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INVESTIGATIONS OF RADIATION RESISTANCE OF STRUCTURAL MATERIALS FOR HEAVY-WATER REACTORS

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ABSTRACT

There are presented results of longstanding investigations of ITEP specialists about structure of materials for provision of stable long-term operation of heavy-water reactors. Based on experimental study the high-frequency hardening was recommended to suppressing the radiation growth in natural uranium fuel and to provide the high burn-up. The stabilizing heat treatment was substantiated to preserve the plasticity of structure materials and to rise their operation time but in some cases the selection of chemical composition was executed. To study defects of crystal lattice the radiography and thermoelectric methods are used which allow to test the content of hydrogen into zirconium too.

1. INTRODUCTION.

The main aim of Institute of Theoretical and Experimental Physics (ITEP, Moscow), which was founded according to the decision of the Russian Government at December 1945, was a development of heavy water direction in reactor's creation for production of fissionable materials required for nuclear weapon. The first research heavy water reactor HWR with thermal capacity 2.5 MWt was commissioned in ITEP at 1949. It was done for the first time in Europe. Then a small series of industrial heavy water were developed and constructed on nuclear enterprise "Mayak" (South Ural): OK-180 (1951), OK-190 (1955), OK-190M (1966), LF-2 (1987). Now reactors OK-180, OK-190, OR-190M have been decommissioned, the reactor LF-2 is operating. The full-scale heavy-water critical assembly "Maket" with volume of heavy water 10 t is continuing to operate in ITEP since 1977; on this assembly it was done a big quantity of experiments for a justification of developed heavy water reactors. In connection with large experimental opportunities of heavy water reactors the researches installations were constructed in China (reactor HWR, 1958) and in Yugoslavia (reactor RA, 1959) under scientific leadership and with participation of ITEP specialists.

Specialists of ITEP carried out a large activity on creation and experimental justification of power reactor KS-150 with electric capacity 150 MWt, carbon dioxide as coolant and heavy water as moderator. This reactor was commissioned on NPP A-1 in Bogunice (former Czechoslovakia) at 1974. After the commissioning of reactor KS-150 experts of ITEP began to develop new power reactor TR-1000 US in prestressed concrete vessel based on principles of ultimate safety, with electric capacity 1000 MWt, carbon dioxide as coolant and heavy water as moderator (Iljichev et al., 2003).

Specialists of ITEP carried out the conceptual study of Accelerator Driven System (ADS) for nuclear transmutation of long-lived radioactive waste (LLRW) since 1990. This technology, perhaps, will decrease an amount of LLRW and improve a state of environment in future.

A number difficult heterogeneous problems of arisen during development of projects for abovementioned reactors that required, in the first place, experimental justification. To such problems the following scientific-technical tasks were concerned, in decision of which specialists of ITEP reactor department took active participation, but in some cases they were initiators of the formulation for experimental study as in ITEP so in other scientific organizations:

- Study of radiation growth and methods of it decreasing (suppression) for given burn-up of natural uranium fuel.
- Study of radiation growth and methods of its decreasing (suppression) for technological channels of zirconium alloy Zr-2.5%Nb, methods of hydrogen' measurements in zirconium tubes and claddings of fuel.

- Justification for opportunity of using of aluminium alloy SAV-1 for components in core of HWR's reactors.
- Study of radiation properties of magnesium-beryllium alloy for claddings of fuel of reactor with carbon dioxide coolant.
- Conceptual studies for choice of radiation-resistant alloy on the base of iron for reinforcing bars of prestressed concrete vessel.

During last 40 years specialists of ITEP are carrying out a lot investigations of resistance for fuel and different structural materials in operation conditions. A most results of these investigations were presented in closed reports and had not been published. Authors decided that it's expedient to present some obtained results in the current paper to inform scientific community.

The current paper is the review of long standing original studies of ITEP for decision abovementioned scientific-technical tasks with aim to provide a long-term radiation resistance of fuel and structural materials for heavy water reactors, besides the item about magnesium-beryllium allow, which have been published earlier (Christenko et al., 1958).

Presented results have a important significance not only for heavy water reactors, but and for thermal reactors of another types. Methods of conducted experiments, as rule, don't described because are well very known besides a new methods for a definition of hydrogen' contain and radiation defects in tubes of zirconium alloy.

Authors, as far as possible, presented the short description of heat treatment regimes besides a cases of such technologies which are the subject of "know-how".

