DYSPROSIUM AND HAFNIUM BASE ABSORBERS FOR ADVANCED WWER CONTROL RODS

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Abstract

Disprosium titanate is an attractive control rod material for thermal neutron nuclear reactors such as WWER and RBMK. Its main advantages are almost non-swelling, no out-gassing under neutron irradiation, quit high neutron efficiency, a high melting point (~1870°C), non-interaction with the cladding at temperatures above 1000°C, simple fabrication, non-radioactive waste and easy to reprocess. The disprosium titanate control rods have worked without operating problems in the reactor MIR during 17 years and in WWER-1000 4 years. After post-irradiation examinations, this long-life control rod type was recommended for using in the nuclear reactors. Dysprosium hafnate is a promising absorber ceramic material. The research results confirmed that it has a large radiation damage resistance. The examination results of hafnium dummies (GFE-1) irradiated in BOR-60 are presented. The maximum accumulated neutron fluence was $3.4 \times 10^{22} cm^{-2}$ (E>0.1 MeV) and the temperature range was 340 to 360°C. Due to high radiation growth (3-4 %) and the absence of an axial gap between the dummy and the upper capsule tip the dummies were bent. The irradiated dummies have high mechanical properties. Other aspects of the expected hafnium irradiation behaviour and the use of hafnium in control rods are discussed. This report presents some experimental data on $Dy_2O_3 \cdot TiO_2$, Hf, $Dy_2O_3 \cdot HfO_2$ and possibilities of their use in WWER control rods.

1. INTRODUCTION

At present, boron carbide (WWER-1000) and boron steel (WWER-1, -2, -3M, WWER-440) are the most widely used in control rods of Russian water reactors. These absorber materials have large radiation damages owing to (n,α)-reaction on ^{10}B isotopes, helium formation and swelling. The first damage of WWER-1000 Rod Cluster Control Assembly (RCCA) due to B_4C swelling and cladding cracking was noticed in the Novovoronezh Nuclear Power Plant.

Long before this accident, the State Scientific Center of the Russian Federation "Research Institute of Atomic Reactor" (SSC RF RIAR) (together with the Moscow Polimetal Plant (MPP)) carried out research on (n,γ) absorbers, which do not swell. More than 60 ceramic absorber materials based on Dy, Eu, Sm, Gd, Hf, Cd, pure Hf and Hf-alloys were investigated.

Post-irradiation examinations have shown that lanthanide oxides ($Ln_2O_3 \cdot MO_2$) with fluorite structure have the largest radiation damage resistance among the ceramic absorber materials. Dysprosium titanate ($Dy_2 \cdot TiO_5$) was selected for WWER-1000 RCCA. It is used in commercial reactors since 1995. Dysprosium hafnate ($Dy_2O_3 \cdot HfO_2$) has attractive properties too. It is characterized by a more stable fluorite structure, larger efficiency and less swelling in comparison with $Dy_2O_3 \cdot TiO_2$. Now dysprosium hafnate research is continued. Hafnium has attractive properties too, especially when it is used simultaneously as absorber and cladding material [1].

2. DYSPROSIUM TITANATE

Natural dysprosium has 5 stable isotopes which have comparatively high absorption cross-sections for thermal neutrons (Fig. 1). Decay products are Ho and Er. All produced radionuclides have small γ-activity and small half-life time. Some results of the γ activity of irradiated $Dy_2O_3 \cdot TiO_2$ are shown in Table I.

