

APPLICATION OF GAMMA ACTIVATION ANALYSIS FOR RESEARCH OF Cs AND I DIFFUSION INTO A GLASSCERAMIC MATRIX

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Nuclear reactions $^{133}\text{Cs}(\gamma,n)^{132}\text{Cs}$, $^{127}\text{I}(\gamma,n)^{126}\text{I}$ were utilized for research of Cs and I diffusion in glassceramic matrices. The glassceramic matrix was manufactured with the help of hot isostatic pressing at 910°C and pressure 100 MPa. Diffusivities of cesium and iodine in a grain and through interphase boundary at 600°C were equal 10^{-11} and $7.9 \cdot 10^{-9}$ sm^2/s , accordingly. The decrease of iodine diffusivity in a grain was observed at 750°C. A method of manufacture of glassceramic matrix for long-lived storage and nuclear-waste disposal ^{129}I is proposed.

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INTRODUCTION

The multibarrier protection of the biosphere against radionuclides [1] for nuclear-waste disposal and long-term storage of high-level waste (HLW) is carried out by means of: 1) a stable matrix, retaining radionuclides; 2) a multilayer engineering barrier; 3) a geologic medium of nuclear-waste disposal.

The geologic medium is a basic barrier for radionuclide diffusion at the time of the nuclear-waste disposal or long-term storage of high-level waste. The synthetic engineering barriers execute protective functions mainly during the period before the final conservation of a storehouse and during the initial period of a geologic storage. In the case of a temporal surface or near-surface storage of HLW, the basic load on isolation of the radioactive waste is realized by means of the engineer barrier.

The borosilicate glass has been considered as a reference industrial matrix for conditioning solutions of fission products (comprising more than thirty chemical elements) resulting from spent-fuel reprocessing operations.

Swelling clays can be used in the engineered barrier system of geologic repositories. Swelling clays placed between the excavated rock and the waste containers in a repository can mechanically fill the open volume, buffer the chemistry around container, and retard radionuclides migration.

The engineering barrier can be improved by means of a spent fuel immobilization. One of perspective methods of the HLW immobilization is to build the barriers made of glassceramic matrix. For prediction mass transfer in the HLW immobilisation during the nuclear-waste disposal, it is necessary to define their diffusive constants. Studies into a joint diffusion of elements with sharply distinguished properties (for example, alkaline and halogens elements) are in particular interest.

EXPERIMENTAL SET-UP AND METHODS

In the present article the diffusion of Cs and I in the glassceramic matrix (70% of granite +30% of kaolin),

manufactured by means of hot isostatic pressing (HIP) was investigated. The HIP-handling was carried out at 920°C and 100 MPa during 5 hours.

The glassceramic material is characterized by high density (relative density more than 0.99). It has satisfactory mechanical fastness, high corrosion stability, and radiation stability and can be applied as a material of the barrier layer for capsulation of the radioactive waste and HLW.

On a polished surface of the glassceramic sample the CsI tracer stratum was coated. The tracer exposed to a short-term heating within 10...15 minutes in gasostat for embodying contact with the sample. The diffusion was carried out in air during 300 hours at $T=600^\circ\text{C}$ and 750°C [2]. The samples were irradiated by bremsstrahlung radiation of an electron accelerator with energy 23 MeV during 3 days after removal of CsI tracer. The penetration profiles of Cs and I were measured by the method of removal layers. The activity of the stratum removed was measured with a Ge(Li)-detector by registering the isotope radiation with energy 668 keV and 388 keV from the reactions $^{133}\text{Cs}(\gamma,n)^{132}\text{Cs}$, $^{127}\text{I}(\gamma,n)^{126}\text{I}$.

RESULTS AND DISCUSSION

The obtained profiles of Cs and I are shown in Fig.1, 2. The full curves are obtained (for Cs and I at $T = 600^\circ\text{C}$, for Cs at $T = 750^\circ\text{C}$) using the least-squares procedure for the diffusion expression [3, 4]. The characteristic dependence of Cs and I isotopes' densities versus the sample depth is observed. The Cs diffusion realize in a grain (0...120 μm for $T=600^\circ\text{C}$, 0...250 μm for $T=750^\circ\text{C}$) and in crystal boundaries (more 250 μm).