2. SUPPRESSION ON RADIATION GROWTH OF METALS.

It's known that the anisotropy diffusion of radiation defects for the crystal lattice and the presence of crystal texture in the products can cause the extension of natural uranium fuels (Christenko et al., 1958) and technological channels from zirconium alloys (Zikanov et al., 1983) that leads to serious difficulties during operation of nuclear reactor.

2.1. Uranium.

One of the first works was concerned to study of uranium texture in natural uranium fuel. The aim of this study was to provide the high burn-up of natural uranium fuel presented as cylindrical rods. In connection with this the texture of uranium pins had been investigated by dilatometric and radiographic methods.

Rods of natural uranium with 4 mm diameter were manufactured from metal uranium with technical quality. One part of rods was in deformation' state, the another part was quenched from γ-phase into water, the third – from β-phase into water, the fourth - from β-phase on air, the fifth was exposed to high-frequency quenching according to the technology of Kharkov Physics-Technical Institute (KPTI). Samples of fuel with length 300 mm were manufactured from abovementioned rods which exposed by etching after polishing. The study by radiography have been before start of irradiation what allows to establish following features:

- Samples of uranium, manufactured by method of drawing after 75% deformation for temperature 300^0C: have hard texture with deposition of [010] direction along axis of rod, crystal grains are strong stretched along axis of rod and have the cross section 3-5 mkm.
- Samples of uranium, quenched from γ- and β-phase into water: have clear structure similar the deformation texture but less clear, crystalline grains have equal axis with cross section 10-20 mkm.
- Samples of uranium, hardening from β-phase on air: crystalline grains have equal axis with size 200-500 mkm; the large granulated texture are formed in the result of hardening on air.
- Samples of uranium, quenched from β-phase with heating in induction heater to the β-phase and cooling by water shower: the structure of samples didn't detect, ration of diffraction' lines corresponds to isotropic state, crystalline grains have equal axis with size 10-20 mkm; the fine granulated texture is formed as the result of high-frequency isotropic quenching. Results of measurements of thermal expansion coefficient for abovementioned uranium samples are given in Table 1.

Titanium tips were welded to ends of uranium samples for its examination. Outside cylindrical surfaces of uranium and titanium tips were covered by protective cladding of Mg-Be alloy. Samples in different intial states were tested in the loop with cooling gas (CO_2) at temperature on inlet 80^0C and, on outlet – 125^0C. Temperature of uranium samples was in range 200^0C (in low part) – 250^0C (in upper part). The special diffractometer was developed for radiography of irradiated samples (Fig. 1).

The samples in different initial state with protective containment of Mg-Be alloy had been examined in reactor loops with gas cooling. The experimental data of radiation growth for natural uranium are presented in Table 1.

Table 1.Coefficients of thermal expansion α and radiation growth $\Delta l/l$ for uranium pins under irradiation till burn-up 5 MWtday/kg

Initiating state	$\alpha.10^6$, $1/^0C$ $(-195 \pm 20)^0C$	$\Delta l/l$, %
Drawing for ~ 300'Ñ. Deformation texture [010] along axis of pin.	7	170
Hardening out β-phase into water. Hardening texture [010] along axis of pin.	12	12
High-frequency hardening out 3-phase. Isotropic finely dispersed structure.	16	1,5

Table 1 shows that the texturing uranium is strong prolonged under irradiation. The hardening significantly decreases the radiation growth but radical method for suppression of radiation growth is high-frequency hardening.

The results of these studies allowed making the decision about the possibility of increasing of burn-up for natural uranium fuel till 10 MWtday/kg. The following operation of these fuel in reactor KS-150 of NPP A-1 with natural uranium fuel were shown that fuel enlargement was less permissible level (3%). The small growth can be explained by thermal cycling.

Further the specialists of the Kharkov Physics-Technical Institute (KPTI) were invited to develop of industrial technology for high-frequency hardening of natural uranium fuel, based on the carried out investigations of ITEP. Chepezk Mechanical plant of former Ministry Middle Machinery (now Minatom) carried out the manufacture of natural uranium fuel with this type of high-frequency hardening.

