SECTION 1

PHYSICS OF RADIATION DAMAGES AND EFFECTS IN SOLIDS

https://doi.org/10.46813/2021-135-003

UDC 621.039:531

MECHANISMS OF RADIATION DAMAGE AND DEVELOPMENT OF STRUCTURAL MATERIALS FOR OPERATING AND ADVANCED NUCLEAR REACTORS

V.N. Voyevodin*, *G.D. Tolstolutskaya, M.A. Tikhonovsky, A.S. Kuprin, A.S. Kalchenko
Institute of Solid State Physics, Material Science and Technology NSC KIPT,
Kharkiv, Ukraine
E-mail: g.d.t@kipt.kharkov.ua

Safety of nuclear reactor (NR) and economic of nuclear power are determined to high degree by structural materials. Study of reasons of change of physical-mechanical properties of materials and of their dimensional stability under irradiation; determination of operation life of elements of nuclear power energetic assemblies in different conditions, selection and development of prospective materials with high radiation resistance are the main objectives of radiation material science. In the presented paper, mechanisms of radiation damage of structural materials for nuclear power and problems of development of radiation-resistant materials for operating and advanced NR of new generation are examined.

INTRODUCTION

The realities of economy and ecology, in spite of tragedies of Chernobyl and Fukushima, forced the humanity to return to the priority development of nuclear power because doesn't yet exist cheaper and ecologically pure electric power. Nuclear energy provides access to clean, reliable and affordable energy, mitigating the negative impacts of climate change. It is a significant part of the world energy mix and its use is expected to grow in the coming decades [1].

Together with the expanding renewable energy sources and fuel switching from coal to gas, higher nuclear power production contributed to the leveling of global CO_2 emissions at 33 Gt in 2019 [2]. Given that energy generation currently accounts for 66% of worldwide greenhouse gas emissions, nuclear energy is considered as important resource in managing atmospheric greenhouse gases and associated climate. Clearly, nuclear power – as a dispatch able low carbon source of electricity – can play a key role in the transition to a clean energy. In 2018, nuclear power produced more than 11 percent of the world's electricity. In Intergovernmental Panel on Climate Change′s (IPCC) own P3 middle-of-the-road scenario nuclear power increases more than a few times from current level (Fig. 1) [3].

At the end of 2017, the 448 operating nuclear power reactors had a global generating capacity of 392 GW (e), which was an increase of about 1.2 GW since 2016 [2]. Thirty countries currently use nuclear power and 28 are considering, planning or actively working to include it in their energy mix.

The advantages of nuclear power in terms of climate change mitigation, energy security, environmental and socio-economic policies are key reasons why many countries intend to introduce nuclear power or expand existing programs.

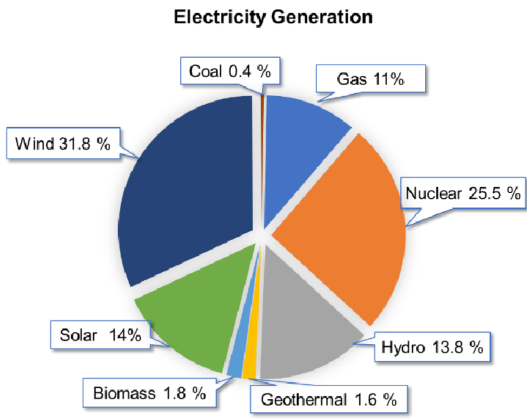


Fig. 1. IPCC identifies pathways to emission reduction to limit climate change to 1.5 °C [3]

Three newcomer countries are building their first nuclear power plants (NPPs) and several others that have decided to introduce nuclear power are at advanced stages of infrastructure preparation. By the state on 31 December of 2017 year 68 nuclear reactors (NR) were in construction; just the same year the construction of 8 new power units was started. The higher number of reactors is constructed in China – 24, Russia – 8, India – 6, USA – 5, Ukraine, Japan and Belarus – by 2 reactors each.

Nuclear power in Ukraine now serves as warrant of energetic independence – 15 working NPP units in 2019 supplied more than 50% of total production of electricity. Beside it, performing of Ukrainian obligations with the adoption of the Paris Climate Agreement in 2015, is possible only under stable functioning of Joining Energetic System, which is supported by nuclear power (Fig. 2) [4].

Detail analysis of the state and prospective of problem solution shows that in spite of considerable efforts of investigators and reactor operators in all countries of the world the economically necessary levels of operation of existing NR are not reached. Despite more than 50 years of fission reactors R&D we still do not have all the science-based tools that we need for advanced nuclear energy. During the last 50 years very slow improvement in burn-up of nuclear fuel (from 2% burn-up in reactors Generation I to 3% in Gen II and till 4…5% in reactors Generation III and III+) had place. This is determined principally by insufficient radiation resistance of main structural materials of exploited now nuclear plants – stainless steels (SS) of different classes and zirconium base alloys.

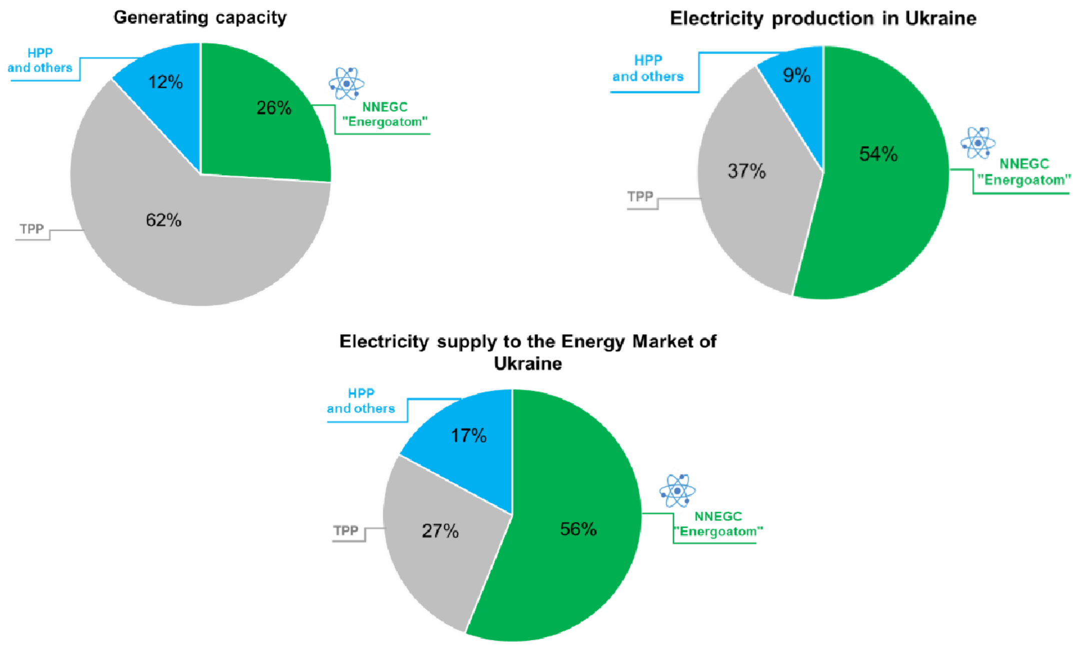


Fig. 2. Part of nuclear power in total production of electricity in Ukraine [4]

Materials in nuclear power engineering play extremely important role. Structural and fuel materials determine safe and economical operation of nuclear power stations. Importance of structural materials consists not only in guarantee of stability of the core geometry during all period of operation and, first of all, in stability of fuel subassemblies and fuel elements, but also in retention of fission products, support of serviceability of control systems and guarantee of minimal consequences in the case of accident, it is mean, in solution of key problems of reactor plants safety.

Well known that irradiation of structural materials at temperatures of reactors operation creates the unprecedented possibility of the change of microstructure, of mechanical properties and even of external dimensions of structural components [4, 5].

Achievement of high burn-up of nuclear fuel is limited by radiation resistance of materials for claddings and ducts of fuel subassemblies and terms of thermal reactor operation is limited by the term of the service of materials for reactor vessels and pressure vessel internals.

The key problem in material science provision of modern nuclear power and power of the future is the study of mechanisms and influence of degradation of initial physical-mechanical characteristics of materials during operation and dimensional stability. Radiation damages are initiated by creation and interaction of point defects on the nanolevel (10^{-9} m), but macroscopic effects, which have determinant influence on reactor's safety, created due to co-evolution of all component of the microstructure, and their roles in the macroscopic response in terms of radiation induced phenomena – swelling, anisotropic growth, irradiation creep, radiation induced phase transformations etc. [5, 6].

The development of radiation tolerant materials is the important part of modern nuclear energetics and very big scientific/technical goal that is specific to the success of sustainable nuclear energy. Radiation tolerance and high burn-up are science challenges with very strong technological implications.

The presented paper shortly summarizes the results of investigations performed in the field of radiation material science by Ukrainian scientists.

1. REACTORS ON THERMAL NEUTRONS

The basis of world nuclear power now presented mainly by thermal reactors with pressurized water cooling or cooled by boiling water (WWER-440, WWER-1000, PWR, BWR) [6]. Fig. 3 provides a schematic overview of the reactor WWER-1000 (36 reactors are operated in the world, 13 – in Ukraine) and shows the materials, conditions of operation and the more dangerous for reactor's safety phenomena. It is necessary to pay attention that different materials which have various crystal lattices perform in reactors diverse functions and work at the whole spectrum of harmful conditions: neutron irradiation, thermal ageing, environment conditions, mechanical stress etc. It will determine appearance of radiation induced phenomena, which are responsible for behavior and safety of the elements and reactor as a whole.

First of all, the main problems of safety for the units of NPP concern the vessel of NR because only the vessel can`t be replaced in the case of its not permissible damage or degradation of material properties, that's why service life of reactor pressure vessel (RPV) mainly determines the limit of service life of modern NPP unit.

It is universally recognized that during operation materials of RPV may embrittle under neutron irradiation and thermal ageing; this may induce the brittle fracture of reactor vessel in whole under the more severe condition of its loading – thermal shock, which emerges under accidental cooling of reactor etc.

The understanding of mechanisms of embrittlement of pressure vessel steels allows assume the behavior of materials during long-term operation. Investigation of microstructure properties of vessel steels for WWER-1000 reactor after irradiation will allow forecast the regime of their radiation embrittlement during their further operation.

