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NANOSTRUCTURED MATERIALS BASED ON NANO-ZrO_2 IN THE NUCLEAR-POWER ENGINEERING

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Abstract: The review of the results of research, development and use of nanomaterials in the nuclear-power engineering and technology have been presented. The basic properties of nanostructured materials are given. The prospects for the use of nanomaterials in the nuclear-power engineering, associated with the creation of nanostructured materials and coatings for structural elements NPEP (nuclear-power engineering plant) and future TNR (thermal nuclear reactor) to increase hardness and strength characteristics, raising corrosion and radiation resistance have been considered.

***Keywords**: nanomaterials, nanotechnology, nuclear fuel cycle, radiation and corrosion resistance.*

1. Introduction

Nuclear-power engineering is the main source of electrical and heat energy and provides energy independence and security of each country. Nuclear-power engineering comprises the extraction and enrichment of nuclear fuel, production of construction materials and fuel elements (FE) for the core of the nuclear reactors, fuel burning in the core of nuclear reactors and power generation, reprocessing of spent nuclear fuel (SNF), the recovery, removal and disposal of radioactive waste (RW). This diversified chain forms closed nuclear fuel cycle (NFC) [1, 2].

Nuclear-power engineering and nuclear industry is very important the issue of modernization of fuel and construction materials for the core of the nuclear reactors. The fuel materials include a wide range of uranium and transuranium elements and their compounds. To the structural materials of nuclear reactors belong austenitic, ferrite, ferrite-martensitic and other grades of steels and alloys, graphite, carbon materials, zirconium alloys, various ceramic materials. In addition, an important thing is a final and appropriate solution of the problem of secure disposal of spent nuclear fuel (SNF) and radioactive waste (RW), as well as development of new quasi-stationary processing methods and minimize the hardness of the neutron spectrum of the SNF. In this regard, one of the tasks is the development of fundamental and applied researches in the field of radioactive materials and radiation technologies. In such research, an important task is to create new fuel and structural materials and new methods of analysis and testing of materials.

Nanotechnology has recently began to be applied in practically all areas of advanced technologies and in fact turned into an interdisciplinary field of science and technology. In the nuclear industry nanotechnology applied before, when they began to use the prefix "nano", as created the fuel and construction materials were largely based on a qualitative change in the properties of materials at the transition to the nanometer range of sizes [3-5].

2. Experimental

The purpose of this paper is a brief overview of the results of research and the latest developments in the use of structural and functional nanostructured materials based on nano-

ZrO_2 in the nuclear energy and technology, as well as the influence of γ - radiation on the nano-ZrO_2 + H_2O system.

The interest in nanostructured materials and nanotechnology is conditional upon a number of important problem reasons:

- nanotechnologies allow to obtain fundamentally new quantum devices and materials with characteristics significantly superior to the current level;
- nanotechnologies brings together the knowledge and techniques in the field of physics, chemistry, materials science, mathematics, biology, medicine, computer engineering.

The term "nanotechnology" refers to a set of methods and techniques, enabling a controlled way to create and modify objects that include components with sizes ranging from 1 to 100 nm, at least in one dimension [3-5]. Accordingly, objects containing structural elements, the dimensions of which at least in one dimension less than 100 nm and having properties of qualitatively new, functional and operational characteristics, referred to nanomaterials. The terms "nanostructure", "nanocomposites" refers to a material formed by a set of nanoparticles of specific size and composition, or obtained by introduction of nanoparticles into any of the matrix to form a qualitatively new object properties associated with manifestation of nanoscale factors. Nanostructures also include macroscopic materials, components of which are nano-objects and nano-scale elements. The primary formations from a small number of atoms ($10 \div 10^4$) of size $0.1 \div 1$ nm are attributed to the nanoclusters. Under the nanoparticles commonly understood intermediate formations of atoms (molecules), and small molecular nanoclusters having a characteristic size < 100 nm. Physical and chemical properties of the cluster depend on the number of atoms in it. When the properties of the cluster no longer depend on the number of atoms, we can assume that in a small volume macroscopic material have been obtained. One-dimensional nanostructures with dimensions less than 100 nm in two dimensions are, for example, carbon nanotubes (CNTs), graphene behaves as an insulator [6]. Thus, depending on the dimension of the nanoobjects quantum-mechanical phenomena can occur in three, two, or in one direction.

