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Letter to the Editors

Dysprosium titanate as an absorber material for control rods

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Abstract

Disprosium titanate is an attractive control rod material for the thermal neutron reactors. Its main advantages are: insignificant swelling, no out-gassing under neutron irradiation, rather high neutron efficiency, a high melting point (~1870°C), non-interaction with the cladding at temperatures above 1000°C, simple fabrication and easily reprocessed non-radioactive waste. It can be used in control rods as pellets and powder. The disprosium titanate control rods have worked off in the MIR reactor for 17 years, in VVER-1000 – for 4 years without any operating problems. After post-irradiation examinations this type of control rod having high lifetime was recommended for the VVER and RBMK. The paper presents the examination results of absorber element dummies containing dysprosium titanate, irradiated in the SM reactor to the neutron fluence of 3.4×10^{22} cm^{-2} ($E > 0.1$ MeV) and, also, the data on structure, thermal–physical properties of dysprosium titanate, efficiency of dysprosium titanate control rods.

1. Introduction

Boron carbide and boron steel are currently used in control rods of Russian power water reactors (VVER-1000, VVER-440, RBMK-1000, etc.). These absorber materials accumulate large radiation induced damages caused by (n,α)-reactions on ^{10}B isotopes, helium formation and swelling. The first failure of the rod cluster control assembly (RCCA) of VVER-1000 caused by B_4C swelling and cladding cracking was detected at the Novo-Voronezh nuclear power plant in 1993.

More than 60 ceramic absorber materials based on Dy, Eu, Sm, Gd, Hf, Cd, pure Hf and Hf alloys have been examined with the purpose to replace (n,α)-absorbers. The post-irradiation examinations demonstrated that lanthanoid oxides ($Ln_2O_3 \cdot MO_2$) with the fluorite structure have the best radiation damage resistance. Dysprosium titanate ($Dy_2O_3 \cdot TiO_2$) was selected for the VVER and RBMK control rods. The dysprosium titanate control rods have been in operation for 17 years in the MIR reactor and did not have any problems. Since 1995 dysprosium titanate has been used in the VVER-1000 RCCAs [1].

2. Material under testing and specimens characteristics

Composition: Dy_2O_3–78.1%; TiO_2–19.7%; Mo–1.8%.

Dysprosium titanate (Dy_2TiO_5) has been synthesised according to the following technology:

- batch mixing (Dy_2O_3, TiO_2, Mo);
- blending;
- drying, batch palletising;
- two-stage sintering;
- crushing, sieving;
- sintering.

The phase composition was a fluorite (2 structures) and traces of hexagonal phase.

The absorber element dummies of two types have been examined: with powder and pellet absorber. The dummies were the austenitic steel claddings (06Cr18Ni10Ti) of 9.6 mm in diameter and 0.60-mm thick. They were filled with dysprosium titanate as a powder (or pellets) and sealed by the plugs on both ends by the argon-arc welding. The dummy length was about 100 mm. These samples have been manufactured at the Moscow Polymetal Plant.

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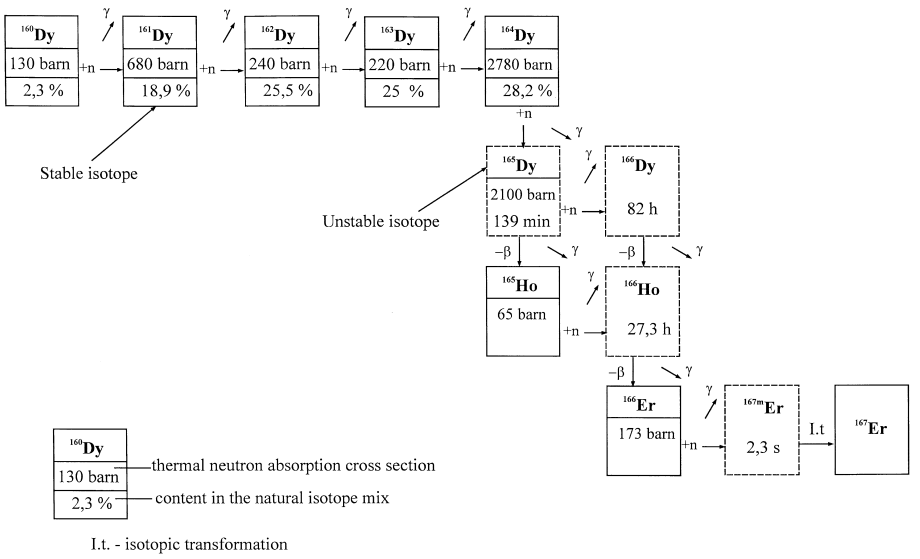

Fig. 1. Transmutations of dysprosium titanate under irradiation.

