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Structure and substructure variations of icosahedral $Ti_{41.5}Zr_{41.5}Ni_{17}$ quasicrystals under irradiation imitating outer space factors

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The article presents the results of studying the changes of coherent length, micro-strain value, density of phason defects and residual macro-stresses in $Ti_{41.5}Zr_{41.5}Ni_{17}$ icosahedral quasi-crystalline ribbons after irradiation by VUV ($h\nu$ = 10.2 eV, duration up to 40 h), electron and proton fluxes ($h\nu$ = 100 KeV with doses D up to $13 \cdot 10^{16}$ cm^{-2}), X-ray bremsstrallung ($h\nu$ = 1 MeV with doses D up to 10000 rad). It is shown that the scale of the substructure changes, defect density, their type and parameters depend on the perfection degree of the original structure and impact energy power.
Keywords: quasi-crystalline, X-ray diffraction, irradiation, structure, substructure.

Представлены результаты анализа изменения размера областей когерентного рассеяния, величины микродеформаций, плотности фазонных дефектов и остаточных макронапряжений в $Ti_{41.5}Zr_{41.5}Ni_{17}$ икосаэдрической квазикристаллической фазе при облучении квантами вакуумного ультрафиолета ($h\nu$ = 10.2 эВ, длительностью до 40 час), потоком электронов и протонов ($h\nu$ = 100 кэВ дозой D до $13 \cdot 10^{16}$ см$^{-2}$), а также рентгеновским тормозным излучением ($h\nu$ = 1 МэВ дозой D до 10000 рад). Показано, что масштаб изменения субструктуры, изменения плотности дефектов, их типа и параметров зависит от степени совершенства исходной структуры и мощности энергетического воздействия.

Зміна структури і субструктури ікосаедричного $Ti_{41.5}Zr_{41.5}Ni_{17}$ квазікристала при радіаційному впливі, що імітує фактори відкритого космічного простору. *С.В.Баздирєва, С.С.Борисова, С.В.Малихін, А.Т.Пугачов, А.М.Бовда, С.Д.Лавриненко, В.В.Абраімов, В.О.Лотоцька.*

Представлено результати зміни розміру областей когерентного розсіяння, величини мікродеформацій, густини фазонних дефектів та залишкових макронапружень у $Ti_{41.5}Zr_{41.5}Ni_{17}$ ікосаедричній квазікристалічній фазі при опроміненні квантами вакуумного ультрафіолету ($h\nu$ = 10.2 еВ, тривалістю до 40 год), потоком електронів та протонів ($h\nu$ = 100 кеВ дозою D до $13 \cdot 10^{16}$ см$^{-2}$), а також рентгенівським гальмовим опроміненням ($h\nu$ = 1 МеВ дозою D до 10000 рад). Показано, що масштаб зміни субструктури, зміни густини дефектів, їх типу і параметрів залежить від ступеня досконалості вихідної структури і потужності енергетичного впливу.

1. Introduction

Studying the behavior of functional materials under conditions of outer space (OS) is an actual problem at present. At the height of 300–400 km from the Earth the most significant factors are the following: microgravity; space vacuum (~$10^{-4}...10^{-5}$ Pa); periodic temperature variations in the range from 120 K to 420 K; the orbital station intrinsic residual atmosphere including the atoms and molecules of O, O_2, N_2, He, H, Ar; micrometeorites; incoming flow of atomic oxygen with energy of 5...10 eV; irradiation by the fluxes of protons ($E \sim 0.1...1$ MeV, 10^8 cm^{-2} c^{-1}), electrons ($E \geq 1.5$ MeV, $5{\cdot}10^5$ cm^{-2}c^{-1}), X-ray and vacuum ultraviolet (VUV) quanta with energy about $1.4{\cdot}10^4$ W·cm^2 [1]. Previously, most attention was focused to studying the phenomena stimulated by irradiation of crystalline metals and aerospace alloys such as aluminum, titanium and their alloys, spring steels and other metals for aerospace purposes [2, 3]. The mechanism and kinetics of photochemical solid-phase reactions occurring on the surface of nanoscale films under VUV irradiation were investigated in [4, 5]. The discovery of stable quasicrystals has given a new impetus for such investigations, because quasicrystals are considered as promising radiation-resistant materials due to their non-periodic structure [6]. It should be noted there are only several works on the quasicrystals under irradiation [7–11]. The aim of this work is studying the variations of structure, substructure and stress state in quasi-crystalline samples under irradiation by different radiation components characteristic for outer space conditions.