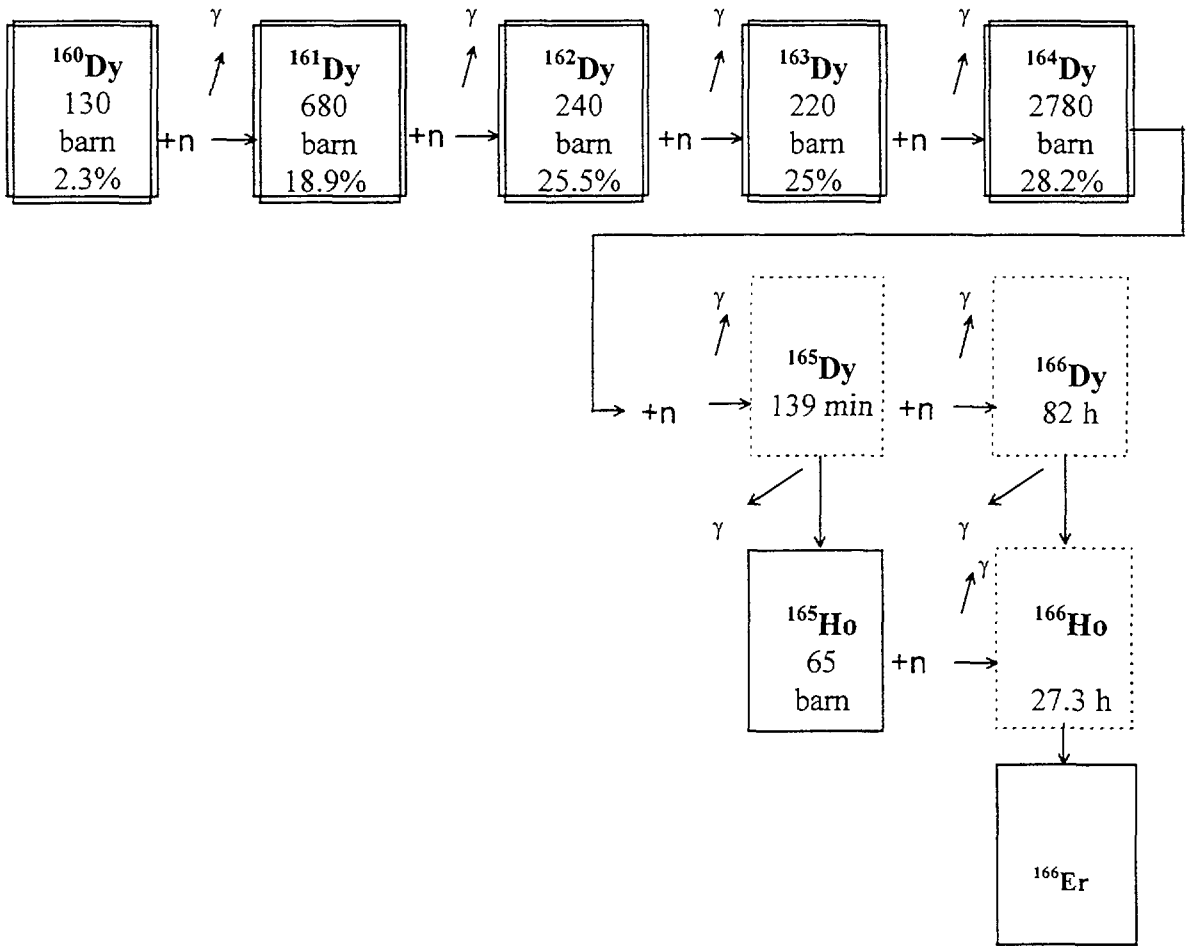
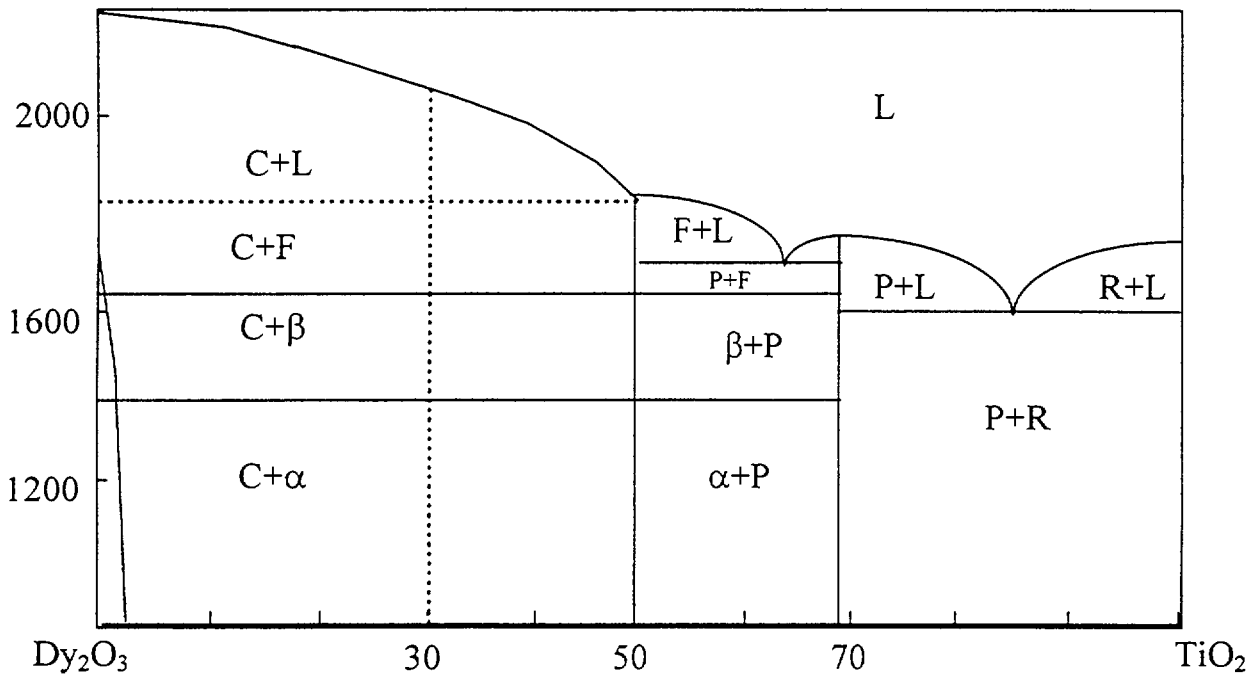


FIG. 1. Transformation of irradiated disprosium

TABLE I. γ ACTIVITY OF $Dy_2O_3 \cdot TiO_2$

Sample	Fluence, $\times 10^{22}$ cm^{-2} (E>0.1 MeV)	Time after irradiation day	Distance m	γ activity μR/s
Pellets of $Dy_2O_3 \cdot TiO_5$ m=2.5 g	0.9	380	0	200±20
			0.35	100±10
			0.80	15±15

According to the $Dy_2O_3 \cdot TiO_2$ phase diagram (Fig. 2), an interaction between Dy_2O_3 and TiO_2 can result in formation of two compounds. They are dysprosium dititanate ($Dy_2 \cdot Ti_2O_7$) and dysprosium titanate ($Dy_2 \cdot TiO_5$), the last is polymorphous (at low temperature it has a the rhombic lattice, with rising temperature it transforms into a hexagonal lattice (~1350°C) and then into a fluoride (~1680°C)). The melting point of $Dy_2 \cdot TiO_5$ is 1870°C. It is possible to obtain $Dy_2 \cdot TiO_5$ with different initial crystal structures verifying heating and cooling regimes. The fluorite structure of $Dy_2 \cdot TiO_5$ has less swelling under irradiation and is more promising to be used as a control rod absorber material. During irradiation the pyrochlore structure can transmute into the fluorite (Fig. 3).

