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REACTOR MATERIALS-MODERN STATUS

N.A. Azarenkov*, I.M. Neklyudov, V.N. Voyevodin****
**Kharkiv National University of V.N.Karazin*
4, sq. Svobody, Kharkov, 61022, Ukraine
***National Science Center "Kharkov Institute of Physics and technology"*
1, Akademicheskaya str., 61108, Kharkov, Ukraine
E-mail: voyev@kipt.kharkov.ua
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This paper presents short description of modern status of reactor materials for nuclear. The fast growing energy demand and concerns about climate changes require nuclear energy to play a role among other energy sources to satisfy future energy needs of mankind. Exactly core materials behaviour provides safe and economy exploitation of nuclear power plants. Metals and alloys used in nuclear service serve in very challenging environments involving high temperatures and stresses, as well as exposure to high irradiation doses. Problems of radiation resistance of materials for exploitation reactors and reactors of next generation are described.
KEY WORDS: nuclear energetic, radiation resistant materials, radiation defects, impurities, reactors on thermal neutrons, fast reactors.

МАТЕРІАЛИ ДЛЯ РЕАКТОРІВ-СУЧАСНИЙ СТАТУС

Н.А. Азаренков *, І.М. Неклюдов, В.Н. Воеводін **
** Харківський національний університет імені В.Н.Каразіна,*
Україна, 61022, м. Харків, пл. Свободи 4
*** Національний Науковий Центр "Харківський Фізико-технічний інститут»,*
Україна, 61108, Харків, вул. Академічна 1
Дана стаття являє короткий опис сучасного стану реакторних матеріалів для ядерної енергетики. Швидко зростаючий попит на енергію і заклопотаність з приводу зміни клімату вимагають від ядерної енергетики відігравати важливу роль серед інших джерел енергії для задоволення майбутніх потреб всього людства в енергії. Саме основна поведінка матеріалів забезпечує безпечну і економічну експлуатацію атомних електростанцій. Метали і сплави, які використовуються в ядерній галузі, працюють в дуже складних умовах при наявності високих температур і напружень, а також впливі високих доз опромінень. У даній статті також описані проблеми радіаційної стійкості матеріалів реакторів, що експлуатуються в наш час, а також реакторів наступного покоління.
КЛЮЧОВІ СЛОВА: ядерна енергетика, радіаційно-стійкі матеріали, радіаційні дефекти, домішки, реактори на теплових нейтронах, реактори на швидких нейтронах.

МАТЕРИАЛЫ ДЛЯ РЕАКТОРОВ – СОВРЕМЕННЫЙ СТАТУС

Н.А. Азаренков*, И.М. Неклюдов, В.Н. Воеводин**
**Харьковский национальный университет имени В.Н. Каразина*
Украина, 61022, г. Харьков, пл. Свободы 4
***Национальный Научный Центр «Харьковский Физико-технический институт»*
Украина , 61108, Харьков, ул. Академическая 1
Данная статья представляет краткое описание современного состояния реакторных материалов для ядерной энергетики. Быстро растущий спрос на энергию и озабоченности по поводу изменения климата требуют от ядерной энергетики играть важную роль среди других источников энергии для удовлетворения будущих потребностей всего человечества в энергии. Именно основное поведение материалов обеспечивает безопасную и экономичную эксплуатацию атомных электростанций. Металлы и сплавы, используемые в ядерной отрасли, работают в очень сложных условиях при наличии высоких температур и напряжений, а также воздействии высоких доз облучений. В данной статье также описаны проблемы радиационной стойкости материалов при эксплуатации реакторов в наше время, а также реакторов следующего поколения.
КЛЮЧЕВЫЕ СЛОВА: ядерная энергетика, радиационно-стойкие материалы, радиационные дефекты, примеси, реакторы на тепловых нейтронах, реакторы на быстрых нейтронах.

Today's nuclear power is the more real in the world that possesses the humanity for the production and supply of low cost electrical and thermal power for distant prospective with guarantee of nuclear, physical, ecological and technical safety in amounts corresponding with society needs.

Three factors emphasize on the nuclear power – exhausting of hydrocarbon resources, environmental contamination, necessity to control the power safety [1].

According to the data of IAEA more than 500 nuclear power units of research and other reactors are now in operation. In spite of Fukushima accident nuclear energetic at the world is developing stable and consequently.

It is just the behavior of structural materials of operated and developed reactors that determines the safe and economical operation of nuclear power stations.

Materials of operating and designed fission reactors may be divided on three groups:

- fuel materials – nuclear fuel: uranium, plutonium, thorium and their alloys.

- structural materials – ferritic-perlitic and ferritic-martensitic steels (pressure vessels of water-water reactors), bainite steels (wrappers and claddings of fuel elements (FE) for fast reactors, pressure vessel internals of water-water reactors, first wall of fusion reactors); ferritic-martensitic steels (wrappers of FU for fast reactors, first wall of fusion reactors); ferritic ODS steels – low-activated steels for fusion reactors and reactors of next generation, zirconium alloys-materials for claddings and channels of thermal reactors (materials of control systems (CR)) – materials absorbing neutrons B, Cd, Hf absorb thermal neutrons, B, Ta, Eu absorb fast neutrons.

The importance of structural materials consists not only in the guarantee of stability of the core geometry for overall operational time and, first of all, stability of fuel assemblies and of fuel elements, but also in the retention of fission products, in the maintenance of serviceability of control systems and in the guarantee of minimal consequences of possible accidents, that is, in the solution of the key problems of reactor plants safety.

Reaching of high burn-up of fuel is limited by radiation resistance of materials for wrappers and ducts of fuel assemblies and the term of operation of reactors on thermal neutrons is limited by the service life of pressure vessel and pressure vessel internal materials.

Unfortunately, structural materials have more potential restrictions for reaching of high levels of radiation damage and impede the reaching of high burn-up of nuclear fuel [2].

Development of structural materials of operating and of developed nuclear plants is extremely complicated science-technical problem. Under the influence of fast particles and radiation complex structure-phase transformations occur in crystalline bodies that cause considerable variation and, unfortunately, degradation of their initial physical-mechanical characteristics [3]. Radiation resistance is determined by the microstructural composition and by structure state of irradiated material. Expediency of the use of the materials in nuclear power plants of definite type depends on special features of NPP, on used coolant, on energy spectrum of neutrons and so on.

The aim of this work is the study and understanding of the properties of materials used in nuclear power and the prospects for improvement in the growing nuclear industry, which is designed to provide humanity soon enough cheap, environmentally friendly and safe energy.

MATERIALS OF REACTORS ON THERMAL NEUTRONS

Now thermal-neutron reactors, pressurized water reactors or boiling reactors serve as the basis of the world nuclear power (WWER- 440. 1000. PWR, BWR). WWER-type reactors are manufactured by Russian plants, PWR,BWR- in foreign countries. The main components of thermal reactors that are subjected to the intensive radiation exposure are the pressure vessels, fuel elements claddings, pressure vessels internals.

The structural materials employed in current power plants both in the pressure vessel and in the core materials, are conventional materials, low allow steels in the case of the pressure vessel (clad internally with stainless steel) and austenitic stainless steels and nickel-base alloys in the case of internal structures.

PRESSURE VESSEL MATERIALS

Materials of pressure vessels must guarantee the safe operation during the whole service life. Typically ferritic-perlitic (Russia) and ferritic-bainitic steels (USA, France, Japan) are used for the fabrication of pressure vessels.

WWER-440 - 15Cr2MoA (C-0.11-0.21; Si-0.17-0.37; Mn-0.3-0.6; S-0.012-0.018; P-0.009-0.0038; Cr-2.5-3.0; Cu-0.09-0.17; Ni-0.19-0.27; Mo-0.6-0.8; V-0.25-0.35);

WWER-1000 – 15Cr2NiMoPA, 15Cr2NiMoPAA (C-0.13-0.18; Si-1; Mn-1; S<0.035; P<0.01; Cr-1.8-2.3; Ni-1.0-1.5; Mo-0.5-0.7; V-1.1-0.12);

PWR, BWR – A533-B (C<0.25; Si-0,15-0.30; Mn-0.15-1.50; S-0,4); P-0.035; Ni-0.40-0.70; Mo-0.45-0.60.

Given in Table 1 data of the operational conditions of thermal neutron reactor show that rather low fluences and rather low operational temperatures are the characteristic properties of pressure vessel material operation for the reactor of such type.

Table 1.

Reactors on thermal neutrons: WWER, PWR, BWR (power 440-1200 Mw)

Mean density of thermal neutron flux in core	$2.7\text{-}4.4.10^{-13}$ n/cm^2 sec
Mean density of fast neutrons in core	$1.9\text{-}4.0.10^{14}$
The rate of dose setting-up	10^{-7}dpa/s
Temperature of coolant (pressure vessel)	On inlet 285-290^{0}C On outlet 320-325^{0}C
Density of fast neutron flux on pressure vessel	1.10^{17}n/cm^{2}sec
Fluence of fast neutrons (E_n>0.1 MeV) on pressure vessel during 40 years of operation	$\Phi t=5.10^{19}-1.10^{20}$n/cm^2
Rate of damaging rate (steel)	10^{-10}dpa/sec
Dose of radiation damage of pressure during 40 years	0.1 dpa

The initial microstructure of these materials is one of the parameters that will influence their behavior under irradiation. Ferritic, tempered martensitic or bainitic microstructures are usually found in RPV steels containing different types of precipitates with size ranging from 10 nm to micrometer.

Exposure to high energy neutron coming from the fission of fuel, together with the overall nuclear reactor core environment (e.g. gamma radiation, neutrons, radiolysis of water), affects significantly the physical and mechanical properties of these materials, resulting in ageing degradation effects during the life of the NPP that could result in early failure of these structural components if not detected or mitigated. Such events or necessary replacements are potentially expensive, impacting not only safety, but also economic viability of nuclear power plants [4].

Typically the wall of the RPV is exposed to high energy (e.g.>0.1 MeV) neutron irradiation, which results in localized embrittlement of the steel and welds in the area of the reactor core (i.e. the RPV core beltline region).

Obviously that such radiation-induced degradation of mechanical properties of pressure vessel steels during operation is the result of microstructure changes of nanostructure scale (nm). Evolution of microstructure under neutron irradiation at temperature of operation of pressure vessel (270- 300^{o}C) depends not only on the migration of point defects formed by irradiation, on their interaction and clustering but also on complex interaction with impurities.

Three main mechanisms responsible for the change of microstructure of pressure vessel steels under irradiation are now considered [4]:

1) Direct damage in the matrix due to the formation of radiation-induced clusters and dislocation loops. . It was detected that matrix damaging evolves with irradiation dose, the rate of dose set up and with irradiation temperature; this damage gives the resulting hardening proportional to the square root of accumulated dose [5].

2) Radiation-accelerated formation during matrix damage of matrix-coherent nano-precipitates and this also causes matrix hardening and embrittlement. Elements of solid solution of pressure vessel steels have the trend to radiation-accelerated clustering and formation of precipitates with nanosize (2-3 nm). These precipitates mainly enriched by copper and called copper-rich precipitates.

It must be noted that chemical composition of these precipitates remains uncertain, different elements are present in these precipitates (Fe, Mn, Ni and possibly Si and P). Even insignificant variation in steel composition and in neutron spectrum causes the significant differences in morphology and concentration of precipitates [6]. In steels of reactor WWER-1000 precipitates are radiation-stimulated and in steels of reactor WWER-440 they are radiation-induced [6].

3) Radiation induced segregation (RIS) on grain boundaries and interphase boundaries of embrittling elements such as phosphorus, sulphur, arsenic, also in combination with matrix damage or attracted into the Cu-rich precipitates

Now the question about relationship of contributions into the radiation embrittlement of different mechanisms demands the further investigation under higher irradiation doses.

Investigation of Ni role in the processes of embrittlement is of special interest because due to the technological causes in pressure vessels of nuclear reactor operating in Ukraine the content of nickel exceeds 1.5 % weight. The deleterious effect of nickel on temper brittleness of steel Cr-Ni-Mo-V was known a long time ago and the existing experimental data on nickel contribution to the radiation embrittlement of reactor steels are limited

Thus, most of these mechanisms are classified as “hardening” ones (matrix damage, copper-rich precipitates, partially also segregations when they are inside grains), but P segregation on grain boundaries is classified as “non-hardening” (non-hardening embrittlement, since not detectable with conventional hardness tests). The last type of embrittlement can manifest itself as intergranular (grain boundary) fracture, rather than the usual transgranular cleavage fracture. Thus, their effect on radiation hardening and embrittlement can be quite different (Fig.1).

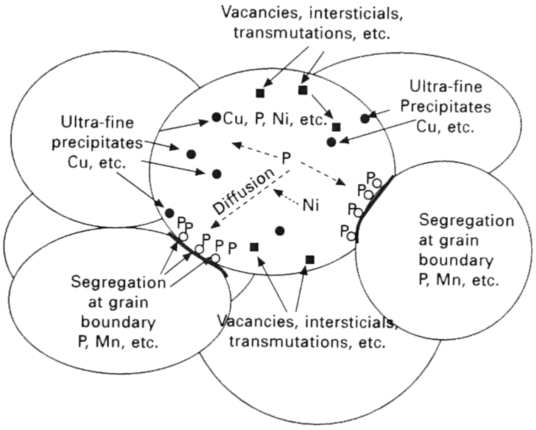


Fig. 1. Schematic embrittlement processes for RPV materials

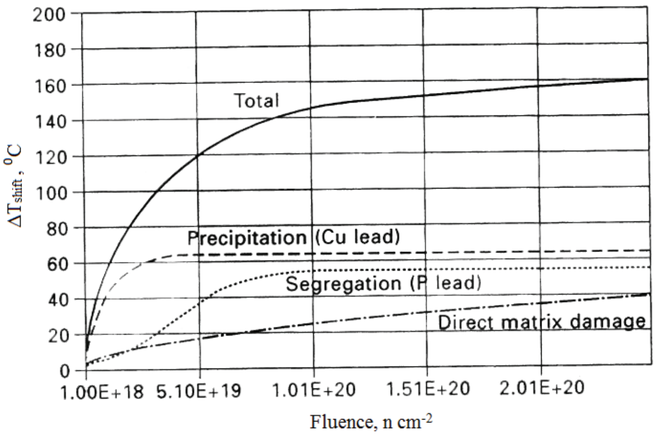


Fig. 2. Schematic diagram showing the effect of three damage mechanisms on irradiation embrittlement of RPV steel

Sum radiation embritterment curve (change of the temperature of brittle-ductile transition) is presented on Fig.2.

In high –nickel (Ni) RPV steels (with Ni content more than approx.1.2 mass %-it is typically for few Ukrainian and Russian units) another damage mechanism can be observed as previously predicted based on thermodynamic considerations and modeling. This “late blooming effect” can cause an additional increase in yield stress and higher transition temperature shifts at larger neutron fluences, where a saturation trend usually takes place (Fig.3).

Key issues are the combined effects of irradiation temperature, content of Ni, Mn and Cu and neutron flux/fluence $6{\cdot}10^{23}m^{-2}$ which are larger than end-of-life fluences for 40 years of PWR operation.

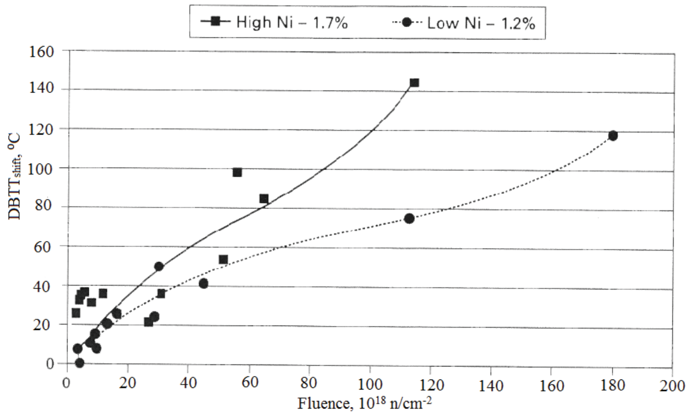


Fig. 3. Late blooming effect in high-nickel WWER-1000 weld metals

An analysis and generalization of great number of the admixtures given about influence on a radiation embrittlement allowed to pull out a requirement about limitation of maintenance of phosphorus and copper accordingly to 0.006 and 0.06% accordingly, and also reduction of total maintenance of antimony, of tin and arsenic(<0.015%).It is assumed that additional alloying by a nickel in an amount 0.6-0.8 % and adjustment of maintenance of chrome(<3%) will provide stability of descriptions became and will allow will get a possible resource no less than 60 with a possible extension 80-100 to [7].

ZIRCONIUM- BASE ALLOYS

Zirconium alloys are of special importance for nuclear power as material of fuel cladding for water-cooled reactors due to unique low cross section of neutron capture (0.18-0.19 barn) and high radiation and corrosion resistance. These elements are subjected to the considerably higher radiation load in comparison with materials of pressure vessels. The main problems revealed under zirconium alloys operation are radiation growth and related phenomenon of radiation creep caused by the anisotropic nature of α-zirconium.

Zirconium alloys (domestic: E110. E125, E635 and foreign Zry-2, Zry-4, M5, ZIRLO) (Table 2) used now in reactors WWER, RBMK, PWR, DWR differ considerably by radiation growth, radiation creep, corrosion resistance, high-temperature strength, hydrogenation and other characteristics that guarantee reliability of articles.

Despite the high number of studied round the world zirconium alloys, including that containing niobium, it is recognized that only five alloys are well studied and prepared for operation in reactors PWR and WWER , namely American Zircaloy-4 and Zirlo, Russian E110 and E635 and French M5 (Table 2 [8]).

The characteristic feature of zirconium alloys of Russian production that are used in nuclear reactors of Ukraine is the presence of niobium. Niobium is the main alloying element for binary and for multi components alloys. Base zirconium alloys of foreign production (Zircaloy-2 and Zircaloy-4 are alloyed by tin, iron, chromium and nickel. Different chemical composition of alloys strongly influence on their radiation and corrosion behaviour.

Alloy E110 is based on the system Zr-Nb where niobium is completely soluble in high-temperature phase of zirconium and is poorly soluble in low-temperature phase (to 1% [8]). Increase of this alloys strength is related with the presence of heterogeneous structure consisted of α-solid solution with inclusions of dispersed particles of β_{Nb}.

This alloy is used in recrystallized state, its ductility reaches 40% but is highly dependent on oxygen content.

Table 2.

Chemical composition of zirconium alloys used in modern reactor

Alloys	Chemical composition, %								
	Nb	**Sn**	**Fe**	**Cr**	**Ni**	**C**	**O**	**N**	**S**
E110	0.9-1.1	-	-	-	-	$\le 2\cdot10^{-2}$	$\le 10^{-1}$	$\le 6\cdot10^{-3}$	-
E110M	0.9-1.1	-	0.1	-	-	$\le 2\cdot10^{-2}$	0.12		
E125	2.5	-	-	-	-	$\le 2\cdot10^{-2}$	$\le 10^{-1}$	$\le 6\cdot10^{-3}$	
Zircaloy -2	-	1.2-1.7	0.07-0.2	0.05-0.1	0.03-0.08	$\le 2.7\cdot10^{-2}$	-	$\le 8\cdot10^{-3}$	-
Zircaloy -4	-	1.2-1.7	0.18-0.24	0.07-0.13	-	$\le 2.7\cdot10^{-2}$	-	$\le 8\cdot10^{-3}$	-
E635	0.9-1.1	1.0-1.5	0.3-0.5	-	-	$\le 2\cdot10^{-2}$	$\le 10^{-2}$	$\le 6\cdot10^{-3}$	-
Zirlo	0.9-1.1	0.9-1.1	0.09-0.11	-	-	$\le 2.7\cdot10^{-2}$	-	-	-
M5	0.8-1.2	-	0.015-0.06	-	-	0.0025-0.012	0.09-0.18	-	≤0.0035

Typically irradiation behaviour of Zr-base alloys is determined by behaviour of structural elements- mainly dislocation in Zr-1%Nb alloy, precipitates in Zr-2.5Nb alloy, dislocation components and aged solid solution-in alloy E635. In conditions of reactor irradiation under the doses higher than 15dpa formation of dislocation loops of the type <c>[0001] is observed in the microstructure of alloy E110. This correlates with the start of the stage of accelerated radiation growth.

It is shown that alloying of Zr-1%Nb with oxygen to concentration 0.19% leads to the suppression of dislocation loops <c> production and, consequently, to the shift of the start of accelerated radiation growth to higher irradiation doses (Fig.4) [9].

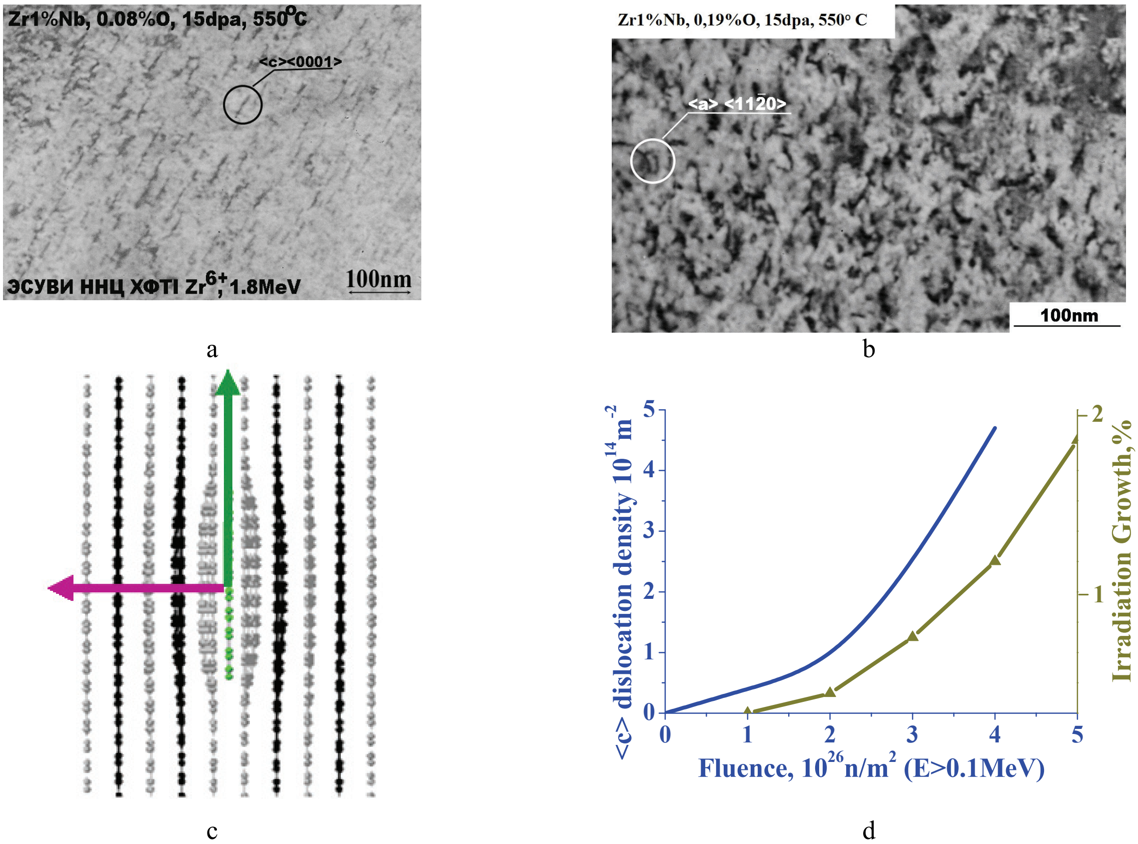


Fig.4. Oxygen influence on <c> components dislocation nucleation in Zr-1%Nb alloy.
a, b-microstructure of alloys; c- scheme of radiation growth in Zr; d- the dislocation density versus fluence.

Alloy E110M (Zr, 1% Nb, 0.1% Fe, 0.12% O) is produced on the base of alloy E110 by alloying with increased content of iron and oxygen (0.1 Fe%, 0.12 O %). This modified alloy demonstrates higher resistance to creep and lower radiation growth (Fig.5).

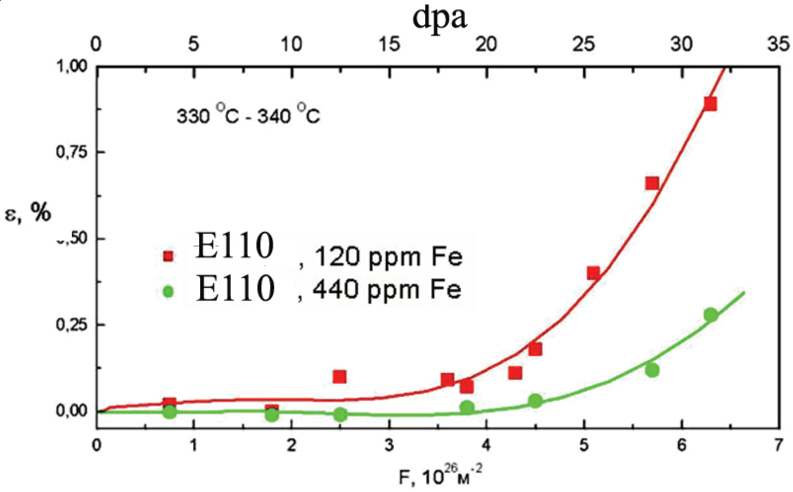
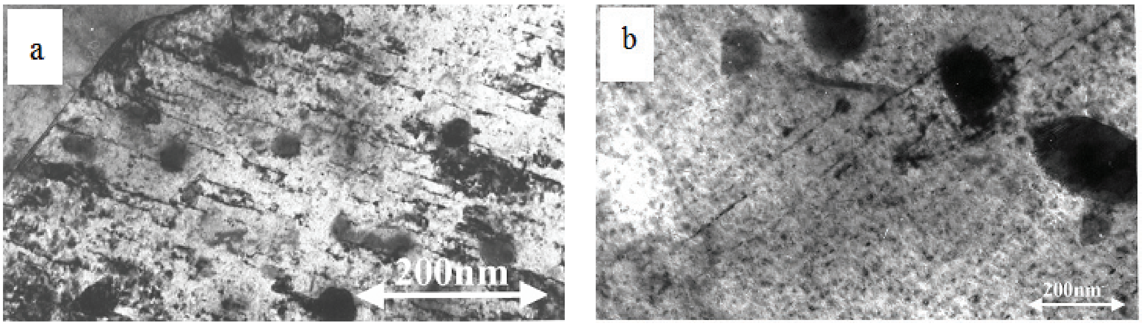


Fig. 5. Radiation growth versus chemical composition E110 alloy

Alloy E125 is specially developed for channel tubes, casings and elements of fuel assembly hangers for reactors RBMK, also for Candu-type reactor. The main requirement for material of channel tubes is the minimal rate of diameter creep (not more 1-1.5$\cdot10^{-5}$ %/hour). The high creep resistance and resistance to radiation growth of this alloy is attained due to the presence in its microstructure of high density of precipitates of β-Nb ($6\cdot10^{20}$m^{-3})

From the point of view of microstructure, the resistance to the radiation growth may be explained by the special features of dislocation structure evolution under irradiation (Fig.6, 7, 8). In alloy E635 with very high resistance to the radiation growth the high concentration of radiation-induced dislocation loops of <c> type responsible for the processes of radiation growth may be formed only under very high irradiation doses (>50 dpa) that are practically unreachable in commercial reactors. This singularity of alloy E635 evolution may be explained by the role of α-solid solution enriched by iron an iron influence on diffusivity of point defects.



a b

Fig. 6. c-component dislocation microstructure of alloys a-E-110, b-E-635

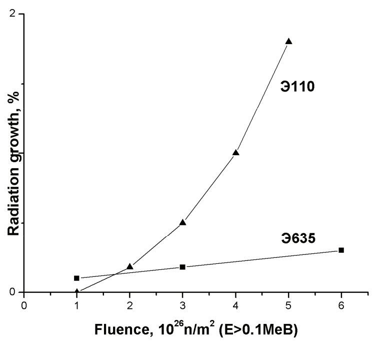


Fig. 7. Plots of the dependence of radiation growth on fluence of neutrons (E<0.1 MeV)

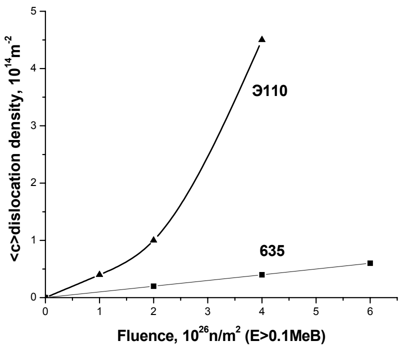


Fig. 8. Density of dislocation loops of c-type on fluence of neutrons (E<0.1 MeV)

MATERIALS OF PRESSURE VESSEL INTERNAL (PVI)

A new important challenge for radiation material science is now the substantiation of radiation resistance of materials of pressure vessel internal (PVI) for reactors PWR and WWER. These structures play an important role as they support the reactor core, they channel the water flow inside the vessel and they support and guide the instrumentation necessary for controlling and monitoring the reactor PVI were designed as not replaceable element of construction with the operation delay equal to the service life of the reactor pressure vessels [10]. Currently, the first commercial WWER units are approaching their design lifetime of 30 years. Consideration is now being given to life extension for another 10 to 30 years. Life extension requires that an assessment be made of the potential behavior of PVI materials under long-term irradiation.

Characteristic property of PVI elements and, first of all of the baffle, produced for Russian reactors of steel Cr08Ni18Ti10 and for reactors of type PWR and BWR, where baffle is manufactured from steel AISI 321, is that during operation they accumulate quite high fluence of neutrons and have the temperature level caused by the absorption of γ-quanta and of neutrons; the considerable volume changes of the material of PVI may occur at such temperature level due to the vacancy swelling under irradiation (Fig.9). This problem is potentially more dangerous for reactors WWER-100 the baffle of which has more complicated shape and is thicker than in reactors PWR. This causes the local increase of temperature up to 460^{o}C and leads to the void formation even without temperature shift. Early the possibility of such radiation swelling in this temperature range was rejected. Recently it became known that this phenomenon may proceed in light-water thermal reactors.

In American, French, Japanese and Russian works voids were detected in PVI of reactors of PWR type (Fig.10) [11, 12].

In the 1990s and 2000s, it was realized that the dpa rate is important, if not more important, than the irradiation temperature in determining the duration of the incubation or transient regime of swelling of austenitic stainless steels [14-16]. Based on experimental data from EBR-II over a wide range of dpa rates a bilinear swelling equation was developed for annealed AISI 304 stainless steel that explicitly incorporated the dpa rate, as well as the total dpa and temperature as variables that determine the development of swelling [16]. The effect of dpa rate on swelling was very pronounced, with the transient regime of swelling reduced very strongly as the dpa rate increased. Despite the fact that a great number of experimental results on radiation effects in 18Cr10NiTi steels is currently available obtained in different reactor and accelerator conditions as well as for different constructional materials, there are still no rated or conventional dependencies of swelling versus the dose, temperature and displacement rate. Approximating function describing 18Cr10NiTi steel swelling over a wide range of dose rates was obtained in [17]. The empirical dependence of 18Cr10NiTi steel swelling against the dose, irradiation temperature and dose rate reads:

$$S=(0.25-0.022\ln k)\cdot\varphi(D-103+0.1T-2.6\ln k)\cdot\exp\left\{-\frac{(T-690-15.5\ln k)^2}{2\cdot(12.3-1.9\ln k)^2}\right\},\qquad(1)$$

where S is swelling in %, D is the damaging dose in dpa; T is the irradiation temperature in °C; k is the dose rate in dpa/s; $\varphi(x)=x\cdot\theta(x)$ and $\theta(x)$ are Heaviside unit step functions; $\theta(x)=1,\quad x>0$ or $0,\quad x\le 0$.

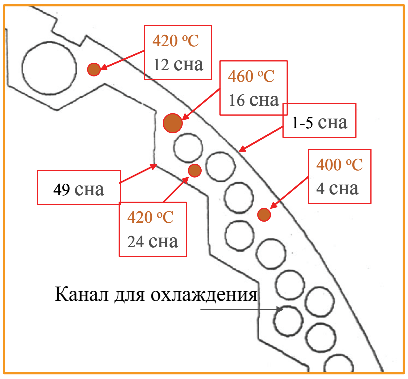


Fig. 9. Temperature-dose field in section with maximum of neutron flux on height [13].

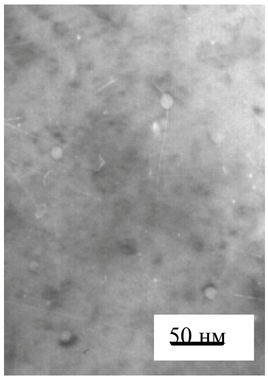


Fig. 10.Voids observed in pressure vessel internal of reactor WWER-1000 (steel 06Cr18Ni10Ti) RNPS –3 [13].

Fig. 11 presents dose-temperature maps of 18Cr10NiTi steel swelling calculated with function (1) with different dose rates typical both for irradiation on an accelerator (k = 10^{-3} dpa/sec) and for fast neutron (k = 10^{-6} dpa/sec) and thermal neutron (k = 10^{-8} dpa/sec) reactors.

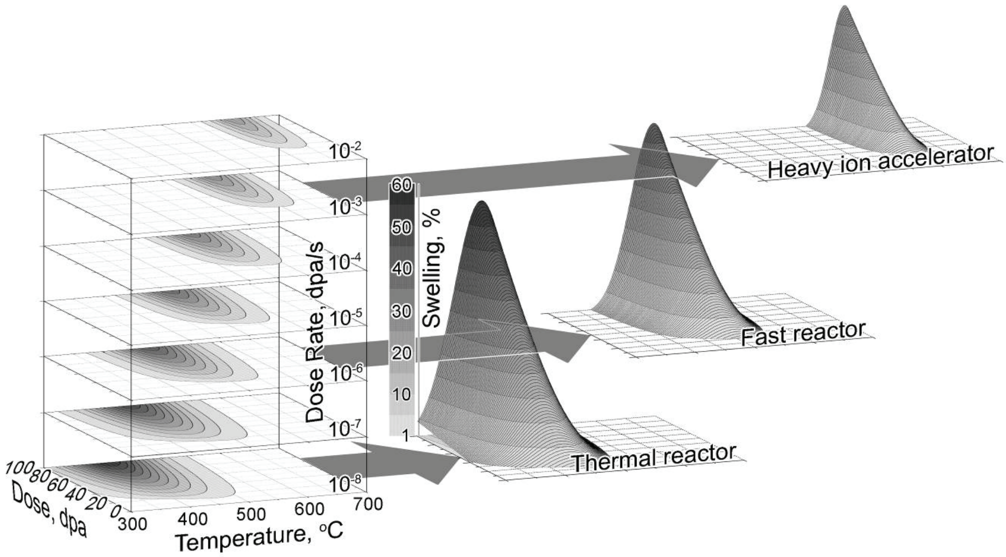


Fig.11. Temperature-dose maps of 18Cr10NiTi steel swelling for different dose rates calculated with modeling function equations (1)

The present results demonstrate that with due attention for dose rate scaling the basic physical processes involved in the swelling phenomenon occur under both heavy-ion and fast reactor irradiation conditions in a very general manner.

Employing simulation by heavy-ion irradiation it has been demonstrated that with a decrease in dose rate toward levels characteristic of WWERs the temperature regime of swelling for 18Cr10NiTi steel will get broader and show a shift of the swelling peak toward lower temperatures. Increased swelling at lower dpa rates develops primarily from a decrease in the incubation period of swelling and an apparent increase in the post-transient swelling rate. Increases in irradiation temperature were also found to decrease the post-transient swelling rate. These results agree with the results of other neutron irradiation studies on this steel and other austenitic steels.

On the basis of the developed empirical equation relatively large levels of swelling are anticipated to occur in the WWER baffle ring, especially at dose levels to be reached following plant life extension. Such information is crucial in making decisions concerning extended operation of WWERs, with or without replacement of the internals.

The main task for the solution of the problem of low-temperature swelling is the study of the operational conditions (rate dose, temperature, doses, environment, synergetic effect of gaseous impurities, stresses, material composition, its initial condition and others).

In nuclear power installations besides creation of radiation defects at co-operating of neutrons with the atoms of materials of PVI of reactors it takes place to formation of foreign atoms from the nuclear reactions of transmutation. The special value of nuclear reactions of transmutation consists in the generation of gas transmutation- helium and hydrogen. In the intercase devices of thermal reactors of type of VVER work of helium and hydrogen for 30 of exploitation of reactor exceeds 1000 and 2000 appm accordingly [18,19]. Such high concentrations of gases can change character of the structural-phase converting into materials. In this connection research of speed of work of gases is a necessity as an additional parameter. Such researches are now conducted in National Science Center "Kharkov Institute of Physics and technology".

MATERIALS FOR REACTORS OF NEXT GENERATION

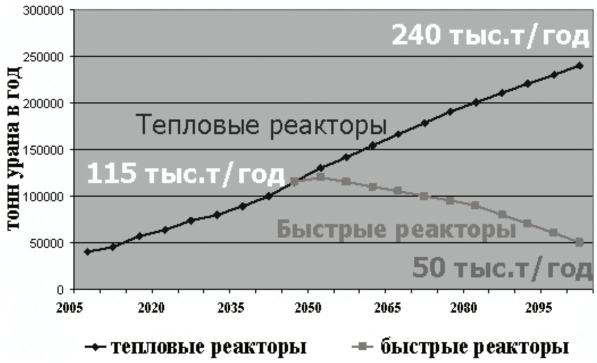


Fig.12. Forecast of the world needs in uranium up to 2100 year [21]

Generation III light water reactors (LWRs) are anticipated to be built in large numbers to replace exist in nuclear power plants or to augment the nuclear production capacity. Beyond the commercialization of best available light water reactor technologies , it is essential to start now the development of break through technologies that will be needed to prepare the longer term future for nuclear power. Fast neutron reactors (sodium , gas or lead cooled) with a closed fuel cycle which afford making an efficient use of uranium resource (more than 80% instead of 1% at most by light water reactors which essentially consume 235U) and minimizing long-lived radioactive waste, thus making nuclear energy more sustainable[20].

Development of large-scale nuclear power is not possible without the use of fast-neutron reactors guaranteeing the nuclear fuel breeding and using in nuclear power cycle of all produced nature uranium and consequently – of thorium (Fig.12).

High temperatures and irradiation doses in reactors fast neutrons (Table 3) lead to the situation that the problem of structural material production for claddings of fuel elements became the key one; such material must have the complex of mechanical and technological properties, compatibility with coolant and fuel material and also stability of properties under irradiation.

Table 3.

Parameters of fast-neutron reactors

Density of neutron flux	3.10^{15}-10^{16}n/cm^{2}sec
Rate of He generation	20-30 appm/year
Rate of dose setting	10-50 dpa/year (Totally 150-200 dpa)
Temperature	400-600^{o}C

These challenging requirements imply that in most cases, the use of conventional nuclear materials is excluded, even after optimization and a new range of materials has to be developed and qualified for nuclear use. Stainless steels of different classes with different alloying and after different thermo-mechanical treatments are more reliable materials as clads and wrappers of such type reactors.

AUSTENITIC STAINLESS STEELS

The most investigated and have technological attractive for the core of fast reactors, are austenitic stainless steels. Austenitic steel shows excellent corrosion resistance, overall mechanical property, but poor irradiation resistance.

These steels were developed intensively in different countries (Table 4).

Radiation swelling up to now is the major problem for using this type of structural materials [22].

Phenomena of swelling in multi component ASS is the result of complex structure-phase transformations during irradiation therefore the achievement of necessary level of resistance of austenitic steels to swelling may be obtained only on the base of understanding of all phenomena involved in the processes of radiation swelling.

In authors opinion the achievement of minimum level of swelling is related with the increase of stability of all structural components (dislocation structure, solid solution, systems of secondary phases precipitates) under irradiation.

Radiation resistance of ASS may be improved at the expense of introduction of insignificant quantities of alloying elements and subsequent thermal-mechanical treatment [23]. Component and impurity composition of steels influencing on energy of stacking fault and energy characteristics of point defects may modify the evolution of dislocation structure during irradiation.

It must be noted that the local variation of composition induced by radiation induced segregation (RIS), leads to the decay of solid solution and forms the precipitates of two types:

► precipitates suppressing the swelling at the expense of accelerated recombination of point defects on interface particle-matrix. These are carbides of type MC (principally TiC, NbC, VC), phosphides Fe_2P or Ni_3Ti (Fig. 13 a, b);

►precipitates produced in the result of solid solution decay (especially due to the segregation of Ni and Si) are the sign of radiation resistance loss on last stages of evolution of structure - M_6C and G-phase (Fig.13 c).

Table 4.

Chemical composition of austenitic steels used in core of nuclear reactors

Steel	Ni	Cr	Mo	C	Ti	Nb	Si	V	P	S	Mn	Others
AISI 316 USA	10.00-14.00	16.0 18.0	2.0-3.0	≤0.08	-	-	≤1,0	-	-	-	≤2,0	B 0.0002
D9 USA	14.0-16.0	14.0	1.4-2.3	-	0.2-0.35	-	0.8-1.0	-	-	-	1.8-2.3	-
PNC316 Japan	13.8	16.5	2.5	-	0.098	0.07	0.93	-	0.031	-	1.78	B 0.0044
15/15Ti, France	14.5-15.0	14.5-15.0	1.3-1.5	-	0.45-0.5	-	0.5	-	0.007	-	1.4-1.6	B 0.0065
FV-548,Great Britain	16.0-17.0	11.5-12.0	1.1-1.2	1.4-1.5	0.9-1.0	-	0.3-0.4	-	-	-		
09Cr16Ni15Mo3B(EI-847), Russia	14.0-16.0	15.0-17.0	2.5-3.0	≤0.09	-	0.8-0.9	≤0.8	-	-	-	≤0.8	-
15Cr15Ni2Mo2GTP (ChS-68) Russia	14,0-15.5	15.5-17.0	1.9-2.5	0.06-0.08	0.2-0.5	-	0.3-0.6	0.1-0.3	0.014	0.004	1.1-2.0	B≤0.005
EK-99 Ukraine	15.0-16.0	15.0-16.0	2.0-2.5	-	0.2-0.4	-	0.2-0.4	-	0.010	-	0.9-1.3	B≤0.005

*base-iron

Key processes leading to instability of fine MC or Fe_2P particles appears to be segregation mechanisms on precipitates surface. After irradiation at a higher dose, precipitates which have a coherent interface or interfaces with low degree of incoherence are observed in the steels. The higher stability of coherent precipitates can be connected with absence of defect sites on coherent interface and minimization of segregation [20]. The change in phase composition with the dose increasing is explained by the infiltration of Ni and Si into MX phases through the incoherence stage of evolution and MX→G-phase transition, where (in G-phase) interstitial elements are dissolved.

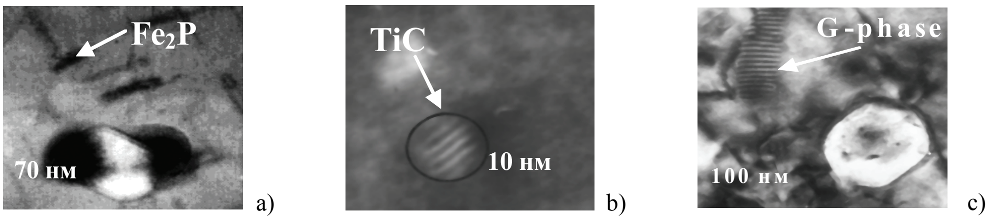


Fig.13. Precipitates of second phases in irradiated ASS
a) phosphydes Fe_2P; b) carbides TiC; c) G-phase $(Ti, V, Nb, Mn)_6(Ni, Co)_{16}Si_7$).

Deceleration of formation G-phase and η-carbides and containing such elements P, Ni and Si, influence on the initiation of voids and its growth.

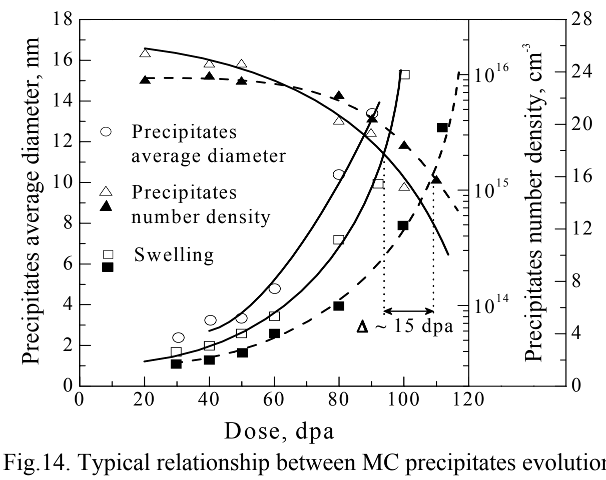


Fig.14. Typical relationship between MC precipitates evolution and swelling in 16Cr15Ni3MoNb (Δ, □) and 16Cr15Ni3MoNbB (▲, ■) steels (Cr^{3+}, E=3 MeV, $T_{irr}=650^0C$)

The principal effect of cold working in these steels is a shift the MC precipitation curve to lower doses and to displace the G-phase curve to higher doses. Cold work provides a higher density of nucleation sites for MC precipitates, beside it, the segregation solute will be distributed between much higher density sinks than in the solution annealed case.

The onset of the regime of swelling at a high rate appeared to be associated with the dissolution of fine titanium - rich MC type precipitates with dose increasing. It's significant that the moment of changing in precipitate form coincides with the beginning of steady state swelling (Fig.14).

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. This "competition" may be extended by the selection of optimal composition and by the thermal-mechanical treatment (Fig.15). Unfortunately, the role of precipitates as the main mechanism suppressing the swelling depends on the matrix surrounding and may vary during irradiation. The alloying elements included into precipitates change the nature of precipitates and modified precipitates interact with point defects in different way under irradiation. Interaction of matrix and precipitates throughout the flows of point defects makes the processes of evolution of microstructure complex and creates some contradictions for understanding of the influence of alloying elements or the role of precipitates.

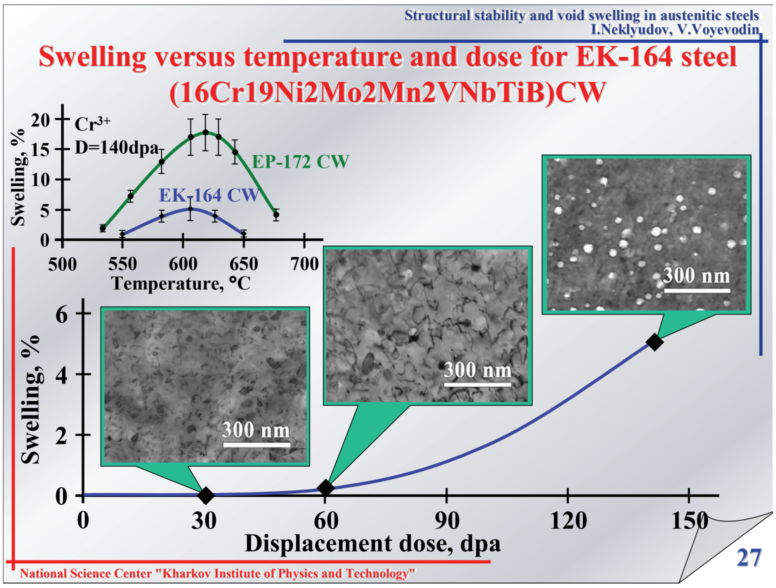


Fig.15. Swelling versus temperature and dose

The obtained results show:

- The maintenance of desirable swelling is directly coupled with maintaining a more stable microstructure during neutron exposure. Alloying influence together with treatment consists in:
- Formation of more stable dislocation structure (mainly existence of slow mobile Frank loops number density) up to higher doses. It can be achieved due to cold work or segregation processes on dislocation components, which restrict dislocation mobility;
- Save small precipitates of carbides and phosphides (prolong their life), which serve as dominant swelling suppressor in these steels, from dissolution - shift dose interval of formation for G-phases and η-carbides to region of higher doses;
- Retarding of G-phase and η-carbides formation will keep in solid solution sufficient quantities of such elements as Ni, Si and P, which mainly influence on void nucleation and growth;
- Typically for all analyzed steels stability of fine precipitates is necessary condition for preventing of high swelling.

FERRITIC-MARTENSITIC STEELS

Ferritic-martensitic steels are now the more attractive materials-candidates for claddings and wrappers of nuclear reactors and for the first wall of fusion reactors due to their low induced activity, low void swelling and creep, high resistance to high-temperature and helium embrittlement.

There are different international programs of development of reactors of 4 generation and of fusion reactors. These programs are based on the use of ferritic-martensitic steels that will operate in the wide range of temperatures under damaging doses of 200 dpa and higher and also of high levels of gases production (of helium and hydrogen) [24-26].

American company "TerraPower" develops a new concept of fast reactor named Traveling Wave reactor (TWR). This reactor concept uses the principle "produce and burn up"; this concept was proposed by Russian scientist Feinberg in 1958. Such reactor may produce more energy than thermal reactor. Depleted uranium or natural uranium may be used as fuel material for this reactor.

The designed burn-up in such reactor will be 20 and possibly 30%. (Let us note that Russian nuclear power poses the task of reaching the fuel burn-up of 20% in fast reactors).

Under such level of burn-up the damaging doses will be 400…500 dpa. In view of this it is necessary to select the structural materials for claddings and wrappers of fuel assemblies and investigations of materials-candidates under super-high irradiation doses are needed.

It is supposed to use ferritic-martensitic steels for claddings in reactor TWR; it is known that these steels have the lower swelling under high doses of irradiation.

The investigation of swelling of industrial ferritic-martensitic steels EP-450 (of Russian production) under irradiation by chromium ions up to the doses of 300 dpa is presented on Fig. 16. Irradiation by heavy ions is used for investigation of radiation resistance of this material. This simulation method is used in KIPT for a long time and gives many useful results during the study of mechanisms of radiation damage and selection of prospective reactor materials [26]. And now this is the only method round the world for reaching the super-high irradiation doses.

Mixing the alloy additives promote the formation of precipitates in ferritic martensitic steels. It has some properties, which important for developing stable micro structure.

F/M STEELS PRECIPITATES BEHAVIOUR

The Cr behaviour in irradiated ferritic steels affects mainly the evolution of the second phase precipitates. It was showed [27] that during irradiation 9% and 12% Cr steels to have formation of a few kinds of second-phase precipitates:

- M_6X and $M_{23}C_6$ precipitates are distributed mainly at grain boundaries and did not change their composition during irradiation.
- α′-phase precipitates are predominantly Cr (up to 85–90%), are ≤10 nm in size, and are uniformly distributed through both ferrite and tempered martensite. Most of the precipitates are coherent. Irradiation of lower Cr-content steels (9% to 10% Cr) can also reduce the amount of Cr sufficiently to cause the formation of the ′α-phase.
- M_2X precipitates exist in 13% as well in 9% Cr steels. They can have a needle-shaped form (in EP-450 steel) and are finely dispersed (in 9Cr-1Mo-NbVB steel).
- New phase - the formation of Si-enrichment precipitates with stoichiometric compositions $(Cr,Fe)_9Nb_3Si_8$, as well as the enrichment of Cr_2N and M_6X precipitates with silicon and vanadium, can serve as proof that segregation processes occur in irradiated ferritic steels.
- Typical for Laves phases $Fe_2(Mo,Nb)$ in 10Cr6MoNbV steel it was founded the phase transformation to $\chi(Fe_{36}Cr_{12}Mo_{10})$ phase according with suggested model of phase transformations.

Table 5.

Chemical composition of some 9-12% chromium steels [28]

Steel mark/ country	C	Si	Mn	Cr	Ni	Mo	V	W	Nb	B	Other elem
EM12 Belgium/France	0.08-0.12	0.30-0.50	0.90-1.20	9.0-10.0		1.9-2.1	0.25-0.35	0.35-0.45			
F82H Japan	0.10	0.20	0.50	8.0			0.20	2.0		0.003	Ta-0.04 N-less 0.01
JLF-1 Japan	0.1	0.05		8.0			0.2	1.95			Ti-0.002 Ta-0.09 N-0.023
EUROFER, Europe	0.10.-0.12	0.05	0.4-0.6	8.0-9.0			0.20-0.30	1.0-1.2		0.004-0.006	Ta-0.06-0.10; n-0.02-0.04
FV448, England	0.10	0.46	0.86	10.7	0.65	0.60	0.14		0.26		N-0.05
EP-450. Russia	0.10-0.15	0.60	0.60	11.0-13.5	0.05-0.30	1.2-1.4	0.10-0.30		0.30-0.60	0.004	
EP-823, Russia	0.10-0.18	1.15-1.3	0.5-0.8	11.3	0.5-0.85	0.6-0.82	0.32	0.5-0.8	0.26-0.4	0.006	Ti 0.004

The main attention is paid to the analysis of swelling in ferritic-martensitic steels. The Fig. 15 illustrated dose dependence of swelling for the most investigated ferritic martensitic steel EP-450 (13Cr2MoNbVB). As it is seen from this Figure the dose dependence of swelling of duplex steel EP-450 have took the traditional form characteristic for all metals and alloys, namely, the presence of incubation period, transient stages with increasing rate of swelling and steady state stages of swelling The high increase of swelling rate in steel EP-450 is related with the high increase of void size (Fig. 16). The mean size of voids under the dose ≥200 dpa makes more than 50 nm and some voids reach the size more than 100 nm and contribute substantially to swelling.

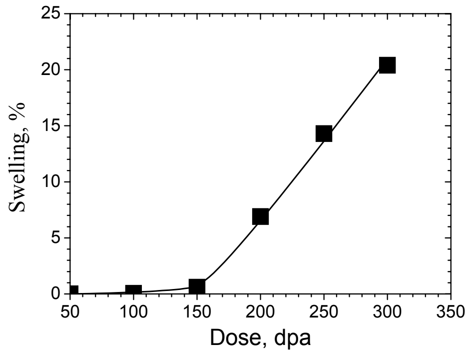


Fig.16. Dose dependence of swelling of steels EP-450 (T=480^{o}C)

During the steady state stage the rate of swelling of steel EP-450 makes 0.14%/dpa. Due to the comparatively high rate the swelling of ferritic steel under the dose 300 dpa reaches~20%. Such swelling of ferritic steel is unexpected because ferritic steels were considered as material with low swelling [26].

DISPERSION-HARDENED STEELS

Many studies are directed toward the development of innovative metallic materials for applications in the nuclear industry [29, 30], fulfilling the design requirements for fission or fusion nuclear reactors. Among these are oxide dispersion strengthened (ODS) alloy materials [31] obtained by powder metallurgy [32] which are of interest as structural materials due to their creep rupture strength at high temperature [33] and their resistance to severe neutron exposure. This high temperature creep strength [34] comes from the presence within the matrix of nanometric size oxide populations, blocking the motion of dislocations and thus making it possible to consider nominal operating temperatures over 1000 C for some ODS materials (Fig.17).

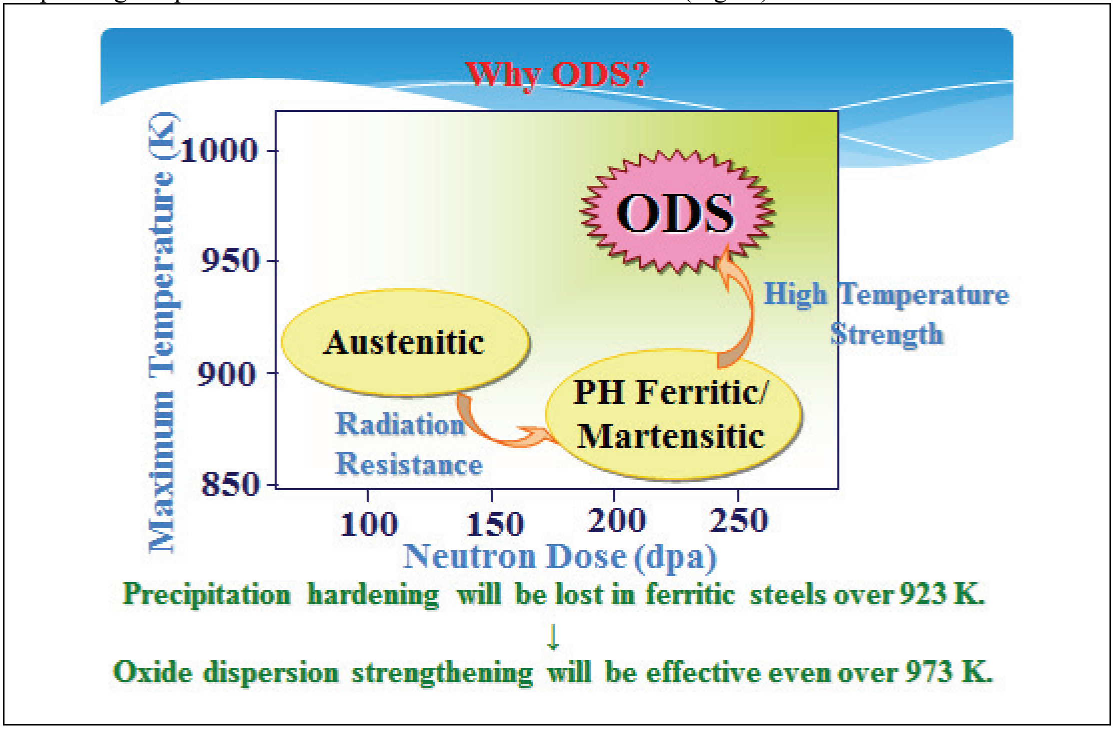
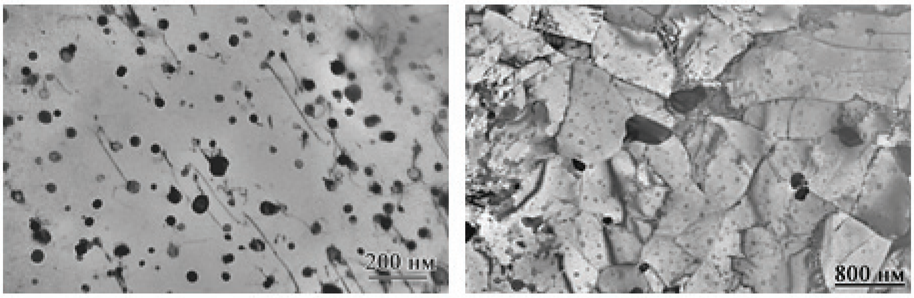


Fig. 17. The preference of dispersion hardened steels

Dispersion hardened ferritic steels(which contain 9-12Cr%) are now ones of the more prospective materials for FA clad of fast reactors and first wall of fusion reactors (FR) and also as structural material of reactors of next generation (See Fig.18).



PM 2000
(HT: recrystallization at 1250⁰C, 1h)

EUROFER 97
(HT: 979⁰C/1h, 51 min + 739⁰C/3 h, 42 min)

Fig. 18. Initial structure of dispersion hardened ferritic steels

The required increase of high-temperature strength is attained by the proper dispersion hardening of fine particles of titanium (TiO_2) and/or yttrium (Y_2O_3). The unique combination of fine grains, of high density of dislocations and nanoclusters containing atoms of solution Y-O and Y-O-Ti supposes the production of materials with unique properties [35-36].

The more important factor influencing on the properties of dispersion hardened steels is the provision of the deformation dissolution in steel matrix of sufficiently “coarse” oxides of yttrium with dimension 40-100 nm and their subsequent precipitation as effectively hardening nanooxides.

The necessity of the investigation of material properties under such severe operational conditions is caused by the last observations that make doubtful the serviceability of ferritic-martensitic steels for their use at high temperatures and high rates of gases generation [24]. Therefore it is necessary to analyze the evolution of microstructure and modification of composition for better understanding not only the nature of low swelling but also the cause of the embrittlement.

The features of these ODS-steel will be nanosize particles introduction of that to the initial matrix gives all material the improvement of his properties. It is such excretions as: Y_2O_3, TiO, $Y_4Al_2O_9$, $YAlO_3$, $Y_3Al_5O_{12}$, $Y_2Si_2O_7$,

Al_2O_3, $Y_2Ti_2O_7$, FeY, Y_2TiO_5, $Y_2Ti_2O_7$, that have different composition, different methods of receipt, but have one goal - increase of descriptions of different types of ODS-steel, that can become construction materials of the future before long. Although irradiation data are scarce, the bcc crystalline structure should present an excellent resistance to swelling.

The necessity of the investigation of material properties under such severe operational conditions is caused by the last observations that make doubtful the serviceability of ferritic-martensitic steels for their use at high temperatures and high rates of gases generation. Therefore it is necessary to analyze the evolution of microstructure and modification of composition for better understanding not only the nature of low swelling but also the cause of the embrittlement. The road map of development of materials for fast breeder reactors is shown on picture (Fig.19).

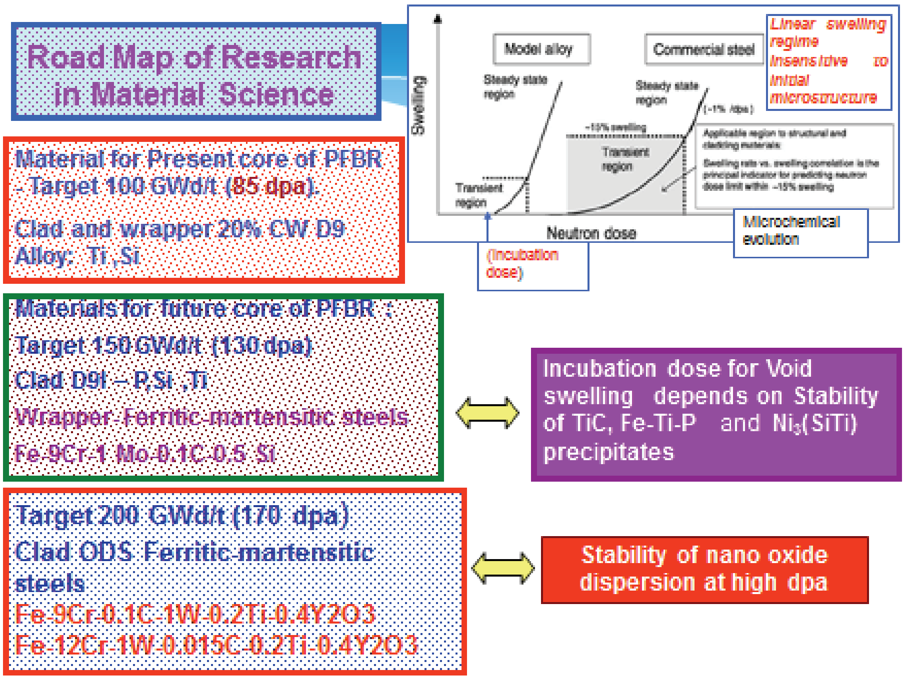


Fig. 19. The road map of development of materials for fast breeder reactors

The main in-service issues, in the low temperature range, remain the effect of the a/a' unmixing on the mechanical properties and, in the high operating temperature domain, the required stability of the oxide dispersion to maintain the improved creep resistance of this type of material and the absence of heavy intermetallic phase precipitation that could degrade the toughness the cladding. Preliminary results under mixed and fast neutron spectrum show that a/a' demixing should allow this type of materials to keep reasonable ductility and fracture toughness. The under irradiation stability of the oxide dispersion is an open issue to be settled. The required increase of high-temperature strength is attained by the proper dispersion hardening of fine particles of titanium (TiO_2) and/or yttrium (Y_2O_3). The unique combination of fine grains, of high density of dislocations and nanoclusters containing atoms of solution Y-O and Y-O-Ti supposes the production of materials with unique properties.

The more important factor influencing on the properties of dispersion hardened steels is the provision of the deformation dissolution in steel matrix of sufficiently "coarse" oxides of yttrium with dimension 40-100 nm and their subsequent precipitation as effectively hardening monoxides.

CONCLUSION

In spite of considerable efforts of researchers in all countries developing the nuclear power the economically necessary levels of operation of existing nuclear reactors are not reached so far.

It is determined in considerable degree by the insufficient radiation resistance of the main structural materials of existing nuclear facilities – of zirconium base alloys and different classes of stainless steels.

Challenges of the 21 Century for radiation material science are the guaranteeing of the problems of security and economy of nuclear power plants.

The main of them are:

1. Substantiation of overhaul period prolongation for operating thermal reactors, that is, study of the influence of the dose, of rate dose, of processes of segregation, special features of material (composition, thermal treatment, structure) on microstructure evolution in structural materials during operational period of reactor.
2. Development of radiation-resistant materials for reactors of new generations. Study of the influence on the material physical – mechanical properties of the dose rate, of stresses, of segregation processes (fast reactors); influence

of the dose, of gas concentration (He, H), of gaseous and solid transmutants (fusion reactors, electronuclear systems (“spallation”).

The presented aims may be realized only on the base of modern understanding of the role of microstructural processes responsible for the evolution of structural state under irradiation and for degradation of initial physical-mechanical properties.

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Azarenkov Nikolay Alekseevich - Academician of National Academy of Sciences of Ukraine, D.Sc., Professor, Honoured worker of science Ukraine, Head of department of nuclear materials, Prorector from scientifically-educationally work of the Kharkiv national university named V.N. Karazin.
Scientific interests: physics of the systems of lacking amenities, nonlinear physics of plasma, cooperation of plasma with substances, radiation materials. An author and coauthor are the over 400 publications.

Neklyudov Ivan Matveevich - Academician-secretary department of nuclear physics and power engineering national academy of sciences of Ukraine, Director general national research center "Kharkov Institute of Physics and Technology", NAS of Ukraine.
Scientific interests: materials, physics of durability and plasticity, radiation firmness of metals and alloys. Publications: coauthor 15 monographs, more than 600 publications and 47 patents and inventions.

Voyevodin Viktor Nikolaevich – Corresponding Member of the Academy of Sciences, D.Sci. of Physics and Mathematics, Professor. Director of the Institute of Solid State Physics, Materials Science and Technology KIPT NASU.
Scientific interests: physics of the radiation phenomena and radiation materials. Author more than 400 publications.