Journal of Thermal Analysis and Calorimetry, Vol. 92 (2008) 1, 155–160

EMANATION THERMAL ANALYSIS STUDY OF BRANNERITE CERAMICS FOR IMMOBILIZATION OF HAZARDOUS WASTE

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Brannerite based ceramics, designed as a matrix for immobilization of high level radioactive waste (HLW), was investigated from the viewpoint of microstructure changes and atomic transport properties caused by leaching of the ceramics at pH 2 and 11, respectively. Scanning electron microscopy (SEM) and emanation thermal analysis (ETA) techniques were used for this purpose. Surface morphology, microstructure changes and transport properties of both 'as-leached' and 'as-prepared' samples were compared and the effect of leaching on the thermal behavior of the ceramics samples heated in the temperature range from 20 to 1250°C was characterized. The mobility of radon in the brannerite ceramics was evaluated by mathematical modeling from ETA results. The thermal behavior of the non-leached brannerite ceramics sample and its natural analogue brannerite mineral was compared using the ETA.

Keywords: *brannerite ceramics, emanation thermal analysis, leaching, radon, SEM*

Introduction

Brannerite ceramics (Uranium titanate, UTi_2O_6) was proposed as a matrix for immobilization of high level radioactive waste (HLW) resulting from nuclear industry facilities [1–3]. The structure of the brannerite can be described considering TiO_6 and UO_6-octahedra [3, 4].

Brannerite ceramics was subjected to several studies dealing with their stability towards leaching in acidic and alkaline fluids [5], since the chemical stability and durability are crucial for its application. It was found that at 40°C the presence of KH-phthalate buffer (pH range of 2–6) had a little effect on the uranium release from synthetic brannerite. In alkaline conditions of kalium bicarbonate (pH 11) the uranium release was increased and the dissolution of brannerite was enhanced. By increasing temperature to 90°C the dissolution of uranium at pH 2 was over 100 times higher than that of Ti and preferential release of uranium over titanium was observed. In alkaline conditions at 90°C, the dissolution of brannerite ceramics was congruent (no preferential release) [5].

In the present study the non-leached and leached brannerite ceramics were characterized by emanation thermal analysis (ETA) and scanning electron microscopy (SEM) in order to evaluate the effect of leaching on properties like surface morphology, microstructure changes and atomic transport properties of the ceramics [6, 7]. In ETA radon atoms were used as microstructure probe and as a tracer to test the ceramics permeability for species of a comparable size to radon atoms (size 0.38 nm) e.g. water molecules. The behavior of the ceramic matrices in simulated repository conditions can be predicted by evaluation of the ETA results using mathematical modeling.

Experimental

Preparation of samples

Synthetic brannerite, UTi_2O_6, was prepared by the alkoxide/nitrate route [1]. Stoichiometric mixtures of UO_2 and TiO_2 (anatase) were dried and calcined in argon at 750°C for 1 h and subsequently wet-milled for 2 h and then dried. The sample contained mainly brannerite phase with minor rutile inclusions (~5% TiO_2) and trace amounts of uranium(IV) oxide (<0.1%) (Fig. 1). The powdered sample (75–150 μm) was prepared by crushing of the monolith and washing the powder with acetone to remove fines from the surface. Surface area of the sample determined by B.E.T. method, was 0.08 $m^2\ g^{-1}$. Static leaching tests were carried out by using 0.01 M solution of HNO_3 (pH 2) and 0.1 M solution of KOH (pH 11), respectively for 7 days at 90°C.

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1388–6150/$20.00

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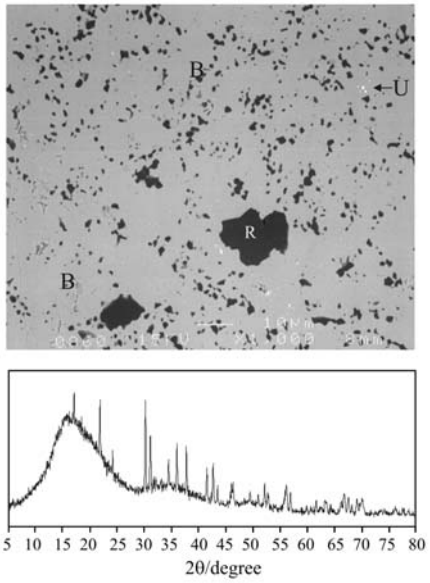

Fig. 1 a – Backscattered electron image of brannerite; B=brannerite, R=rutile, U=UO_2). b – XRD pattern of synthesized sample. All peaks correspond to brannerite

Methods of characterization

ETA [6, 7], based on the measurement of the release of inert gas (radon) atoms from solids, was used to characterize microstructure changes and transport properties of the samples under in situ conditions of heating [8].