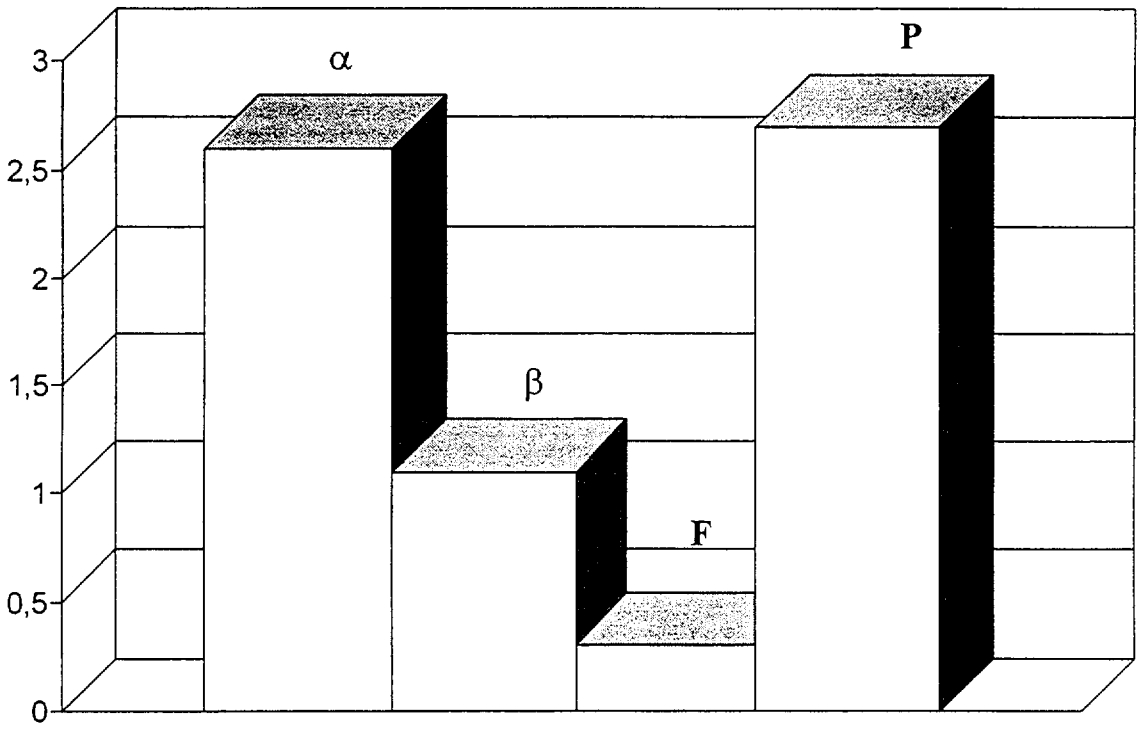


α – rhombic
β – hexagonal

L – liquid
F – fluorite

P – pyrochlore (cubic)
R – rutil

FIG. 2. Dy_2O_3·TiO_2 phase diagram



α – rhombic
β – hexagonal

F – fluoride
P – pyrochlore

FIG. 3. Volume variation of phase components of dysprosium titanate after irradiation ($F=1\times10^{22}$ n/cm^{-2}, T=250-450°C)

The initial physical efficiency of $Dy_2 \cdot TiO_5$ ($\rho \sim 5$ g/cm^3) in WWER-1000 environment is 15% smaller than that of natural B_4C ($\rho \sim 1.7$ g/cm^3). On the other hand, $Dy_2 \cdot TiO_5$ has a higher life-time (Fig. 4) due to existence of daughter isotopes characterized by high absorption cross-sections. It makes $Dy_2 \cdot TiO_5$ very attractive for use in control rods. The physical efficiency of $Dy_2 \cdot TiO_5$ control rod decreased only by 5-6 % within 17 years of operation in the research reactor MIR (RIAR) ($F = 2.2 \times 10^{22}$ cm^{-2} (E>0.1 MeV))

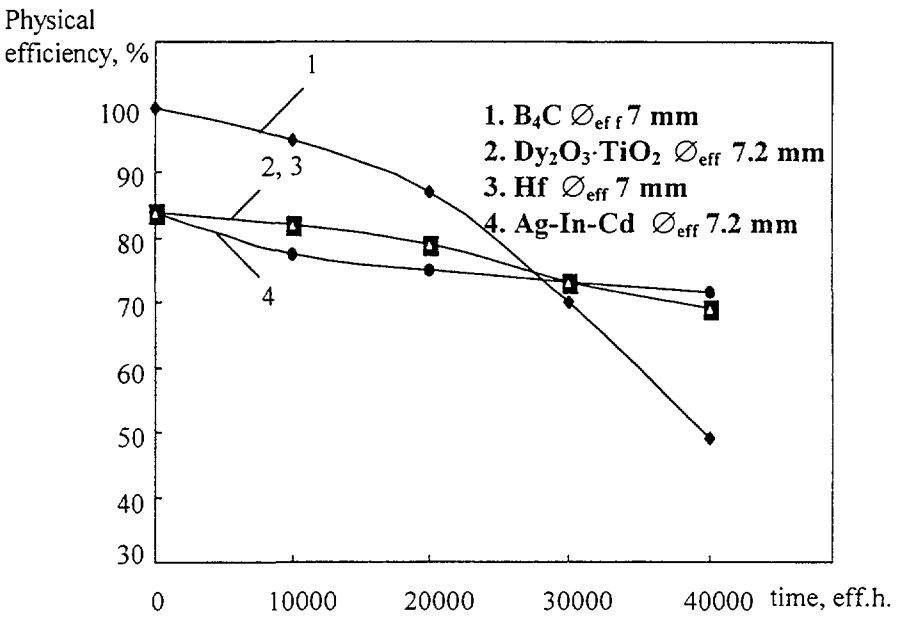


FIG. 4. Dependence of efficiency of absorbing materials during irradiation in WWER-1000

Some thermo-physical properties of $Dy_2 \cdot TiO_5$ are given in Figs. 5 - 7 and the lattice volume increase upon radiation in Fig. 8. At a temperature of 350°C, the heat capacity (Cp) is equal to 0.441 J/gK, the thermal conductivity (λ) of powder ($\rho = 4.8$ g/cm^3) is 0.33 W/mK, the thermal expansion coefficient (α) of pellets ($\rho = 6.2$ g/cm^3) is equal to $(8.52 \pm 0.15) \times 10^{-6}$ K^{-1}. $Dy_2 \cdot TiO_5$ is characterized by a good chemical inertness. Dysprosium titanate does not interact with the austenitic steel cladding at temperatures between 280 and 320°C during 146 000 h and at 1000°C during 1 h.

