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# Effect of gamma irradiation on the physical properties of melt span alloys of $Ti_{30}Zr_{45}Ni_{25}$

O.E. Dmytrenko, I.V. Kolodiy, V.I. Dubinko

*National Science Center "Kharkov Institute of Physics and Technology"*
*Kharkov 61108, Ukraine*

Gamma irradiation of the melt span samples of $Ti_{30}Zr_{45}Ni_{25}$ up to the dose of $10^4$ rad did not result in any substantial changes of their physical properties (micro hardness and electric resistivity), which is consistent with a high degree of disorder in the initial microstructure that does not change significantly under irradiation. The present results show that these materials can be considered as radiation resistant hydrogen absorbers (HABs) for the mitigation of hydrogen hazards in severe accidents in nuclear power plants.

**Keywords**: hydrogen absorption, amorphous alloys, Laves phase, irradiation.

Гамма-опромінення зразків швидко загартованого сплаву $Ti_{30}Zr_{45}Ni_{25}$ до дози $10^4$ рад не призводить до суттєвих змін їх фізичних властивостей (мікротвердості і питомого електричного опору), що узгоджується з високим ступенем безладу в вихідної мікроструктурі, яка не зазнає суттєвих змін при опроміненні. Представлені результати показують, що ці матеріали можуть розглядатися в якості радіаційно-стійких водневих поглиначів для зменшення ризиків, пов'язаних з витоком водню в аварійних умовах на атомних електростанціях.

**Ключові слова**: поглинання водню, аморфні сплави, фази Лавеса, опромінення.

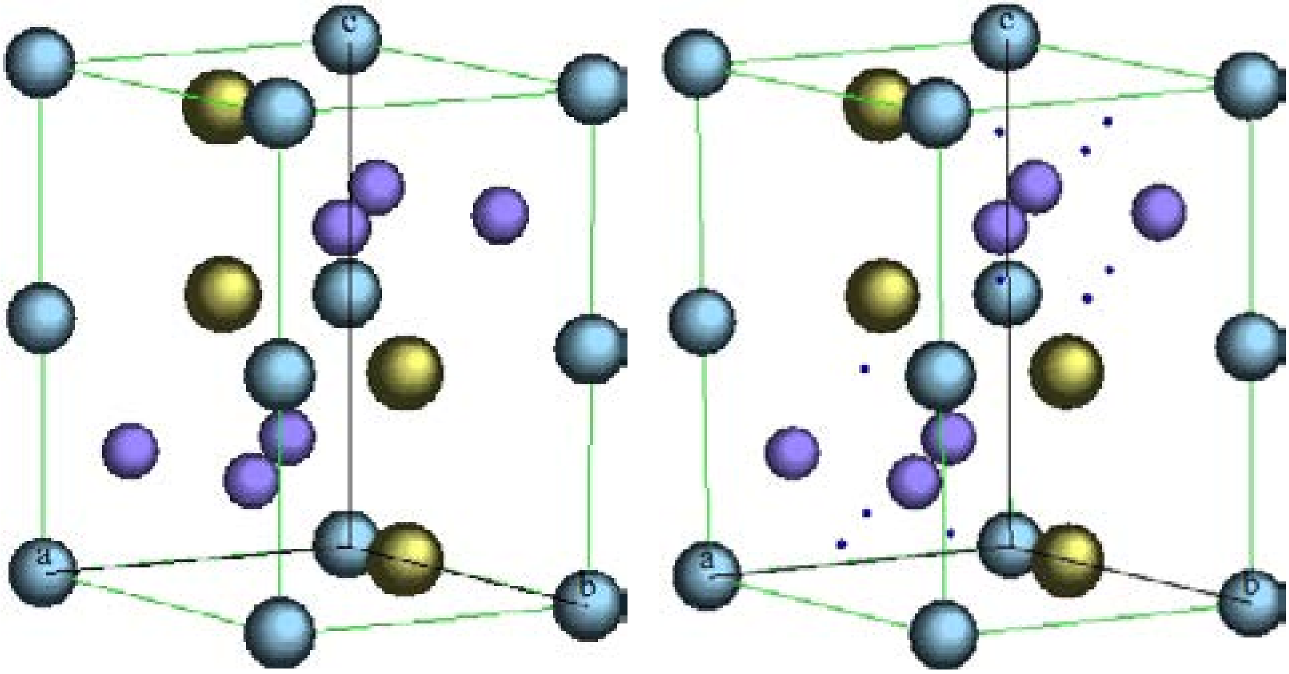
Гамма-облучение образцов быстро закаленного сплава $Ti_{30}Zr_{45}Ni_{25}$ до дозы $10^4$ рад не приводит к существенным изменениям их физических свойств (микротвердости и удельного электрического сопротивления), что согласуется с высокой степенью беспорядка в исходной микроструктуре, которая существенно не изменяется при облучении. Представленные результаты показывают, что эти материалы могут рассматриваться в качестве радиационно-стойких водородных поглотителей для уменьшения рисков, связанных с утечкой водорода в аварийных условиях на атомных электростанциях.