In this study radon ^{220}Rn atoms were used as a structural probe. The samples were labeled using adsorption of ^{228}Th and ^{224}Ra from acetone solution and the acetone solvent was dried out after five minutes. The specific activity of the sample was 10^5 Bq g^{-1}. The labeled samples were stored in dry conditions. The ^{224}Ra and ^{220}Rn atoms were incorporated into the samples due to the recoil energy (85 keV atom^{-1}) gained by the radionuclides during α-spontaneous decay. The maximal penetration depths of the recoiled ^{224}Ra and ^{220}Rn atoms in the brannerite ceramics were 59.2 nm as calculated by Monte Carlo method by using TRIM code [9]. The theoretical density 6.35 g cm^{-3} was considered in the calculation.

The labeled samples (amount 0.1 g) were heated in the temperature range 20–1250°C at the rate of 6°C min^{-1} in the constant flow of argon (flow rate 50 mL min^{-1}), which took the radon released from the sample into the measuring chamber of radon radioactivity.

The modified Netzsch DTA-ETA Equipment, Model 404, was used for the measurement. The values of the radon release rate, E, are presented (in relative units) as $E=A_\alpha/A_{total}$, where A_α is α-radioactivity of radon released in unit time from the labeled sample, and A_{total} is the total γ-radioactivity of the labeled sample. The A_{total} 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.

SEM equipment by Philips, Type 3020 was used for the characterization of surface morphology of the 'as prepared' and 'as leached' samples.

Results and discussion

From SEM micrographs in Fig. 2 it followed that the surface morphology of the brannerite ceramics samples before leaching and after leaching at pH 2 was similar. Small surface alterations of sample leached at pH 11 can be ascribed to congruent dissolution of brannerite ceramics [5].

ETA was used to characterize differences in transport properties of the sample that may result due

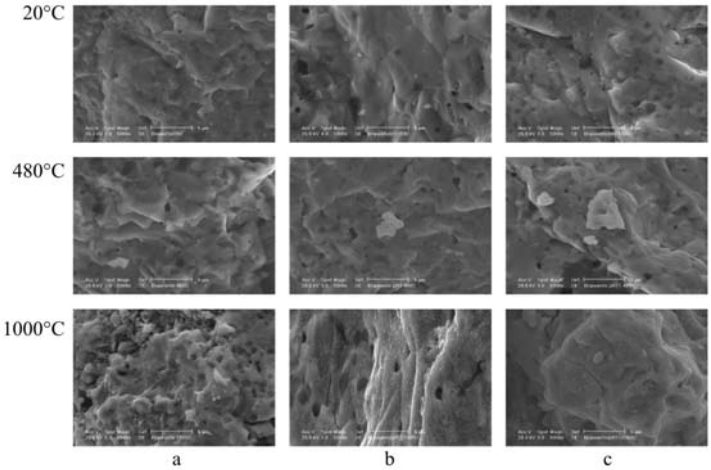

Fig. 2 SEM micrographs of brannerite ceramics samples: a – non-leached sample, b – sample leached at pH 2, c – sample leached at pH 11