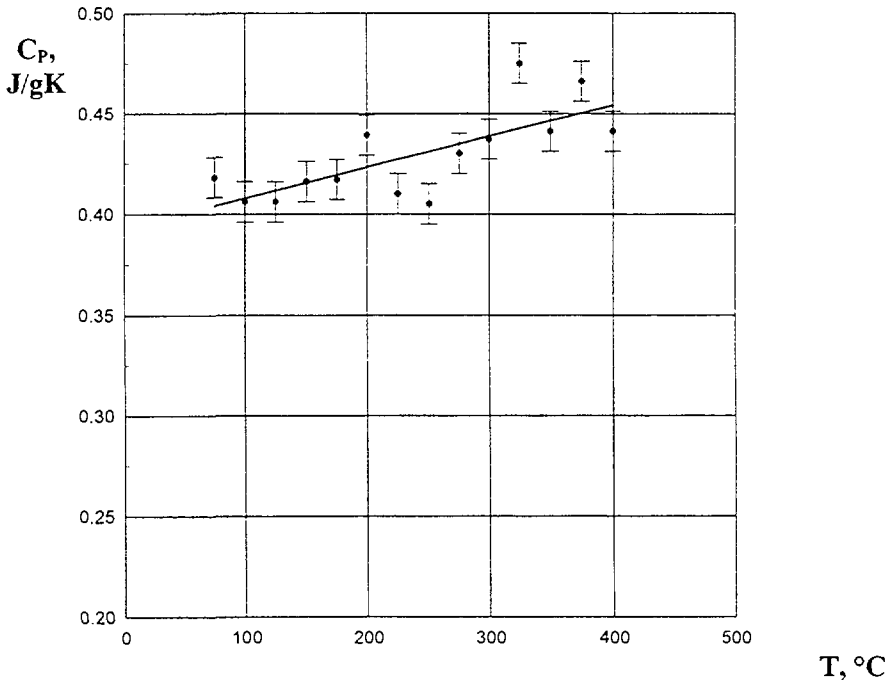


FIG. 5. Dependence of $Dy_2O_3 \cdot TiO_2$ heat capacity (C_p) upon temperature

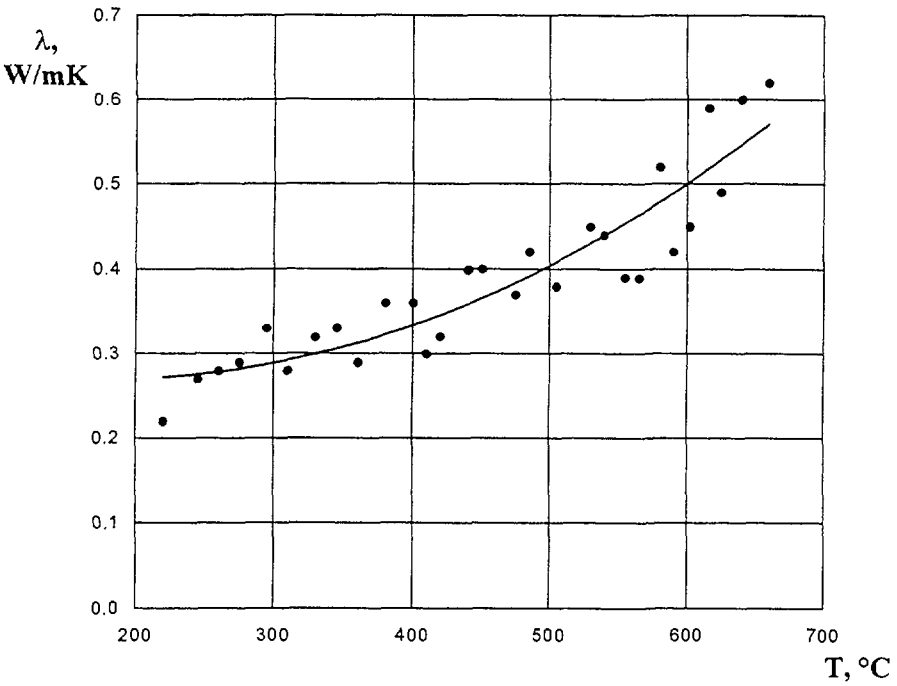


FIG. 6. Dependence of $Dy_2O_3 \cdot TiO_2$ thermal conductivity (λ) upon temperature (ρ_{POWDER}=4.8 g/cm^3, P_{He}=0.1 MPa)

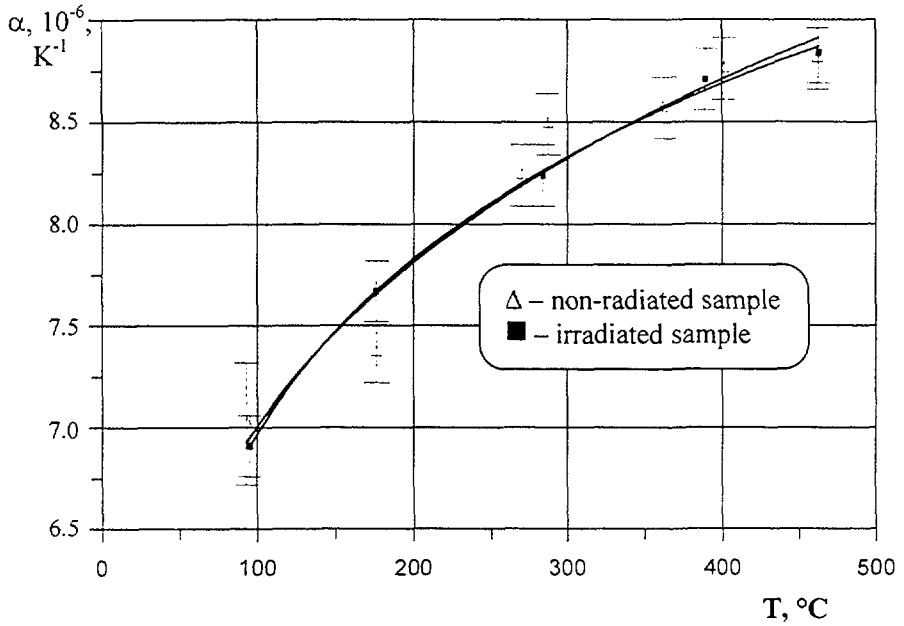


FIG. 7. Temperature dependence of thermal coefficient (α) of $Dy_2O_3 \cdot TiO_2$ (ρ=6.2 g/cm^3)

$Dy_2 \cdot TiO_5$ ($D_2 \cdot Ti_2O_7$) could be used in control rods as powder or in pellet form. In the first case, as a rule, its density is equal to 4 - 5 g/cm^3, in the second case, it is more than 6 g/cm^3. Some results of $Dy_2 \cdot TiO_5$ pellets and powder dimension stability after irradiation by neutron fluence 3.4×10^{22} cm^{-2} (E>0.1 MeV) are given in Table II. These results show that $Dy_2 \cdot TiO_5$ is characterized by the low swelling rate. The powder does not sinter and freely extract from the cladding, the lattice volume, pellet diameters, lengths and volumes increased (due to micro-cracking (Fig. 9)) at 1.7%, 0.5÷0.7%, 0.2÷0.7 % and 1.2÷2.3 %, accordingly. Dysprosium titanate pellets were cracked and fragmented on pieces of 1 - 5 mm at a temperature gradient of more than $\Delta T \geq 60$°C/mm. It is a ceramic material characterized by brittleness and low plasticity. But it is not a large problem because these absorber pellets do not interact with the cladding and do not deform it (as is with $Dy_2 \cdot TiO_5$ powder). The out-gassing absence and good corrosion properties in water at a temperature of 300°C are very important advantages of dysprosium titanate too.

