Journal of Thermal Analysis and Calorimetry, Vol. 60 (2000) 691–698

EMANATION THERMAL ANALYSIS OF PRECURSORS FOR RUTHENIA-BASED MATERIALS

V. Balek[1,3*], *T. Mitsuhashi*[2], *J. Šubrt*[3], *P. Bezdička*[3] *and J. Fusek*[3]

[1]Nuclear Research Institute, CZ-25068 Ře , Czech Republic
[2]National Institute for Research in Inorganic Materials, 1-1 Namiki, Tsukuba, Ibaraki 305-0044 Japan
[3]Institute of Inorganic Chemistry AS CR, CZ-25068 Ře , Czech Republic

Abstract

Emanation Thermal Analysis (ETA) was used to characterize microstructure changes of hydrous ruthenia and hydrous ruthenia-titania as precursors for preparation of RuO_2 and $(RuO_2)_{0.9}$–$(TiO_2)_{0.1}$ by heating in the temperature range of 20–600°C in argon. A good agreement was found between ETA, TG and DTA results, X-ray diffraction patterns and surface area measurements of intermediate products of the thermal treatment

Keywords: DTA, ETA, hydrous ruthenia, hydrous ruthenia-titania, RuO_2 , $(RuO_2)_{0.9}$–$(TiO_2)_{0.1}$, TG, X-ray diffraction

Introduction

Ruthenium oxide, RuO_2, is the main constituent of materials designed as catalysts for numerous reactions of great technological and environmental importance [1–4]. RuO_2 is also known as the corrosion resistant material possessing a metal-like conductivity and excellent thermal resistance characteristics [5–7]. In order to obtain materials of tailored properties it is necessary to have detailed knowledge about the microstructure development of the precursors during heating.

In this paper hydrous ruthenium oxide and Ti containing hydrous ruthenium oxide were used as precursors for preparation of RuO_2 and $(RuO_2)_{0.9}$–$(TiO_2)_{0.1}$. Emanation thermal analysis (ETA) [8, 9] was used in order to characterize microstructure changes of the precursors under in-situ conditions of their heating.

Experimental

Preparation of precursors

A reagent grade $RuCl_3 \cdot nH_2O$ (Furuya Metal) and $TiCl_4$ (Kanto Chemicals) were used as starting materials. Ruthenium chloride solution was prepared by dissolving

---

[*] Author for correspondence: fax: +4202 2094 0567, e-mail: bal@nri.cz

1418–2874/2000/ $ 5.00

Akadémiai Kiadó, Budapest
Kluwer Academic Publishers, Dordrecht

$RuCl_3 \cdot nH_2O$ in a 0.1M hydrochloric acid. For the preparation of hydrous ruthenia containing 10% of titania the solutions of Ti and Ru chlorides dissolved in the respective overall ratios were used. The solutions were added by drops to the 2M ammonia. The precipitates of obtained hydrous oxides were washed, filtered and dried at 120°C.

The samples for the ETA measurements were labelled by adsorption of the radionuclides of ^{228}Th and ^{224}Ra from acetone solution on the surface of the precipitates. After the labelling the acetone was evaporated at approximately 80°C. The specific activity of the labelled sample was 10^5 Bq per gram. Atoms of radon ^{220}Rn have been formed by the spontaneous α-decay of ^{228}Th and ^{224}Ra. The labelled samples were stored at least three weeks prior to the ETA measurements in dry conditions to allow the radioactive equilibrium between the ^{228}Th and ^{224}Ra nuclides to be established. The layer of the maximum depth of 100 nm was labelled by ^{224}Ra and ^{220}Rn recoiled atoms, whereas the remaining atoms of ^{228}Th were adsorbed on the sample surface, serving as a source of ^{224}Ra and ^{220}Rn.