3. Dysprosium titanate structure

The natural dysprosium consists of five stable isotopes having rather high thermal neutron-absorption cross-sections (Fig. 1). The decay products are Ho and Er. All the radionuclides have a low gamma activity and a short half-life period [2].

In the Dy_2O_3–TiO_2 system two compounds can be formed in accordance with the equilibrium phase diagram (Fig. 2) [3]. They are dysprosium dititanate ($Dy_2Ti_2O_7$) and dysprosium titanate (Dy_2TiO_5) having the polymorphs. The latter is crystallized into the orthorhombic lattice at the low temperatures. With temperature increase, it transforms into hexagonal lattice

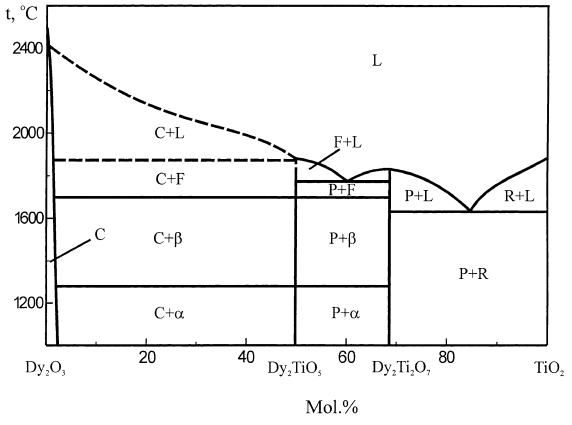

Fig. 2. The phase diagram of Dy_2O_3–TiO_2: C – solid solution based on Dy_2O_3, L – liquid, α – orthorhombic phase, β – hexagonal one, F – cubic solid solution with the fluorite structure, P–$Dy_2Ti_2O_7$ (pyrochlore), R–TiO_2 (rutile).

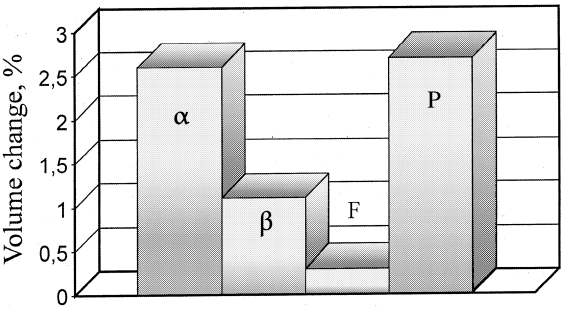

Fig. 3. The volume change of the phase component of dysprosium titanate after irradiation ($F = 1 \times 10^{22}$ cm^{-2}, $t = 250$–450°C): α – rhombic phase; β – hexagonal one; F – fluorite; P – pyrochlore.

(~1350°C) and then into the fluorite one (~1680°C). The melting temperature of $Dy_2 \cdot TiO_5$ is 1870°C. The different crystal structures of dysprosium titanate can be obtained by changing heating and cooling conditions. The fluorite structure has the smaller swelling under irradiation and is more promising absorber material for control rods (Fig. 3). Under irradiation the pyrochlore structure can be transformed into the fluorite.

4. Thermal–physical properties

Some thermal–physical properties of Dy_2TiO_5 are presented in Figs. 4–6 [4,5]. At 350°C the heat capacity (C_p), the thermal conductivity (λ) of powder with density of ($\rho = 4.8$ g/cm^3), the thermal expansion coefficient (α) of the pellets with density of $\rho = 6.2$ g/cm^3 were

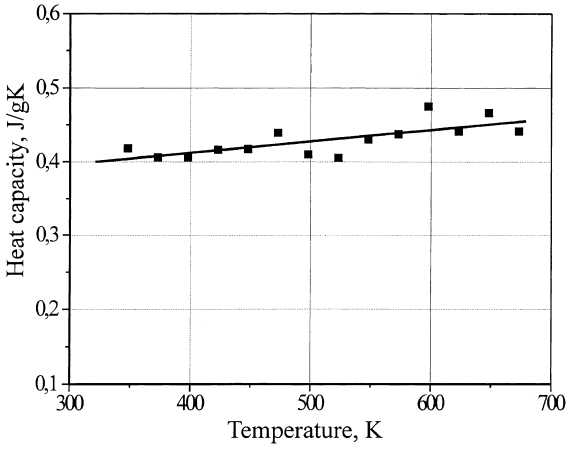

Fig. 4. Temperature dependence of $Dy_2O_3 \cdot TiO_2$ heat capacity (C_p).