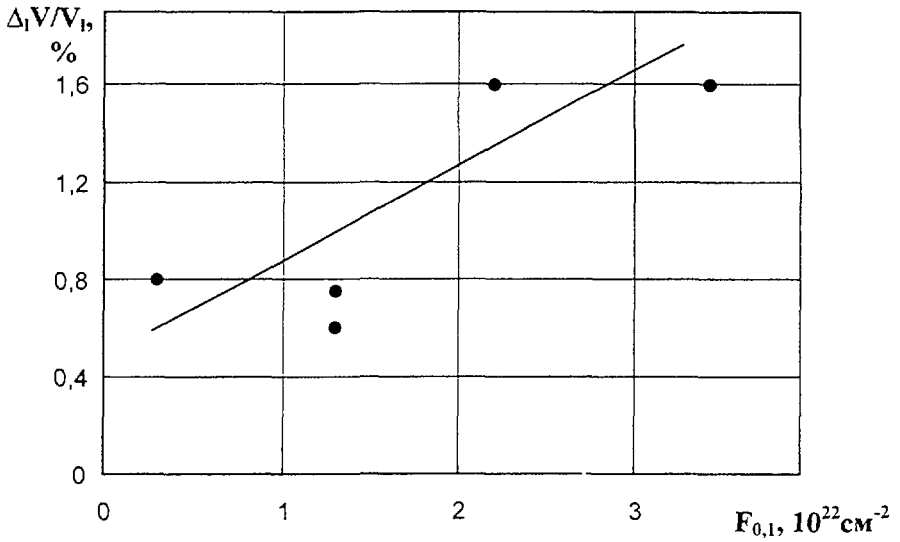


FIG. 8. Dependence of lattice volume ($\Delta V_l/V_l$) increase of fluorite $Dy_2O_3 \cdot TiO_2$ upon irradiation

TABLE II. DIMENSION STABILITY OF $Dy_2O_3 \cdot TiO_2$
($F_{max}=3.4\times10^{22}$ cm^{-2}, E>0.1 MeV)

Test	**Powder**	**Pellets**
Visual observation	freely emptied, sintering is absent	a) at the t=345-360°C, Δt=(3-5)°C/mm pellets are not destroyed, press on cladding is absent; b) at the t=150-500°C, Δt>60°C/mm pellets are destroyed on fragments due to thermal stress, press of cladding is absent
Size dimension	–	at temperature =345-360°C Δd/d=(0.5-0.7)%, ΔH/H=(0.2-0.7)%, ΔV/V=(1.2-2.3)%.
X-ray picture	a = 5.1692±0.003 Å ΔV/V=1.7%	–

3. HAFNIUM

Hafnium is used in the world (e.g. in the USA) as absorber and cladding material from the end of the seventies. Many attractive properties of hafnium were already discussed and published. Nevertheless, there are some factors restraining the more widely use of hafnium in control rods. These are the relatively high cost, the absence of reliable experimental results on radiation behaviour and hydrogenation, sometimes low mechanical properties, the absence of industrial production in Russia, etc. From our point of view, hafnium remains one of the most promising materials for using in water reactor control rods, especially it is used as absorber and cladding simultaneously.

Hafnium investigations on various fabrication, technology and composition are carried out in Russia more than 20 years. The main results received up to 1993, were published in the book "Hafnium in Atomic Technics" [1]. Pure hafnium really possesses unique nuclear, physical, mechanical and corrosion properties. Most essential demands made to hafnium control rods without cladding are presented in Table III.

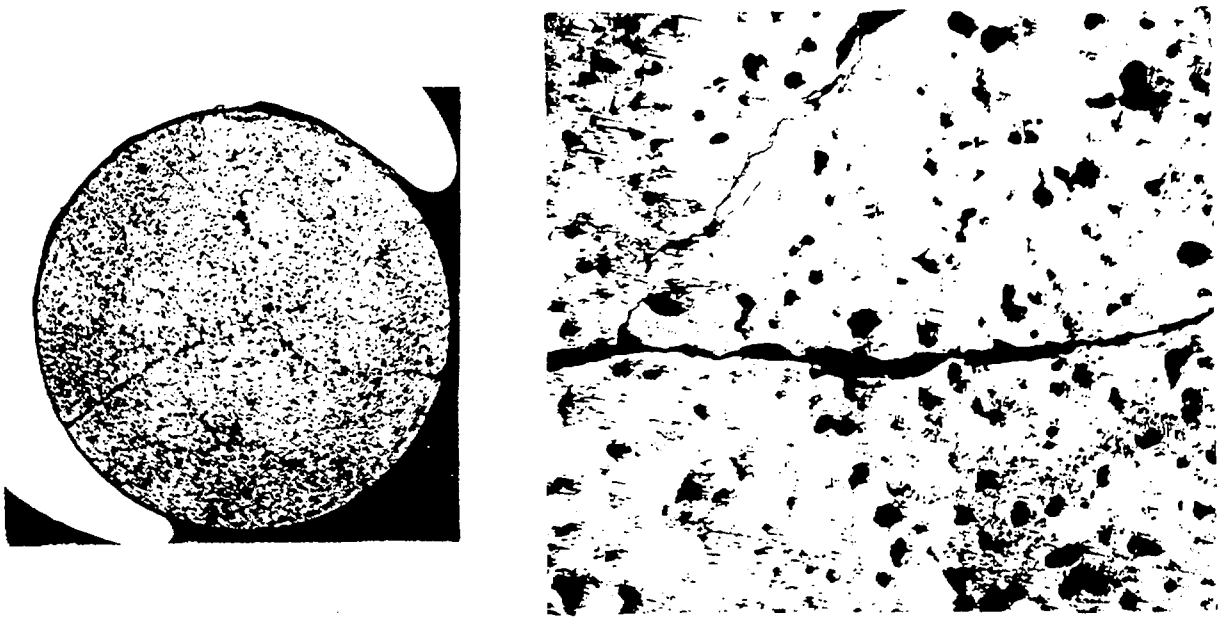


FIG. 9. Structure of Dy_2TiO_5 pellets after irradiation by neutron fluence $F=3.4\times10^{22}$ cm^{-2} (E>0.1 MeV) at the temperature 340 - 460°C, ×200

TABLE III. MAIN REQUIREMENTS PRESENTING TO HAFNIUM CONTROL RODS

Chemical contents	O – 0.03	Cr – 0.01	Mo – 0.02
	H – 0.003	Fe – 0.03	Al – 0.01
	N – 0.01	W – 0.01	Co – 0.005
	C – 0.01	Ta – 0.02	Pb – 0.005
	Cu – 0.005	Nb – 0.01	Zr – 1.0
	Ni – 0.005	Ti – 0.01	Hf – base
	V – 0.005	^{235}U – 7×10^{-6}	
Hf+Zr	> 99.8%		
Contents of gas additions	min		
Grain dimension	< 10 mkm		
Texture	not		
Mechanical properties	H_μ<1900 MPa σ_B=420 - 560 MPa σ_{02}=270 - 310 MPa δ_p>30%		
Metal	Absence of internal cracks and blisters		
Surface of control rods	Absence of micro-cracks after mechanical treatment and absence of Cu, N, Ni and W on the rod surface		

The use of hafnium control rods without cladding is more expedient. There exist many positive experimental operation results of such water reactor control rods. For instance, these control rods worked without any problems off more than 15 years in the Shippingport reactor [2]. Since 1991,

control rods without cladding were used in the research reactor RBT-6 (RIAR). Their planned lifetime is more than 20 years.