**Ключевые слова**: поглощение водорода, аморфные сплавы, фазы Лавеса, облучение.

## Introduction

One of the most important issues of the nuclear power plants operation is the mitigation of hydrogen hazards in severe accidents in nuclear power plants. To avoid severe damage of the containment and thus loose the confinement function for radioactivity release some hydrogen control and risk mitigation measures exist [1]. In particular, passive auto catalytic recombiners (PARs) have been developed and have become commercially available in the last decades. PARs are simple devices, consisting of catalyst surfaces arranged in an open-ended enclosure. In the presence of hydrogen (with available oxygen), a catalytic reaction occurs spontaneously at the catalyst surface and the heat of reaction produces natural convection flow through the enclosure, exhausting the warm, humid hydrogen depleted air and drawing fresh gas from below. Thus, PARs do not need external power or operator action. However, PAR capacities are ultimately subject to mass transfer limitations and may not keep up with high hydrogen rates in some scenarios so that flammability limits can be reached or exceeded (e.g. in the immediate vicinity of the hydrogen release). Thus, working in high concentrations (>8%) can initiate deflagration in the PARs due to the hot surfaces of the catalyst, which shows the need for research to create other means of hydrogen removal in addition to PARs, which is addressed in the present paper.

It is known that some metals and alloys can be very strong hydrogen absorbers (**HAB**s), and the rate and efficiency of hydrogen absorption depends strongly on temperature and material structure. Therefore HABs can be used in some scenarios where PAR capacities are not sufficient, such as high hydrogen concentrations or places where exothermic reactions taking place at PAR surfaces are not desirable. In this respect, **melt span alloys** of Ti-Zr-Ni may present a good alternative, since, according to our research, they can absorb large quantities of hydrogen (up to 1.7 wt%) without producing extra heat [2, 3]. Their absorption capacity and rate strongly depend on temperature and show the best characteristics between 400 and 500 $^{o}$C, and so HABs made from these alloys can be used in the hot areas of the reactor. Application of a thin Pd coating dramatically reduces the loading time and