2.2. Zirconium alloy N-2,5

Alloy N-2,5 (Zr-2,5% Nb) is used as structural material for core of nuclear reactors with water coolant. The operation of reactors RBMK and WWER shows that there are the radiation growth of zirconium channels. However it was no information about possible radiation growth of zirconium channels in conditions of heavy water reactors so that it’s required detailed study of this phenomena. According to estimation of ITEP specialists high-frequency hardening of zirconium rods were manufactured by cold drawing can be one of possible measure of decreasing the radiation grow of zirconium channels. With this aim experiments were conducted to study of impact of different regimes of high-frequency hardening. Initially ITEP specialists with the participation of KPTI scientists carried out a study of radiation growth of zirconium samples in research heavy water reactor HWR. The following method was used for preparation of zirconium samples. Zirconium rods were subjected to multirepeated cold drawing to diameter 4 mm. After that the samples were heated, regimes of which are indicated in Table 2, then the chemical treatment was conducted in the special etching installation to diameter 1 mm. The irradiation of zirconium samples, placed into aluminium ampoule, was conducted in the HWR reactor channel of placed through ring fuels at neutron flux $0.56.10^{13}$ $cm^{-2}s^{-1}$ (E > 0.16 joule) during effective 30 days. During irradiation temperature of samples didn’t exceed 150^0C. Results of measurements for **c**oefficients of thermal expansion α and radiation growth $\Delta l/l$ are given in table 2.

Table 2. Coefficients of thermal expansion α and radiation growth $\Delta l/l$ for zirconium pins under irradiation at neutron fluence 10^{19} cm^{-2} ($E \geq$ pjoule) and temperature $\sim 150^0C$.

Initiating state	$\alpha.10^6$, $1/^0C$ $(-195 \pm 20)^0C$	$\Delta l/l$, %
Annealing for 500^0C, 24 h, in vacuum. Deformation texture.	5,05	0,022
High-frequency hardening (according to KPTI technology) +annealing for 550^0C, 24 h, in vacuum. Isotropic fine dispersed texture	6,6	0,000

Table 2 shows that high-frequency hardening very effectively suppresses the radiation growth because the hardening forms up the isotropic structure.

At Fig.2. there are presented the results of measurements for the wide of diffraction lines at radiographs of investigated samples. The points, corresponding to reflection (0002) out tightly packing surfaces, don't place at line connecting two other experimental points. By comparison low wide of line (0002) is explained by the domination of atomic packing defects in hardening dislocations. After annealing at 700^0C the anomaly of wide for abovementioned line is preserved that indicates on high temperature stability of packing defects. Perhaps these defects and radiation dislocations are mutually destroyed by interaction, which positive affects on radiation resistance of alloy.

Afterwards based on carried out investigations of the KPT1 experts had developed the industrial technology for high-frequency hardening of Zr tubes. The radiation examinations of hardening Zr alloy samples, carried out in Research Institute of Atomic Reactors, were shown the lack of radiation growth till neutron fluence 8. 10^{22} cm^{-2} [Zelenski et al., 1990].

3. PROVISION OF MARGIN FOR DUCTILITY OF STRUCTURE MATERIALS FOR NUCLEAR REACTORS.

3.1. Aging aluminium alloy SAV-1.

Alloy SAV-1 (Al + 0,7% Mg + l% Si) was chosen for heavy-water vessel and calender tubes of research and industrial heavy-water reactors and reactor KS-150 due to their suitable nuclear, thermal, mechanical, technological and corrosion stability in working media. However this alloy was instable in working conditions after traditional heat treatment (hardening for 530^0C and artificial aging during 12 h for 150-160^0C).

At Fig. 3 there are presented the results of mechanical examinations of some parts of industrial heavy-water reactor channel, which was operating during 350 day under neutron fluence ~2,23.10^{20} cm^{-2}. It shows that the properties of channel's low part correspond to properties of initiating material, but the properties of channel's upper part are significantly changed: the strength is increased and the ductility is decreased. The radiographic and electron-microscope investigations shown aging of alloy accompanied by emission of Mg_2Si particles.

The plasticization process, described in the Dr.V.Nikitin's patent (heating during 10 hours for 225^0C, endurance during 20 hours at this temperature and cooling during 10 hours till room temperature), was used to suppress the fragility of alloy [Nikitin, 1978]. The artificial aging of alloy for such heat treatment provides enlargement of Mg_2Si particles. The irradiation of alloy in this initial state doesn't influence on his fragility. At Fig. 4 there are presented the results of mechanical examination of plasticized alloy after irradiation at different temperatures. It shows that the plasticity is increased with growth of irradiation temperature. The strength and plasticity are not practically changed at temperature $\sim 80^0$C.

3.2. Granulated aluminium alloy.

To increase the radiation resistance of aluminium structure alloy, the experts from ITEP and the Russian Institute of Light Alloys (RILA) had developed the new aluminium alloy with high radiation resistance for technological channels of nuclear reactors [Dobatkin et al., 1973]. Initially the hardening granules are extracted from melted Al+1,5% Nb+1,5% Zr which then are pressed into briquettes at temperature 400 ^{0}C. After that the sheets, pins and tubes are manufactured by warm rolling. The particles of Al_3Zr and Al_3Nb intermetallides are extracted from supersaturated solid solution in technological process.

The mechanical properties of alloy depend from temperature of annealing making after warm rolling (Fig.5). The experimental points indicated at this figure are concerned just as to material in initial state so to alloy irradiated in reactor. The results of Fig. 5 show that the irradiation doesn't change mechanical properties of alloy. It allows using this Al alloy in nuclear engineering widely.

3.3. Alloy Fe-Ti.

The aim of investigations of solid solutions, which were carried out ITEP specialists together with experts of the Institute Metallophysics (this Institute enters in Research Institute of Black Metallurgy**,** Russian Academy of Science), was to search the structure materials with more radiation resistance on the base of iron. The experiments on the influence of reactor irradiation had shown that alloy Fe-Ti had preserved relative elongation after radiation at the conditions when other solid solutions on the base Fe had significantly lost the plasticity [Batenin at al., 1964].

The influence the titanium content on mechanical properties of iron is presented at Fig.6. These experimental data show that the hardening significance of Ti with the conservation of alloy relatives elongation at enough high level. The concentrations of admixture's elements are at level of theirs contains in Armco iron.

The variation for the fracture toughness of Fe-Ti alloys at examination temperature for different titanium's contains is presented at Fig.7. The temperature of ductile-brittle transition for all samples was less 200^0C that provided the reliable work at operating conditions.

The comparative examination of alloy Fe+1,3%Ti and steel 22K for boilers on impact strength had shown the evident advantages of alloy as in initial state as after irradiation (Fig. 8). As shown from Fig. 8 the level of the impact strength for irradiated alloy Fe-Ti with temperature more 80^0C is several times higher then for steel of boilers.

4. STUDY OF RADIATION DEFECTS OF CRYSTAL LATTICE FOR METALS.

4.1. Method of radiography

The scheme of radiography diffractometer allowed to study a radioactive samples is presented at Picture 1. The root-mean-square value of atom's displacements to the direction of normal to reflected flatness defined from dependence

$$\ln (I_r/I_c) = -2\pi^2 \bullet u^{-2} \bullet \Sigma\eta^2/3\alpha^2 \quad \text{where}$$

I_r/I_c — change of intensity for radiography line in result of irradiation,
u^2 — standard deviation of atom's position in junction of lattice,
$\Sigma\eta^2$ — sum of squares for indexes of reflected plane
α — parameter of crystal lattice.

The dependence $\ln (I_r/I_c) = \int (\Sigma\eta^2)$ for α-phase of carbon steel under irradiation of fluence 10^{20} cm^{-2} (E>0,16 pjoule) is presented at Fig. 9. Experimental points, corresponded to indexes (222), (400) and (444) lie on straight line 2, points corresponding to another indexes – on straight line 1. It arises an interest of metallophysicists.

4.2. Thermoelectric method for investigations of defects in crystal lattice

Authors of paper [Sharov et al., 1995.] have proposed the new method for study of the defects in crystal lattice which allows to divide a vacancy disturbance in a lattice from a defects of implantation.

The results of ITEP specialist's investigations of radiation defects in electrolytic nickel (wire of Φ O,l8 mm) and in iodide zirconium (wire of Φ 0,095 mm) are presented below.

The junction of thermocouple was the bend of wire. The samples of junctions were annealed in vacuum at temperature 600^0C during 5 hours. Then one arm of thermocouple was irradiated by electrons with energy 220 keV and fluence $2{,}3.10^{-3}$ dpa at room temperature. The free ends of thermocouple were connected to + cleat of voltmeter. The thermoelectromotance (TE) was measured during cooling of thermocouple junction in fluid nitrogen. In this case TE must be positive if the implantation defects dominate in the irradiated arms of thermocouple and negative if the vacancy defects dominate. After measurement of TE E_1, which corresponded to temperature of annealing $t_1 = 20^0$C, thermocouples were subjected to step-by-step annealing and each time TE was measured for increasing temperatures. The results of these measurements are presented at Fig.10 and they allow making the following conclusions:

- The decreasing of TE for nickel thermocouple can be explained by the destruction of comprehensive defects - the aggregations of intergranular atoms.
- The decreasing of TE for titanium thermocouple can be explained by the motion of vacancies discharging of which produces the negative component of E.
- TE is increased in case of their elimination in consequence of incompensating influence for implantation defects.
- The increasing E is probably explained by destruction of complexes of intergranular atoms.

Now it's considered the possibility to provide the conditions for mutual destruction of radiation defects and initial, for example, annealing defects. To study this process it's proposed to use thermoelectric method of investigations.

5. DEFINITION OF TENDENCY FOR ZIRCONIUM ALLOYS TO HYDROGENATION

The test allows to obtain characteristics of special thermocouple, one bough of which saturated by hydrogen in the electrolyzer, but another bough was in initial state. The junction of thermocouple (bend of wire) was cooled, the TE on free ends measured by microvoltmeter.

It's known that hydrogen forms zirconium hydride $ZrH_{1.5}$ at room temperature. Calculations are showed that concentration of hydride' molecules is the ration of the amount of zirconium atoms in the same volume and by equation can be described:

$C_r = Eq/k\ \Delta T1.5$, where

E – the thermoelectromotance

q - charge of electron

k - constant of Boltzman

ΔT - difference of temperatures for junction and free ends

Good reproduced results were obtained under cooling of thermocouple' junction by liquid nitrogen. This method allows to choice the zirconium alloy, slightly absorbing hydrogen, and covering for protection from penetration of hydrogen too.

6. CONCLUSION.

The complex of experimental investigations on physical metallurgy, carried out by ITEP specialists together with experts from other scientific centers during long-term period, has allowed to solve a lot of problems for structure materials of heavy-water reactors (research, industrial and power) and to provide the reliable operation of these reactors.

The high-frequency hardening is chosen for metallic uranium fuel and calender tubes from zirconium alloy providing the suppression of theirs radiation growth.

The mode of artificial aging is recommended for aluminium alloy SAV-1 (for heavy-water vessels and calender tubes) to provide the preservation of theirs plasticity.

The granulated aluminium alloy Al-Nb-Zr (for calender tubes) and iron deleted titanium (for vessel of reactor) are recommended as structure material with high radiation resistance.

Thermoelectric method is proposed for investigations of defects in metal crystal lattice with hardening's and deformation's disturbances.

REFERENCES.

[1] Iljitchev, B.I., Kiselev, G.V., Kochurov, B.P., et al., January 2003. The ultimate in safety. Nuclear Engineering International, p. 23.

[2] Christenko, P.I., Petrov, P.I., Mitropolevski, V.A., et al., 1958. Fuel assembly with pins for heavy-water power reactor with gas cooling. Proceedings of Second International Conference on Peaceful Application of Atomic Power. Paper Ns 2053, Geneva.

[3] Zikanov, V.A., Davidov, E.F., Kuprienko, V.A., et al., 1983. Variation of sizes for products of zirconium alloys irradiated in reactor SM-2 to high fluence. Atomnaya energy, v. 55, iss. 4, p.p.211.

[4] Zelenski, V.F., Stukalov, A.I., Nekljudov, I.M. et al., 1990. Rapid high-frequency heat treatment and radiation growth of zirconium alloy. Proceedings of International Conference on radiation physics metallurgy, KPTI, part 4, p. 55.

[5] Nikitin, V.L., 1978. High - temperature strength, plasticity and corrosion of AVIAL. M., Metallurgy, p. 152.

[6] Dobatkin, V.I., Elagin, V.I., Fedorov, V.M., 1973. Alloy on the base of aluminium. Russian Federation Patent № 378483, Bulletin of patents, M., № 19.

[7] Batenin, I V., Krizkaya, V.K.,. Sharov, B.V., et al., 1964. Influence of neutron radiation on crystal structure and properties of metals and solid solution. In collected volume: Problems of physics metallurgy and metal physics. M., Metallurgy, № 8, p. 112.

[8] Sharov, B.V., Kalantarov, V.D., 1995. Investigation of deformation's defects for crystal lattice by thermocouple method. Reports of Russian Academy of Science, v.342, № 3, p.333.