to leaching of the brannerite ceramics with acidic and alkaline fluids. The ETA experimental data characterizing the brannerite ceramics on heating in argon in the temperature range from 20 to 1250°C are presented in Fig. 3. The increase of the radon release rate in the temperature range 20–250°C was due to the radon diffusion along surface and subsurface structure irregularities that served as radon diffusion paths. It was assumed that the radon diffusion in this temperature range was controlled by random 'single jump' mechanism. The leaching at pH 2 as well as at pH 11 influenced the transport properties of the sample characterized by the temperature dependence of the radon release rate $E(T)$. The E values in the temperature interval 20–250°C were relatively highest for the non-leached sample, while for the 'as leached' samples the E values were lower due to decreased amount of the radon diffusion paths. The break observed at about 250°C and the subsequent decrease of the radon release rate $E(T)$ in the range 250–500°C are due to the thermal annealing of the radon diffusion paths. The decrease of $E(T)$ was more significant for the non-leached sample. For the 'as leached' samples the decrease of $E(T)$ was less intense in accordance with the assumption, that a number of radon diffusion paths was reduced by leaching. The surface morphology of the non-leached and leached samples prepared after heating to 480 and 1000°C, respectively are presented in Fig. 2. No changes of the surface morphology were observed by SEM micrographs of the samples heated to 480°C.

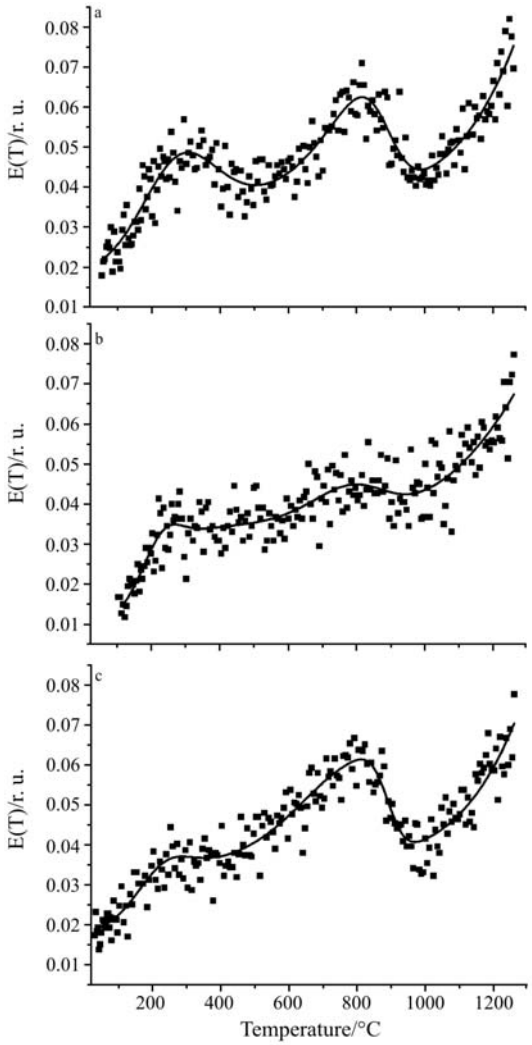

Fig. 3 ETA ■ – experimental results of the brannerite ceramics samples measured during heating from 50 to 1250°C with the — – model curves representing temperature dependencies of radon release rate $E(T)$.
a – non-leached sample, b – sample leached at pH 2, c – sample leached at pH 11

On further heating above 500°C the increase of the radon release rate $E(T)$, was supposedly due to the radon diffusion along grain boundaries. The break observed about at 800°C and the subsequent decrease of $E(T)$ was ascribed to the sintering of the ground solid particles brannerite ceramics. The SEM micrographs in Fig. 2 are in favor of this interpretation. In its turn, the enhanced radon release observed in the range 1000–1250°C was due to the radon diffusion by the bulk diffusion mechanism in the sintered ceramics body.

Evaluation of the ETA experimental data

The experimental ETA data were evaluated by using the mathematical model [10]. It was supposed that the radon released from the labelled samples by: *i*) recoil energy of the radon atoms, E_R, *ii*) diffusion in open pores and *iii*) bulk diffusion in the solid. The total measured radon release rate, E_{TOTAL} can be written as

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

The second term of the Eq. (1) is a product of two functions: $E_D(T)$ characterizing the radon permeability along structure irregularities that served as radon diffusion paths, and $\Psi(T)$ characterizing the changes in the number of the radon diffusion paths.