The physical efficiency of hafnium, as well as that of dysprosium, slowly decreases during operation (Fig. 4). Hafnium does not swell too. Its dimensional changes are connected with a radiation growth, as its crystal lattice is hexagonal close packed (hcp). The radiation growth deformation can change in a large range, it depends on the fabrication method and the thermo-mechanical treatment (Fig. 10). The lengths of some hafnium samples increased by 3-4% after irradiation by a neutron fluence of 3.4×10^{22} cm^{-2} (E>0.1 MeV) at temperatures between 320 - 360°C and their diameters decreased by 2-3%. Because of the absence of an axial gap in the radiation equipment some of them were curved (Fig. 11).

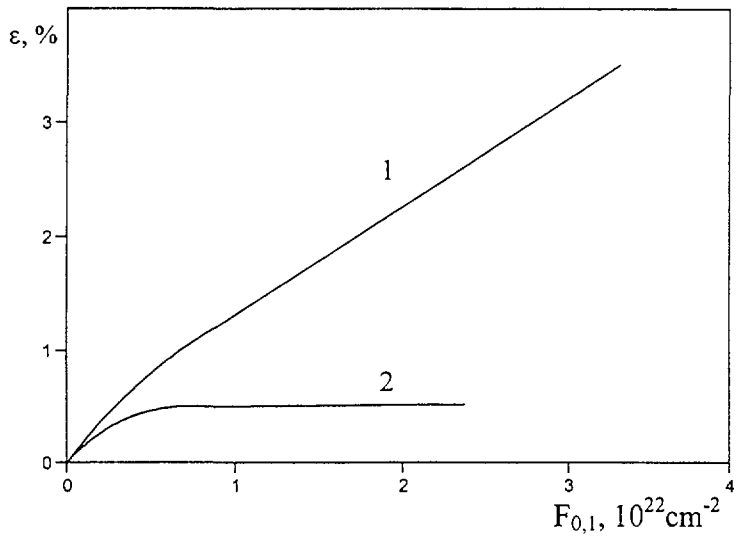


FIG. 10. Radiation growth of hafnium
1 – GPhA-1 (t=340 - 360°C); 2 – GPhI-1 (t=280 - 320°C)

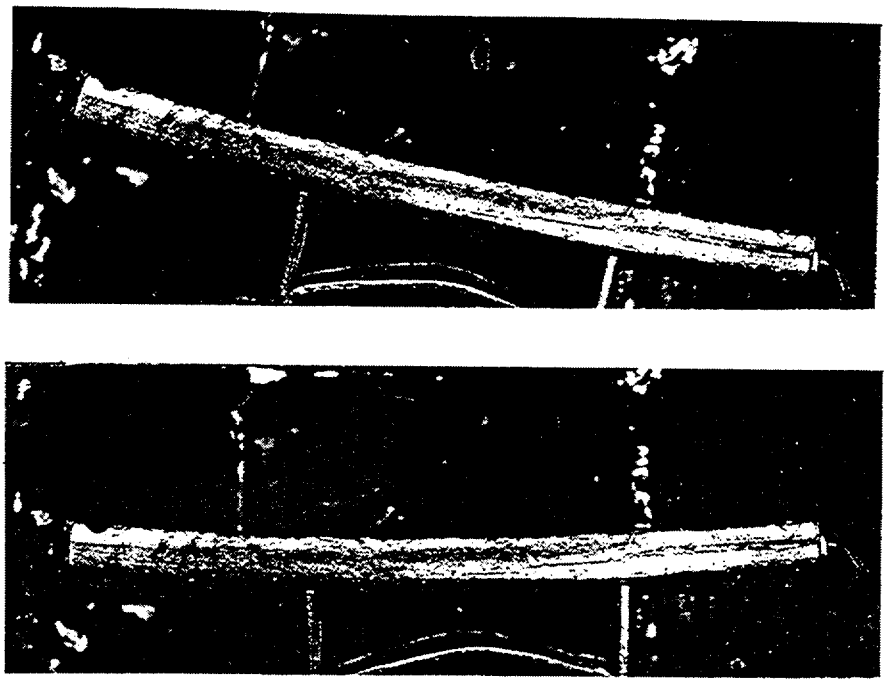


FIG. 11. View of Hf rodlets (GPhA-1) after irradiation by neutron fluence $F=3.4 \times 10^{22}$ cm^{-2} (E>0.1 MeV) at the temperature 340 - 460°C

Hafnium structural damage appears in changes of its dislocation structure (mainly dislocation loops) due to an accumulation of nuclear reaction products (transmutants), e.g. tantalum (Ta) and lutetium (Lu), and hydrogenation. More than 2% of Ta is contained in hafnium after irradiation by a neutron fluence of $2\text{-}3\times10^{22}$ cm^{-2} (E>0.1 MeV). It is necessary to take into account at the development of hafnium alloys. We suppose that only pure unalloyed hafnium must be used in control rods.

There is a good correlation between the dislocation loop concentration and the hafnium microhardness (Fig. 12). Dimensions of loops are equal to 25 - 50 Å after irradiation by a neutron fluence of 2×10^{22} cm^{-2} (E>0.1 MeV) at temperatures between 230 - 340°C, density is 5×10^{16} cm^{-3}.

The hafnium mechanical properties depend widely on a hydrogen absorption and the hydride phase appearance. At the oxidation film thickness 3 - 20 mm, hydrogen contents in irradiated hafnium is not more than 2×10^{-2}%. Relative lengthening of irradiated hafnium samples, as a rule, is 2 - 4%. The view of the ring samples of irradiated hafnium after mechanical tests are shown in Fig. 13.