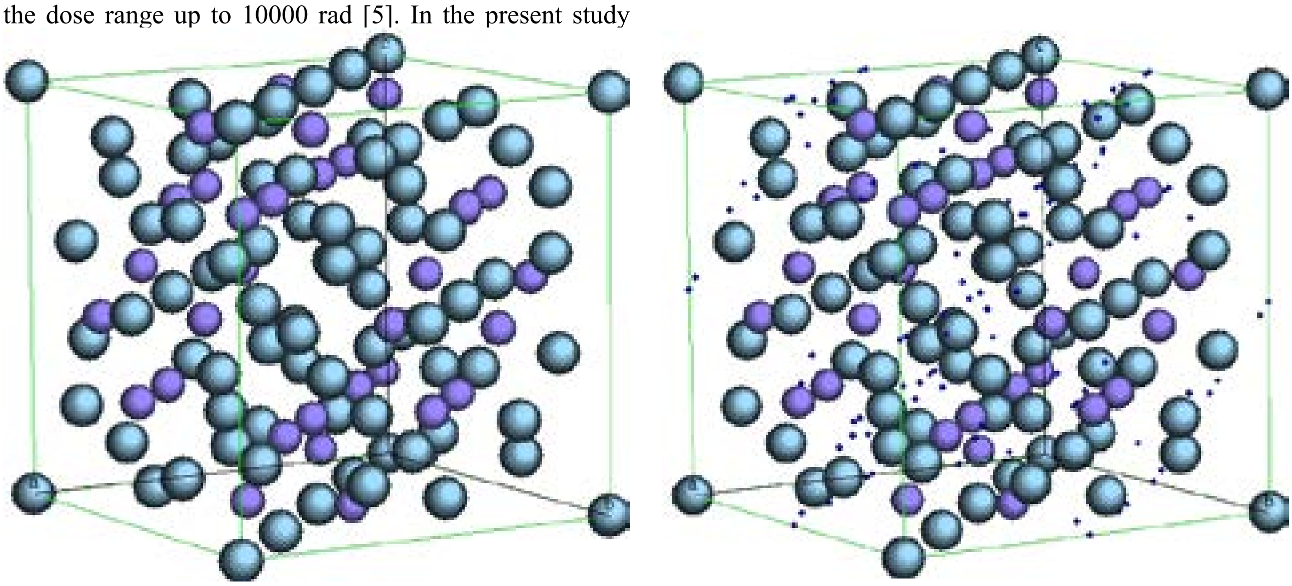
*a* *b*

*Fig. 1.* Crystal structure of the L-TiZrNi phase before hydrogenation (a) and L-TiZrNi$H_{2.12}$ after hydrogenation (b).

enables absorption at room temperature [4], which shows the potential of these materials as HABs for power plant applications.

One of the main questions concerning the applications of melt spun alloys with a complex structure as HABs for nuclear power plants is their *stability under irradiation*. The main constituent of the irradiation fields in nuclear power plants are gammas which are hard to shield. Few existing studies of the effect on gamma irradiation on **$Ti_{41,5}Zr_{41,5}Ni_{17}$ and $Ti_{41,5}Hf_{41,5}Ni_{17}$** quasicrystals have shown their resistance to the radiation-induced phase transitions in the dose range up to 10000 rad [5]. In the present study we investigate the effect of gamma irradiation on the physical properties of $Ti_{30}Zr_{45}Ni_{25}$ melt spun alloys, which demonstrate high absorption rate and capacity due to a large fraction of amorphous phase in the initial state prior to irradiation.

In the following section, the structure and hydrogen absorption kinetics of $Ti_{30}Zr_{45}Ni_{25}$ melt spun alloys are presented. In section 3, the gamma irradiation setup of the $Ti_{30}Zr_{45}Ni_{25}$ samples is described, and the effect of irradiation on their micro hardness and electric resistivity is presented.



*a* *b*

*Fig. 2.* Crystal structure of the $(Ti,Zr)_2Ni$ phase before hydrogenation (a) and $(Ti,Zr)_2NiH_{2,5}$ after hydrogenation (b).

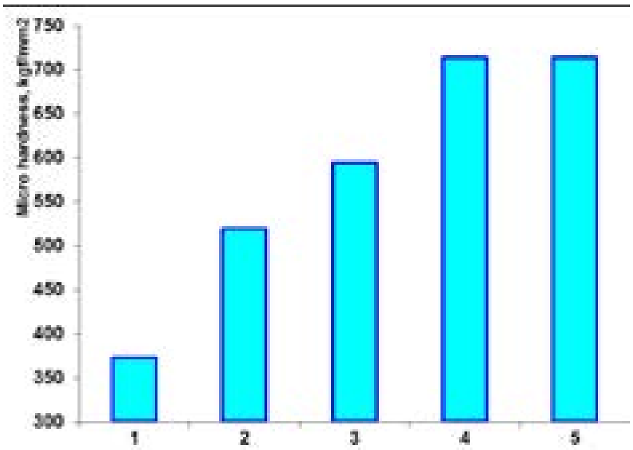



*Fig. 3.* Micro hardness of $Ti_{30}Zr_{45}Ni_{25}$ in different states [2] : 1 – crystalline ingot; 2 – melt span films before hydrogenation; 3- melt span films after hydrogenation at 400 °C; 4- melt span films after hydrogenation at 450 °C; 5- melt span films after hydrogenation at 500 °C.