2. Samples and methods of research

The samples were ribbons of $Ti_{41.5}Zr_{41.5}Ni_{17}$ alloy with thicknesses from 20 to 100 mm, prepared by rapid quenching at the single disc. The details of preparation procedure are given in [12, 13]. The structure of the samples was investigated by X-ray diffraction. Phase identification and indexing of the quasi-crystalline phase were carried out according to the J.W.Cahn procedure with two-index notation (N, M) [14]. To characterize the quasi-crystalline phase, the quasi-crystalline parameter a_q was used, which magnitude was related to the diffraction vector Q_{II} in physical (parallel) space by the ratio,

$$Q_{II} = \frac{4\pi\sin\theta}{\lambda} = \frac{\pi}{a_q}\sqrt{\frac{N + M\tau}{2 + \tau}},$$

where $\tau = 1.618034$ — irrational number, which is so-called "golden section". The total six-dimensional diffraction vector for the quasi-crystals consists of two three-dimensional terms: $\mathbf{Q}_{6D} = \mathbf{Q}_{\text{II}} + \mathbf{Q}_{\perp}$. The last term ($Q_{\perp}$) is a component of the diffraction vector in the additional (perpendicular) space.

Irradiation experiments were carried out using VUV photons (with exposure time up to 40 h), X-ray bremsstrallung irradiation, electron and proton fluxes. The source of vacuum ultraviolet was a barrier discharge lamp BAR [15] emitting the continuum spectrum with wavelengths $\lambda > 120$ nm (argon) and photon flux with densities from ~10^{16} to 10^{17} cm^{-2}c^{-1}. The lamp was placed close to the sample surface. Irradiation exposures were carried out in several successive stages. For X-ray irradiation the apparatus "TEMP-A" NSC KIPT IFTTMT was used, based on the pulse accelerator of relativistic electrons. The maximum energy of photons $h\nu_{max} = 1$ MeV, and the maximum dose D up to 10000 rad were used. The absorbed dose was measured with a special receiver placed in the irradiation chamber. Irradiation by protons and electrons with energy of 100 keV and doses $D = (1.8;\ 3.6;\ 8.5;\ 13){\cdot}10^{16}$ cm^{-2} was carried out with the experimental facility made in ILTPE NASU. Such experiments simulated a long-term holding under conditions of OS. The maximum irradiation dose was equivalent to 10-year presence at the orbit.

The residual macrostresses in textured quasicrystals were determined by X-ray diffraction using $\sin^2\psi$-method, where angles ψ corresponded to crystallographic angles between the reflecting plane and the plane perpendicular to the texture axis [16]. To study the substructure characteristics we used the modified approximation method described in detail in [17]. This method allows to evaluate coherence length (L), average value of micro-strain (ε) and density (N) of phason defects specific to the quasi-crystals. The phason as a defect induces some local topological and chemical disorder into the structure. The presence of the phasons is manifested by variations of the diffraction peaks parameters, depending on Q component of the diffraction vector [19–21].

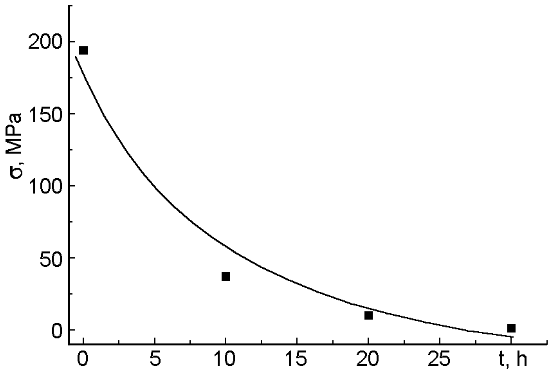

Fig. 1. The variation of the residual macro-stresses magnitude under VUV irradiation during 40 h.