The temperature dependence of the radon release obtained by the ETA was used for the evaluation of the transport properties and of microstructure development characterization of the samples on heating. Following equations were used to evaluate ETA data. Based on the mathematical model the radon release rate due to diffusion was expressed as

$$E_D(T)=A[F(T_0)-F(T)] \quad (2)$$

where $F(T)=1/[k_{D0}\exp(-Q_D/RT)+\lambda_{Rn}]$, $A=\lambda_{Ra}C_{Ra}$ is a coefficient of concentration transformation, $\lambda_{Ra}=2.2035\cdot10^{-6}$ s^{-1}, C_{Ra} is equilibrium concentration of ^{224}Ra, $\lambda_{Rn}=1.2464\cdot10^{-2}$ s^{-1} is the decay constant of ^{220}Rn, B is T_0 is the initial temperature of heating,

Table 1 Parameters of radon mobility in brannerite ceramics samples evaluated from ETA measurements on heating in argon

Sample	Radon mobility parameters					
	20–250°C		500–800°C		1000–1250°C	
	D_0/cm^2 s^{-1}	Q_D/kJ mol^{-1}	D_0/cm^2 s^{-1}	Q_D/kJ mol^{-1}	D_0/cm^2 s^{-1}	Q_D/kJ mol^{-1}
As-prepared	$2.2\cdot10^{-9}$	40	$6.2\cdot10^{-6}$	143	$1.3\cdot10^{-5}$	230
As-leached at pH 2	$2.4\cdot10^{-7}$	58	$1.5\cdot10^{-6}$	150	$1.2\cdot10^{-7}$	173
As-leached at pH 11	$4.5\cdot10^{-9}$	44	$7.0\cdot10^{-8}$	113	$2.4\cdot10^{-5}$	240

k_D – rate constant of radon diffusion, depending on temperature according to Arrhenius relationship,

$$k_D=k_{D0}\exp(-Q_D/RT) \quad (3)$$

where Q_D is activation energy of radon diffusion, R=8.314 J mol^{-1} K^{-1} is molar gas constant.

For the description of the changes in the number of the radon diffusion paths following temperature dependence was used:

$$\Psi(T)=1-\frac{\kappa}{2}\left(1+\mathrm{erf}\,\frac{1-T_m/T}{\Delta T\sqrt{2}/T}\right) \quad (4)$$

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 and κ is the parameter describing the contribution of the respective solid state process to the change in the number of the radon diffusion paths. The values of the radon diffusion parameters calculated from ETA are summarized in Table 1.

Effect of leaching on thermal behavior of brannerite ceramics

Figures 3a–c depicts the results of the mathematical modeling that describe the temperature dependences of the radon release rate $E(T)$ based on fitting with the ETA experimental data. The model curves are represented as full lines, the experimental ETA data are represented as full points. The model curves are compared in Fig. 4 were used to demonstrate the effect of leaching on the thermal behavior of brannerite ceramics.

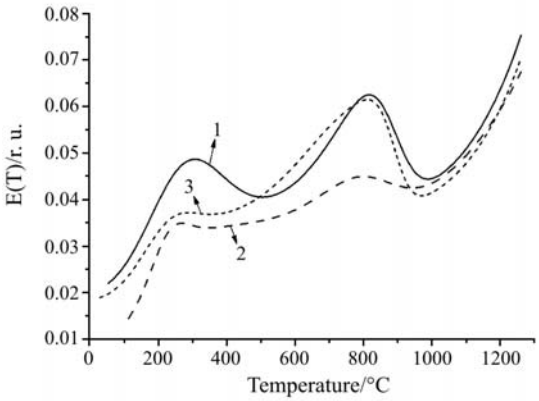

Fig. 4 Temperature dependences of the radon release rate, $E(T)$, obtained by mathematical modeling of ETA experimental data that characterized thermal behavior of brannerite ceramics. Curve 1 – non-leached sample, 2 – sample leached at pH 2, 3 – sample leached at pH 11