Calculation of diffusion element in the matrix is carried out by the expression [4]:

$$\frac{\bar{c}(y)}{C_0} = \operatorname{erfc}\left(\frac{\eta}{2}\right) + \frac{\eta \sqrt{D_{ma}t}}{b\pi} \times \quad (1)$$

$$\times \int_1^\infty \frac{d\sigma}{\sigma^{3/2}} \exp\left(-\frac{\eta^2}{4\sigma}\right) \left\{ e^{-X^2} - \sqrt{\pi} * X * \operatorname{erfc}(X) \right\}$$

$$X = (\sigma-1)/2 \cdot \beta, D_{ma} = D_m / (1 + \rho_m \cdot K_d / \epsilon_m), \quad (2)$$

$$D_{fa} = D_{fa} / (\epsilon_m + \rho_m K_d), \quad (3)$$

$$\eta = \frac{y}{\sqrt{D_{ma}t}}, \beta = \frac{\Delta}{\sqrt{D_{ma}t}}, \Delta = \frac{aD_{fa}}{D_{ma}}, \quad (4)$$

where a is a half-width of a fissure, b – a half-interval, C_0 – initial tracer concentration of solution, D_f – fissure diffusion coefficient, D_{fa} – fissure apparent diffusion coefficient, D_{ma} – apparent diffusion coefficient in pore water of matrix, K_d – adsorption coefficient, ϵ_m – the matrix porosity, ρ_m – the matrix density, y – distance from the specimen surface in the direction of depth.

The first term on the right-hand side of the eq.(1) represents the direct diffusion into grains and is a function of y only. The second term represents the contribution of the diffusion through the fissure.

Diffusion coefficient is determined by means of minimization function [5]:

$$F = (\sum (y_{th} - y_{exp})^2) / (k-s), \quad (5)$$

where y_{th} , y_{exp} – theoretical and experimental values the reaction yield, accordingly, k – the measurements' number, s – the number of connections (number of degrees of distribution). The minimal function values were realized at $b=50 \mu\text{m}$ (radius of the grain).

The Cs and I diffusivities in the grains and through grain borders are equal to 10^{-11} and $7.9 \cdot 10^{-9} \text{sm}^2/\text{s}$ at $T=600^\circ\text{C}$, accordingly. An essential difference in the iodine profiles is visible at $T=600^\circ\text{C}$ and 750°C . At $T=750^\circ\text{C}$ the maximal iodine density value is observed at $200 \mu\text{m}$. For Cs at the same temperature the smooth lowering of the density is observed.

It is known that due to the Coulomb attraction a polyvalent cation together with cationic vacancy forms a complex cluster «admixture–cationic vacancy». At presence of such complexes the diffusivities of the cations D_+ and anions D_- are equal [6]:

$$D_+ = 4 \cdot a^2 \cdot f \cdot v_o \cdot \exp((S_{m+})/k) \cdot \exp((-H_{m+})/k \cdot T), \quad (6)$$

$$D_- = (4 \cdot a^2 \cdot f \cdot v_o / c) \cdot \exp((S_{m-})/k) \cdot \exp((-H_{m-})/k \cdot T), \quad (7)$$

where v_o is the effective vibration frequency of an ion being near the equilibrium position (is supposed identical to the anionic and cationic vacancies), f – the correlation factor, and a – distance between the anion and cation, c – isovalent atom density, S_{m+} , H_{m+} – entropy and enthalpy of migration of the cations, S_{m-} , H_{m-} – entropy and enthalpy of migration of the anions, k – the Boltzmann constant, T – temperature. It is apparent that the anion diffusivity is inversely proportional to the isovalent atom density.

Generally, the glassceramics obtained consists of feldspar ($\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2$), mullite ($2\text{SiO}_2 \cdot 3\text{Al}_2\text{O}_3$), glass, and other minerals and is characterized by the presence of the cations of different valence. The expressions 6, 7 adjusted describe the cation self-diffusion in a lattice such as NaCl at presence of isovalent admixtures. Therefore, in our case, these expressions can serve as estimation.

Note, the cations c^+ and c^- density agreed with Lida-jrd [6] is:

$$c^+ \cdot c^- = \exp(-G_s/k \cdot T), \quad (8)$$

where G_s is Gibbs free energy of the Schottky couple formation. Therefore, the cesium diffusion increases and iodine diffusion decreases over a period of time.

This fact exhibits the different character of these elements concentration dependence (Fig.1,2). The cation diffusion increases, whereas anion diffusion decreases for the cation density less than $10^{-2}\%$ (see, [3]).