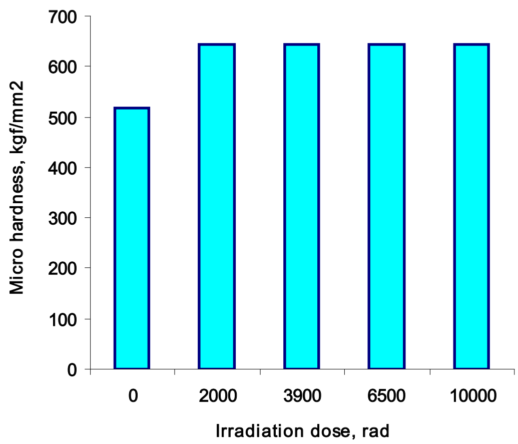



*Fig. 4.* Micro hardness of the melt span samples after different irradiation doses.

**Structure and hydrogen absorption properties of $Ti_{30}Zr_{45}Ni_{25}$**

Ingots of $Ti_{30}Zr_{45}Ni_{25}$ were made of iodine Ti (99,98%), iodine Zr (99,98%) and electrolytic Ni (99,99%) in the arc furnace with tungsten electrode in the Ar atmosphere. Melt span films of thickness 40÷60 microns were obtained at the cooling rate of $10^5$ K/s [2]. The microstructure of as-received and hydrogenated samples was analyzed means of X-ray diffraction at XRD installation DRON-4-07 and scanning electron microscope QUANTA 200 3 D with micro-analyzer Pegasus 2000.

Ingots of $Ti_{30}Zr_{45}Ni_{25}$ contain two phases. 98 wt% is occupied by hexagonal Laves phase L-TiZrNi (C14, $MgZn_2$ type [6]) shown in Fig. 1a. Its lattice parameters are **a** = 5,2250Å, **c** = 8,5509Å, and the elementary cell volume **V** = 202,17Å$^3$. The remaining 2 wt% is taken by the α-(Ti,Zr) based solid solution.

After melt spinning, the main phase L-TiZrNi retained its geometry with somewhat increased lattice parameters: **a** = 5,2294Å; **c** = 8,5621Å, **V** = 202,78 Å$^3$, and decreased fraction - 86.2 wt%. Additional cubic phase occupying 13.8 wt% was formed by melt spinning - $(Ti,Zr)_2Ni$, with **a** = 11,913Å; **V** = 1690,69Å$^3$, which is mediated by 0.132 wt% of oxygen present in the matrix (Fig. 2).

Hydrogenation of samples was done for 4 hours in a heated vacuumed chamber under initial hydrogen pressure of 0.5 bar at 400 °C , 450 °C and 500 °C [2]. The maximum hydrogen content of 1.3 wt% was achieved at 450 °C, which resulted in a significant increase of micro-hardness from 520 to 700 kgf/mm$^2$ (Fig. 3).

Analysis of the microstructure of samples hydrogenated at 400 °C for 4 hours has shown that it consists of three phases. The main one (82 wt%) is the hydride of the Laves phase L-$TiZrNiH_{2.12}$ (Fig. 1b) with increased volume: **a** = 5,4280Å; **c** = 8,9191Å, **V** = 227,58Å$^3$. The second phase (9.6 wt%) is $(Ti,Zr)_2NiH_{2.3}$ with **a** = 12,586Å **V** = 1993,72Å$^3$ (Fig. 2b) and the third phase (8.4 wt%) $(Ti,Zr)_4Ni_2O$ with **a** = 11,398Å, **V** = 1480,76 Å$^3$. The relative increase of the volume of the first two phases, **ΔV/V** = 12,7% and 17,9%, respectively, corresponds to the accumulation of hydrogen in them.