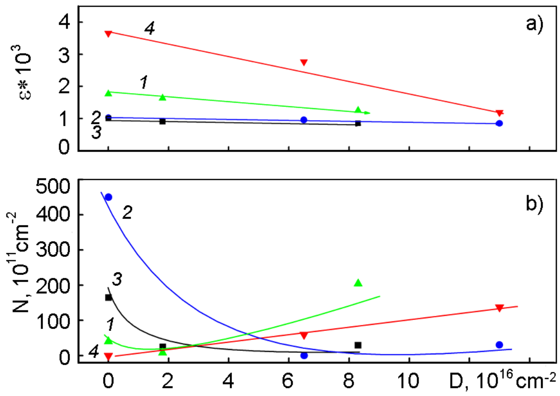

Fig. 2. The dependences (a) between variations of micro-strain (ε) and (b) the phason defects density (*N*) on the dose of irradiation in the crossed streams of electrons and protons. *1*, *2* – samples obtained at the quenching disk linear velocity of the 15 m·s^{-1} ; *3*, *4* – samples obtained at the quenching disk linear velocity of the 25 m· s^{-1}.

3. Results and discussion

As shown by the results of previous studies [13, 22], $Ti_{41.5}Zr_{41.5}Ni_{17}$ samples obtained at quenching disk linear velocities of 15, 19.5 and 25 m·s^{-1} contained only single icosahedral quasi-crystalline phase in the initial state. This phase was textured and had the texture cap half-width of about 15...20 degrees. Depending on regime of the sample preparation the quasi-crystalline parameter a_q varied from 0.51940 to 0.52100 nm.

By the results of X-ray diffraction no qualitative changes of diffraction patterns (total number of reflections) were revealed after exposure to different irradiation types. Consequently, the stimulated phase changes were absent. The quasi-crystalline phase was found to be stable to all of the applied radiation types. All observed variations of the diffraction patterns were reduced to changes in position, intensity and width of the diffraction lines. According to the theory of scattering by M.A.Krivoglaz [18] such changes can indicate substructure variations, namely, structural defects distribution, their type, density, and parameters.

Analysis of the results we began from irradiation by VUV having the lowest energy per atom. Figure 1 shows variations of the residual macro-stresses with increasing exposure durations. It is seen that in the initial state the samples obtained at disk linear velocity of 19.5 m·s^{-1} have tensile macro-stresses about +200±20 MPa. But already after 20 h of exposure, the tensile macro-stresses were fully annealed and had no further modifications. The similar character of the residual macro-stresses reducing was characteristic for all experiments by VUV irradiation of the ribbons. Decrease of the macro-stresses is accompanied by decreasing the quasi-crystalline parameter (measured for the unstrained section) from 0.52037 nm to 0.52000 nm. Similarly, the coherence length decreases from 200 nm to about 50 nm. The phason defect density decreases linearly from 90·10^{11} cm^{-2} to 0.23·10^{11} cm^{-2}. The micro-strain average value decreases linearly from 1.86·10^{-3} practically to zero for exposure time τ = 30 h and further grows up to 0.9·10^{-3}. The observed changes can be classified as stimulated annealing. These can be occurred, for example, by heating in vacuum. As a result of irradiation the density of initial quenching induced defects decreases. Movement of randomly distributed dislocations related to micro-strains, releases stress, and dislocation alignment into the wall results in coherence domain fragmentation. All the defects are annealed including chaotically distributed phasons. The phasons trend to generate the walls [23], especially near the dislocations, thus reducing the excessive strain. However, in this case the localized (or zero-dimensional) defects transform to the extended defects type causing different diffraction effects [18]. Perhaps, the effect of micro-strains increases after the long-term exposures is related with such transformations.

The next by energy impact were experiments by irradiation in the crossed streams of electrons and protons. In the ribbons ob-

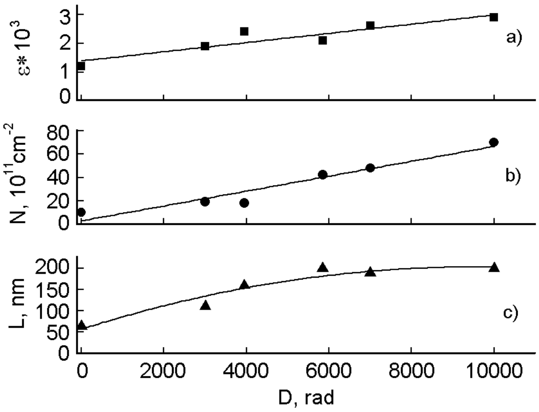

Fig. 3. Variations of (a) micro-strain level, (b) phason defect content and (c) coherence length on the dose irradiation of with X-rays bremsstrallung.