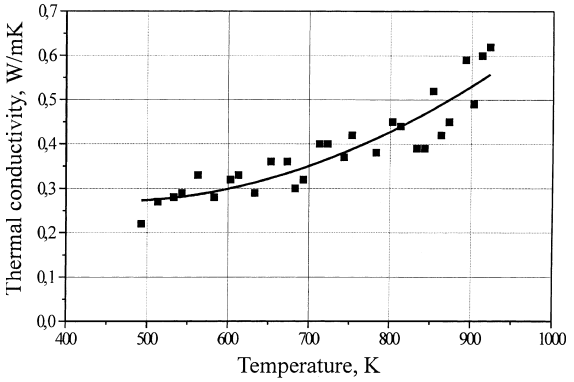

Fig. 5. Temperature dependence of $Dy_2O_3 \cdot TiO_2$ thermal conductivity (λ) ($\rho_{powder} = 4.8$ g/cm^3, $P_{He} = 0.1$ MPa).

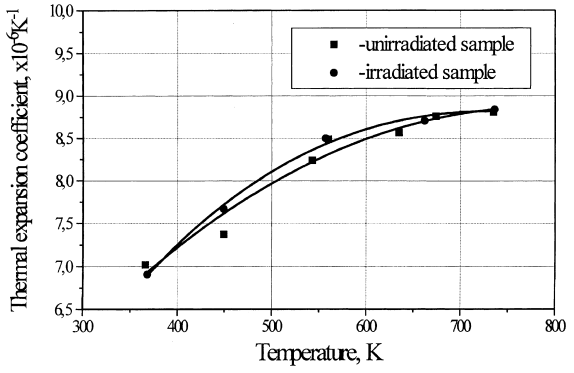

Fig. 6. Linear expansion coefficient (α) of $Dy_2O_3 \cdot TiO_2$ vs temperature ($\rho = 6.2$ g/cm^3).

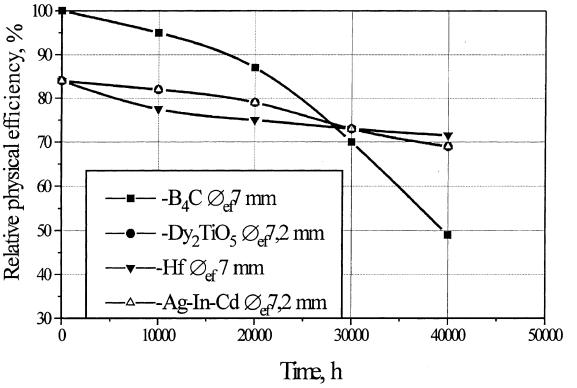

Fig. 7. Dependence of the absorber material efficiency under irradiation in the VVER-1000.

0.441 J/g K, 0.33 W/m K, $(8.52 \pm 0.15) \times 10^{-6}$ K^{-1}, respectively. Dysprosium titanate has a high chemical resistance. It does not interact with the austenitic steel cladding at 280–320°C for 146 000 h and at 1000°C for 1 h. The irradiation does not practically influence on the thermal conductivity and the thermal expansion coefficient. No irradiation effect on the compression strength of 100–130 MPa has been observed.

5. Efficiency

Dysprosium titanate has practically equal efficiency of neutron absorption with hafnium and 80%Ag–15%In–5%Cd alloy in the VVER-1000 core environment. At the beginning of operation the dysprosium titanate efficiency is 15% lower than boron carbide with the natural content of ^{10}B and ^{11}B isotopes (Fig. 7) [6]. The efficiency of $Dy_2O_3 \cdot TiO_2$ control rods decrease at a slower rate due to the daughter isotope chain having high neutron absorption values. After 4–5 years of operation it exceeds the efficiency of the B_4C control rods.