Methods

Emanation thermal analysis (ETA) [8, 9]

The apparatus used for ETA measurements was constructed on the basis of Netzsch DTA 409 equipment. The heating rate of 5 K min^{-1} , the cooling rate of 2.5 K min^{-1}, and the argon flow rate of 50 ml min^{-1} were used. DTA and TG measurements were carried out in the same conditions using Netzsch STA 409 Equipment.

During an ETA measurement the sample in the amount of 0.05 g was placed into a corundum crucible which was situated in a furnace being overflowed by the constant flow of argon, which carried the radon released from the sample into the measuring chamber of radon radioactivity. ETA results are presented as temperature dependences of emanating rate, E (in relative units); $E=A_\alpha/A_\gamma$, where A_α is the α-radioactivity of radon released in unit time from the labelled sample, and A_γ is the total γ-radioactivity of the labelled sample, (where the radioactive equilibrium between ^{220}Rn and its daughters, including ^{208}Tl, has been established). The A_γ value 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. Because of different efficiencies of radioactivity counting by the detectors used, the parameter E is expressed in relative units.

X-ray diffraction patterns (XRD)

XRD were recorded with a Philips diffractometer using CuK_α, Ni-filtered radiation.

Surface area

Surface area was determined by B.E.T. method based on the nitrogen adsorption measurement using Coulter SA 3100 apparatus.

Results and discussion

RuO_2 precursor

ETA results of hydrous ruthenia used as a precursor for RuO_2, are presented in Fig. 1, curve 1.The initial sample was amorphous (for XRD pattern Fig. 2), surface area determined by B.E.T. was 204 $m^2 g^{-1}$.

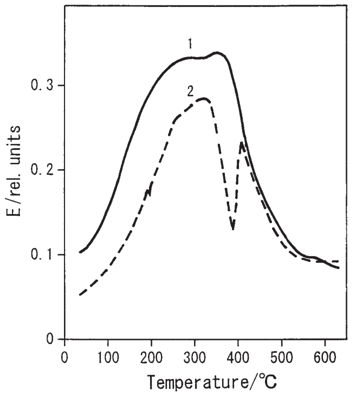

Fig. 1 Results of ETA of hydrous oxides as precursors for preparation of RuO_2 (curve 1) and $(RuO_2)_{0.9}$–$(TiO_2)_{0.1}$ (curve 2) during heating in argon, (Heating rate: 5 K min^{-1})

The increase of the emanating rate, *E,* observed on the ETA curve in the temperature range of 60–170°C reflected the liberation of water from the sample surface of the hydrous ruthenia. In this temperature interval, 34.6% of the water initially present in the sample was released. (For TG results Fig 3, curve 1.)

On further heating from 170 to 300°C, the emanating rate increased tending to a steady level which characterized the amorphous partially dehydrated RuO_2 precursor (for XRD see Fig. 2). From TG results in Fig. 3 it follows that the sample still contained 35% of the initial water amount.

On further heating the decrease of emanating rate was observed above 360°C (Fig. 1, curve 1) corresponding to the onset of the sample crystallization. The exothermal effect observed on the DTA curve (Fig. 3, curve 1′) confirmed the crystallization of RuO_2 in the bulk sample in the temperature range of 408–450°C. The comparison of ETA and DTA results (curves 1 Figs 1 and 3, respectively), is in support of our statement that the emanating rate decrease, starting at 380°C, indicated the onset of the crystallization process.

The decrease of emanating rate continued during the sample crystallization in the bulk. Surface area of the sample heated to 500°C decreased to 52 $m^2 g^{-1}$. As confirmed by XRD patterns (Fig. 2) a partially crystallized ruthenia was found in the sample heated to 500°C. During the heating, the water content in the sample continued to decrease. In the heating to 500°C the amount of 4% of initial water content was