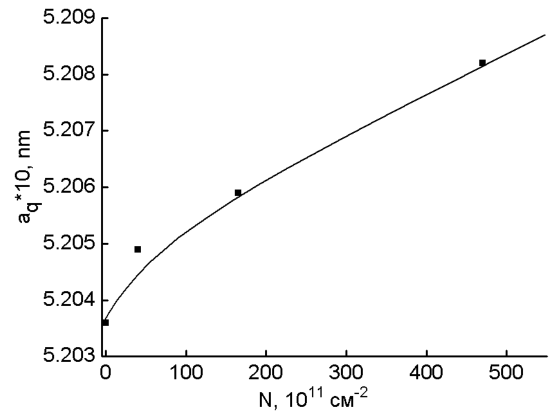

Fig. 4. Dependence of the quasi-crystalline parameter (a_q) on the phason defect density under irradiation in the crossed streams of electrons and protons.

tained at quenching disk linear velocities 15 m·s1 and 25 m·s1, in the initial state the residual tensile macro-stresses up to 100 MPa were revealed. Under irradiation the macro-stresses were also annealed. The micro-strain variations are shown at Fig. 2a, and the quantities of phason defects are in Fig. 2b. It is seen that the micro-strain level lowers as the irradiation dose increases. This decreasing is more significant in the samples with greater level of initial micro-strains and insignificant in the initially relatively perfect samples. In the last ones, the concentration of phason defects is found to be higher initially, and it is reduced as a result of irradiation. Figure 2b shows that the extent of phasons annealing is the greater, the more of phason were in the initial state. In the case of small initial content of phasons, they were accumulated as the radiation dose increased. This accumulation is more significant when the micro-strain annealing becomes more intensive. The coherence length either does not change in the samples with initially large (about 200 nm), or reaches this value, when large coherence length L was smaller (30...60 nm) in the initial state. Thus, we can conclude that in the case of electron-proton irradiation the annealing of initial defects and the accumulation of new ones occurs in succession. The nature and extent of these processes depend on the state of the initial structure.

X-rays bremsstrallung irradiation was used as the most energetic. Variations of the micro-strain level, phason defects content and coherence length with increasing radiation dose are shown in Fig. 3.

It is seen that the irradiation exposure promotes the linear increase of micro-strain (ε) corresponding to increasing the density of randomly distributed dislocations in the coherence domain. Similarly, the density of phason defects (N) increases. Increasing the coherence length and decreasing the density of dislocations forming the walls are linear up to 6000 rad dose, then the saturation takes place. The quasi-crystalline parameter increases monotonically from 0.51950 nm to 0.52000 nm.

From the described experimental results we can make important conclusions. Firstly, the correlated changes of L and ε values do not contradict to the classical knowledge about behavior of pre-deformed material under annealing. Secondly, any substantial variation of micro-strains is necessary accompanied by accumulation of phason defects. This is indeed possible when dislocations move by sliding in non-periodic structure [19, 20, 24]. The phasons annealing is observed only in the case of the constant micro-strains level. Thirdly, there is an interesting fact for all types of radiation: the greater is the density of phason defects, the higher is the quasi-crystalline parameter (a_q), and vice versa. Fig. 4 shows the data for the samples irradiated by electrons and protons. The nature of phason defects ("phasons") is currently widely discussed [25]. It is believed [26] that phasons are small dislocation dipoles. Taking into account that these are stacking faults inside the dipoles, it is possible to explain the observed selective displacement and broadening of the diffraction lines with strictly defined indices. However, stacking faults or large prismatic dislocation loops create anisotropic strains. Thus, the interstitial loops of radiation nature cause the largest increase of the interplanar spacing in the planes where there are. To determine the quasi-crystalline parameter we selected the reflection (136, 220), which should be least sensitive to presence of phasons. Nevertheless, we observed the displacement of the reflection. So, we assume that the phasons act like interstitial atoms or small complexes and create anisotropic strain, resulting the a_q increasing. But the phasons cause broadening other reflections as well. From observed diffraction effects and based on the scattering theory [18], we assume that the phasons generated both during quenching and as a result of strain, are similar to the small dislocation interstitial loops.

