ANNEALING OF GLASS SURFACE ROUGHNESS AND SUBSURFACE IRREGULARITIES CHARACTERISED BY MEANS OF EMANATION THERMAL ANALYSIS

V. Balek[1], *T. Banba*[2], *I. N. Bekman*[3], *Z. Malek*[1] *andJ. Šubrt*[4]

[1]Nuclear Research Institute Rez pic, CZ-250 68 Rez, Czech Republic
[2]Department of Environmental Sciences, Japan Atomic Energy Research Institute, Tokai-mura Ibaraki-ken 319-1195, Japan
[3]Department of Radiochemistry, Lomonosow Moscow State University, 119899 Moscow GSP-3 Russia
[4]Institute of Inorganic Chemistry, Czech Academy of Sciences, CZ-25068 Řez, Czech Republic

Abstract

Emanation thermal analysis (ETA) was used for characterization of the thermal behaviour of a boro-silicate glass, designed for the vitrification of hazardous waste. Changes of release rate of radon atoms from the glass sample were measured continuously during heating in an air flow from 20 to 1000°C. Annealing of surface roughness, cracks and technological defects was indicated in the temperature range of 275-400°C by a decrease of radon release rate. A decrease of viscosity of the glass sample (in the proximity of the glass transition temperature, T_g) was indicated by the increase of the radon release rate starting at 430°C, whereas the decrease in the radon release rate starting, at 600°C, corresponded to the glass softening. Mathematical modelling was used for the description of the kinetics of radon release from the labelled glass sample and for the simulation of the ETA curve. Good agreement between the experimental data and the results of mathematical modelling of the ETA curve was found.

Keywords: emanation thermal analysis, surface roughness, thermal behaviour of borosilicate glass and cracks annealing, vitrified hazardous waste

Introduction

Chemical durability is important for the assessment of potential environmental risk connected with the disposal of vitrified hazardous waste products [1-5]. The characterization of the behaviour of glasses under simulated repository conditions requires a detailed knowledge about the glass surface and subsurface defects.

For the purpose of direct comparison of the results obtained from leach testing of the borosilicate glasses used for encapsulation of hazardous waste it is necessary to standardize test specimens and methods [1]. It is obvious that surface area and cracks in the glass sample may substantially influence the rate of the interaction of glass surfaces with liquids in early stages of the alteration.

The aim of this paper is to demonstrate emanation thermal analysis (ETA) [6, 7] as a tool for the characterization of borosilicate glass samples, especially the annealing of surface roughness and irregularities (cracks, micropores) of subsurface region.

Experimental

Method

Emanation thermal analysis [6, 7] consists in the measurement of the rate of radon release from samples previously labelled. Atoms of radon ^{220}Rn are formed by the spontaneous α-decay of ^{228}Th and ^{224}Ra according to the scheme:

$$^{228}\text{Th} \rightarrow ^{224}\text{Ra} \rightarrow ^{220}\text{Rn} \rightarrow$$

The thorium nuclide ^{228}Th used for labelling samples to be tested, has a suitable half-life (1.9 years) to serve as a quasi-permanent source of radon ^{220}Rn (half-life 55 s). The half-life of ^{220}Rn ensures that the steady state between ^{224}Ra and ^{220}Rn is established within several minutes, which makes it possible to investigate even rapid changes in solids and on their surfaces. Radon formed by the spontaneous α-decay of ^{228}Th and ^{224}Ra was incorporated into samples to a maximum depth of 100 run from the surface, due to the energy (85 keV/atom) of recoiled atoms.

The radon atoms can be directly released by recoil, or trapped at the lattice defects, vacancy clusters, grain boundaries and pores. The defects in the solids can serve both as traps and diffusion paths for radon. It follows from theories of diffusion and recoil processes [6], that the rate of radon release depends on the surface area of the solid-gas and solid-liquid interfaces, and on the radon diffusion parameters in the solid matrix.