The experimental ETA data were evaluated by the mathematical model described in the previous paragraph, assuming 'single jump' random diffusion in the surface and subsurface of the sample (in the range 50–250°C), by diffusion via grain boundaries (500–800°C) and by bulk diffusion mechanisms (1000–1250°C), respectively. Table 1 summarizes values of radon diffusion parameters calculated from the ETA data in the respective temperature intervals. From the calculated activation energy Q_D it is obvious, that in the temperature ranges 250–500 and 800–950°C the diffusion of radon in the sample leached at pH 2 is the values of Q_D are increased, supposedly due to the decrease of the amount of radon diffusion paths in the sample. On the contrary, in the temperature interval 1000–1250°C, where bulk diffusion mechanisms is supposed, the activation energy Q_D has relatively smallest value for the sample leached at pH 2. This can be due to incongruent dissolution of brannerite, since at the temperature of 90°C the dissolution of uranium at pH 2 was over 100 times higher as compared to the dissolution of Ti, corresponding to the preferential release of uranium over titanium in the brannerite [5].

Moreover, from Fig. 4 it followed that the intensity of microstructure changes, characterized by the decrease of $E(T)$, in the temperature ranges 250–500 and 800–950°C, respectively, differed for the non-leached sample and the sample leached at the respective pH. The processes of the annealing of structure irregularities in the respective temperature ranges were assessed from the ETA results by using the model $\Psi(T)$ function described in Eq. (4) of the previous paragraph.

The calculated $\Psi(T)$ functions are shown in Fig. 5. On sample heating up to 500°C the $\Psi(T)$ function characterized the decrease of the number of radon diffusion paths due to annealing of surface and subsurface structure irregularities in the samples. From Fig. 5, curve 1 it followed that the most intense annealing the structure irregularities was observed

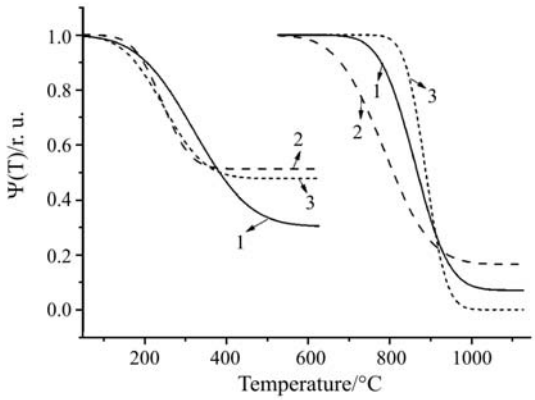

Fig. 5 Ψ(*T*) functions obtained by modeling to describe the annealing of structure irregularities.
Curve 1 – non-leached sample, 2 – sample leached at pH 2, 3 – sample leached at pH 11

with the non-leached ceramics. On the contrary, the relatively lowest intensity of the annealing was observed with the 'as leached' sample at pH 2 (Fig. 4, curve 2). From the decrease of $E(T)$ in the range 700–1000°C it followed that the annealing of grain boundaries due the sintering took place with different intensity as well. The temperature dependences of Ψ(*T*) functions in this temperature range (Fig. 5) made it possible to characterize the decrease of the number of radon diffusion paths due to sintering. From the intensity of the decrease it followed that the most intense sintering was observed with the sample leached at pH 11 (curve 3, Fig. 5). The relatively smaller intensity of the decrease was observed with the sample leached at pH 2 (curve 2, Fig. 5). This behavior is in agreement with the findings of Zhang *et al*. [5], that at pH 2 the brannerite ceramics was depleted in uranium and enriched in Ti. It can be therefore assumed that the surface of the Ti-enriched ceramics possessed higher thermal stability.

It was of interest to compare behavior of brannerite ceramics with its natural analogue. The ETA results of the non-leached brannerite ceramics sample and then brannerite mineral are presented in Fig. 6. It is obvious, that during the heating up to 800°C, the ETA curves of both samples are similar. The thermal behavior of both samples however differed due to the annealing of metamict mineral stage and its crystallization observed in the range 900–1050°C [11]. This process was not observed with the sample of brannerite ceramics, that was mainly crystalline as observed in Fig. 1. It is also to note, that at the final stages of the heating, where radon diffusion in the bulk material takes place, the ETA curves of the brannerite ceramics and its natural analogue coincide, indicating that the microstructure characteristics of both samples at high temperatures were similar. From curves 1a and 1b in Fig. 6 measured during cooling of the both samples preheated to 1050°C it followed that their transport properties differed. For the brannerite mineral based sample diffusion of radon was affected by the presence of impurity elements like Pb, Ca, Th, Y on the U-site and Si, Al or Fe on the Ti-site [12].