4. Conclusions

Thus, it has been established that even maximum doses of irradiation by VUV, electron and proton fluxes, and X-rays bremsstrallung result in no phase transformations in icosahedral quasi-crystalline phase $Ti_{41.5}Zr_{41.5}Ni_{17}$. All types of irradiation result in changes of the diffraction patterns from indicating the following substructure changes: average micro-strain value, coherent scattering length, and phason defect density. The scale of the substructure variations depends on the perfection degree of the original quasi-crystal structure and irradiation impact power.

References

1. M.I.Panasuk, L.S.Novikov, Model Space, KDU, Moscow (2007) [in Russian].
2. B.E.Paton, Space: Tecnologiji, Materials science, Constructions, ed. by B.E.Paton IEW, NAS Ukraine, Kiev (2000) [in Russian].
3. A.A.Kos'ma, S.V.Malykhin, *Functional Materials*, **6**, 262 (1999).
4. I.F.Mikhailov, S.S.Borisova, L.P.Fomina et al., *Functional Materials*, **13**, 85 (2006).
5. I.F.Mikhailov, S.V.Malykhin, S.S.Borisova et al., *Functional Materials*, **13**, 381 (2006).
6. Sh.Khananov, *FMM*, **75**, 26 (1993).
7. R.Chatterjee, D.Kanjilal, A Dunlap, *Nucl.Instrum.Met. Phys.Res., B*, **156**, 201 (1999).
8. G.Coddens, A.Dunlop, H.Dammak, *Nucl. Instr. Met. Phys. Res., B* 211, 122 (2003).
9. S.Mechler, C.Abromeit, N.Wanderka, *Nucl. Instr. Met. Phys. Res., B* 245, 133 (2006).
10. R.Wang, X.Yang, H.Takahashi, S.Ohnuki, *Condens.Matter.*, **7**, 2105 (1995).
11. K.Sato, F.Baier, W.Sprengel, H.E.Schaefer, *Phys. Rev. B*, **66**, 092201/1 (2002).
12. V.Azhazha, S.Dub, G.Khadzhay et al., *Phil. Mag.*, **84**, 983 (2004).
13. V.Azhazha, S.Dub, O.Grib, B.Merisov et al., *Vistnik Karkivskogo Nacionalnogo Universitety, Ser.Physika*, No.9, 103 (2006).
14. J.Cahn et al., *J.Mat.Res.*, **1**, 30 (1986).
15. G.A.Volkova, N.N.Kirilova, E.N.Pavlovskaja et al., *Zh. Prikladnoj Spektroskopii*, **41**, 691 (1984).
16. S.V.Bazdyrieva, S.V.Malykhin, A.T.Pugachov, Trudy 55-th Mezdunarodnoj Konf. "Aktualniji Problemy Prochnosti", Kharkiv (2014) p.169.
17. S.V.Bazdyreva, N.V.Fedchuk, S.V.Malykhin et al,, *Functional Materials*, **20**, 81 (2013).
18. M.A.Krivoglaz, Diffraction of X-rays and Thermal Neutrons by Real Crystals, Naukova Dumka, Kiev (1983) [in Russian].
19. V.Franz, M.Feuerbacher, M.Wollgarten, K.Urban, *Phil.Mag.Lett.*, **79**, 333 (1999).
20. A.Letoublon, F.Yakov, F.Livet et al., *Europhys.Lett.*, **54**, 753 (2001).
21. M.Jono, Y.Matsuo, K.Yamamoto, *Phil.Mag.*, **81**, 2577 (2001).
22. V.M.Azhazha, A.M.Bovda, S.D.Lavrinenko et al., *PAST, Ser. Vacuum, Pure Mater., Superconduct.*, **4(16)**, 82 (2007).
23. M.Ju.Gutkin, I.A.Ovidko, Defects and Plasticity mechanisms in nanostructures non-crystalline materials, SPb., Janus (2001) [in Russian].
24. M.Feuerbacher, P.Schall, Y.Estrin, Y.Brechet, *Phil.Mag.Lett.*, **81**, 473 (2001).
25. M.De Boissieu, in: Proc. 9th International Conf. Quasicrystals, 22-26 May, Iowa State University, Ames, USA (2005), p.301.
26. M.Kleman, *Europhys.Lett.*, **31**, 315 (2003).