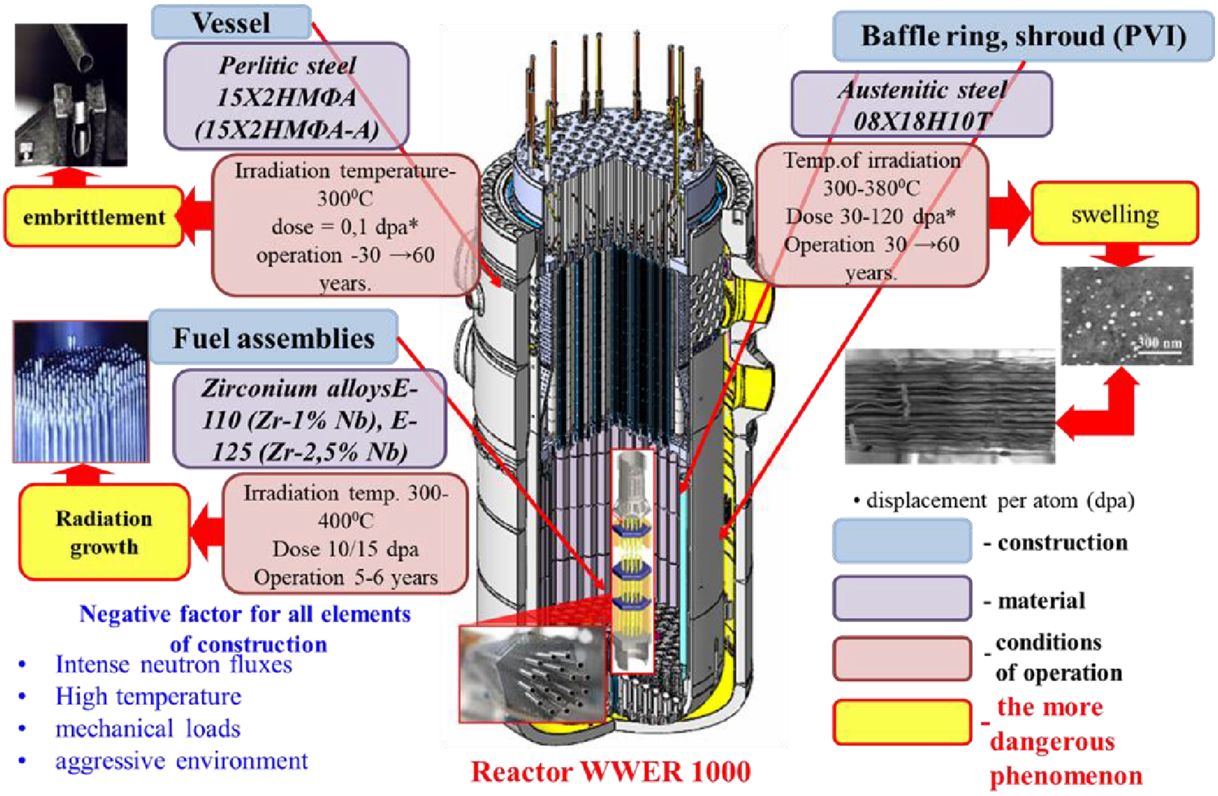


Fig. 3. Overview of cross section of the reactor WWER-1000

Radiation-induced variations are the cause of complex synergetic changes in steel behavior that can`t be explained only by one mechanism. It is supposed in paper [6] that evolution of radiation damage in pressure vessel steels occurs as follows: formation of primary defects → nanostructure evolution → strengthening → embrittlement (shift of temperature of brittle-ductile transition). Numerous investigations had showed that during operation pressure vessel materials strengthen – their yield strength increases. The yield strength of pressure vessel steels after irradiation to fluence 10^{22} n/cm^2 at the temperature of 240…290 °C increases by 20…40% [9].

It is assumed that hardening is the cause of embrittlement of these steels in the result of the irradiation, mainly at the expense of formation of ultra-fine precipitates of copper and copper-enriched zones or copper-vacancy clusters [7]. Processes of formation of grain-boundary or intragrain segregation of impurities (mainly of phosphorus) play the important role in the irradiation embrittlement due to the influence of hardening mechanism (radiation-induced changes in phase composition, formation of dislocation loops and precipitates) and not-hardening mechanism (formation of grain boundary and intergranular segregation) [8, 9] (Fig. 4).

In pressure vessel steels for reactor WWER-1000 the content of phosphorus and copper was considerably decreased. In the same time for reactors WWER-1000 that operate under higher pressures in comparison with reactors WWER-440 the steel 15Cr2NiMoFA with Ni addition was developed. Increase of this steel hardenability is attained at the expense of additional alloying by nickel that also increases the toughness. Unfortunately, some pressure vessels of Ukrainian reactors have nickel content that exceeds considerably the specified value (KhNPS – 1.88%, SUNPS – 1.72%).

Because in RPV steels of Ukrainian NPS the content of phosphorus and copper is rather low and nearly the same for all units and the concentration of nickel and manganese are much different effect of the shift of temperature of brittle-ductile transition under irradiation may be related with different content of nickel in steel.

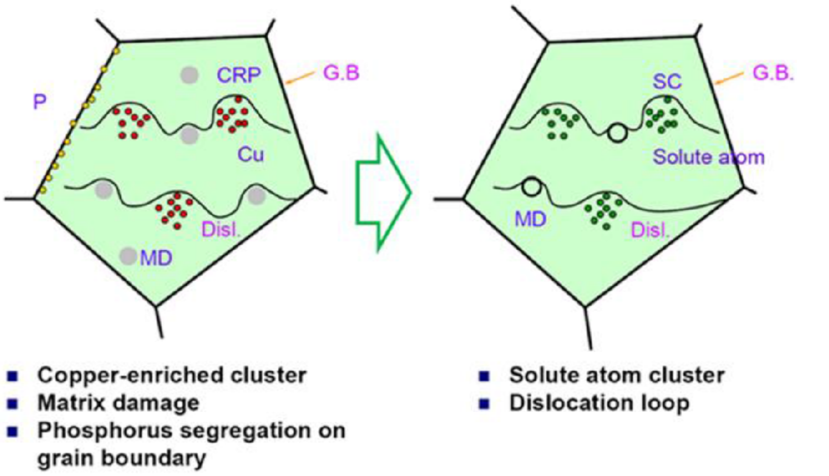


Fig. 4. A schematic overview of the radiation-induced changes in phase composition-formation of dislocation loops and precipitates and formation of grain boundary and intergranular segregation [9]

Dependence of embrittlement coefficient A_F for vessels (welds metal) of Ukrainian NPPs versus nickel content (Fig. 5), shows that up to Ni content near 1.6%, influence of nickel on level of radiation embrittlement is negligible [10]. At nickel value close to 1.7 wt.% the significant change in the A_F level is fixed – from the lowest (A_F ~ 10 °C) to the highest (A_F ~ 23 °C), which exceeded the normative value by 20 °C. It is shown that at 1.88 wt.% nickel (weld metal of the reactor vessel, unit No. 1 of KhNPS) the highest degree of embrittlement (A_F = 25 °C) take place.

Thus, for the welds metal with a nickel content from 1.1 to 1.88 wt.% recorded its limit value in the range of 1.5 to 1.6 wt.% below which the effect of nickel is negligible.

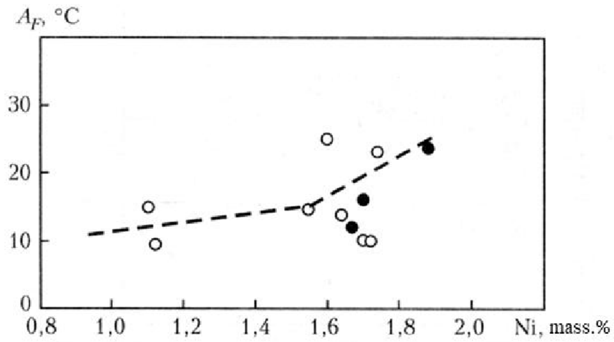


Fig. 5. Dependence of the radiation embrittlement coefficient A_F on the nickel content for the weld metal of reactor vessel [10]

However, according to [11], "late blooming phases" (LBPs) should be formed at sufficiently high fluences in low Cu steels, which contain a significant amount of Ni and Mn. Specific feature of formation of these phases consists in the long incubation period and rapid grow thereafter. Therefore, formation of LBPs should result in sudden severe embrittlement, so, it can be dangerous for RPV under long time operation condition.

The expected forecast of the radiation embrittlement needs the accelerated irradiation of specimens in test reactors to fluences near and higher the designed fluencies [12, 13]. The recent investigation of wells in reactors WWER-1000 revealed the presence of the effect of dose rate, namely demonstrated systematic differences in kinetics of radiation embrittlement of steels irradiated with difference fluxes (increased embrittlement at low flux [14, 15]). Therefore, the use of data, obtained at accelerated irradiation for extension of service life must be justified. This requires the precise understanding and evaluation of mechanisms responsible for effect of the flux.

In XX century used materials and technologies were directed to guarantee the specified life of reactors during 30 years. Just in this period it is became clear that single-mined development of technologies may cause the reconsidering of norms at the expense of decrease of evaluation conservatism and influence considerably on increase of materials service life. Now in all country's new units of NPP are oriented on reaching of specified life not less 60 years with possibility to it increase as minimum by 20…30%, that is to 80…90 years. The orientation on such long service life forces to revalue the problems of operation of the units of NPP [16].

Development of material science caused the considerable progress in development of technologies of steels production – increase of accuracy of introduction and monitoring of alloying elements and impurities, increase of the level of refinement of steel from undesirable components, increase of the degree of processes control (continuous mass-spectrometry, express analysis of gases and oxygen, temperature, protective atmospheres) [17].

Analysis and generalization of high quantity of data on effect of impurities on radiation brittleness allowed to put forward the requirement about decrease of phosphorus and copper content to 0.006 and 0.06% respectively, also as decrease of general content of antimony, tin and arsenic (total < 0.015%). It is supposed that optimal alloying by nickel 0.6…0.8% and correction of chromium (< 3% mass) and molybdenum content (0.5…0.8% mass) will provide thermal and radiation stability of steels and extend the life of pressure vessel not less than 60 years with possibility of extension to 80…100 years [18].

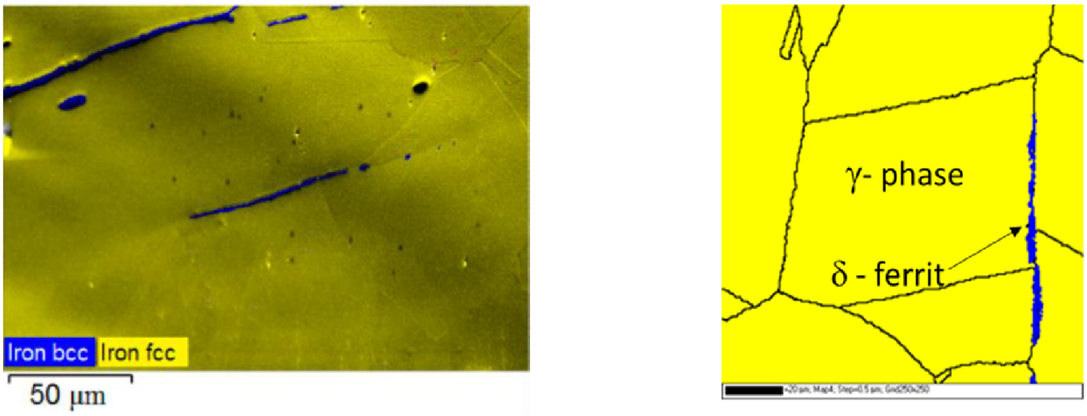
2. MATERIALS OF PRESSURE VESSEL INTERNALS

The problem of lifetime extension of Eastern pressurized water reactors up to 60 years is primarily connected with the life time of irreplaceable equipment-RPV and reactor vessel internals (RVI) [19]. One of important challenge for radiation material science is substantiation of radiation resistance of materials for RVI of reactors WWER-440 and WWER-1000 which were designed as irreplaceable element of construction with operation term which is equal to the operation life of RPV.

The void swelling of SS is one of the major factors that were found to limit the lifetime of the internal structural components under fast reactor irradiation conditions, although it was previously considered that under conditions characteristic of water-cooled reactors that swelling would not occur [20]. In 1994 it was predicted that swelling would most likely occur as a consequence not only of gamma-heating of thick plates but also as a consequence of the lower dpa rate characteristics of PWRs [21].

Numerous experiments show that high doses of neutron irradiation characteristic for operation of PVI will cause the considerable degradation of physical-mechanical properties of 18Cr10NiTi SS (decrease of ductility and crack resistance, nucleation and increase of radiation swelling). Low temperature boundary of void occurrence in materials irradiated in different reactors makes 300…310 °C [22]. The features of swelling in conditions of thermal reactors are the shortening of incubation period of swelling and significant decrease of temperature of void production. Potentially this problem is much more dangerous for reactors WWER-1000 baffle ring which has more complicated shape and higher thickness than in reactors PWR. This induces the local increase of the temperature up to 400 °C and void production even without effect of temperature shift. Besides its austenitic SS 18Cr10NiTi in solution treated condition most prone to swelling.

Only a few studies were carried out for samples after real neutron irradiation in light water reactors (with the corresponding neutron spectrum and typical operating times) [23]. PVI specimens cut from the decommissioned in 2016 WWER-440 unit after 45 years of operation have been studied [19]. Noted that neutron irradiation can lead to austenitic (γ) to ferrite (α) transformation that can drastically decrease the fracture toughness and plasticity of PVI. In addition, ferrite can also form in the initial state under thermo-mechanical treatment (Fig. 6,a). The same ferrite plates were observed in NSC KIPT on samples of aged steel, which were cut from the cover of steam generator of Rivne NPP [24]. The structure of aged steel 18Cr10NiTi was two-phase. Along with austenitic grains there are grains of δ-ferrite in the form of narrow layers (see Fig. 6,b).



a *b*

Fig. 6. Typical EBSD-images of 18Cr10NiTi steel: a baffle in WWER-440 unit after 45 years of operation [19] (a); a cover of steam generator of Rivne NPP after 145.8 thousand hours of operation [24] (b)

It is possible to suggest strong influence of segregation processes during thermal ageing. Therefore, investigation of influence of thermal ageing on swelling at high irradiation doses seems very prospective.

Topical line of investigation is analysis and generalization of the law of the effect of different operational factors, such as irradiation temperature, damaging dose, mechanical stresses, dose rate, concentration of helium and hydrogen and others on swelling and microstructure of steels of austenitic class, forecasting of serviceability of reactor elements under high damaging doses typical for life extension procedures.

Results of tremendous investigations (Programs of material science accompaniment of safe operation of PVI for reactors WWER-1000 of NPS of Ukraine) have improved prediction of behavior for PVI materials at long terms of operation.

Using accelerator irradiations with Cr^{3+} and Ar^{+} ions allowed studying effects of dose rate, different initial structure state and implanted ions on features of structure evolution and main mechanisms of degradation including low temperature swelling and embrittlement of the 18Cr10NiTi steel [25, 26]. It was shown that differences in dose rate at most irradiation temperatures mainly exert their influence on the duration of the swelling transient regime. A decrease of dose rate causes swelling to start at lower temperatures.

The literature data [27] on the swelling of AISI 304 (18Cr9Ni) steel after irradiated in a fast reactor EBR-II were analyzed. A correlation between the transient stage of swelling and the steady state swelling rate was revealed (Fig. 7). The longest transition stage is observed at the peak swelling temperature, followed by a steady-state stage with the highest swelling rate. The transition stages are shortened, and the steady-state swelling rates are decreased at temperatures below and above the peak swelling temperature.

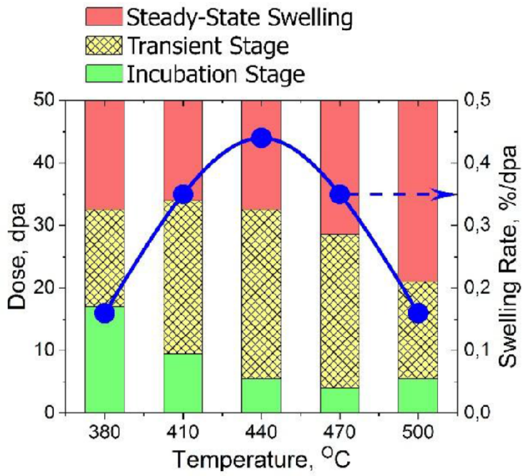


Fig. 7. Correlation between transient stage durations and steady-state swelling rates in AISI 304 steel

The maximum swelling rate of AISI 304 steel irradiated at a dose rate of $5\cdot10^{-7}$ dpa/s is observed near a temperature of 440 °C (see blue curve in Fig. 7). This temperature, in turn, is the temperature of the maximum swelling. A fairly long transient stage is observed at this temperature (see yellow shaded area in Fig. 7).

The swelling rate of steel decreases by about a quarter, and the transient stage preceding it decreases by about 10% when the temperature dropped or raised by 30 °C relative to the peak swelling temperature.

The tendency to shorten the transient stage and a decrease in the swelling rate are even more pronounced when the temperature changes by 60 °C relative to the peak swelling temperature, herein the transient stage is almost halved, and the swelling rate drops by about three times.

Substantiation of the service life of PVI and supporting elements of reactor WWER-1000 and also providing of strength and service life of RPV of WWER on life extension up to 60 years and more requires the development of methods and recommendations on choice of starting data (swelling, change of mechanical properties and others).

3. ZIRCONIUM BASE ALLOY

In the nearest 50…60 years thermal reactors will dominate in park of commercial nuclear power units which produce electric energy. The main material of the core of these reactors is structural materials on the base of zirconium. Due to the optimal concentration of nuclear (particularly of so called “neutron penetrability”), corrosion, mechanical, thermal and other physical-mechanical properties zirconium alloys were non-alternative structural materials for nuclear power, especially, for complete set of the cores of light-water reactors with operation temperature of coolant 300…350 °C [28]. Zirconium alloys alloyed by Nb (E110, E125) or Sn, Fe, Cr, Ni (E635, Zirlo, Zry-2, Zry-4) are widely used in core of water-cooled NR [29].

Unfortunately, the accident on Japan NPS “Fukusima” requires the critically increasing safety of zirconium base alloys, which served as claddings of NPP on thermal neutrons, especially reduction of the possibility of steam-zirconium reaction. Providing of operational safety, specified life and safety of nuclear plants allowing for economic and ecological factors may be realized on claiming of very severe demands which considered degradation of structural materials of fuel elements (FE) and fuel subassemblies under the influence of high temperature, neutron irradiation and corrosion into coolant.

Zirconium alloys which are used now as claddings in reactors WWER, RBMK, PWR, BWR, CANDU differ considerably as to deformation of radiation growth, radiation creep, corrosion resistance, high-temperature strength, hydrogenation and other properties that guarantee reliability of products. Relationship of operational parameters and criteria, performance of production with high number of technological operations and products characteristics is the subject of deep study [30].

The total quantity of alloying elements (weight %) in zirconium alloys doesn’t exceed 2.5…3.0% and even low variations of composition changes considerably its radiation and corrosion resistance. Therefore, any change of alloy composition demands the high attention and testing from point of view of reliability and safety. For instance, decrease of tin content from 1.5 to 1.0% in alloy Zry-4 demanded testing during 10 years.

On solving the above-mentioned tasks, it is necessary to consider the following phenomena which cause the degradation of characteristic of zirconium alloys: hydrogenation, oxidation, radiation-thermal creep, radiation growth, change of mechanical properties, microstructure changes.

Alloy E110 is used now on Ukrainian NPP; this alloy has high resistance to uniform attack, is subjected to noticeable forming in reactor and to corrosion under boiling and increase content of oxygen in coolant. As to the phenomena which influence negatively on operational characteristics, these are: deformation of radiation growth, radiation-thermal creep and corrosion [31]. Radiation growth of tubes is determined as their elongation in axial direction without stresses; this elongation depends on alloys composition, initial dislocation structure, texture, fluence of neutrons and temperature.

In NSC KIPT phenomenological mechanisms of the phenomenon of radiation growth is proposed [32]. Thermal mechanical treatment used on production of tubes for FE produces the anisotropic orientation of zirconium grains. Radial oriented grains dominate into texture of FE, that is, the direction of axe **c** is chiefly radial (in certain range of angles; this is named the structure scattering), and direction **a** is chiefly tangent**.** Such texture of FE claddings is the reason of that during radiation growth the increase of the length of FE occurs with simultaneous contraction.

Under displacing irradiation formation and evolution of radiation defects in the form of dislocation loops of

a- and **c**-types occurs which have Burgers vector 1/3 [1120] and 1/2 [0001], respectively. **c**-component loops are deposited on base of pyramid planes of hcp lattice and have vacancy character. Dislocation loops of **a**-type are interstitial. On early stages of irradiation dislocation loops (mainly interstitial) form in prismatic planes with Burgers vector of **a**-type; this is accompanied by moderate radiation growth. After reaching of some threshold fluence (is different for alloys of different composition) formation of **c**-component dislocation loops is observed, this induces the acceleration of radiation growth. With the increase of irradiation dose, the density of dislocation loops of **c**-type increases because the vacancies are directed on base of pyramidal planes and interstitials stabilize **a**-loops in prismatic planes.

Necessity of reaching of fuel elements burn-up up to 75…80 MWt·d/kg uranium; increase of service life from 30000 to 46000 effective hours; increase of cladding temperature to 358 °C; possibility of power variation needs the development of new zirconium materials with higher radiation and corrosion resistance for prospective fuel cycles. All this requires the study of mechanisms and laws of composition influence on formation of structure-phase state of alloys and their physical-mechanical characteristics under irradiation.

Analysis of trends of development of zirconium alloys for nuclear power shows that the main alloying elements are: Sn, Nb, Fe. Low additions of Cr, Cu, V may promote the resistance to corrosion and saturation by hydrogen; Sn, Fe, O and their content into solution with Zr guarantee strength and resistance to creep and radiation growth; increase of the degree of cold deformation (from 65 to 95%) increases the creep; increase of recrystallization degree decreases the creep; texture determines anisotropy of mechanical properties, of creep and orientation of hydrides; **c**-dislocations into microstructure increase the rate of radiation growth; type intermetallic particles, their size and density and change them under neutron field are of high significance for corrosion, creep and radiation growth.

Oxygen which is contained in zirconium alloys dissolves in α-zirconium in rather high quantity [33]. In low quantity (900…1400 wt. ppm) oxygen doesn't influence on corrosion of zirconium but hardened it considerably. Mechanism of hardening is that the region around dislocations represents the sink for vacancies and interstitials. For instance, at temperature 300 °C atoms of oxygen in zirconium interact with dislocations and harden considerably unirradiated material. Therefore, oxygen must be considered not as impurity but as alloying element. High quantities of oxygen are not used due to its embrittling effect on zirconium alloys [33]. However, chemical-thermal treatment of finished fuel tubes in gaseous media containing oxygen (or nitrogen) leads to a significant solid solution hardening of the surface layer of the tubes, which increases their resistance to cavitation wear and abrasion [34]. In this case, the mechanical properties of the tubes (tensile strength, yield stress, long-term strength and plasticity) remain at the same level or even increase [35]. At the same time the surface layer saturated with oxygen (nitrogen) hinders the penetration of hydrogen into the body of the tubes and reduces the number of hydrides, which causes the so-called hydride cracking [36]. Note that processing in gaseous environments is a fairly simple, well-controlled process and it can be carried out on existing industrial equipment for the final annealing of tubes.

In recent years new way for material characteristics improvement are widely studied; they are connected with the formation of nanostructured and ultra-fine-grained states. The more prospective way for production of materials of such class is severe plastic deformation, realized by different methods. In NSC KIPT several methods of severe plastic deformation are developed such as multicycle process of upsetting-extrusion and its combination with deep deformation by drawing, by rolling, by quasi-hydroextrusion at room, high or cryogenic temperatures [37].

In [38] evolution of microstructure, texture and structural parameters of pure zirconium are thoroughly investigated during severe plastic deformation by different methods. It is revealed that warm deformation of zirconium by the method "upsetting-extrusion" at temperature near 500 °C fines the grain effectively up to submicron values. So, at total logarithmic deformation $e_{tov} \approx 4$ the average size of the grain is 320 nm. The cold deformation of starting ingot by "upsetting-extrusion" causes non-monotonous change of mean size of grain. The minimal obtained size of grain is near 250 nm at deformation $e_{tov} = 8$, that is doesn't reach the nanostructured boundary. The cold deformation by drawing of recrystallized zirconium with starting size of grain 5…15 μm induced the high fragmentation of grains and the mean size of grain at deformation degree $e_{tov} = 6.2$ makes approximately 100 nm. Analogous grain size is realized on drawing of extruded rod with starting grain size 380 nm with deformation degree $e_{tov} = 5.6$. In other words, in spite of difference of starting size of grain more than one order the final size of grains turned out to be practically the same and reached the limit value, which can be realized at this type of intense plastic deformation. The cases of such restriction may be processes of recovery of dynamic recrystallization, which are realized at high degree of accumulated deformation. Zirconium and its alloy with niobium in submicron and nanostructural states have high strength characteristics and can have increased radiation resistance. However, the question remains of the thermal stability of such a material under operating conditions in NR.

4. MODERN STATE OF DEVELOPMENT INTO THE FIELD OF PRODUCTION OF NUCLEAR FUEL RESISTANT TO ACCIDENTAL CONDITION FOR WATER-COOLED REACTORS

Improvement of the economy of nuclear power is directed on increase of power of isolated units of Nuclear Power Stations, increase of operating period and nuclear fuel burn-up, possibility to maneuvering by reactor power. All this also as necessity to guarantee safety of NPS in case of emergency, especially with the loss of coolant, increases substantially the requirements to structural materials of reactor core. Now these are mainly zirconium alloys because their low cross-section of thermal neutron capture, high radiation and corrosion resistance, long-term operation in reactors.

The main problems of existing zirconium alloys are: decrease of corrosion resistance at temperatures of coolant above 400 °C, intensive oxidation with the release of high quantity of hydrogen in accident with the coolant loss (LOCA), fretting-wear, accumulation of high quantity of hydrogen and embrittlement with fuel burn-up more than 50 GW·d/MtU (gigawatt day for metric ton of uranium) [39].

The higher danger in light-water reactors is the accident with the loss of coolant. In the case of such accident on switching-on of the system of passive cooling the reactor core continues to release the heat of radioactive decay and water will transform into vapor. With the increase of vapor temperature, the oxidation of fuel claddings produced of Zr-alloys will accelerate and, in the result, high quantity of explosive hydrogen will be produced so as the considerable quantity of additional heat due to the high enthalpy of ZrO_2 production. Quick oxidation of fuel elements of Zr-alloys starts in the range 700…1000 °C at high pressure of vapor. Besides, breaking of fuel rods cladding may starts at temperature higher ~ 900 °C, because the Zr-alloys loss mechanical strength at temperature > 850 °C. In the case of pressure drop in the result of the tube rupture hydrogen explosion can occurs and products of radioactive decay will get in environment [40]. The example of such accident is the accident on Japanese station Fukusima in 2011. The severity of the nuclear event at Fukushima Daiichi has been rated 7 on the International Nuclear and Radiological Event Scale (INES), the highest level and the same as the 1986 Chernobyl NPP accident [41].

Now round the world exist two main approaches in development of new fuel claddings resistant to accidental conditions (*ATFC – accident-tolerant fuel claddings*): revolutionary one and evolutionary [39].

Revolutionary approach (long-term > 15 years) – development and introduction of fuel cladding produced of new materials: SiC/SiC-composites, FeCrAl-alloys, metal-ceramics hybrids, Mo-alloys.

As example for new fuel cladding SiC/SiC-composites may be used instead traditional zirconium alloys. The main advantage of such composites is very high oxidation (up to 1500 °C) resistance. But these composites have also essential disadvantages: production is very complicated, it is difficult to guarantee the pressure tightness of cladding, they have low toughness and may dissolve in coolant at operational temperature with the formation of volatile hydroxides [42]. Usual austenitic SS have higher resistance to oxidation than zirconium alloys and high mechanical properties but they have not sufficient quantity of Cr and Ni for providing protection at temperature 1200 °C and higher. High concentrations of nickel are also unacceptable due to formation of long-lived isotopes. One of possible candidates for new claddings of fuel elements may be molybdenum or molybdenum alloys due to their high melting temperature (2623 °C), high strength and creep resistance at high temperatures. The serious disadvantage of such alloys is radiation embrittlement, higher than in zirconium, cross-section of neutron capture and formation of volatile (MoO_3) compound in oxidizing conditions, that is, they can`t be used without protective coatings. Possibility to replace zirconium alloys by Fe-Cr-Al-alloys is widely investigated; these alloys have high oxidation resistance in normal operational conditions and at high temperatures, high strength and high workability. They also have some disadvantages: relatively lower melting point, higher cross-section of neutron capture, relatively high permeability for hydrogen isotopes than Zr-alloys and lack of information about their radiation resistance.

Evolutionary approach (mean-term, < 10 years) – this is surface modification of zirconium alloys by protective coatings. Modern zirconium alloys used as materials for fuel claddings may be divided according their main alloying elements on two forms which have niobium (E110, E125, M5) and have tin (Zircaloy-2, Zircaloy-4). Significant efforts in the field induced the development of improved alloys alloyed simultaneously by tin and niobium (Opt. ZIRLO, J-Alloys, AXIOM, MDA, E635, HANA, and others). The smallest thickness of oxide film at high burn-up of fuel has alloy M5 [43]. New alloyed zirconium alloys may satisfy requirements of higher burn-up of the fuel, increase of cycle duration (from 12 to 24 months), somewhat higher temperature of coolant but they can`t guarantee the necessary resistance in accident conditions.

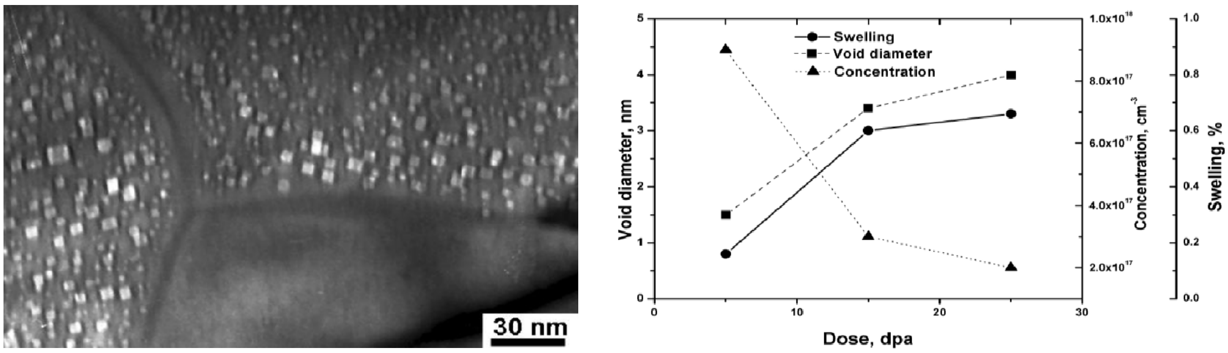
Use of protecting coatings is prospective and economically favorable solution because it is possible existing zirconium claddings and technologies of their production [44]. The oxidation-resistant coating can protect the zirconium alloy cladding from a chemical reaction with high-temperature water, which was the primary source of the H_2 explosion in the Fukushima accident.

Material of protecting coating on zirconium may possess following properties: high corrosion resistance in coolant at normal operation of reactor; high resistance to oxidation at higher temperatures (to 1200 °C) in vapor and on air; melting temperature not lower than that in zirconium (1852 °C); low cross-section of thermal neutron capture; low hydrogen permeability; high thermal conductivity; high hardness and good adhesion to zirconium; radiation resistance not lower than that of zirconium; doesn't produce long-lived radioactive isotopes.

Materials which meet these conditions are: chromium, some oxides Y_2O_3, Cr_2O_3, Al_2O_3, and also nitrides ZrN, CrN, TiN, and carbides ZrC, Cr_3C_2, SiC. The highest resistance to oxidation at high temperatures has SiC but its use is limited by it dissolution into coolant under normal conditions of operation and very low ductility in comparison with zirconium. The new prospective class of materials which can be used for protection of zirconium claddings are composites on the base of MAX-phases with stoichiometry $M_{n+1}AX_n$ (n = 1, 2, 3), where M – transition metal; A – element of IIIA or IVA group and X – carbon or nitrogen [45]. These materials with structure of nanolaminates have extraordinary combination of ceramic and metallic properties: are subjected to mechanical treatment, are thermally stable, have high strength, thermal conductivity, resistance to thermal shocks and high-temperature oxidation, their ductility increases at ~ 1000 °C, they are also radiation resistant. As to protection of zirconium claddings coatings of composition Ti_3SiC_2 and Ti_2AlC are considered [46].

Now the majority of coatings developed for protection of zirconium alloys from oxidation are obtained by magnetron sputtering and cathodic arc evaporation methods. Cathodic arc evaporation method is widely used in industry for deposition of hard coatings (TiN, CrN, DLC etc.) on the machining tools and also for corrosion-erosion protection of different units of machines (turbine blades, for instance) [47]. This method is characterized by high degree of ionization of material flux which is deposited that guarantees the high quality and adhesion of obtained coatings.

Radiation-induced microstructural changes in sub-microcrystalline chromium coatings deposited by cathodic arc evaporation method on zirconium alloy (E110) after irradiation by 1.4 MeV argon ions at 400 °C investigated by TEM [48]. Temperature-independent increasing of grain size from 250 to 295 nm in the chromium coatings is observed under irradiation dose of 25 dpa. Size of radiation-induced voids increases with the increasing of the irradiation dose and its concentration decreases (Fig. 8).



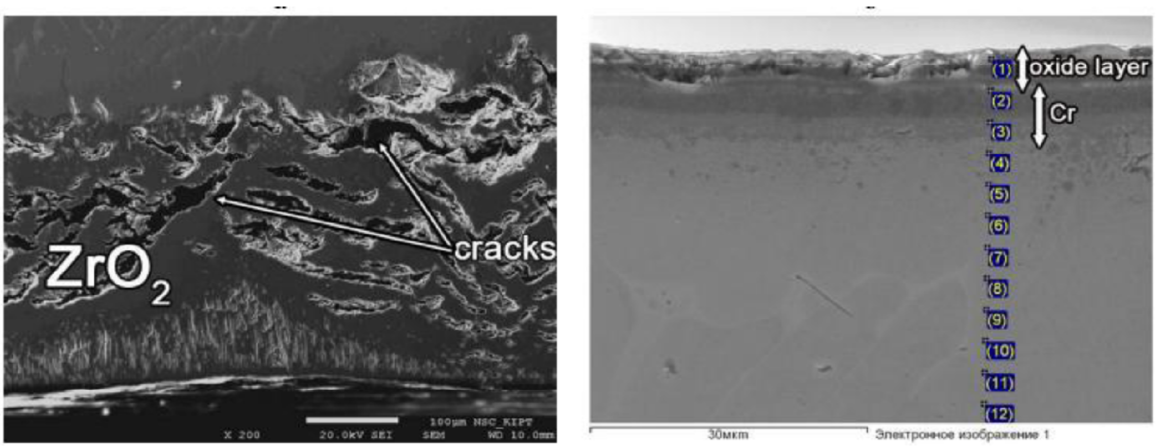
a *b*

Fig. 8. TEM images of Cr coatings irradiated up to 25 dpa (a). Dose dependence of average size, concentration of voids and swelling in irradiated Cr coatings (b) [48]

Radiation-induced swelling is 0.16% under dose 5 dpa and attains 0.66% under the dose of 25 dpa that an order of magnitude lowers than the allowable swelling for the core materials of the reactor. The present results indicate that chromium coatings have a good radiation resistance and can be used as the protection of zirconium alloys fuel claddings for PWR- and BWR-type reactors.

In institutes of NAS of Ukraine the special attention is paid to development of advanced technologies of treatment of zirconium alloys. For instance, in IW named by E.O. Paton electron-beam technology of coating deposition on the base of SiC is developed.

In NSC KIPT during last 5 years vacuum-arc protective nanostructured (multilayers) coatings with thickness 10…20 µm on Zr1Nb alloy claddings are successfully developed. This chromium-based coating can effectively protect Zr-alloy claddings in the case of accident with the loss of coolant (LOCA) not less than 1 h (which is sufficient for accept of correct solving by station operator) and increase their operational possibilities in conditions of normal operation of reactor [48–50]. The high resistance to oxidation of the developed coatings is determined by the formation of a dense chromium-oxide layer on their surfaces (Fig. 9) [50].



a *b*

Fig. 9. SEM micrographs of metallographic cross sections of E110 tubes after air oxidation at 1100 °C during 3600 s: uncoated (a) and with protective Cr coating (10 µm) (b) [50]

The NSC KIPT scientists are involved in the development of SiC-based materials using method of high-speed hot pressing (HSHP) [51], and also, in the studies into the influence of alloying additives on the mechanical characteristics of the SiC [52] and its corrosion resistance under hydrothermal conditions [53]. The best corrosion resistance under hydrothermal test conditions was shown by the SiC ceramics with Cr additions.

Many types of potential accident-tolerant fuel-cladding systems were discussed and three concepts under active development: Cr-coated Zr-based cladding, FeCrAl and SiC/SiC-cladding.

It is expected that one or more of the discussed systems will be implemented in commercial reactors. However, although the study of these new materials is motivated by accidents, it is important to note that other parameters must be considered such as creep, long time corrosion, radiation resistance, hydrogen pickup, adhesion or cladding ballooning etc. Intensive research is needed not only on the properties of various new materials and coatings, but also on improving the technologies for their creation.

5. MATERIALS FOR REACTORS OF GENERATION IV

Low efficiency of NR in comparison with thermal electrical station (TES) with solid fuel (nuclear ~ 33…34%, TES ~ 45% and higher and the planned one are in construction in Europe ~ 55%), adoption of "system of passive safety" on stage of NR designing excluding elements of electric automatic equipment (due to their damaging) and minimization of the influence of operators on NR operation (so called human factor) requires the development of reactor plants of new generation.

Three systems which are working on neutrons of fast spectrum (SFR, GFR, LFR, one – on thermal neutrons (SCWR) and two systems (MSR, VHTR), which allowed to work as at fast, and thermal spectrum were selected by world nuclear community [7] as the main objective of Generation IV (Gen IV) reactors – producing an abundant, reliable, proliferation resistant, safe and of course competitive energy.

All these innovative systems are based on a higher running temperature associated to more severe irradiation conditions (higher irradiation dose, fast neutrons). As it is easily understandable the combination of high temperature, high neutron dose and severe environment is a major challenge for the viability of structural materials.

Now is clear that the development of *radiation tolerant materials* is the big scientific/technical goal that is specific to the success of sustainable nuclear energy. Realization of presumptuous programs for development of Gen IV reactors requires the solution of problems of radiation-resistant structural materials capable of operate in fast reactor (E > 0.1 MeV) at fluences to $2 \cdot 10^{16}$ n/(cm^2·s) to damage doses 200 dpa at temperatures 370…710 °C.

These materials must meet following demands [54]:

- have low creep at temperatures to 700 °C and stability of sizes, life ~ 9 years;
- have high radiation resistance to neutron irradiation dose up to ~ 200 dpa;
- provide radiation resistance of cladding material at increased characteristics of high-temperature strength;
- have high mechanical properties: high ultimate strength > 300 MPa at 700 °C, long-term strength > 120 MPa during 10^4 h at 700 °C, percentage elongation > 1%;
- have high corrosion resistance in coolant at increased temperature and chemical compatibility with fuel;
- in contact with fuel and flux of sodium have high chemical compatibility.

Current efforts on R&D of materials for future nuclear technologies are concentrated principally on two directions: improvement of existing materials (mainly austenitic and ferritic-martensitic steels) and creation of innovative materials – oxide dispersion strengthened (ODS) steels and high entropy alloys that will be able to meet the different challenges for the new generations of NR (Gen IV, spallation, fusion).

Austenitic SS (mainly Fe-Cr-Ni system) are of higher interest for their use in core (as claddings and wrappers) of NR which are in operation or under development [55]. Advantages of austenitic SS are well known: a good heat resistance, high corrosion resistance to coolant and fuel. These steels have a good technological ability and have much data on irradiation.

A lot of modification of austenitic steels were developed and investigated. Worlds experience shows that any changing in chemical composition and thermo-mechanical treatment will lead to drastic changing in radiation behavior because it will influence on physical parameters of processes which are involved in phenomena of radiation damage. From this point of view can be important such positions:

- main (basic) components composition;
- alloying elements choice and amount;
- synergistic in alloying elements influence;
- thermo-mechanical treatment.

The neutron irradiations are essential to evaluate and qualify materials for Gen IV systems therefore it is important to note that the effective radiation effects experiments can be performed also using ion-beam facilities.

Really current situation with achievement of high damage doses is very complicated. Now many of these facilities with high neutron flux are shut down (FFTF, DFR, PFR, EBR-II, BN-350, PFR and others).

Kharkov Institute of Physics and Technology (KIPT) during many years was involved into the Program of simulation of Radiation Damage in reactor materials. This simulation method gave a lot of useful results during the study of mechanisms of radiation damage and selection of prospective reactor materials [56].

Experiments in KIPT were carried out on many kinds of austenitic steels and allowed to understand main mechanisms their radiation behavior (Fig. 10) [57].

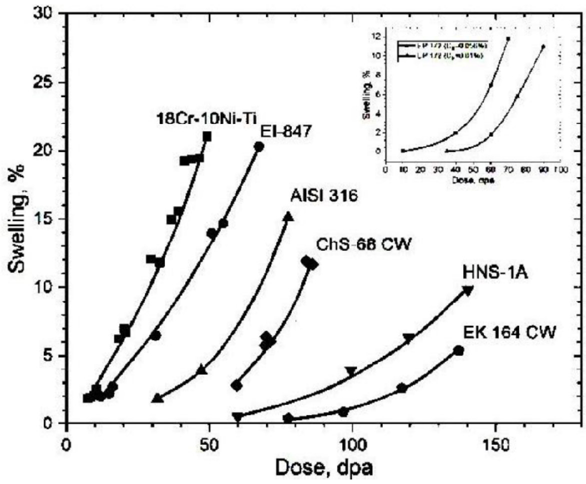


Fig. 10. Dose dependences of swelling for few austenitic steels ($T_{irr} = T_{max\ sw}$) (investigated at KIPT in 1983–2000 years). The inset shows data for samples of EP-172 steel with different B content [57]

Fig. 10 clearly shows that up to now radiation swelling is the very important factor limiting the use of austenitic SS as structural materials for reactors of next generations, because various nuclear concepts require low void swelling of structural steels at very high exposure (≥ 200 dpa). Achievement of necessary level of swelling resistance of austenitic steels with appropriate alloying and thermal-mechanical treatment suitable for commercial use may be obtained only with understanding of all phenomena involved into processes of radiation swelling, because the radiation swelling in multi components austenitic SS is the result of complicated structure-phase transformation under irradiation [54].

It is well known that level of swelling is determined by quantity of surviving points defects which avoid mutual recombination and annihilation on any kinds of point defects sinks which or exits at material before irradiation or were created by irradiation. Any element of defect structure and any element of chemical composition influence on sinks' behavior and diffusion properties under irradiation which as result generally determine swelling level.

Really, design of new radiation resistant steels and prognoses of behavior of these steels under high damage doses possible only as result of understanding of all mechanisms which are involved in processes of radiation damage. The key point of philosophy is that radiation resistance of investigated materials is determined by cooperative interaction of defect structure elements (mainly dislocation components), decaying solid solution and system of the second phase precipitates. Void swelling development is a last step of this evolution. Achievement of acceptable level of swelling is directly related with formation of more stable microstructure under irradiation.

For today the obtained results show that influence of alloying and treatment consists in following:

- production of more stable dislocation structure (conservation of low mobile Frank loops) and increase of the recombination level point defects. It may be reached due to the solution treatment or by the processes of segregation of alloying elements on dislocation components that decreases their mobility;
- saving of fine carbides precipitates (TiC) and phosphides (Fe_2P) up to higher damage doses;
- delay of formation of G-phase and η-carbides will keep in the solid solution the sufficient quantity of such elements as Ni, Si, and P which strongly influence on nucleation and growth of voids.

Evolution of defected structure is the result of "competition" between the evolution of phases preventing the swelling, and phases produced in the result of decay of solid solution or otherwise a competition between swelling resisted phases (MC, Fe_2P) and phases resulted in decay of solid solution (γ', G, and M_6C). This "competition" may be extended by the selection of optimal composition and by the thermal-mechanical treatment. Roles of precipitates as a dominant swelling suppression mechanism, highly depend on the matrix alloying elements that can to change the nature of the precipitates [57].

As a summary, attempts to increase radiation resistance of austenitic SS were done by alloying and cold worked deformation till 20…30%: Nb alloying (16Cr15Ni3MoNb – steel EP-847); addition of B + solid solution stabilization (16Cr15Ni3MoNbB – steel EP-172); multi-stabilization and refining of carbides (Ti,V) (15Cr15Ni2Mo2MnTiVB – steel ChS-68); rare earth addition (16Cr11Ni3MoTiSc – steel EK-99); increasing of Ni content, multi-stabilization and refining carbides (Ti, V, Nb) (16Cr19Ni2Mo2MnTiVNbB – steel EK-164).

Unlike the steels with fcc-structure, which have stable phase component of austenite, in ferritic steels with bcc-structure evolution of all components of defected structure can go in different ways depending on their chemical composition and thermal treatment. It is possible to obtain the different components: ferrite and tempered martensite with different initial structures. It allows to get different types of structure, distribution of precipitates and effect on the radiation resistance.

Well known that swelling of bcc-materials (Fe-Cr steels) typically is much lower than widely used austenitic base alloys. Results show difference in swelling for steels with different Cr-content. Typically swelling of steels with 9 Cr % and which have mainly martensitic structure is lower than in 12% steels, structure of whom consists as from martensite as ferrite (Fig. 11).

It was also shown influence of structure state on processes of nucleation and growth of voids. In duplex steel EP-450 voids appear earlier and growth faster in ferrite than in tempered martensite. It can be explained by this fact that dislocation components in ferrite and tempered martensite serve as defect sinks in different way that may be associated with different degree of impurity atoms interaction with dislocations in ferrite and tempered martensite. Different concentration of carbon in ferrite and tempered martensite may also influence on this effect.

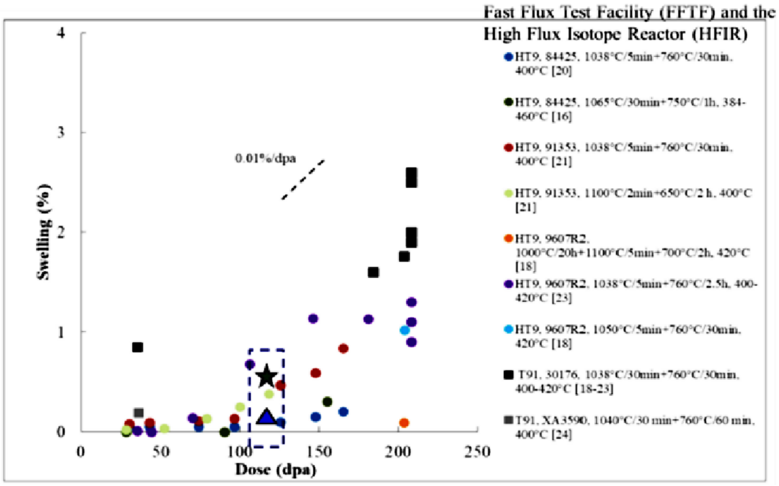


Fig. 11. Compilation of data for steels HT9 and T91 irradiated in a reactor to a dose 208 dpa at temperatures from 400 to 443 °C [58] and ferrite (★), and martensite (▲) T91 [59]

It was established that bcc-iron and ferritic alloys on its base have immunity to high rate of swelling. But the question remains: if always α-alloys will have low rate of swelling and if can swelling of these alloys under high dose of irradiation (more than 100 dpa) reach the value of several tens of percent's?

The effect of high-dose irradiation on swelling of ferritic alloys has been identified in [60]. After long-term incubation stage ~ 150 dpa the transition is observed to steady state stage of swelling with the rate 0.14%/dpa and swelling of steel with bcc-lattice may reach the value more than 20%. Dependences of swelling on irradiation dose are shown on Fig. 12. It was also demonstrated that for steel HT-9 (American production) and for alloy Fe-9Cr-1Mo the rate of swelling may be compared with the rate of swelling detected in pure alloy Fe-12Cr but after considerably higher incubation period [61].

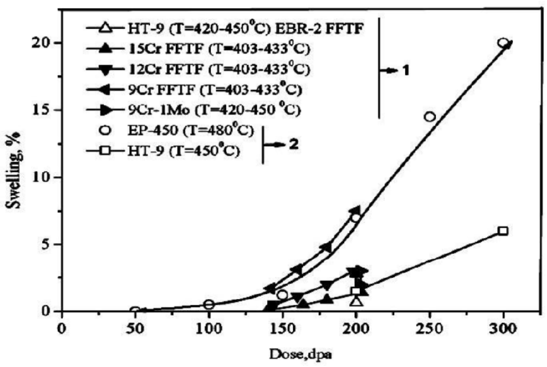


Fig. 12. Dose dependence of swelling for Fe-Cr binary alloys and F/M steels [60, 61]

As noted above, one of the directions in which current effort on R&D of materials for future nuclear technologies are concentrated – *creation of innovative materials* – ODS steels and high entropy alloys.

One of the suggested methods of this problem solution is increase of radiation resistance and high-temperature strength as austenitic and ferritic steels at mechanical alloying of steel matrix by nanoscaled oxide particles [62]. Secondary oxides formed on thermal-mechanical treatment of mechanically alloyed steels are precipitates of complex nanosized non-metallic compounds with covalent bond. They may be stable to temperatures 1400 °C and have high radiation resistance (higher 150 displacements per atom), and also guarantee augment resistance of plastic deformation of steel and this had determined the terminology "oxide-dispersion strengthened steel" (ODS-steel). Unfortunately, modern status of knowledge for ODS behavior under irradiation is far from being sufficient for nuclear application and needed a lot of investigation for implementation of ODS steels to nuclear industry.

In NSC KIPT the experimental technology of fabrication of austenitic ODS steel 18Cr10NiTi is developed. The composition of base nanoscaled powders of oxides of the system Y_2O_3-ZrO_2 and conditions of mechanical-thermal treatment are defined. It is established that in obtained by this technology bands of ODS steel after final thermal treatment the austenitic matrix steel have grain size 1.2…2 µm and the density of precipitates of complex nanooxides changes in the range $(1.7…7.3)\cdot10^{15}$ cm^{-3} at mean size near 10 nm. The higher density of precipitates at lower mean size and higher homogeneity of their distribution by volume is observed in specimens alloyed with nano-oxides of composition 80 mol.% Y_2O_3-20 mol.% ZrO_2 [63].

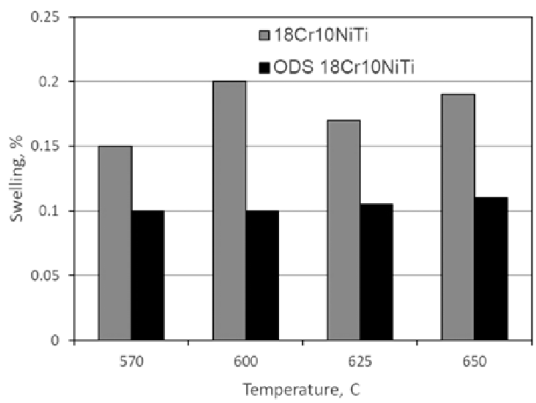


Fig. 13. Evolution with temperature of the swelling for 18Cr10NiTi and ODS 18Cr10NiTi [64]

Investigation of swelling features in ODS 18Cr10NiTi + 0.5% (80 mol.% Y_2O_3-20 mol.% ZrO_2) after irradiation at accelerator of heavy ions showed that level of swelling at determined swelling maximum was 2 time less relatively base steel 18Cr10NiTi (Fig. 13) [64].

Suppression of swelling is caused by the increase of possibility of point defects recombination on sinks. Sinks are boundaries of “nanooxides-matrix” and grain boundaries. The strength of nanooxides-sinks is $4.86 \cdot 10^{14}$ m^{-2} in this case and this is 35 times higher than sinks strength ($1.41 \cdot 10^{13}$ m^{-2}) which is provided by grain boundaries of the size ~ 1.2 µm.

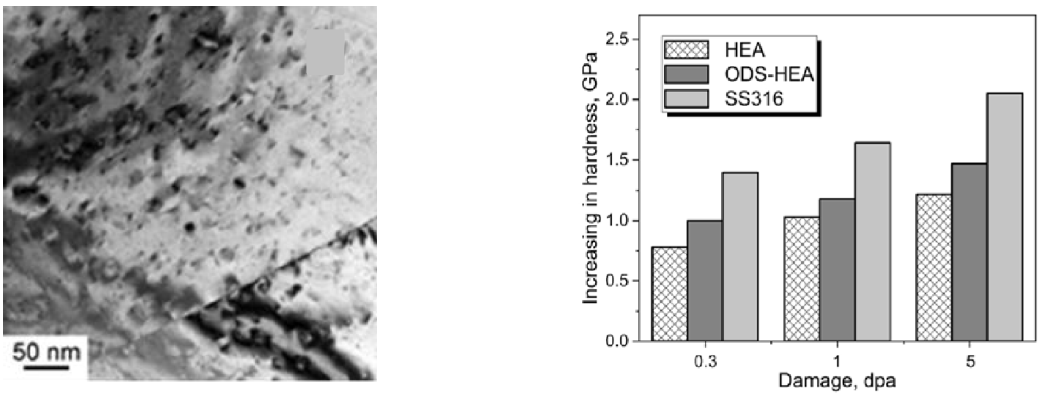
At the same time, characteristics of strength of produced ODS steel also are improved considerably. Especially substantial advantage is observed at temperature of testing 700 °C (this is the maximum operational temperature of fuel element cladding for fast reactors) where the conventional yield strength of ODS steel in three time higher than in base steel 18Cr10NiTi. Ductility on this is some lower but remains on level sufficient for technologic and operational purposes [62].

Later it was shown that even insignificant variation of quantity of added powder ZrO_2 to nanooxide Y_2O_3 in base austenitic steel as well as variation in technological procedures induces the considerable decrease of dimension of grain and precipitates of secondary oxides and also increases the uniformity distribution through specimen of oxides type $Y_2(Ti_{1-x}Zr_x)_2O_7$ which have semi-coherent boundaries with austenitic matrix [65] and positive influence on the strength characteristics of ODS steels at elevated temperatures.

One more promising line for solving the problem of production of radiation resistant and high-temperature strengthened steels consists now into the use of new class of ferritic-martensitic radiation resistant steels strengthened by particles of oxides of nanometer size. These steels have high strength, high thermal stability and good mechanical properties. This trend is intensively developed in countries with developed infrastructure of nuclear power (Russia, USA, Japan, China, France) [66]. NSC KIPT scientists took part in investigation of radiation tolerance of different kind of ODS ferritic steels after very high damage doses [67].

High entropy alloys (HEAs) are principally novel effort in R&D of materials science and engineering [68, 69]. These alloys have multiple metallic elements of nearly equimolar compositions. The high configurational entropy leads to reduce the tendency of forming intermetallic phases and stabilize solid solution state and leads to receiving unique physical-mechanical properties. The prospects for using HEAs in nuclear and thermonuclear power industry are of a great interest. The results obtained in the study of different aspects of HEAs behavior under irradiation with particles of different type were summarized in [70, 71].

Promising features of HEA behavior under irradiation, such as higher resistance to a radiation-induced defect formation, lower void swelling, higher microstructural stability and limited radiation-induced hardening in alloys, have been found in a number of studies. For example, the cobalt free 20Cr-40Fe-20Mn-20Ni (at.%) high entropy alloy and it’s strengthened with yttrium-zirconium nanooxides version have been investigated in relation to the development of hardening phenomenon under the irradiation [72]. The irradiation effects in HEAs were compared with hardening behaviour of 316 austenitic SS irradiated under an identical condition. The main irradiation defects observed in HEAs were defect clusters at low doses and dislocation loops at higher doses (Fig. 14,a).

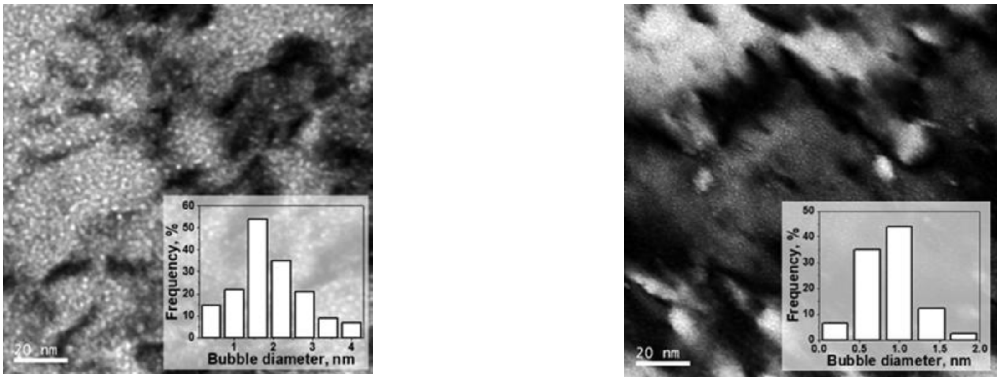


a *b*

Fig. 14. TEM micrographs of ODS-20Cr-40Fe-20Mn-20Ni high entropy alloys irradiated at room temperature with 1.4 MeV Ar ions to 1 dpa (a) and nanohardness increments of the irradiated HEA, ODS-HEA alloys and SS316 [72]

The nanohardness of all studied materials increases with damaging dose and approaches the quasisaturation mode at high fluencies (see Fig. 14,b). Irradiated HEA and ODS-HEA demonstrate lower increase in radiation-induced nanohardness as compared with SS316. These observations suggest that high entropy alloys must lose less plasticity in comparison with conventional austenitic steels of nuclear power. We also note that ODS HEA, like ODS steels, have significantly higher strength characteristics in comparison with alloys without nanooxides [73].

Result of interaction of high-energy particles with atoms of materials is not only atomic displacements but also production of foreign atoms as a consequence of nuclear transmutation reactions. The most important product of nuclear transmutation reactions is gaseous – helium and hydrogen. To simulate the processes occurring with the participation of these atoms, the microstructure Cr-Fe-Ni-Mn high-entropy alloy and 18Cr10NiTi stainless steel after irradiation with helium ions to 4.8 dpa and 11.7 at.% at T_{room} and post-irradiation annealing was investigated [74] (Fig. 15).



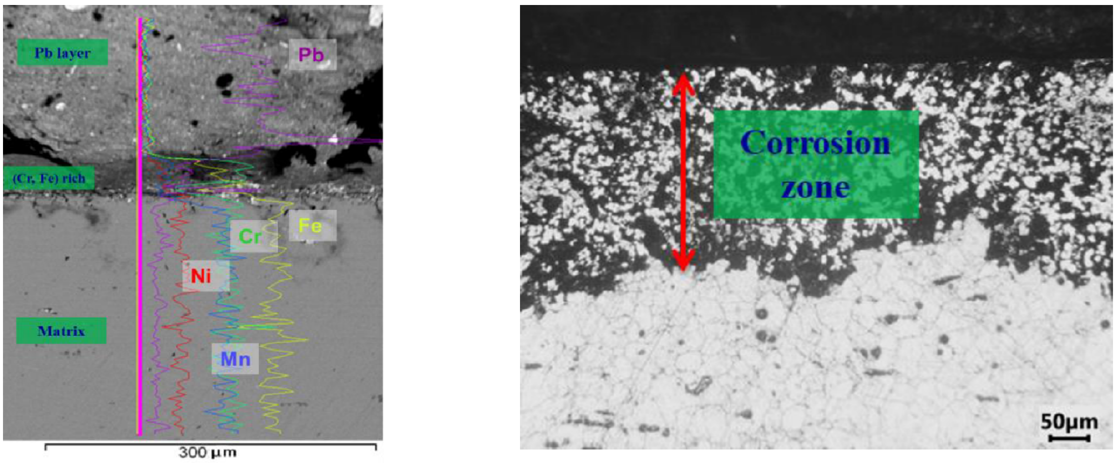
a b

Fig. 15. The morphology and distribution of the He bubbles in irradiated and subsequently annealed 18Cr10NiTi steel (a) and 20Cr-40Fe-20Mn-20Ni high entropy alloy (b) [74]

Irradiation promoted the formation of a high density of bubbles in HEA and steel. Comparison of the parameters of helium porosity in these materials showed that the swelling in CrFeNiMn alloy is about two times smaller than that in 18Cr10NiTi steel. The obtained result indicates that CrFeNiMn HEA is much more resistant to the formation of helium bubbles than conventional 18Cr10NiTi stainless steel.

The potential of HEAs to be used in high-temperature applications is remarkable due to their high-temperature microstructural stability and excellent mechanical properties. However, while the number of publications reporting on HEAs mechanical properties is impressive, far less were dedicated to the evaluation of their corrosion behavior at high temperatures.

Moreover, there were only few publications and communications regarding HEA corrosion behavior exposed to the fluids foreseen in advanced NR Gen IV. Scientists from NSC KIPT (Kharkiv) and Karpenko Physical-Mechanical Institute (Lviv) have been performed evaluation of the compatibility of high-entropy Cr-Fe-Mn-Ni alloys and their hardened by nanooxides version with a liquid lead coolant [75]. Corrosion test were performed at 480 and 580 °C for exposure of 100, 250, 500, and 1000 h (Fig. 16). It was established that for studied alloys compositions at 480 °C the main mechanism of corrosion damage of the surface layers is intergranular corrosion, which consists in the etching of grain boundaries, lead penetration into the matrix and dissolution of chromium, nickel and manganese in liquid lead (see Fig. 16,a).



a b

Fig. 16. Elements distribution on the surface layer of HEAs alloy (500 h exposure at 480 °C) (a) and structure of the surface layer of alloy after 500 h exposure at 580 °C (b) [75]

Increasing the temperature to 580 °C contributes to the implementation of the combined mechanism of corrosion damage, which is realized by the combination of intergranular corrosion, as well as at a temperature of 480 °C, and the diffusion of oxygen from the melt into the matrix and, as the result, implementation of the internal oxidation of chromium and manganese process (see Fig. 16,b). It is demonstrated that the dispersion hardening of HEAs with radiation-resistant nanooxides Y_2O_3-ZrO_2 strongly increases their corrosion resistance. Using these alloys in contact with the lead melts can be recommended to a temperature of 500 °C. Possible options for increasing the operating temperature are optimization of the HEAs composition and additional alloying.

CONCLUSIONS

Nuclear power meets the best the principles of sustainable development; the main requirement of such development is the presence of sufficient fuel-energetic resources on their stable consumption in long-term prospects. Nuclear power of Ukraine is the reliable base of energetic independence of the state, the more developed and highly technologic sector of economy is now the main source of electric and thermal energy.

Materials in nuclear power play extremely important role. The more important peculiarity is that fuel and structural materials of nuclear power plants in comparison with materials for traditional power plants operate in specific and more severe conditions. Development of structural materials of operating and improved nuclear plants if the more complicated scientific-technical problem the solving of which guarantees the radiation material science.

Radiation material science which studies the influence of irradiation by high energy particles of different origin and energy on properties of materials and operational characteristics of nuclear plants makes its important contribution into the solving of these tasks because only on the base of modern scientific ideas about the role of microstructural processes in degradation of base physical-mechanical characteristics the posed goals may be realized.

The further development of fundamental and applied researches in the field of radiation material science, radiation technologies and new nuclear-power sources are needed for increasing the role of nuclear power as a one of the main sources of low carbon energy in the world.

ACKNOWLEDGEMENTS

The work was financially supported by the National Academy of Science of Ukraine (program "Fundamental scientific research on the most important problems of the development of scientific and technical, socio-economic, socio-political, human potential to ensure Ukraine's competitiveness in the world and sustainable development of society and the state") and was prepared within the project No 2020.02/0327 "Fundamental aspects of the new materials creation with unique physical, mechanical and radiation properties based on the concentrated multicomponent alloys", implemented with the financial support of the National Research Foundation of Ukraine.

REFERENCES

1. S. Chu, A. Majumdar. Opportunities and challenges for a sustainable energy future // *Nature*. 2012, v. 488, p. 294-303.

2. Nuclear Technology Review (GC (62) / INF / 2), 2018, 47 p.

3. *The Intergovernmental Panel on Climate Change.* Special Report Global Warming of 1.5 °C.

4. A course of lectures "Nuclear Energy" delivered by specialists of the National Atomic Energy Generating Company "Energoatom" at the Odessa National Polytechnic University (May 14 – 17, 2019).

5. G.S. Was. *Fundamentals of Radiation Materials Science*: *Metals and Alloys.* Springer, Berlin, 2007.

6. V.N. Voyevodin, I.M. Neklyudov. *Evolution of the structure-phase state and radiation resistance of structural materials.* Kiev: "Naukova dumka", 2006, 378 p.

7. M. Akamutsu et al. Influence of some alloying elements on the formation of vacancy defects in ferritic steels during irradiation at 288 °C // *Effect of Radiation on Materials: Proc. of 16-th Intern. Symp., ASTM STP 1175.* 1993, p. 516.

8. G.R. Odette, G.E. Lucas. Recent progress in understanding reactor pressure vessel steel embrittlement // *Radiation Effect and Defects in Solids*. 1998, v. 144, p. 189-231.

9. Naoki Soneda. Current understanding on the mechanism of neutron irradiation embrittlement of RPV steels // *IAEA-ICTP Workshop on Environmental Degradation of Components in Nuclear Power Reactors,* 5–16 March 2012, Trieste (Italy).

10. E.U. Grinik et al. Analysis of the influence of nickel on the radiation embrittlement of the metal of the seams of the WWER-1000 reactor vessels of the Ukrainian NPP // *Collection of scientific articles under the direction of B.Ye. Paton "Problems of resource and safety of operation of structures and machines".* Kyiv, 2009, 709 p.

11. G.R. Odette, E.V. Mader, G.E. Lucas. The effect of flux on irradiation hardening of pressure vessel steels, Effects of Radiation on Materials // *Proc. of 16-th Intern. Symp., ASTM STP.* 1994, v. 1175, p. 373.

12. B. Gurovich et al. Evolution of structure and properties of VVER-1000 RPV steels under accelerated irradiation up to beyond design fluences // *J. Nucl. Mater.* 2015, v. 456, p. 23-32.

13. D.Y. Erak, D.A. Zhurko, V.B. Papina. Interpretation of accelerated irradiation results for materials of WWER-1000 reactor pressure vessels // *Strength Mater.* 2013, v. 45, p. 424-432.

14. E.A. Kuleshova et al. Assessment of segregation kinetics in water-moderated reactors pressure vessel steels under long-term operation // *J. Nucl. Mater.* 2016, v. 477, p. 110-122.

15. M. Lambrecht et al. On the correlation between irradiation-induced microstructural features and the hardening of reactor pressure vessel steels // *J. Nucl. Mater.* 2010, v. 406, p. 84-89.

16. G.P. Karzov, V.A. Nikolaev, G.N. Filimonov. Development and improvement of radiation-resistant steels for vessels of water-cooled atomic reactors // *Problems of Materials Science*. 2006, v. 1(45), p. 111-122.

17. A. Dub. *Progress in the field of technologies.* REA (ROSENERGOATOM), 2012, v. 1, p. 22-27.

18. A.M. Morozov, G.N. Filimonov, A.A. Tsukanov. Basic principles of alloying steels for VVER-type nuclear reactor vessels // *Problems of Materials Science*. 2006, v. 1 (45), p. 103-110.

19. E.A. Kuleshova et al. Microstructure degradation of austenitic stainless steels after 45 years of operation as VVER-440 reactor internals // *J. Nucl. Mater*. 2020, v. 533, p. 152124.

20. F.A. Garner. Chapter 6: *Irradiation performance of cladding and structural steels in liquid metal reactors*, v. 10 A of Materials Science and Technology:

A Comprehensive Treatment, VCH Publishers, 1994, p. 419-543.

21. F.A. Garner, L.R. Greenwood, D.L. Harrod. Potential high fluence response of pressure vessel internals constructed from austenitic stainless steels / R.E. Gold, E.P. Simonen (Eds.) // *Sixth International Symposium on Environmental Degradation of Materials in Nuclear Power Systems – Water Reactors.* The Minerals, Metals and Materials Society, 1993, p. 783-790.

22. F.A. Garner. *Void swelling and irradiation creep in light water reactor (LWR) environments: Understanding and mitigating ageing in nuclear power plants* / Ed. by Philips G. Tipping. Woodhead Publishing Limited, 2010, p. 308-356.

23. K. Fujii, K. Fukuya. Irradiation-induced microchemical changes in highly irradiated 316 stainless steel // *J. Nucl. Mater*. 2016, v. 469, p. 82-88.

24. *Estimation of the effect of thermal aging on the swelling of the materials of VKP WWER reactors*: Report on research work on the program “Problems of resource and safety operation of structures, buildings and machines” (No state registration 0110U004273), 2011.

25. O.V. Borodin et al. Swelling and post-irradiated deformation structures in 18Cr-10Ni-Ti irradiated with heavy ions // *J. Nucl. Mater*. 2004, v. 329-333, p. 630-633.

26. O.V. Borodin et al. Microstructure evolution and degradation mechanisms of reactor internal steel irradiated with heavy ions // *J. Nucl. Mater*. 2009, v. 385, p. 325-328.

27. F.A. Garner, B.J. Makenas, S.A. Chastain. Swelling and creep observed in AISI 304 fuel pin cladding from three MOX fuel assemblies irradiated in EBR-II // *J. Nucl. Mater*. 2011, v. 413, p. 53-61.

28. V.N. Voyevodin. Structural materials of nuclear power – challenge to 21 century // *Problems of Atomic Science and Technology*. 2007, N 2, p. 10-22.

29. V.N. Voyevodin. Current status of zirconium materials in nuclear energy // *Bulletin of the NAS of Ukraine.* 2012, #7, p. 18-20.

30. A.V. Nikulina. Zirconium alloys in nuclear power engineering // *Metallurgy and heat treatment of metals.* 2004, N 11, p. 8-12.

31. D. Gilbon et al. Irradiation Creep and Growth Behavior, and Microstructural Evolution of Advanced Zr-Base Alloys // *12th International Symposium on Zr in the Nuclear Industry,* Toronto, Canada, 1998; ASTM STP 1354, G.P. Sabol and G.D. Moan, Eds., ASTM International, West Conshohocken, PA, 2000, p. 51-73.

32. V.V. Novikov et al. Investigation of the microstructure of zirconium alloys irradiated with zirconium ions on an accelerator // *Atomic Energy.* 2013, v. 1, p. 255-260.

33. O.V. Borodin et al. Influence of oxygen content on evolution of the structure of alloy Zr1%Nb under ion irradiation // *Problems of Atomic Science and Technology.* 2008, N 2, p. 53-61.

34. V.S. Trush et al. Influence of thermochemical treatment on properties of tubes from Zr-1Nb alloy // *Problems of Atomic Science and Technology*. 2019, N 2(114), p. 70-75.

35. V.S. Trush et al. Influence of modification of the surface layer by penetrating impurities on the long-term strength of Zr-1% Nb alloy // *Materials Science.* 2020, v. 55(4), p. 585-589.

36. P.I. Stoev et al. Effect of hydrogenation on the anisotropy of mechanical properties of the fuel elements pipes of an alloys Zr1%Nb // *Problems of Atomic Science and Technology*. 2016, N 2(102), p. 38-45.

37. M.A. Tikhonovsky, A.G. Shepelev, L.V. Panteyenko. Nanomaterials: analysis of trends of development, based on information flow data // *Problems of Atomic Science and Technology*. 2003, N 5, p. 103-110.

38. I.V. Kolodiy et al. Features of zirconium structure formation after severe plastic deformation // *Problems of Atomic Science and Technology*. 2015, N 5(96), p. 98-104.

39. S.J. Zinkle, K.A. Terrani, J.C. Gehin, L.J. Ott, L.L. Snead. Accident tolerant fuels for LWRs: a perspective // *J. Nucl. Mater.* 2014, v. 448, p. 374-379.

40. C. Tang, M. Stueber, H.J. Seifert, M. Steinbrueck. Protective coatings on zirconium-based alloys as accident-tolerant fuel (ATF) claddings // *Corrosion Rev*. 2017, v. 35, p. 141-165.

41. N. Minin, T. Vlček. Post-Fukushima performance of the major global nuclear technology providers // *Energy Strategy Reviews*. 2018, v. 21, p. 98-110.

42. K. Terrani. Accident tolerant fuel cladding development: promise, status, and challenges // *J. Nucl. Mater*. 2018, v. 501, p. 13-30.

43. K.A. Terrani et al. Hydrothermal corrosion of SiC in LWR coolant environments in the absence of irradiation // *J. Nucl. Mater*. 2015, v. 465, p. 488-498.

44. A.T. Motta, A. Couet, R.J. Comstock. Corrosion of Zirconium Alloys Used for Nuclear Fuel Cladding // *Annual Review of Materials Research*. 2015, v. 45, p. 311-343.

45. M.W. Barsoum. The MN+1AXN phases: a new class of solids: thermodynamically stable nanolaminates // *Progress in Solid State Chemistry*. 2000, v. 28, p. 201-281.

46. D.J. Tallman et al. Effect of neutron irradiation on select MAX phases // *Acta Materialia*. 2015, v. 85, p. 132-143.

47. I.I. Aksenov et al. *Vacuum arc: plasma sources, deposition of coatings, surface modification*. Kiev: “Naukova dumka”, 2012.

48. A.S. Kuprin et al. Irradiation resistance of vacuum arc chromium coatings for zirconium alloy fuel claddings // *J. Nucl. Mater*. 2018, v. 510, p. 163-167.

49. A.S. Kuprin et al. Vacuum-arc chromium coatings for Zr-1Nb alloy protection against high-temperature oxidation in air // *Problems of Atomic Science and Technology.* 2015, N 2(96), p. 111-118.

50. A.S. Kuprin et al. Vacuum arc chromium-based coatings for protection of zirconium alloys from the high-temperature oxidation in air // *J. Nucl. Mater*. 2015, v. 465, p. 400-406.

51. V.N. Voyevodin et al. Improvement of microstructure and mechanical properties of high-dense SiC ceramics manufactured by high-speed hot pressing // *Problems of Atomic Science and Technology*. 2017, N 2(108), p. 97-102.

52. K. Lobach et al. Optimization of properties of silicon carbide ceramics with the use of different additives // *Functional Materials.* 2018, v. 25(3), p. 496-504.

53. K.V. Lobach et al. Corrosive resistance of SiC-based ceramics under hydrothermal conditions // *Materials Science*. 2020, v. 55(5), p. 672-682.

54. N.A. Azarenkov, I.M. Neklyudov, V.N. Voyevodin. Reactor materials-modern status // *Bulletin of Kharkov National University named by V.N. Karazin, Series physics "Nuclei, particles, fields"*. 2012, N 1017(3), p. 4-20.

55. *Structural Materials for Generation IV Nuclear Reactors /* Editor Pascal Yvon. Woodhead Publishing. 2016, p. 684.

56. V.N. Voyevodin. Accelerator simulation and theoretical modelling of radiation effects in structural materials // *IAEA Nuclear Energy Series*. 2018, No NF-T-2.2, p. 23-48.

57. F.A. Garner et al. Use of self-ion bombardment to study void swelling in advanced radiation-resistant alloys // *Proc. 17th International Conference on Environmental Degradation of Materials in Nuclear Power Systems – Water Reactors*. 2015, Ottawa, Ontario, Canada.

58. E. Getto et al. Void swelling and microstructure evolution at very high damage level in self-ion irradiated ferritic-martensitic steels // *J. Nucl. Mater*. 2016, v. 480, p. 159-176.

59. V. Voyevodin et al. Structural features and operational characteristics of steel T91 // *East Eur. J. Phys***.** 2020, v. 3, p. 93-98; DOI:10.26565/2312-4334-2020-3-12.

60. O.V. Borodin et al. Radiation swelling of ferritic-martensitic steels EP-450 and HT-9 under irradiation by metallic ions to super high doses // *Problems of Atomic Science and Technology*. 2011, N 2(97), p. 10-15.

61. F.A. Garner, M.B. Toloczko, B.H. Sencer. Comparison of swelling and irradiation creep behavior of fcc-austenitic and bcc-ferritic/martensitic alloys at high neutron exposure // *J. Nucl. Mater*. 2000, v. 276, p. 123-142.

62. S.V. Starostenko et al. Microstructure of 08Kh18Ni10Ti austenitic steel mechanically alloyed with nanooxides of the Y_2O_3-ZrO_2 system // *Materials Science.* 2016, v. 51, N 6, p. 827-832.

63. A.N. Velikodnyi et al. Structure and properties of austenitic ODS steel 08Cr18Ni10Ti // *Problems of Atomic Science and Technology.* 2014, N 4(92), p. 94-102.

64. I.V. Kolodiy et al. Effect of argon-ion irradiation on cavity formation in 18Cr10NiTi austenitic steel and its strengthened version // *Problems of Atomic Science and Technology.* 2020, N 4(128), p. 11-16.

65. S.V. Starostenko et al. Influence of irradiation by heavy ions Cr^{3+} on microstructure of steel 08X18H10T ODS, mechanically alloyed by nano-powder of system Y_2O_3-ZrO_2 // *Problems of Atomic Science and Technology.* 2016, N 4(104), p. 3-8.

66. R.L. Klueh et al. Oxide dispersion-strengthened steels: A comparison of some commercial and experimental alloys // *J. Nucl. Mater*. 2005, v. 341, p. 103-114.

67. M.B. Toloczko et al. Ion-induced swelling of ODS ferritic alloy MA957 tubing to 500 dpa // *J. Nucl. Mater*. 2014, v. 453, p. 323-333.

68. D.B. Miracle, O.N. Senkov. A critical review of high entropy alloys and related concepts // *Acta Mater*. 2017, v. 122, p. 448-511.

69. T.S. Srivatsan, M. Gupta. *High-entropy alloys: Innovations, Advances, and Applications.* Boca Raton: CRC Press, 2020, 758 p.

70. E. Pickering et al. High-entropy alloys for advanced nuclear applications // *Entropy*. 2021, v. 23, p. 98-129.

71. A.V. Levenets et al. High entropy alloys as a prospective class of new radiation–tolerant materials. Research development analysis based on the information databases // *Problems of Atomic Science and Technology*. 2021, N 2(132), p. 3-15.

72. V.N. Voyevodin et al. Effect of irradiation on microstructure and hardening of Cr-Fe-Ni-Mn high-entropy alloy and its strengthened version // *Phil. Mag*. 2020, v. 100(7), p. 822-836.

73. I.V. Kolodiy et al. Microstructure and mechanical properties of oxide dispersion strengthened high-entropy alloys CoCrFeMnNi and $CrFe_2MnNi$ // *Problems of Atomic Science and Technology*. 2021, N 2(132), p. 87–94.

74. A.S. Kalchenko et al. Comparative study of helium bubble formation in Cr-Fe-Ni-Mn high-entropy alloy and 18Cr10NiTi steel after irradiation and post-irradiation annealing // *Problems of Atomic Science and Technology*. 2019, N 5(123), p. 25–29.

75. V.M. Fedirko et al. Influence of the Dispersion Hardening with Nanooxides on the Corrosion Resistance of High-Entropy Alloys of the Cr-Fe-Mn-Ni System in Lead Melts // *Materials Science*. 2020, v. 55, p. 529-535.

Article received 11.08.2021

МЕХАНИЗМЫ РАДИАЦИОННЫХ ПОВРЕЖДЕНИЙ И РАЗРАБОТКА КОНСТРУКЦИОННЫХ МАТЕРИАЛОВ ДЛЯ ДЕЙСТВУЮЩИХ И БУДУЩИХ ЯДЕРНЫХ РЕАКТОРОВ

В.Н. Воеводин*, *Г.Д. Толстолуцкая, М.А. Тихоновский, А.С. Куприн, А.С. Кальченко

Безопасность ядерных энергетических установок (ЯЭУ) и экономичность атомной энергетики во многом определяются конструкционными материалами, из которых изготовлены элементы ЯЭУ. Изучение причин изменения физико-механических свойств материалов и их размерной стабильности при облучении, определение ресурса работы элементов ЯЭУ в различных условиях, выбор и разработка перспективных материалов с высокой радиационной стойкостью являются основными задачами радиационного материаловедения. В статье рассматриваются механизмы радиационного повреждения конструкционных материалов ядерной энергетики, проблемы и перспективы создания радиационно стойких материалов для действующих реакторов и реакторов нового поколения.

МЕХАНІЗМИ РАДІАЦІЙНИХ ПОШКОДЖЕНЬ І РОЗРОБКА КОНСТРУКЦІЙНИХ МАТЕРІАЛІВ ДЛЯ ДІЮЧИХ І МАЙБУТНІХ ЯДЕРНИХ РЕАКТОРІВ

***В.М. Воєводін*, Г.Д. Толстолуцька, М.А. Тихоновський, О.С. Купрін, О.С. Кальченко**

Безпека ядерних енергетичних установок (ЯЕУ) і економічність атомної енергетики багато в чому визначаються конструкційними матеріалами, з яких виготовлені елементи ЯЕУ. Вивчення причин зміни фізико-механічних властивостей матеріалів і їх розмірної стабільності при опроміненні, визначення ресурсу роботи елементів ЯЕУ в різних умовах, вибір і розробка перспективних матеріалів з високою радіаційною стійкістю є основними завданнями радіаційного матеріалознавства. У представленій статті розглядаються механізми радіаційного пошкодження конструкційних матеріалів ядерної енергетики, проблеми та перспективи створення радіаційно стійких матеріалів для діючих реакторів і реакторів нового покоління.