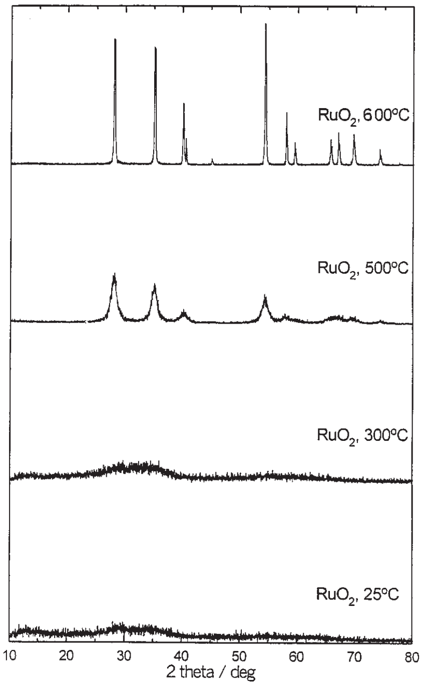

Fig. 2 X-ray diffraction patterns of hydrous ruthenia samples heated in argon to indicated temperatures

present in the sample. The well crystallized rutile structure of ruthenia resulted after heating to 600°C when no more water was found in the sample. This is in an agreement with the results by Málek *et al.* [10].

$(RuO_2)_{0.9}$–$(TiO_2)_{0.1}$ *precursor*

The initial sample was amorphous (for XRD pattern Fig. 4). Thermal behaviour of hydrous ruthenia-titania used as the precursor for $(RuO_2)_{0.9}$ –$(TiO_2)_{0.1}$ preparation is characterized as follows.

The ETA curve (Fig. 1 curve 2) showed an increase of the emanating rate in the temperature range of 60–350°C indicating the water release from the sample, similarly as observed during heating of pure hydrous ruthenia. TG curve in Fig. 3 showed that in this temperature range, 82% of initially present water was released from the sample. In the temperature range of 350–480°C , the loss of the remaining 10% of water took place.

On the ETA curve (Fig. 1, curve 2), a decrease of emanating rate was observed above 360°C, characteristic of the annealing of sample surface prior to the crystallization of the bulk sample, which (according to the exothermal effect on the DTA curve in Fig. 3, curve 2′) took place in the temperature range of 460–480°C.

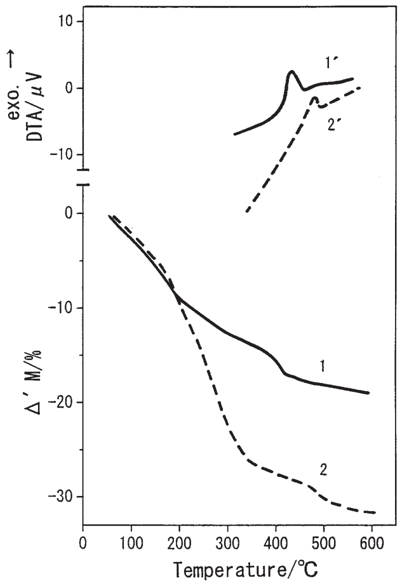

Fig. 3 TG and DTA results of hydrous oxides used as precursors for preparation of RuO_2 (curve 1) and $(RuO_2)_{0.9}$–$(TiO_2)_{0.1}$ (curve 2) during heating in argon. (Heating rate: 5 K min^{-1})

The abrupt increase of the emanating rate observed on the ETA curve in the range of 390–420°C (Fig. 1, curve 2) revealed that the crystallization of the sample was preceded by a significant change of the sample microstructure due to the formation of a metastable highly disordered intermediate product. The XRD pattern of the sample heated to 400°C (Fig. 4) corresponded to a poorly crystalline rutil structure. Consequently, we have supposed that the formation of a solid RuO_2–TiO_2 solution with the rutile structure took place in this temperature range. The decrease of the emanating rate was observed in the range of 425–500°C corresponding to the annealing of highly disordered sample leading to the crystallization.