Elementary cell of L-$TiZrNiH_{2.12}$ consists 12 metal atoms and 10.5 hydrogen atoms that fill about 20% of the vacant hydrogen positions. At 100% occupancy one would have the phase L-$TiZrNiH_{12}$ with 48 hydrogen atoms per 12 metal atoms, i.e. with exceedingly high ratio H:M = 4:1. On the other hand, the maximum hydrogen occupancy in the second phase $(Ti,Zr)_2NiH_4$ is 128 H per 224 positions amounting to the maximum ratio H:M = 4:3. It means that for the best performance of this material as the hydrogen absorber, we need to get rid of oxygen in the system, which mediates the transformation of L-TiZrNi into $(Ti,Zr)_2Ni$.

**Effect of gamma irradiation on $Ti_{30}Zr_{45}Ni_{25}$**

Gamma irradiation of the samples was done by *Bremsstrahlung* gammas produced by 350÷500 keV electrons from the impulse electron accelerator passing

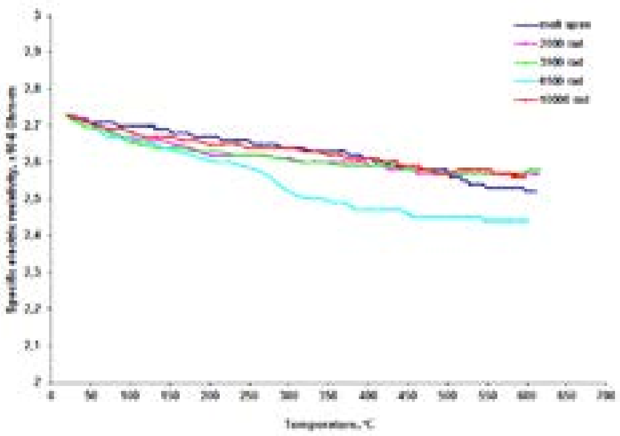


*Fig. 5.* Specific electric resistivity of melt span samples after different irradiation doses.

through a molybdenum converter. The electron beam current in the impulse was ~ 2÷5 kA and the impulse duration ~ (1.5÷5) $10^{-6}$ s. The dose rate of gamma irradiation was ~ (3.5÷5) $10^{8}$ rad/s.

The micro hardness of the melt span $Ti_{30}Zr_{45}Ni_{25}$ samples increases after irradiation from 520 to 700 kgf/ $mm^2$ (Fig. 4). However, the effect quickly saturates and does not seem to depend on the irradiation dose, which may be due to the random nature of the microstructure change with increasing irradiation dose. Similarly, there is no clear tendency in the change of electric resistance of the samples with increasing irradiation dose (Fig. 5), which seems to confirm this hypothesis.

**Conclusions and outlook**

Hydrogenation of the melt span samples of $Ti_{30}Zr_{45}Ni_{25}$ results in formation of two phases: L-$TiZrNiH_{2.12}$ and $(Ti,Zr)_2NiH_4$. The former phase has a potential to absorb up to 4 H atoms per a metal atom. On the other hand, the maximum hydrogen occupancy in the second phase 4:3. It means that for the best performance of this material as the hydrogen absorber, we need to get rid of oxygen in the system, which mediates the transformation of L-TiZrNi into $(Ti,Zr)_2Ni$.

Gamma irradiation of the melt span samples of $Ti_{30}Zr_{45}Ni_{25}$ did not result in any substantial changes of their physical properties (micro hardness and electric resistivity) with increasing irradiation dose up to $10^4$ rad, which is consistent with a high degree of disorder in the microstructure that does not change significantly under irradiation.

The present studies have been done on materials *after* irradiation. However, the problem needs further investigations, especially under *in situ* irradiation, which is hardly possible to do under reactor conditions due to obvious technical problems. Existing reports on the hydrogen behavior in metals under *in situ* electron irradiation [7] conclude that *"excitation of vibrations occurs in the hydrogen subsystem"* which greatly accelerates diffusion and release of hydrogen isotopes from metals at low temperature. The main constituent of the irradiation fields in nuclear power plants are gammas which are hard to shield as compared to electrons. Gammas are converted *inside the material* into electrons of the same energies due to the photoelectric effect and ultimately result in radiation-induced formation of defects and *localized atomic vibrations* (LAVs). The existence of LAVs, known also as *discrete breathers*, has been demonstrated in solids of different types and structures ranging from metals to insulators and from crystals to amorphous medium [8-12]. Recently the interest of researchers has extended to the study of the role of LAVs in solid state physics and their impact on the reaction rates in non-equilibrium conditions, such as exposure to irradiation, oscillating magnetic field, temperature and stress gradients [13-18]. We expect that LAVs produced in may catalyze various reactions, including the hydrogen diffusion and storage. These processes will be investigated in in a subsequent paper.

