THE IRRADIATION EFFECT ON STRUCTURE AND PHYSICAL-MECHANICAL PROPERTIES OF PROTECTIVE CORDIERITE AND CORDIERITE-ZIRCON CERAMICS FOR RADIOACTIVE WASTES IMMOLIZATION

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Research of irradiation effect on the structure and physical-mechanical properties of protective cordierite (Mg₂Al₂Si₄O₁₂) and cordierite-zircon ceramics (Mg₂Al₂Si₄O₁₈ + ZrSiO₄) for radioactive wastes (RAW) immobilization was carried out. The necessary γ-irradiation dose absorbed by ceramic container was determined by means of computer modeling. The ceramic container was produced from the cordierite or cordierite-zircon ceramics and cement matrix was obtained by solidification of liquid simulated radioactive wastes with activity 1 Ci/l on ¹³⁷Cs. Results shown that irradiation dose 1MGy does not effect on investigated ceramic material properties degradation.

INTRODUCTION

A great number of radioactive wastes of the high, average and low specific activity are produced during Atomic Power Station (APS) exploitation process. On average, from 0.15 to 0.35 m³ liquid and from 0.1 to 0.3 m³ hard RAW on 1 MW of electric power are formed for a year depending on power and type of the reactor [1].

A common approach to localization of the RAW is the principle of creation of system of protective engineering barriers. The concept of an environment protection is a basis of the complex approach at the creation of multi-barrier system of RAW isolation with using mineral-matrix and barrier materials. The basic requirements for reliable immobilization of the radioactive waste in the engineering barrier are corrosion and radiation resistance of a container material.

Research on development of processes of ceramic and glass ceramic materials producing for immobilization of radioactive wastes are traditionally carried out in NSC “Kharkov Institute of Physics and Technology” [2–4].

One of the most promising materials for container producing is the high density oxide ceramics on the basis of (Mg₂Al₂Si₄O₁₈). Cordierite materials possess good mechanical properties, have a high chemical resistance, resistance to thermal and thermal shock loads, a low thermal coefficient of linear expansion, etc. [5].

The substantial improvement of properties of ceramic based on cordierite is possible by introduction of different modifying additions. The most solid composites can be obtained in mixtures of cordierite with zircon [6–8].

Addition of zirconium dioxide at the synthesis of cordierite quartz-like structures is favorable for formation of zircon ZrSiO₄, characterized by a relatively low values of thermal coefficient of linear expansion and physical-chemical properties closed to cordierite. Adding ZrO₂ to cordierite in an amount of 5...15 weight % allows to extend the interval of ceramics sintering.

An effective way to enhance the properties of cordierite ceramics is the introduction of modified adding of zirconium dioxide in the process of saturation of the cordierite mixture by aqueous solution of zirconium oxychloride (ZrOCl₂·H₂O) with the following heat treatment. As a result of the conducted before investigations [9], was shown that cordierite-zircon ceramics possess higher physical-mechanical properties compared to pure cordierite.

The aim of the study was effect of irradiation on the structure and physical-mechanical properties of cordierite-zircon ceramics.

MATERIALS AND METHODS

For cordierite ceramic preparing chemically pure oxides of Al₂O₃, MgO and SiO₂ were used in stoichiometric composition of cordierite. Zirconium oxychloride (ZrOCl₂·8H₂O) was used for cordierite-zircon ceramics formation as zirconium based addition.

Mixing of materials was made at the planetary mill “Pulverisette 6” (GFR) during 2 hours at a speed of 150 turns/min. Prepared mixture was heat treated in the muffle furnace Nabertherm P310 (GFR) at temperature 1000 °C during 1 hour. The heat-treated materials were grinded in a planetary mill at a speed of 200 turns/min for the obtaining of particles size < 5 μm, according to the parameters reported in reference [10]. The samples molding was performed by pressing method with a based pressure - 80 MPa.

Sintering of cordierite ceramic samples from oxide mixture was made at a temperature of 1400 °C during one hour. An open porosity and relative density were evaluated by standard methods according to GOST 473.4-81.

Mechanical strength of ceramic samples was measured by the of diametrical compression method [11].

For determination of heat-resistance the standard of EN 820-3:2004 was used. The heat-resistance was characterized by the temperatures drop ΔT, at which cracks appear in samples.

Phase composition of materials after heat treatment was investigated by means of X-ray analysis method (DRON – 1.5; Cu Kα-radiation with a nickel filter).

Analysis of the ceramic samples microstructure was made by scanning electron microscopy method (JEM-7001 F).
Simulation irradiation of samples was performed on a linear electron accelerator KUT-1 by braking irradiation of $\gamma$-quanta energy $\sim 5$ MeV ($E_{\text{max}} = 10$ MeV) up to a maximum dose of 1 MGY.

The estimation of an absorbed dose, collected by cordierite-zircon container with a matrix solidified during cementation of liquid RAW process, was made by the universal package Geant 4 for estimation of ionizing radiations interaction with the matter [12]. The calculation is based on suggestion, that a cement matrix possesses specific activity 1 Ci/l on 137Cs, which is a basic contribution to the dose of radiation, absorbed by a ceramic matrix. The dose range was corresponded to a dose accumulation in matrix up to decrease mechanical strength of the radiation-exposed cordierite samples during the terms of material storage with the reducing of initial activity approximately in 100 times. Element composition of cordierite and cement, density of cement matrix of 2.24 g/cm$^3$ [13, 14] were taken into account in the calculations. The density of cordierite ceramic samples was equal 2.8 g/cm$^3$ corresponded to the average density of the ceramic samples according to GOST 473.4-81.

RESULTS AND DISCUSSIONS

As an example of standard metallic barrel of 200 l volume was used for the calculation of an absorbed dose produced for 150 years of exploitation of the cordierite container with the cemented radio-active wastes of the initial activity 1 Ci/l on 137Cs. The geometrical model of the ceramic container and his sizes is presented on a Fig. 1.

According to preliminary estimation of activity of $10^{-3}$ Ci/l the cement matrix made from cordierite with the wall thickness of 10 cm can accumulated up to 1.2 kGY (on 137Cs) during the first year of exploitation. Furthermore, the rate of an accumulation of $\gamma$-radiation absorbed dose is significantly decreased with reducing of the caesium activity [14, 15].

Fig. 1. The geometric model of ceramic container for the calculation of radiation absorbed dose after exploitation time of 300 years: 1 – cover; 2 – ceramic container, made from cordierite; 3 – cement matrix with initial activity 1 Ci/l on $^{137}$Cs

On Fig. 2 the calculated change of $\gamma$–radiation absorbed dose in a cement matrix and ceramics depending on time with reducing of $^{137}$Cs activity is presented. The absorbed dose in a cement matrix increase up to value of 1 MGY for half-value period radionuclide (30.17 years), and at the full activity decay (up to 150 years) for five indicated terms of time $< 1.8$ MGY. After 180 years of exploitation, an absorbed dose has not practically changed. Results demonstrate that for the cordierite container for RAW immobilization a border an absorbed dose is about 0.85 MGY after 50 years and about 1.0 MGY after 75 years of exploitation. Based on the simulation results the imitation irradiation of ceramic materials was made.

Fig. 2. An absorbed dose in cement matrix and ceramic container depending on time (cemented radio-active wastes with initial activity 1 Ci/l on $^{137}$Cs. Energy $\gamma$-quantum 0.662 MeV, half-value-period 30.17 years)

Samples made from cordierite and cordierite-zircon ceramics were used for radiation resistance tests.

Fig. 3.a shows the X-ray diffraction analysis of ceramics. The presence of the basic phase – cordierite ($\text{Mg}_2\text{Al}_5\text{Si}_3\text{O}_{18}$) was identified. The XRD analysis of cordierite–zircon ceramics is presented on Fig. 3.b. The presence of prevailing phase of cordierite ($\text{Mg}_2\text{Al}_5\text{Si}_3\text{O}_{18}$) and zircon ($\text{ZrSiO}_4$) formed by reactions of zirconium dioxides $\text{ZrO}_2$ and silicon $\text{SiO}_2$ and some amount of secondary undefined phases was observed.
Physical-mechanical properties of ceramic material samples before and after are γ-irradiation tests are presented in a table. According to table data, cordierite ceramic samples have the open porosity – 10...15%, relative density – 85%, tensile strength at a compression – 70...80 MPa, heat-resistance – 400 °C. The samples of cordierite-zircon ceramics possess higher parameters in comparison to cordierite samples: open porosity – 1...3%, relative density – 95%, tensile strength at a compression – 120 MPa, heat-resistance – 500 °C.

<table>
<thead>
<tr>
<th>Composition of ceramics</th>
<th>Open porosity, %</th>
<th>Relative density, %</th>
<th>Tensile strength at a compression, MPa</th>
<th>Heat-resistance, Δ T, °C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>before</td>
<td>after</td>
<td>before</td>
<td>after</td>
</tr>
<tr>
<td>Cordierite</td>
<td>10...15</td>
<td>12</td>
<td>85</td>
<td>85</td>
</tr>
<tr>
<td>Cordierite-zircon ceramics</td>
<td>1...3</td>
<td>3</td>
<td>≥95</td>
<td>95</td>
</tr>
</tbody>
</table>

The samples of cordierite-zircon and cordierite ceramics irradiated by dose 1 MGy have the same characteristics before and after irradiation process as presented in Table. Therefore, the irradiation dose up to 1 MGy did not lead to the degradation of physical-mechanical properties of ceramic materials.

The properties of ceramics are significantly determined by the structure. Scanning electron microscopy (SEM) analysis was made for obtained results explanation. SEM analysis of ceramics demonstrates the improvement of mechanical properties of ceramics due to dense fine-grained structure, presented mainly by cordierite and uniformly spaced zircon.

The microstructure of ceramic materials before and after γ-irradiation tests is presented in Fig. 4. The microstructure of the ceramic was formed by the cordierite crystals of prismatic form, with the main size of 2...3.5 μm, and crystals of zircon, with the main size of 0.5...1.5 μm and pores sizes of 0.5 μm. The structure of ceramics, both pure cordierite and cordierite with zircon was not changed after γ-irradiation according to SEM analysis. There was some increasing of ultra-disperse crystal phase of ZrSiO₄ in the cordierite-zircon ceramic after γ-irradiation process.
CONCLUSIONS

The calculation of the dose absorbed by ceramic container made from the cordierite with a cement matrix inside obtained by solidification of liquid radioactive wastes with activity 1Ci/l on $^{137}$Cs after 300 years of exploitation was presented in the study.

The irradiation simulation of the pure cordierite ceramic and ceramic composition (cordierite + zircon) by the braking $\gamma$-radiation up to maximal absorbed dose about 1MGy was made.

Results shown that irradiation doze 1 MGy did not effect on ceramic material properties degradation.

The results of electron microscopy analysis presented in the table demonstrated the improvement of the physical-mechanical properties of cordierite-zircon ceramic compared to pure cordierite.

The cordierite–zircon ceramics are perspective for application as protective material for RAW immobilization.

REFERENCES


ИССЛЕДОВАНИЕ ВЛИЯНИЯ ОБЛУЧЕНИЯ НА СТРУКТУРУ И ФИЗИКО-МЕХАНИЧЕСКИЕ СВОЙСТВА ЗАЩИТНОЙ КОРДИЕРИТОВОЙ И КОРДИЕРИТОЦИРКОНОВОЙ КЕРАМИКИ ДЛЯ ИЗОЛЯЦИИ РАО

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Проведены исследования влияния облучения на структуру и физико-механические свойства защитной кордиритовой (Mg₂Al₃Si₂O₁₈) и кордиритоцирконовой керамики (Mg₂Al₃Si₂O₁₈ + ZrSiO₄) для изоляции радиоактивных отходов (РАО). С использованием компьютерного моделирования определена необходимая поглощенная доза γ-облучения, набираемая керамическим корпусом (инженерным барьером), который выполнен из исследуемого материала и заполнен цементной матрицей, полученной отверждением жидких РАО с активностью 1 Ки/л по ¹³⁷Cs. Показано, что доза облучения 1 МГр не приводит к ухудшению свойств исследуемого керамического материала.

ДОСЛІЖЕННЯ ВПЛИВУ ОПРОМІНЕННЯ НА СТРУКТУРУ ТА ФІЗИКО-МЕХАНІЧНІ ВЛАСТИВОСТІ ЗАХИСНОЇ КОРДІЄРИТОВОЇ ТА КОРДІЄРИТОЦИРКОНОВОЇ КЕРАМІКИ ДЛЯ ІЗОЛЮЦІЇ РАО

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Проведені дослідження впливу опромінення на структуру та фізико-механічні властивості захисної кордиритової (Mg₂Al₃Si₂O₁₈) та кордиритоцирконової керамики (Mg₂Al₃Si₂O₁₈ + ZrSiO₄) для ізоляції РАВ. З використанням комп’ютерного моделювання встановлена необхідна поглинена доза γ-опромінення, що набирається керамічним корпусом (інженерним бар’єром), який виконаний з досліджуваного матеріалу і заповнений цементною матрицею, отримана отверженням рідких радіоактивних відходів активністю 1 Кіл/за ¹³⁷Cs. Показано, що доза опромінення 1 МГр не приводить до погіршення властивостей досліджуваного керамічного матеріалу.

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