Consequently, the temperature of 390°C indicated on the ETA curve by the decreased minimum value of emanating rate can be considered as the onset of sample crystallization. During crystallization the remaining 10% of initial water content was released from the sample. As demonstrated in Fig. 4 $(RuO_2)_{0.9}$–$(TiO_2)_{0.1}$ solid solution of a perfect rutile structure resulted after heating to 610°C.

In order to obtain more detailed picture of the microstructure changes taking place before and during the crystallization of the $(RuO_2)_{0.9}$–$(TiO_2)_{0.1}$, an additional set of ETA measurements were carried out under following experimental conditions:

– first run heating at the constant rate of 5°C min^{-1} from 20 to 400°C followed by sample cooling at the same rate to room temperature,

– recycled heating of the sample heated to 400°C from 20 to 610°C at the constant rate of 5°C min^{-1} followed by sample cooling at the same rate to room temperature.

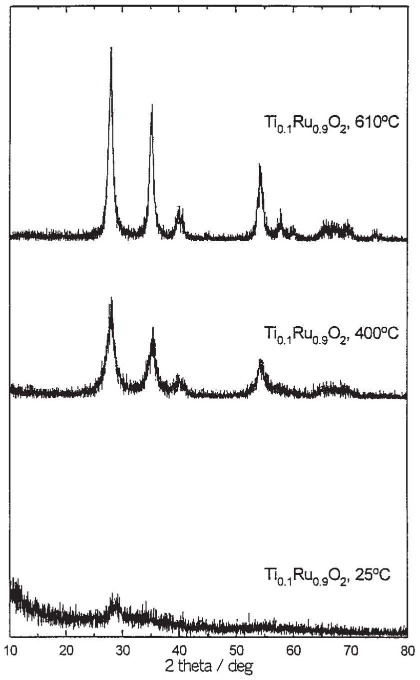

Fig. 4 X-ray diffraction patterns of Ti containing hydrous ruthenia samples as precursor for $(RuO_2)_{0.9}$–$(TiO_2)_{0.1}$ heated in argon to indicated temperatures

The ETA results are presented in Fig. 5. It should be pointed out that ETA results give an information about processes taking place in surface layers labelled with the radon atoms to the max. depth of 100 nm.

The increase of emanating rate *E* observed in the temperature range of 30–350°C (Fig. 5, curve 1) corresponded to the liberation of the free surface as a result of the water release from the sample. The slowing down of *E* indicated that parallel to the water release from the sample, an annealing of surface roughness took place. This phenomenon was already observed in Fig. 1, curve 2, demonstrating a good reproducibility of the ETA results.

The ETA curve measured on sample cooling from 400°C to room temperature confirmed that the microstructure changes were irreversible. ETA results measured during the second run heating of the sample heated to 400°C (curve 2 in Fig. 5) characterized thermal behaviour of the partially annealed sample containing 12% of the initially present water.

The formation of the intermediate metastable stage indicated on the ETA curve in the temperature range of 390–420°C (Fig. 1, curve 2) by the abrupt increase of the emanating rate was not observed during the recycled heating of the sample previously heated to 400°C.