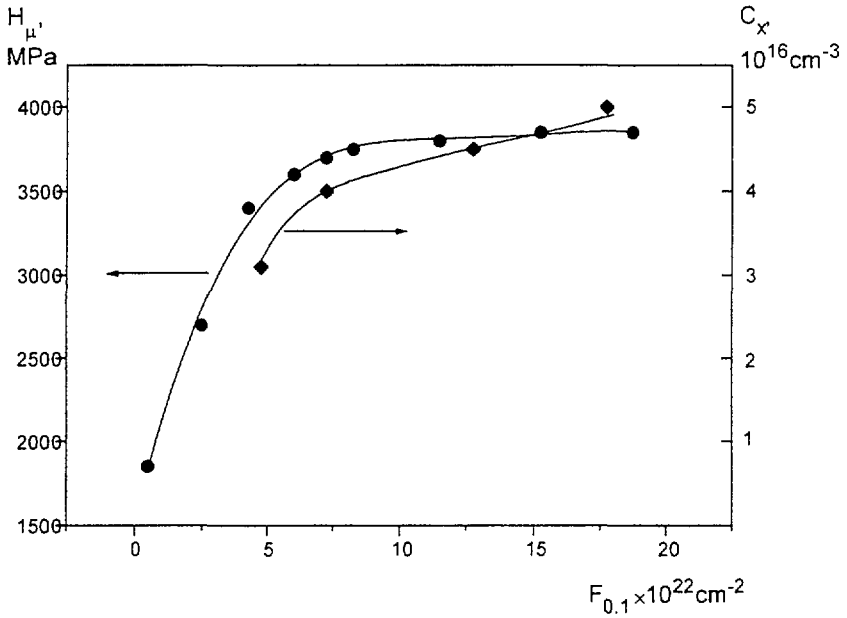
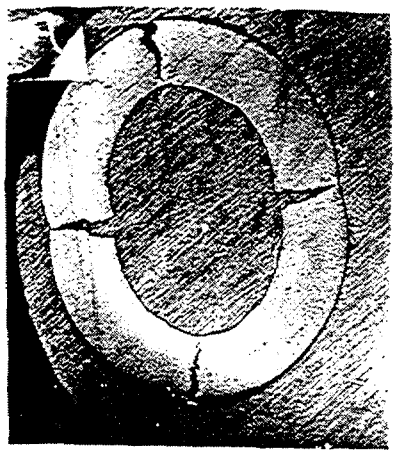


FIG. 12. Dependence of microhardness and dislocation loops upon neutron fluence (E>0.1 MeV) an temperatures between 280 - 340°C

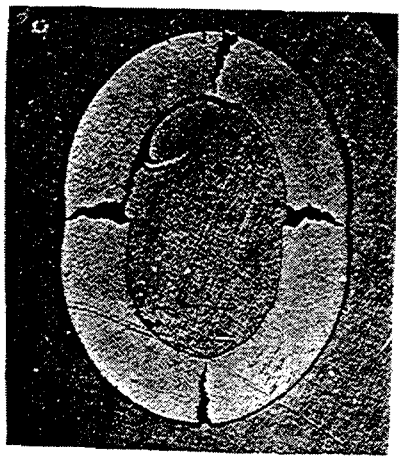
4. DYSPROSIUM HAFNATE

Dysprosium hafnate is considered as a possible material for water reactor control rods. It has a higher neutron absorbing ability and lifetime, in comparison with $Dy_2O_3{\cdot}TiO_2$, since Ti atoms are replaced by the second absorber Hf. Hafnate disprosium has also a stable fluorite structure and a higher radiation resistance.

$Dy_2O_3{\cdot}HfO_2$ pellets (∅6×10 mm, ρ=6,2 g/cm^3) were irradiated by a fast neutron fluence 1×10^{22} ñm^{-2} (E>0.1 MeV) in helium in the BOR-60 (RIAR) at temperatures between 360 - 480°C. All pellets saved their shapes and the initial structure after irradiation (Fig. 14). The pellet diameter increased by 0.3%. The fluorite crystal structure did not change and the lattice volume increased by 0.6%. There is good agreement with the results of the volume measurements of the $Dy_2O_3{\cdot}HfO_2$ pellets. Some dimension stability results of irradiated B_4C, in comparison with (n,γ)-absorber materials based on Dy and Hf, are given in Fig. 15.



20°C



150°C

250°C

300°C

FIG. 13. View of irradiated hafnium samples after mechanical tests

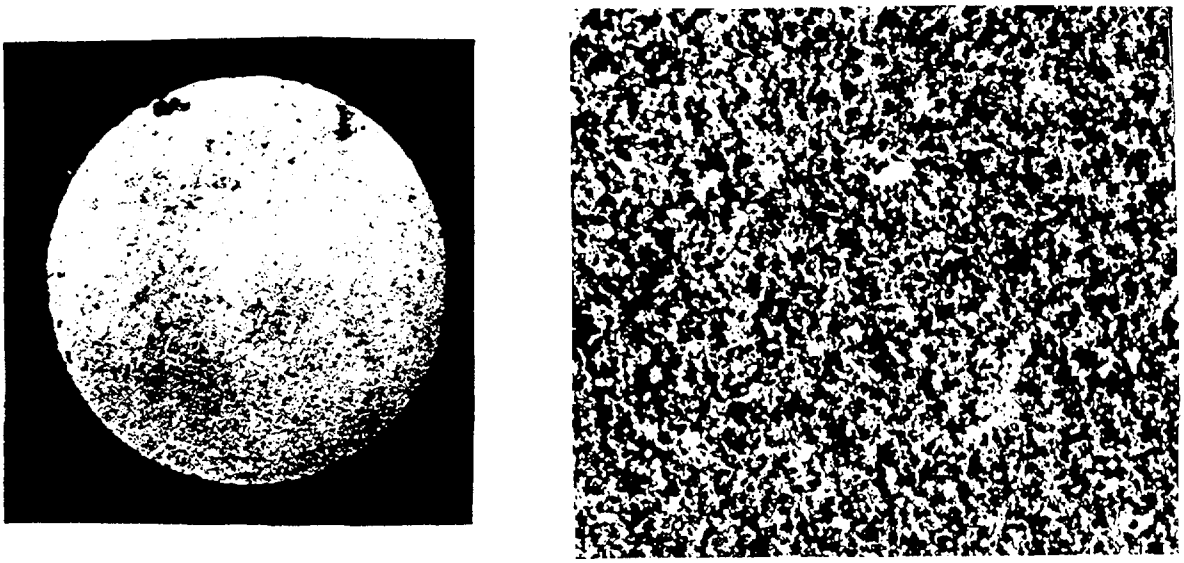


FIG. 14. Structure of irradiated pellets of $Dy_2O_3 \cdot HfO_2$ ($F=1\times10^{22}$ cm^{-2}, $E>0.1$ MeV, $t=360-480°C$), ×200