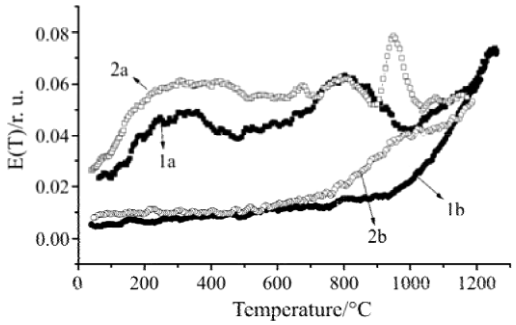

Fig. 6 Temperature dependences of radon release rate $E(T)$ of curve 1 – non-leached brannerite ceramics and
2 – brannerite mineral obtained during argon • Curve 1b – heating and curve 2b – subsequent cooling

Conclusions

The ETA brought about additional information about the thermal behavior of brannerite ceramics and characterized the effect of leaching on transport properties of the ceramics samples during heating from 30 up to 1250°C. From the evaluation of the ETA results it followed that the intensity of thermal annealing of microstructure irregularities depended on leaching conditions. It can be supposed that in the brannerite ceramics leached in acidic media (pH 2) the number of structure irregularities that served as radon diffusion paths decreased and considerably influenced the transport properties and microstructure development of the ceramics samples on heating. Radon atoms served in this study as diffusion structural probe and as a tracer of the samples permeability in their subsurface up to approximately 60 nm.

Acknowledgements

This work was supported in part by Ministry of Education of Czech Republic (projects ME-896 and LA-292) and the Academy of Sciences of the Czech Republic (Project AV0Z403005). The cooperation with the Australian Nuclear Science and Technology Organization was carried out in the frame of the IAEA Coordinate Research Programme under Research Agreement No. CZR-10,646.

References

1 A. E. Ringwood, S. E. Kesson, K. D. Reeve, D. M. Levins and E. J. Ramm, Radioactive Waste Forms for the Future, W. Lutze and R. C. Ewing, Eds, 1988, p. 233.
2 B. B. Ebbinghaus, R. A. Van Konynenburg, F. J. Ryerson, E. R. Vance, M. W. A. Stewart, A. Jostsons, J. S. Allender, T. Rankin and J. Congdon, Ceramic Formulation for the Immobilization of Plutonium,Waste Management 98 (CDROM), Tucson, AZ, USA, 5 March, 1998.
3 K. B. Helean, A. Navrotsky, G. R. Lumpkin, M. Colella, J. Lian, C. R. Ewing, B. Ebbinghaus and J. G. Catalano, J. Nucl. Mater., 320 (2003) 231.
4 J. Lian, L. Wang, G. R. Lumpkin and R. C. Ewing, Heavy ion irradiation of brannerite-type ceramics, Materials Research Society Symposia Proceedings, 650 (2001) R3.17.1-6.
5 Y. Zhang, B. S. Thomas, G. R. Lumpkin, M. Blackford, Z. Zhang, M. Colella and Z. Aly, J. Nucl. Mater., 321 (2003) 1.
6 V. Balek and J. Tölgyessy, Wilson and Wilson's Comprehensive Analytical Chemistry, Part XIIC, Elsevier Sci. Publ., (1984), pp. 43–71.
7 V. Balek, Thermochim. Acta, 192 (1991) 1.
8 V. Balek, J. Šubrt, T. Mitsuhashi, I. N. Beckman and K. Györyová, J. Therm. Anal. Cal., 67 (2002) 15.
9 J. F. Ziegler and J. P. Biersack, The Stopping and Range of Ions in Solids, Pergamon Press, New York 1985.
10 I. N. Beckman and V. Balek, J. Therm. Anal. Cal., 67 (2002) 49.
11 V. Balek, E. R. Vance, V. Zeleňák, Z. Malek and J. Šubrt, J. Therm. Anal. Cal., 88 (2007) 93.
12 R. O. Ifill, W. C. Cooper and A. H. Clark, CIM Bull., 89 (1996) 93.

DOI: 10.1007/s10973-007-8754-8