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# Estimating the number of solutions equation of N-point gravitational lenses algebraic geometry methods

A.T. Kotvytskiy[1], S.D. Bronza[2], S.R. Vovk[3]

*V.N.Karazin Kharkov National University, Ukraine[1,3]*
*Ukrainian State University of Railway Transport[1,2]*
*kotvytskiy@gmail.com[1], bronza_semen@mail.ua[2]*

One of the main problems in the study of system of equations of the gravitational lens, is the computation of coordinates from the known position of the source.

In the process of computing finds the solution of equations with two unknowns. The difficulty lies in the fact that, in general, is not known constructive or analytical algorithm for solving systems of polynomial equations In this connection, use numerical methods like the method of tracing.

For the N-point gravitational lenses have a system of polynomial equations. Systems Research is advisable to start with an assessment of the number of solutions. This can be done by methods of algebraic geometry.

**Keywords**: gravitational lenses, algebraic geometry, Bézout's theorem.

Однією з основних завдань, при дослідженні системи рівнянь гравітаційної лінзи, є обчислення координат зображення за відомим положенням джерела.

У процесі обчислень доводиться знаходити рішення системи рівнянь з двома невідомими. Складність полягає в тому, що в загальному випадку не відомий конструктивний або аналітичний алгоритм для вирішення систем нелінійних рівнянь. У зв'язку з цим вдаються до чисельних методів подібним методу трасування.

У разі N-точкових гравітаційних лінз система рівнянь є полиномиальной. Дослідження такої системи доцільно почати з оцінки числа рішень. Ми проводимо це дослідження методами алгебраїчної геометрії.

**Ключові слова**: гравітаційні лінзи, алгебраїчна геометрія, теорема Безу.

Одной из основных задач, при исследовании системы уравнений гравитационной линзы, есть вычисление координат изображения по известному положению источника.

В процессе вычислений приходится находить решение системы уравнений с двумя неизвестными. Трудность состоит в том, что в общем случае не известен конструктивный или аналитический алгоритм для решения систем нелинейных уравнений. В связи с этим прибегают к численным методам подобным методу трассировки.

В случае N-точечных гравитационных линз система уравнений является полиномиальной. Исследование такой системы целесообразно начать с оценки числа решений. Мы проводим данное исследование методами алгебраической геометрии.

**Ключевые слова**: гравитационные линзы, алгебраическая геометрия, теорема Безу.

## Introduction

According to the general theory of relativity, the light beam, which passes close to a point source of gravity (gravitational lens) at a distance $\xi$ from it (in case $\xi >> r_g$) is deflected by an angle

$$\vec{\alpha} = \frac{2 \cdot r_g}{\xi^2}\vec{\xi} = \frac{4 \cdot G \cdot M}{c^2 \cdot \xi^2}\vec{\xi}, \quad (1)$$

where $r_g$ - gravitational radius; $M$ - mass point of the lens; $G$ - gravity constant; $c$ - velocity of light in vacuum.

The detailed derivation of the formula (1) can be found in many classic books [1-3]. For $N$ - point of the gravitational lens, in the case of small tilt angles have the following equation in dimensionless variables [4], [5]:

$$\vec{y} = \vec{x} - \sum_i m_i \frac{\vec{x} - \vec{l}_i}{\left|\vec{x} - \vec{l}_i\right|^2}, \quad (2)$$

where $\vec{l}_i$ - dimensionless radius vector of point masses outside the lens, and the mass $m_i$ satisfy the relation $\Sigma m_i = 1$.

The Equation (2) in coordinate form has the form of system: