NEUTRON DIFFRACTION OF γ - RADIATION - STIMULATED PHASES IN THE VARIOUS CLASSES ALLOYS

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The structure and properties of crystals are sensitive to various external influences, including gamma radiation. In the present work the influence of γ-radiation on the structure of interstitial alloys of various classes was studied by means of neutron (λ = 0,1085 nm) and X - ray (λ = 0,15418 nm) diffraction methods. Irradiation of the samples was carried out in the γ - field of ^{60}Co with the intensity of ~ 2200 R/s.

Our results show that, before gamma irradiation, $TiN_{0,26}H_{0.15}$ has hexagonal structure (sp. gr. $P6_3$ /mmc) in which nitrogen atoms randomly occupy octahedral interstices, while hydrogen atoms reside in both octahedral (50 %) and tetrahedral (50%) interstices, in agreement with our earlier data [1]. X-ray diffraction measurements showed that the material was single-phase and homogeneous, with lattice parameters $\boldsymbol{a}$=0.2978± 0.003 and $\boldsymbol{c}$ = 0.4795±0.002 nm. According to X-ray diffraction data, the material irradiation up to a gamma dose of 8×10^9 R remained single- phase and belonged to the same structure type. In the neutron-diffraction scan, we observed 6 to 16 % changes in the relative intensity of the strongest diffraction peaks, situated at small angles, where the effect of thermal vibrations is insignificant. Note that the accuracy in our intensity measurements was 3 % or better. Therefore, it was reasonable to assume that gamma irradiation changed the distribution of nitrogen and hydrogen atoms over interstitial positions in the hexagonal close-packed (HCP) titanium matrix. Refinement by the full-pattern fitting Rietveld routine [2] (fig. 1) yielded the smallest R - factor

(R_p = 0.98%; R_{wp} = 1,3 %; R = 5,2 %) when all of the nitrogen atoms and 73,3 % of the hydrogen atoms were assumed to occupy octahedral interstices in a random manner, and the remaining 26.7 % of the hydrogen atoms were placed in tetrahedral interstices of the HCP matrix .

Considering that there are two octahedral and four tetrahedral interstices per unit cell, we find that the occupancy of hydrogen on the tetrahedral sites is far lower than that on the octahedral sites.

The assumption that half of the hydrogen atoms reside in octahedral interstices and half in tetrahedral interstices leads to R_{Br}= 8.5 % and to a notably poorer agreement between the observed and calculated intensities of the first three diffraction peaks. Therefore, the former model appears more likely. Note also that gamma irradiation increases the lattice parameters of the solid solution ($\boldsymbol{a}$ = 0.2994±0.002 nm, $\boldsymbol{c}$ = 4.823 ±0.001 nm).

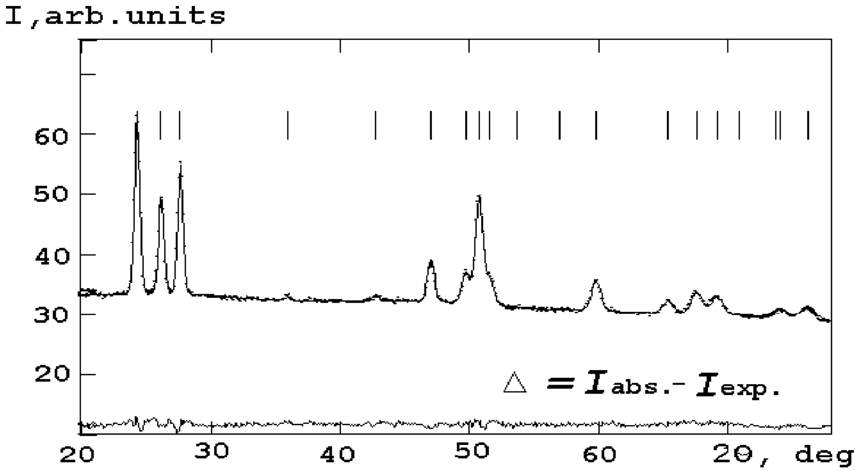

Fig.1. Profile fit difference plot gamma-irradiated $TiN_{0,26}H_{0,15}$

Thus, the hydrogen atoms in the gamma-irradiated $TiN_{0.26}H_{0.15}$ solid solution are situated largely in octahedral interstices, presumable because gamma irradiation increases the amplitude of their thermal vibrations, favoring their ordering in octahedra, whose volume ($r = a/\sqrt{2}$) is notable larger than that of the tetrahedra ($a\sqrt{3}/\sqrt{2}$).

The increase in the lattice parameter upon gamma irradiation is probable due to static atomic displacements.

It is of interest to study the influence of γ-radiation on the structure both superconducting and non-superconducting non-stoichiometric ceramics $YBa_2Cu_3O_{7-x}$, because the effect of γ-radiation can either cause the formation of various structure defects or initiate new phase transformations which are not corresponding to the equilibrium phase diagram of the system. The influence of γ-radiation has been studied on the powder samples $YBa_2Cu_3O_{6.98}$ and $YBa_2Cu_3O_{6.77}$ [3] . The first one had the critical temperature of the superconducting transition $T_c = 89$ K and had usual orthorhombic structure. The second one had semiconducting behaviour of temperature dependence of electrical resistance in interval of 77 - 300 K. This sample is characterized by essential oxygen non-stoichiometry over O(1) and O(4) positions, oxygen in O(5) position being absent completely. The structure of the samples (before and after γ-radiation) was studied by neutron diffraction method. Irradiation by γ-rays up to dose of 3.65×10^{10} R was carried out in the γ - source with intensity of 2200 R/s in evacuated and sealed quartz ampoules.

The same neutron diffraction patterns observed before and after irradiation. Therefore, the irradiated samples remained monophase with the initial structure type. The treatment of neutron diffraction pattern of $YBa_2Cu_3O_{6.77}$ by means of profile Rietveld method showed that practically there were no noticeable changes in the structure . However, the large scatter of experimental points revealed in the neutron pattern of the irradiated sample of near stoichiometry composition ($YBa_2Cu_3O_{6.98}$), and the changes observed in proportion of diffraction reflexes intensities and in doublet reflexes form, which are visually well detected at the Wolf-Bragg andles of $2\theta>40^0$. It is obviously that the large statistic scatter of experimental points testifies that large statistic distortions arise in the structure exposed to γ-radiation. The other changes of diffraction pattern can be caused by change in atom arrangement over the various position or in atom concentration. The treatment of diffraction patterns by Rietveld method showed that a good agreement between experimental and calculated reflex intensities (and the least discrepancy index R) can be obtained when supposed that oxygen content in the sample decreased significantly (7-x) = 6.64, oxygen atoms having gone away from O(1) and O(4) positions (fig. 2). If Meissner effect was observed in the starting sample, after irradiation this effect was not found. Thus, the results caused by γ-radiation of powder sample

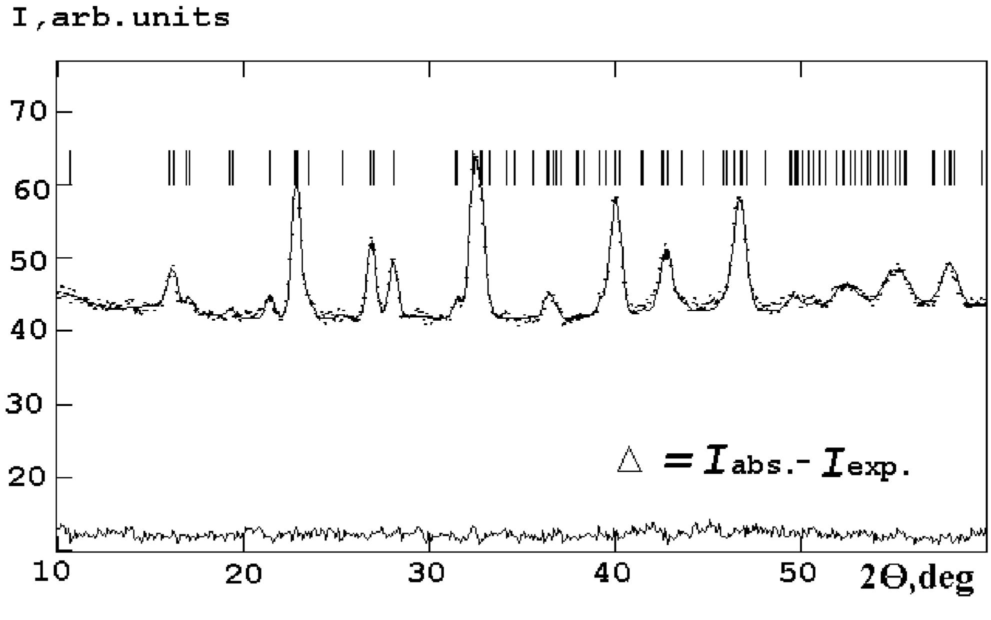

Fig. 2. Neutron diffraction pattern of $YBa_2Cu_3O_{6.98}$ after gamma-radiation

Y $Ba_2Cu_3O_{6.98}$ in evacuated ampoule are analogous to those obtained by annealing at a temperature about 450 - 570 K under persistent evacuation, the difference is that the large statistic distortions of the lattice a rise in irradiated sample. Different consequences ofeffect of heat treatment and γ-radiation on the $YBa_2Cu_3O_{6.98}$ structure are caused by various mechanisms of these factors. In the case of heat treatment the atom diffusion plays the main role in these structure changes; in the case of gamma-irradiation mechanisms are much more complicate. Under the effect of long-term irradiation, the particular material structure is formed, which is caused by radiative heating (thermal diffusion), radiation-stimulated diffusion, formation of radiation-induced defects and their interaction with various defects of initial structure and local distortions of the electron structure of crystals. Irradiation of the samples non-stoichiometric on oxygen, doesn't lead to noticeable modification of their structure. Therefore, the structure of the powder non-stoichiometric samples is more radiation-resistant than of stoichiometric one.

The interesting result was obtained for irradiated titanium dihydride TiH_2: γ - quanta initiated phase transition from cubic system to tetragonal one with the lattice para- meters a = 0,3160; c = 0,4415 nm. The crystal structure of the radiation-stimulated phase belongs to sp. gr. I4/mmm with the next atoms arrangement: 4 Ti atoms - in 4 (e) positions with coordinates 0; 0; 0 and 8 H atoms - in 8 (g) positions with 0; 1/2; 0,206 ± 0,003. Within the framework of the model we obtained the discrepancy index R_{Br} = 0,05.

It was also shown that in solid solution of nitrogen in α- Zr γ-rays stimulated a decay, and short range order parameter α altered its sign from negative ($\alpha < 0$) to positive ($\alpha>0$) [4].

Thus, the results of neutron - and X - ray - structure investigations showed that γ - rays caused various changes of crystal structure. It may be bound up with distinction in electron structure and defect-formation degree in the crystal lattice of interstitial alloys.

In conclusion, it should be noted that this work was financed by Fund of support of fundamental investigations of Uzbekistan Academy of Sciences.

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