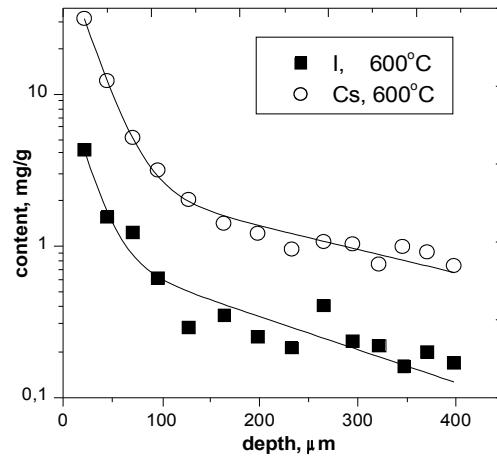


Fig.1. Penetration profiles of I and Cs in a glassceramic after diffusion during 300 hours at 600°C

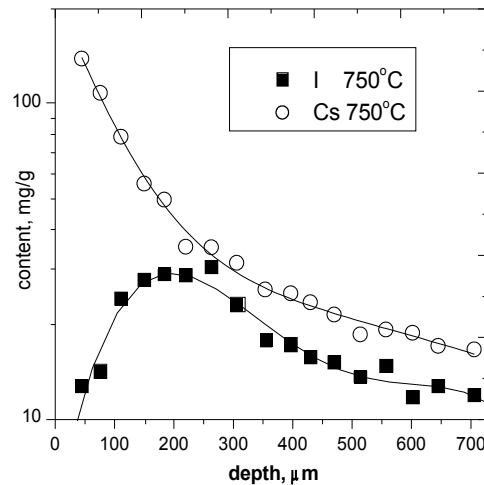


Fig.2. Penetration profiles of I and Cs in a glassceramic after diffusion during 300 hours at 750°C

It should be noted that the frequency factor change for Cs⁺ (atomic radius 1.69 Å) in comparison with other alkaline ions is more significant, than for I⁺ (atomic radius 2.16 Å) in comparison with other halogens.

The absence of inconvertible natural minerals containing I at an age of about 10⁸ years causes the problem of matrix synthesis the nuclear-waste disposal of ¹²⁹I. Apparently, our results obtained and presented here can be used in manufacturing of a prime glassceramic matrix with considerable density of ¹²⁹I (0.3% mass.). Stabilization of ¹²⁹I is realized by the alkaline elements.

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ПРИМЕНЕНИЕ ГАММА-АКТИВАЦИОННОГО АНАЛИЗА ДЛЯ ИССЛЕДОВАНИЯ ДИФФУЗИИ Cs И I В СТЕКЛОКЕРАМИЧЕСКОЙ МАТРИЦЕ

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Ядерные реакции ¹³³Cs(γ,n)¹³²Cs, ¹²⁷I(γ,n)¹²⁶I использовались для исследования диффузии Cs и I в стеклокерамической матрице. Стеклокерамическая матрица изготовлена при помощи газостатического прессования при 910°C и давлении 100 МПа. Коэффициенты диффузии цезия и йода в зерне и по границам зерен при 600°C составили 10⁻¹¹ и 7,9·10⁻⁹ см²/с, соответственно. Обнаружено уменьшение коэффициента диффузии йода в зерне при 750°C. Предложен способ создания матрицы для захоронения ¹²⁹I.

ЗАСТОСУВАННЯ ГАММА-АКТИВАЦІЙНОГО АНАЛІЗУ ДЛЯ ДОСЛІДЖЕННЯ ДИФУЗІЇ Cs ТА I В СКЛОКЕРАМІЧНІЙ МАТРИЦІ

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Ядерні реакції ¹³³Cs(γ,n)¹³²Cs, ¹²⁷I(γ,n)¹²⁶I використовувалися для дослідження дифузії Cs та I у склокерамічній матриці. Склокерамічна матриця виготовлена за допомогою газостатичного пресування при 910°C і тиску 100 МПа. Коефіцієнти дифузії цезію і йоду в зерні і по границях зерен при 600°C склали 10⁻¹¹ та 7,9·10⁻⁹ см²/с, відповідно. Виявлено зменшення коефіцієнта дифузії йоду в зерні при 750°C. Запропоновано спосіб створення матриці для поховання ¹²⁹I.