	15.7056	237.7 14.4	1280 – 1100 °C 630 – 100 °C
2B				11.8956	267.7 12.2	1300 – 1150 °C 660 – 100 °C
3A	80.62	0	19.38	11.3505	295.1 9.3	1310 – 1100 °C 700 – 100 °C
3B				12.2888	259.6 10	1300 – 1080 °C 600 – 100 °C

Table 4. Basic characteristics of the YSZ simulated waste forms

4A	90.64	4.68	4.68	12.4186	213.2	1250 – 1050 °C
					10	700 – 100 °C
4B				12.3945	267.7	1260 – 1060 °C
					6.4	560 – 100 °C
5A	71.53	18.98	9.49	3.9144	305.4	1300 – 1150 °C
					8.6	660 – 100 °C
5B				6.0868	276.3	1300 – 1100 °C
					8.6	620 – 100 °C
6A	51.84	24.08	24.08	16.4998	295.1	1270 – 1170 °C
					11.5	530 – 100 °C
6B				15.6219	276.3	1290 – 1150 °C
					8.6	470 – 100 °C

The ETA results, measured for the YSZ samples with varying content of Nd and Ce, are summarized in Figs. 21 and 22.



2A



3A







leaching (for chemical composition of the samples see Table 4)





6A



4B



Fig. 22 Temperature dependences of radon release rate measured during heating and subsequent cooling run of the YSZ samples with varying content of Nd and Ce denoted as curves 1B to 6B. The samples (B) correspond to YSZ waste forms after leaching (for chemical composition of the samples see Table 4)

It follows from Figs. 21 and 22 that for YSZ samples doped with Ce or Nd (denoted 2A and 2B; 3A and 3B) no significant differences in radon mobility before and after sample leaching were observed. On the other hand the small effect of the simultaneous presence of Ce and Nd on the radon mobility before and after leaching was observed for the samples 4A - 4B, 5A - 5B and 6A - 6B. The most important synergic effect resulting in the slight decrease in the chemical durability was observed for samples 4A - 4B where both additives Ce and Nd were present up to total 9.2 wt.%.

Using the ETA data where no significant changes between behaviour of the YSZ samples before and after leaching were observed, we can say that the YSZ matrix containing Ce/Nd admixtures is chemically durable towards leaching in acidic environment used according to the MCC-1 protocol. Nevertheless slight differences, observed for individual samples between the ETA curves measured during heating and cooling respectively, revealed that the during heating in air the annealing of defects in surface and near surface layers took place. The values of the activation energy Q of radon diffusion calculated from the temperature dependences E(T) obtained during cooling of the samples did not significantly differ (see Table 4).

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