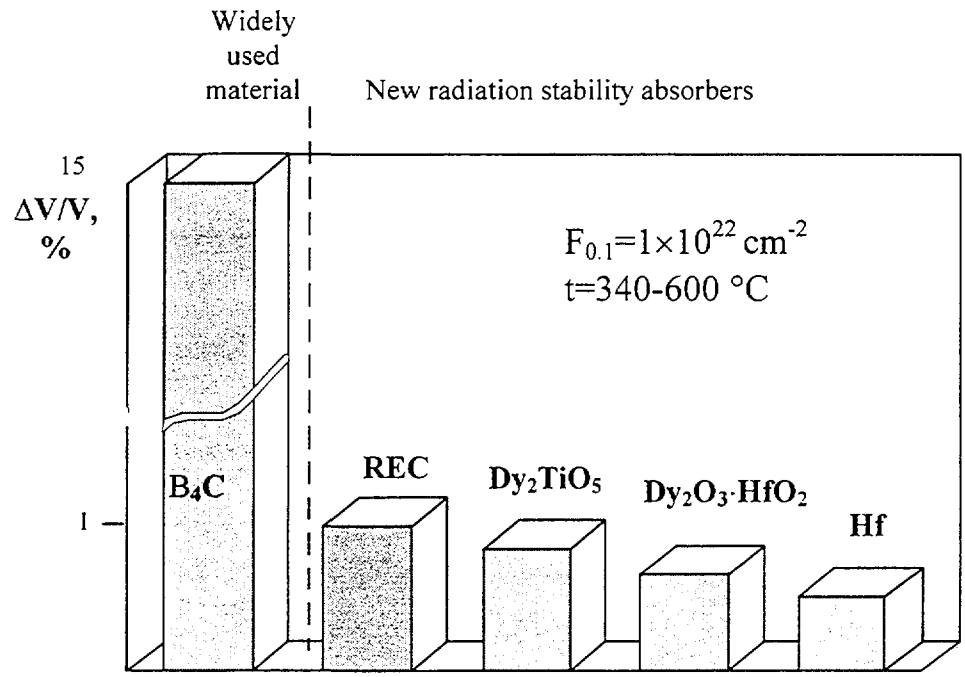


FIG. 15. Dimension stability of absorber materials after irradiation in WWER-1000 RCCA (REC-$Ln_2O_3 \cdot TiO_2$; Ln -Dy, Gd, Eu, Sm)

5. (n, γ) ABSORBER MATERIALS IN WWER CONTROL RODS

At present time the main reasons of WWER control rod degradation and their small life-time in reactors are cladding deformations due to absorber pin swelling and losses of cladding mechanical properties during irradiation. Claddings, for instance, from X18H10T and SS304 steels, crack and distract, as a rule, at the deformation more than 0.5% (Fig. 16). In using absorber pins which do not swell, the WWER-1000 control rod resource may be increased from 2 - 5 years, for B_4C, to 15 - 20 years.

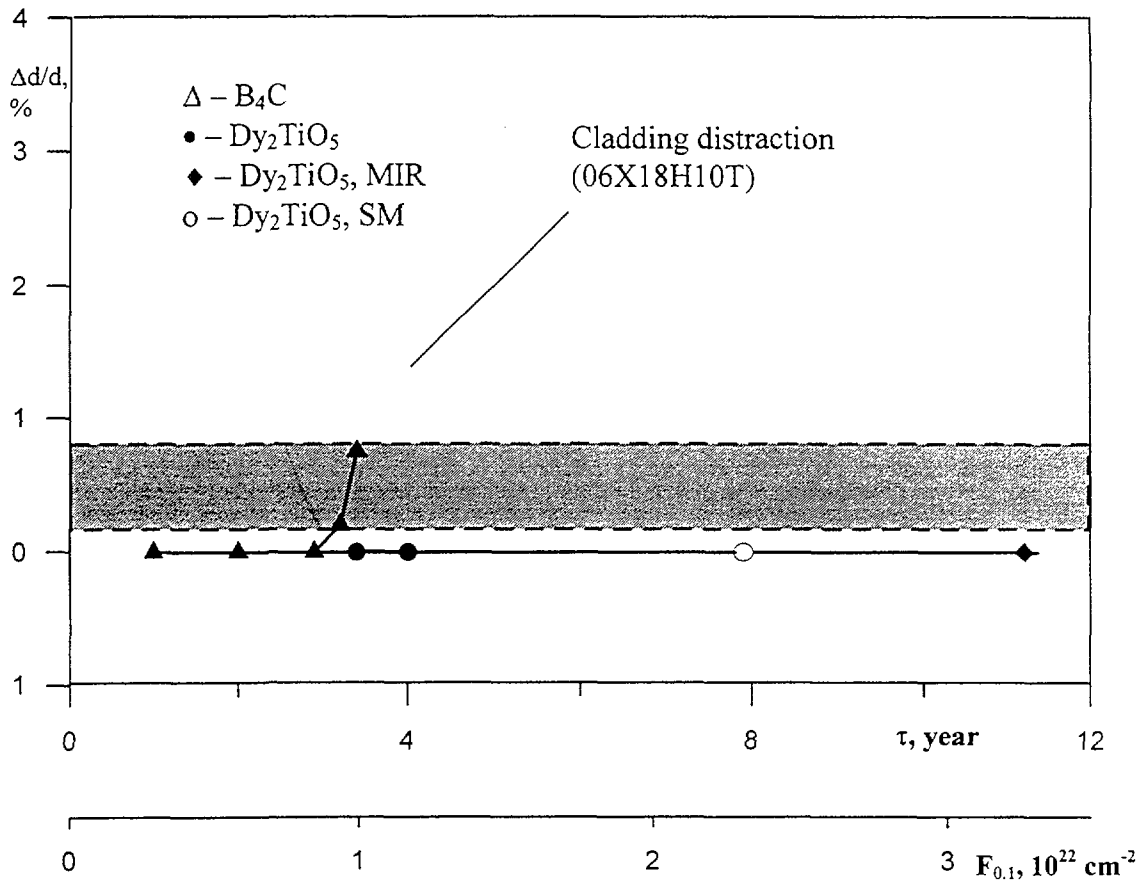


FIG. 16. Dependence of diameter cladding change ($\Delta d/d$) with $Dy_2O_3 \cdot TiO_2$ upon fluence ($F_{0.1}$) and operating time (τ)

From 1995, RCCAs containing $Dy_2 \cdot TiO_5$ powder (the bottom part) and B_4C powder (the upper part) are used in Russian WWERs-1000 and, from 1997, RCCAs containing Hf and B_4C are used in Ukrainian reactors.

6. CONCLUSION

New (n,γ) absorber ceramic materials of $Dy_2O_3 \cdot TiO_2$, $Dy_2O_3 \cdot HfO_2$ and Hf for WWER control rods were investigated. The use of these materials allow to raise the reliability and the safety of operation and, also, to increase the lifetime of control rods in comparison with rods containing B_4C. The use of RCCAs containing $Dy_2 \cdot TiO_5$ and Hf in WWER-1000 has taken place. Tests and research on $Dy_2O_3 \cdot HfO_2$ are continued.

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