6. Radiation damage

Dysprosium titanate Dy_2TiO_5 ($Dy_2Ti_2O_7$) can be used in control rods as powder (density of 4–5 g/cm^3) or pellets (density of 6 g/cm^3 and more). Same results of dimension stability of Dy_2TiO_5 pellets and powder after irradiation by the fluence of 3.4×10^{22} cm^{-2} ($E > 0.1$ MeV) are given in Table 1. It is obvious that dysprosium titanate has a low swelling rate. The powder is not sintered and is freely emptied from the cladding, the crystal lattice volume was increased by 1.7% (Fig. 8).

Due to microcracking of material the pellet diameter, height and its volume increased by (0.5–0.7%), (0.2–0.7%), (1.2–2.3%), respectively (Fig. 9). The dysprosium

Table 1
Dimensional stability of $Dy_2O_3 \cdot TiO_2$

Test	Powder	Pellets
Visual inspection	Is poured empty, sintering is absent	(a) at $t = 345$–360°C, $\Delta t = (3$–$5)$°C/mm, $F_{max} = 3.4 \times 10^{22}$ cm^{-2} ($E > 0.1$ MeV). Pellets were not broken, cladding pressure was absent; (b) at $t = 150$–500°C, $\Delta t > 60$°C/mm, $F_{max} = 2.7 \times 10^{22}$ cm^{-2} ($E > 0.1$ MeV). Pellets were broken into fragments as a result of thermal stresses, the cladding pressure was absent.
Dimensional stability	–	At 345–360°C $\Delta d/d = (0.5$–$0.7\%)$, $\Delta H/H = (0.2$–$0.7\%)$, $\Delta V/V = (1.2$–$2.3\%)$.
X-ray diffraction analysis	$a = 5.1692 \pm 0.003$ Å $\Delta V/V = 1.7\%$	–

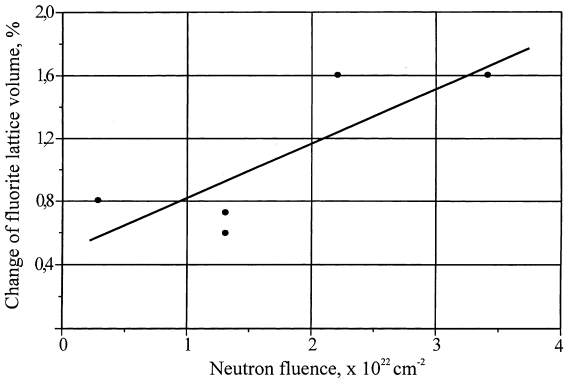

Fig. 8. Change of fluorite lattice volume of $Dy_2O_3 \cdot TiO_2$ on neutron fluence.

titanate pellets are cracked and fragmented into pieces of 1–5 mm at a temperature gradient of $\Delta T \geqslant 60$°/mm. This is a ceramic material characterized by brittleness and low plasticity. But it is not a great problem in powder (or pellets) form since the absorber does not interact with the cladding and does not strain it.

The interaction between $Dy_2O_3 \cdot TiO_2$ and the claddings 06Cr18Ni10Ti and EP-630U alloy (41–43% Cr, 1.0–1.5% Mo, 0.10–0.01% Ce, the rest-Ni) is completely absent under irradiation during 8160 h at 330–360°C. No interaction was observed between dysprosium titanate and 06Cr18Ni10Ti under irradiation during 28 800 efh in VVER-1000 conditions ($t = 320$–350°C, $F = 1.2 \times 10^{22}$ cm^{-2} ($E > 0.1$ MeV)).

The gamma dose rate of irradiated dysprosium titanate pellets was measured (Table 2). The samples have low induced γ-activity.

An important advantage of dysprosium titanate is the lack of gas release under irradiation and its good corrosion properties in water at 300°C.

7. Performance

The $Dy_2O_3 \cdot TiO_2$ full-scale control rods that have been in operation for 17 years in MIR ($F_{max} = 2.2 \times 10^{22}$ cm^{-2} ($E > 0.1$ MeV)), 4 years in the automatic control regime in VVER-1000 ($F = 1.2 \times 10^{22}$ cm^{-2} ($E > 0.1$ MeV)) and 2 years in Leningrad RBMK-1000 ($F = 0.6 \times 10^{21}$ cm^{-2} ($E > 0.1$ MeV)) have been subjected to post-irradiation examination. There were no remarks on their performance. All the control rods