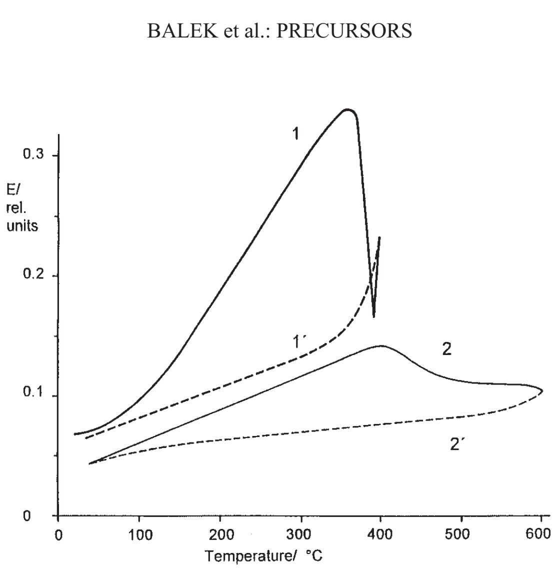

Fig. 5 Results of ETA measured during first and subsequent second run heating of precursors for $(RuO_2)_{0.9}$–$(TiO_2)_{0.1}$ heated in argon from 20 to 400°C and recycled in argon from 20 to 610°C: curves 1 and 1′ correspond to the first run heating of $(RuO_2)_{0.9}$–$(TiO_2)_{0.1}$ and the subsequent cooling in argon, resp., curves 2 and 2′ correspond to the recycled heating of the sample heated to 400°C and the subsequent cooling in argon, resp.

We can therefore suppose that the metastable intermediate product was annealed during the first run heat treatment to 400°C of the $(RuO_2)_{0.9}$–$(TiO_2)_{0.1}$ precursor. The decrease of the emanating rate observed during heating above 430°C corresponded to the bulk sample crystallization. The irreversible character of these changes was confirmed by the ETA cooling curves (Fig. 5, curves 1′ and 2′).

Conclusions

ETA made it possible to characterize microstructure changes taking place under in situ conditions during heating of precipitated hydrous oxides as precursors for preparation of RuO_2 and $(RuO_2)_{0.9}$–$(TiO_2)_{0.1}$. Temperature intervals of the microstructure changes determined from the ETA results are in a good agreement with the results of DTA, TG, XRD and surface area measurements. Optimal conditions for preparation of RuO_2 and $(RuO_2)_{0.9}$–$(TiO_2)_{0.1}$ with tailored properties by heating of corresponding hydrous oxides in argon were determined.

* * *

This work was carried out in the frame of the cross-over research project on underlying technology of nuclear energy promoted by the Science and Technology Agency of Japan and the bilateral co-operation in Science and Technology between the Czech Republic and Japan supported by the Ministry of Education of the Czech Republic. The financial support received by the Grant Agency of the Czech Republic (project Nr. 104/00/1046) has been highly appreciated. The authors are indebted to their co-workers for experimental assistance during the work, namely: Mr. A. Watanabe, NIRIM

Tsukuba, Japan, prepared the samples of precursors, Mrs. E. Klosová, Nuclear Research Institute, Ře (CZ) carried out the ETA measurements, Mrs. E. Vecerniková, Institute of Inorganic Chemistry, Ře (CZ) provided us with the results of DTA/TG measurement.

References

1 G. Blondeel, A. Hariman, G. Porter, D. Urwin and J. Kiwi, J. Phys. Chem., 87 (1983) 2629.
2 K. Ravindranathan Thampi, J. Kiwi and M. Graetzel, Nature, 327 (1987) 506.
3 P. Baltzer, R. S. Davidson, A. C. Tseung, M. Graetzel and J. Kiwi, J. Amer. Chem. Soc., 106 (1984) 1504.
4 T. Kawai and T. Sakata, Chem. Phys. Lett., 72 (1980) 87.
5 K. Kuramasu, S. Saito, K. Okano and Y. Takahashi, J. Ceram. Soc. Jap., l04 (1996) 840.
6 Y. E. Roginskaya, V. I. Bystrow and S. M. Shub, Zh. neorg. Khim. (in Russian), 22 (1977) 201.
7 T. Mitsuhashi and A. Watanabe, Proc. of 14th IUPAC Conference on Chemical Thermodynamics, Osaka, August 1996, p. 224.
8 V. Balek, Thermochim. Acta, 192 (l99l) 1.
9 V. Balek and J. Tölgyessy, in: Wilson and Wilson's Comprehensive Analytical Chemistry, Part XII. C, Elsevier Sci. Publishers, Amsterdam 1984, p. 304.
10 J. Málek, A. Watanabe and T. Mitsuhashi, Thermochim. Acta, 282/283 (1996) 131.