Nanostructured materials exhibit significant differences in almost all physical properties compared with the macroscopic or microscopic objects. The main manifestations of size effects are as follows:

- a total cause of differences in the properties of nanosystems on the properties of macroscopic systems - is comparable sizes of their structural elements with a wavelength of collective excitations;
- reducing lead time of different processes with decreasing nanostructures’ size;
- a major role in the properties of nanostructures plays tunnel effect;
- a proportion of surface atoms increases with decreasing particle size. For nanoparticles almost all of the atoms are “surface atoms”, so their chemical activity is very high;
- with decreasing grain size, the role of interfaces increases;
- properties of the surface in the nanometer range different from microstructural surface;
- crystallite size is comparable to the mean free path of the carriers in the analysis of transport phenomena.

For metals the influence of grain size of nanometals and nanoalloys on the electronic properties can manifest itself only for a very small crystallites or in very thin films.

Analysis of the evolution of structural-phase state of metallic materials, in particular the changes of phase diagrams due to size effects cause considerable difficulties due to the lack of a number of values of the thermodynamic parameters. For example, it is known, that the eutectic temperature in a number of systems is reduced by the amount of grains less than tens of nanometers, although it must be borne in mind, that the calculations are estimates in the simplest approximation of regular solutions. Phase transformations in nanoparticles of oxides depending on the size may vary due to the contribution of the elastic energy, so in ZrO_2 nanoparticles recorded simultaneous formation of the monoclinic (the region of the existence $T < 1440$ K) and tetragonal (T = 1440-2640 K) modification [7]. Changing the dynamic vibration atoms manifests itself in changing the melting point of the lattice component of thermal conductivity and associated with increasing of the amplitudes of atomic vibrations in nanocrystals, and with appearance in the phonon spectrum additional both low frequency (spectrum softening) and high frequency modes. The observed increase in heat capacity for nanomaterials is due to a strain in the preparation of nanoparticles. Reducing the size of the crystallites decreases the characteristic temperature. Change in the phonon spectrum of nanomaterials is also manifested in the reduction of the melting temperature, which is set for a multi-component systems. In homogeneous single-component nanomaterials at temperatures close to the melting point intensive crystallization occurs and nanostructure disappears. [7]

Therefore, on the other hand, when creating a nanostructure in pure form with a characteristic sizes at least one direction of less than 100 nm, nanocrystalline materials exhibit both high strength and plasticity. Even nanocrystalline ceramics is plastic at low temperatures. It is in connection with these contradictions by the existing classification disperse and ultrafine particulate material is separated into a macroscopic (coarse-grained), microscopic (sub-microcrystalline) and nanocrystalline.

A separate class forms amorphous alloys or metallic glasses obtained by rapid cooling of the melt. Nature of the bonds in metallic glasses is preserved. Amorphous alloys as well as nanocrystalline ones, by a number of characteristics surpass their crystalline analogs. The strength of about twice the strength of steel, impact resistance - three times. Viscosity increases with increasing strain rate.

At this time is problematic to predict the processes of formation, evolution and stability of nanomaterials, mainly due to lack of uniquely interpreted experimental results and the complexity of the calculations. However, the transition to nanostructured materials promotes to reduce the energy of formation of defects, increase the diffusion mobility of the components, regulate the physical and mechanical properties, controle structural and phase transformations during the formation of non-equilibrium phases and segregation. All this allows extensive use of nanomaterials in the nuclear-power engineering and technology.

Applications of nanotechnology in the atomic energetics are very diverse and cover the whole range of problems of the nuclear fuel cycle and producing fusion cycle [1 -13]:

- the creation of new high-density nuclear fuel nano-additives, fuel compositions for the fuel assemblies of the core of the Atomic Power Stations;
- a research and development of materials for fast reactors and future reactors of 4th generation;
- microstructural prediction possibility of extending the reactor lifecycle: housing (embrittlement);
- intercase steels (intumescence), nanomembranes and nanofilters for technologies for the treatment of SNF (spent nuclear fuel) and RW (radioactive waste);
- ceramic materials for burning radiolytic hydrogen.
- development of metrological support for use of structural and functional devices based on nanomaterials for nuclear installations;
- research and development of materials for future fusion reactors.