The rate of radon release from the sample (called also the emanation release rate, E) can be expressed, in a simplified way, as follows:

$$E = E_{recoil} + E_{diff} = S\ [K_1 + K_2(D/\lambda)^{1/2}] \qquad (1)$$

where E_{recoil} is the part of the radon release due to recoil, E_{diff} is the diffusion part of the released radon, S is the surface area, K_1 is the temperature independent constant, proportional to the penetration depth of Rn recoiled atoms, D is the coefficient of radon diffusion in the sample, λ is the decay constant of Rn, and K_2 is a constant depending on temperature.

The release of radon atoms previously incorporated into the glass sample is measured, serving as a probe of microstructure. An increase in the radon release rate (E) indicates an opening of the structure and/or an increase of the surface area of the interfaces, whereas a decrease in E reflects a densification of the structure, closing of pores and/or a decrease in the surface area of the interfaces.

Preparation of samples for ETA and radioactivity measurements

The samples for ETA measurements were labelled using adsorption of radionuclides of ^{228}Th and ^{224}Ra on the sample surface from acetone solution. The specific activity of the sample was 10^5 Bq per gram. For a measurement, approximately 0.1 g of the sample was used. The labelled samples were stored for, at least three weeks in dry condition prior to the ETA measurements to allow the radioactive equilibrium between the ^{228}Th and ^{224}Ra nuclides to be established. The layer of 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.

The ETA results are presented as a temperature dependence of the radon release rate E (in relative units); $E = A_\alpha/A_\gamma$ where A_α is the alpha radioactivity of radon released in unit time from the labelled sample, and A_γ is the total gamma radioactivity of the labelled sample.

The $A\gamma$ 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.

Equipment for ETA

The ETA apparatus (Fig. 1 in [8]) consisted of the sample holder situated in a furnace, the detector of α-radioactivity, the counts-meter and the carrier gas system. The sample was subjected to the constant flow of the carrier gas (air: flow rate 50 ml min^1) which took the radon released from the sample into a chamber for measuring radon radioactivity.

Materials

The borosilicate glass containing simulated radioactive waste elements was prepared at JAERI by melting at 1150°C for 2 h. Subsequently the glass was poured into a graphite mold, held at 600°C for 2 h and then slowly cooled to room temperature. The glass sample was ground. Similarly to the requirements of corrosion tests of simulated nuclear waste glasses, a selected fraction (0.065-0.35 mm grain size) was used as the sample to be labelled for ETA measurements. The chemical composition of the borosilicate glass containing radioactive waste simulants is given in Table 1.

Mathematical modelling

The aims of the mathematical modelling were to obtain the temperature dependence of the radon release rate from the glass sample, and to demonstrate the ability of emanation thermal analysis to reflect processes taking place during heating of a real glass sample.

Table 1. Chemical composition of borosilicate glass and radioactive waste simulant

Constituent	Content [wt%]	Constituent	Content [wt%]
Glass components		CdO	0.03
SiO_2	45.1	SnO_2	0.02
B_2O_3	13.90	Sb_2O_3	0.01
Li_2O	2.00	TeO_2	0.23
Na_2O	9.79	Pr_6O_{11}	0.49
Al_2O_3	4.89	Nd_2O_3	1.65
CaO	4.00	Sm_2O_3	0.32
ZnO	2.47	Eu_2O_3	0.06
Waste simulants		Gd_2O_3	0.04
Rb_2O	0.12	SeO_2	0.02
SrO	0.34	RuO_2	0.80
Y_2O_3	0.20	Fe_2O_3	2.90
ZrO_2	2.64	NiO	0.40
$MoO3$	1.73	Cr_2O_3	0.50
MnO_2	0.26	P_2O_5	0.30
Cs_2O	0.98	Ru	0.12
BaO	0.62	Rh	0.15
La_2O_3	0.50	Pd	0.43
CeO_2	1.91		
Ag_2O	0.03	Total	100.00