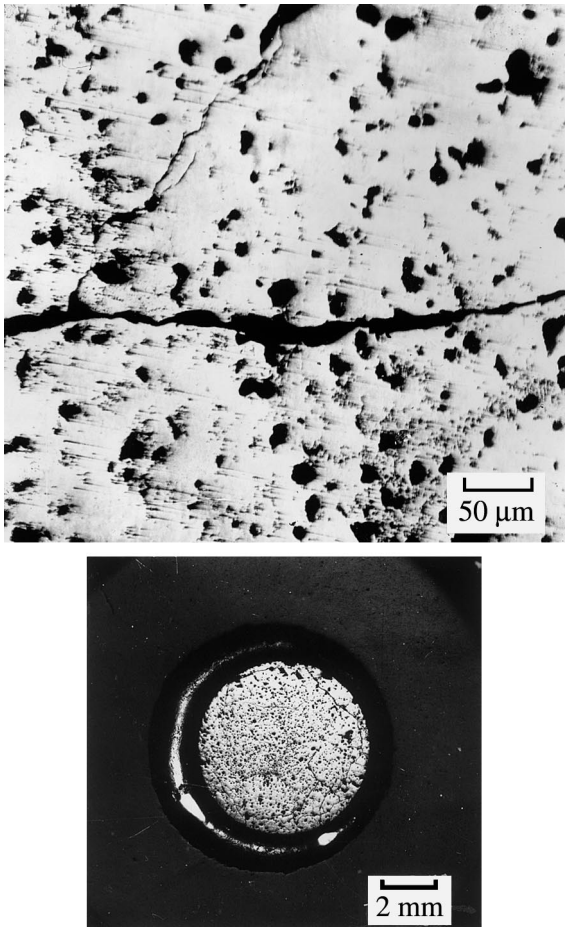

Fig. 9. Structure (top: microstructure; bottom: macrostructure) of Dy_2TiO_5 after irradiation ($F = 3.4 \times 10^{22}$ cm^{-2} ($E > 0.1$ MeV)) at 345–360°C.

Table 2
Exposure rate of $Dy_2O_3 \cdot TiO_2$

Sample	Fluence ($\times 10^{22}$ cm^{-2}) ($E > 0.1$ MeV)	Post irradiation period (days)	Distance (m)	Exposure rate (μR/s)
$Dy_2O_3 \cdot TiO_5$ pellets $m = 2.5$ g	0.9	380	0	200 ± 20
			0.35	100 ± 10
			0.8	15 ± 15

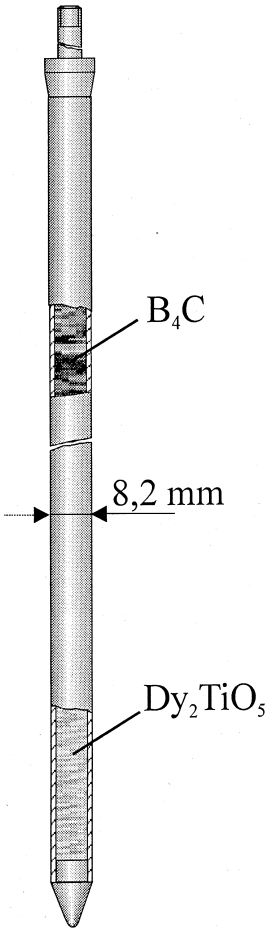

Fig. 10. Design of the B_4C and Dy_2TiO_5 combined absorber element.

saved the preserved shape, integrity and dimensions. The PIE showed that their lifetime characteristics are not degradated.

One of the basic criteria limiting the efficiency of control rods is the ultimate cladding strain limitation (not more than 0.5–0.7%). The higher deformation results in the cladding damage. This was proved experimentally, in particular during the examination of the B_4C control rods. When using $Dy_2O_3 \cdot TiO_2$ as an absorber core, no cladding deformation is observed. Therefore, the only factor limiting the lifetime of dysprosium titanate control rods will be loss of efficiency. Besides, there is an opportunity to develop combined control rods [7]. Dysprosium titanate will occupy the part with the highest radiation dose, and boron carbide, for example, will occupy the other part (Fig. 10). Such control rods are being fabricated for the VVER-1000 reactors. It is planned to use dysprosium titanate in the RBMK-1000 (1500) reactors.

8. Conclusion

Dysprosium titanate has high dimensional and structural stability. It does not practically swell and does not effect on the cladding under irradiation up to high damage doses that makes it possible to manufacture control rods having the high lifetime period. Currently cluster assemblies containing dysprosium titanate control rods are used in the VVER-1000 reactors.

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