With the implementation of these problems are developed pilot-scale technology for production of functional materials and products using nanotechnology and nanomaterials for nuclear and thermonuclear hydrogen and conventional energetics, medicines. Let us consider some of the results of research and development of nanostructured materials in nuclear-power engineering.

Energy strategy envisages the gradual introduction of new nuclear-power engineering technologies on fast neutrons with the closing of the nuclear fuel cycle with MOX (mixed uranium-plutonium oxide fuel). The further development of atomic-power engineering requires the inclusion of the fast reactors into the structure of the APS capacity. Today from all the types of fast reactors industrially developed ones are sodium-cooled reactors (FN). One of the conditions for increasing the efficiency of the APS is to increase the burn-up of the nuclear fuel. To ensure high burn-up of the fuel it is necessary to create coarse-grained structures of the nuclear fuel with controlled porosity.

The initial homogeneous state has turned into an ordered structure of the new phase with a period of a few nanometers. Formation in solid solution nanostructured sublattice of short-range ordering clusters - traps vacancies and interstitials with the period 5-10 nm, comparable to the mean free path of radiation point defects is the most effective way of ensuring radiation resistance. This interesting effect that provides superior properties of reactor materials, found in some alloys.

3. Results and discussion

Zirconium dioxide (ZrO_2) is one of the materials that are widely used in science and technology. ZrO_2 is used to make nuclear reactor fuel cells, which convert chemical energy into electrical energy. Fuel cells of the devices operating at high temperatures. The use of zirconia for fuel cells due to the high ionic conductivity, which is conditional upon the transfer of anionic oxygen vacancies [14-16]. In order to ensure their high quality nanoscale powders are used. The nanoscale systems differ in many ways from conventional single crystalline systems. Therefore, the study of their properties under the influence of γ - radiation is of practical and scientific interest.

In this paper, in order to determine the effect of zirconia on the radiolysis of water the kinetics of accumulation of molecular hydrogen in the radiolytic decomposition of water in the system $ZrO_2 + H_2O$ at T = 300 K, ρ_{H2O} = 5 mG/cm^3 and D = 0,33 Gy /s have been investigated.

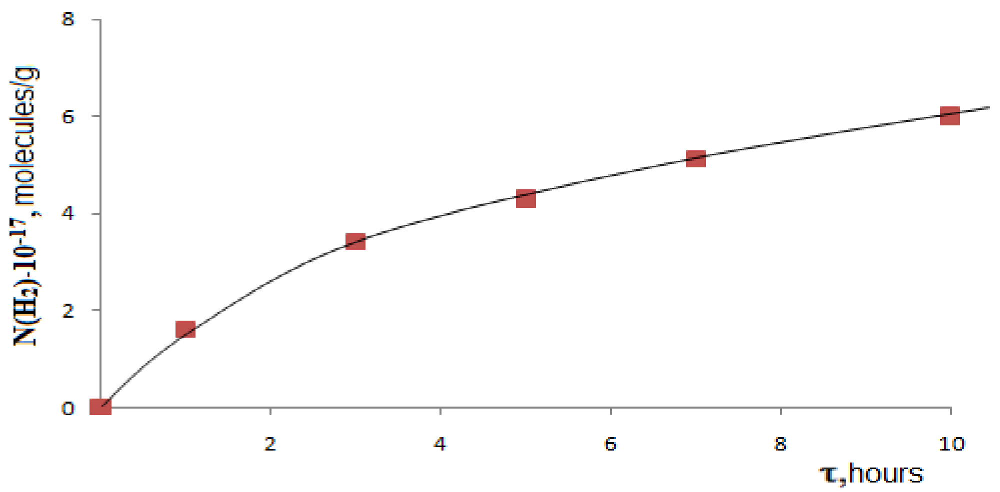

Fig.1 The kinetics of accumulation of molecular hydrogen in the radiolysis of water in the presence of nano-ZrO_2 at T=300 K, ρ_{H2O} = 5 mG/sm^3 and D = 0,33 Gy /s

Based on the kinetic curve the value of the process rate and the radiation-chemical yield of molecular hydrogen $G(H_2)$, rated per energy absorbed by water have been defined. In so doing it is revealed that the radiation-chemical yield of molecular hydrogen $G(H_2)$ at T = 300 K equals 2.14 molecul/100 eV, higher than for pure water, which is $G(H_2)$ = 0.45 molecul/100 eV. The observed increase in the values of $G(H_2)$ in the radiolysis of water in the presence of ZrO_2 in comparison to the output of the radiolysis of pure water can be explained by the contribution of δ - electrons emitted from ZrO_2 under the influence of γ- quanta and the formation the active water decomposition centers on the metal oxide surface.Under the conditions of exploitation of the nuclear reactor structural material (ZrO_2) are simultaneously exposed to heat and radiation in contact with the coolant. Therefore, in order to identify regularities of the radiation, the radiation-thermal processes in contact with the coolant nanopowder ZrO_2, which is the material of nuclear reactors with water cooling, the kinetics of accumulation of molecular hydrogen by the action of γ -radiation at different temperatures have been studied. In order to identify the contribution of radiation-heterogeneous processes into heterogeneous radiation-thermal processes, under identical conditions radiation-thermal and thermal processes of decomposition of water at T = 373 K, ρ_{H2O} = 5 mG/cm^3 and D = 0,33 Gy/s have been carried out. Based on the initial linear portions of the experimental kinetic curves the values $W_{rt}(H_2)$ and $W_t(H_2)$ rates have been determined.

The rate of radiation component $W_r(H_2)$ of the radiation-thermal process of accumulation of hydrogen is determined from the difference in rates of radiation-thermal and thermal processes:

$$W_r\,(H_2) = W_{rt}\,(H_2) - W_t\,(H_2)$$

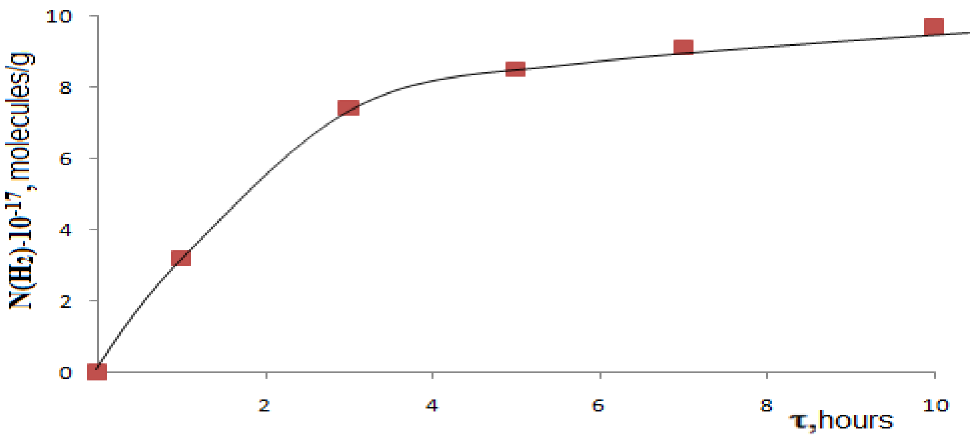

Fig.2 The kinetics of accumulation of molecular hydrogen in the radiolysis of water in the presence of nano-ZrO_2 at T=373 K, ρ_{H20} = 5 mG/sm^3, D = 0,33 Gy/s.

The results show that increasing of the temperature from 300 to 373 K causes an increase radiochemical yield of the molecular hydrogen from 2.14 to 4.58 molecul/100 eV. The observed increase in the radiation-chemical yield of molecular hydrogen with the temperature shows that there is the influence of temperature on the energy transfer in the system $ZrO_2 + H_2O$.

4. Conclusions

It is clear from presented results that nanostructured materials become an important role in the nuclear-power engineering as structural and functional materials practically in all stages of the nuclear fuel cycle. It is extremely important the formation in nanostructured materials after exposure ordered nanostructure from the new phase with a period of a few nanometers, promoting preservation the properties of materials under high irradiation. The observed phenomenon may be the beginning of a new trend of radiation materials sciences - creating structural materials, "positively" responding to radiation exposure.

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