Background considerations used in the modelling

We considered the release rate of radon to be the probability of the release of radon atoms, formed by radioactive α-decay of the parent nuclide. Two mechanisms of radon release, namely recoil and diffusion along two independent diffusion paths (channels) were considered. In the modelling we shall write Eq. (1) in the form:

$$E=A_0S(T)M(T) \qquad (2)$$

where A_o is a constant, $S(T)$ is the formula describing changes of the surface area upon sample heating, Γ is the temperature. An integral Gauss function was used to express $S(T)$ as an S-like curve, describing the decrease of the surface area from an upper limit value to a lower limit value. Hence, we can write:

$$S(T)=1-[B/2][1+erf(z)] \qquad (2a)$$

where $z=(T-T_m)/\sigma(2)^{1/2}$, $\sigma=\Delta T/3$; T_m is the temperature corresponding to the maximum rate of surface area change, ΔT is the temperature range in which the surface area change takes place, B is a parameter comprising the size and shape of the sample grains, the recoil path of radon atoms, the rate of heating, etc. The function $M(T)$ can be expressed as follows:

$$M(T)=C+Fexp(-Q/2\boldsymbol{R}T) \qquad (2b)$$

where C is a constant comprising the size and shape of the sample, etc., F is a constant comprising the pre-exponential factor of the temperature dependence of radon diffusion coefficient, Q is the activation energy of radon diffusion, $\boldsymbol{R}$ is the molar gas constant, T is the temperature.

Results and discussion

Results of experimental measurements

ETA results for the ground glass sample measured during constant rate heating are presented in Fig. 1 (as black points). The increase of the radon release rate in the temperature range from 40 to 300°C can be ascribed to radon diffusion in surface cracks and micropores in the subsurface region. The break observed on the curve at 300°C corresponds to onset of the annealing of the surface roughness, cracks and micropores [9] of the glass sample labelled with radon atoms up to the maximum depth of 100 nm from the surface. The increase of the radon release rate observed at 430°C indicates the enhanced diffusion mobility of radon in the glass sample. This effect may also be connected with the onset of a decrease in the glass viscosity. A DSC measurement, carried out to determine the glass transition point T_g, confirmed this interpretation. It should be mentioned here that 'condensed' defects, formed during previous glass cooling, begin to move above the glass transition temperature. A steep increase of oxygen self-diffusion was reported [10] in this temperature range for at least three different glass compositions.

The subsequent decrease of the radon release rate in the temperature range of 590-700°C corresponded to the glass softening (in this temperature range the glass is plastic). This decrease observed on the ETA curve corresponds to the characteristic behaviour of inorganic glasses in the plastic stage, observed at pre-melting temperatures [9-11].

No effects were observed on the ETA curve measured on cooling of the sample to room temperature. This is consistent with the general hypothesis that the above described processes were irreversible. The ETA curve measured during the re-cycled heating of the previously treated sample was identical with the previous ETA curve measured during cooling of the sample.

Results of mathematical modelling

From the ETA experimental results (Fig. 1) it follows that, during heating of the glass samples, two temperature ranges can be distinguished, namely 20-400 and 400-700°C. The annealing of surface roughness, cracks and other technological defects on sample heating, was reflected by the decrease of radon release rate in the temperature range 275-400°C. The sintering of the powdered glassy sample at higher temperatures was reflected in the temperature range 600-700°C by a decrease in the radon release rate. In order to characterize both low and high temperature processes taking place on sample heating, Eq. (2) was used in the modelling of ETA curves, using varying values of parameters. Generally, in the modelling of high temperature processes, higher values of activation energy for radon diffusion in the bulk glass sample were considered in comparison with those considered for the low temperature process, where radon release along defects in the sample surface and subsurface was assumed.

It was considered, in the modelling, that changes of the radon release rate, E, due annealing of surface roughness, cracks and other technological defects, are superimposed on the ETA curve characterizing the thermal behaviour of the annealed glass.

Consequently, the results of ETA of the glass sample, describing its thermal behaviour in the temperature range 20-1000°C, can be analysed as the sum:

$$E=E_1+E_2 \qquad (3)$$

where E_1 and E_2 correspond to the processes described by Eq.(2a), using various values of the parameters. In the temperature interval of 20-400°C:

$$E_1=A_{10}S1(T)\ M_1(T) \qquad (4)$$
$$S_1(T)=1-(B_1/2)(1+\mathrm{erf}(z_1)) \qquad (4a)$$
$$M_1(T)=C_1+F_1\ exp(-Q_1/2\boldsymbol{R}T) \qquad (4b)$$

In the temperature interval 400-700°C, we believe that the shape of the ETA curve is controlled by two processes: radon diffusion release and sintering of sample. Consequently:

$$E_2 = A_{20} S_2(T) M_2(T) \tag{5}$$
$$S_2(T) = 1 - (B_2/2)(1 + \mathrm{erf}(z_2)) \tag{5a}$$
$$M_2(T) = C_2 + F_2 \exp(-Q_2/2RT) \tag{5b}$$

The values of the parameters A_o, C, F, B, T_m and AT used in the expressions for E_x and E_2 – see Eqs (4a), (4b), (5a) and (5b) - are listed in Table 2.

Table 2 Parameters used in the modelling of ETA curves characterizing the thermal behaviour of borosilicate glass

Temperature range/°C	A_o	C	F	B	T_m/°C	ΔT	Q, kJ/mole
20-400	$1.2 \cdot 10^5$	10^{-18}	10^{-5}	1	340	125	7.52
400-70	$3.4 \cdot 10^7$	10^{-11}	$2.5 \cdot 10^{-8}$	0.92	650	75	37.63

It follows from the ETA experimental results presented in Fig. 1, that the annealing of the surface roughness, cracks and other technological defects was reflected by the decrease of radon release rate E in the temperature range 275-400°C. In the modelling the width of this interval was set as $Ar=125$°C, the value of the temperature at the maximum annealing rate was set as $r_m=340$°C and 100% annealing of existing cracks was considered. The value selected for the activation energy of radon diffusion in this low temperature range was $Q=7.5$ kJ mol.
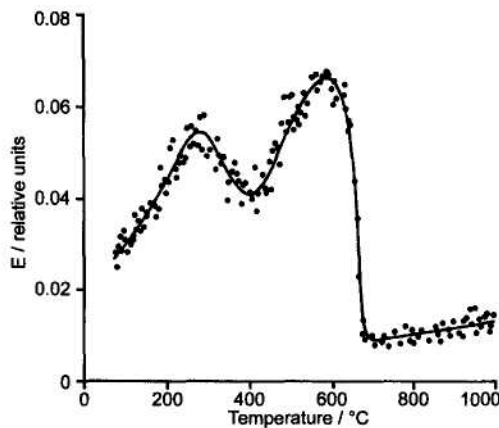

Fig. 1 Experimental ETA results (black points) of borosilicate glass sample compared with the results of mathematical modelling (full line)

The ETA high temperature effect observed on heating of the glass sample above 600°C corresponded to the sintering due to glass softening. A 92% compactization was assumed and the parameters were $T_m=650$°C, $\Delta T=75$°C. The value of the activation energy of radon diffusion in this temperature range was $Q=37.5$ kJ mole. A diffusion mechanism was assumed to be the process controlling the radon release from the glass sample on heating above 700°C.

Results of the mathematical modelling of the ETA curves, presented in Fig. 1 as the temperature dependence of the radon release rate, are in excellent agreement with the experimental ETA results. This agreement confirms the validity of the model and the parameters used in the mathematical modelling.

Conclusions

Temperature intervals corresponding to the annealing of surface roughness, micro-cracks and other defects, produced by manufacture and/or by subsequent treatment of glass samples were determined using ETA. The agreement of the experimental and model ETA curves demonstrated that ETA can be used in the characterization of the thermal behaviour of borosilicate glasses used for vitrification of

hazardous waste. In general, ETA can be recommended for characterization of the annealing of surfaces roughness, micro-cracks and other defects in surfaces and subsurfaces of glass samples.

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