MODIFICATION OF Ti-Zr-Ni ALLOYS BY POWERFUL PLASMA STREAM OF DIFFERENT GASES

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The effects of irradiation by hydrogen, helium and argon plasma heat loads of 0.4 … 0.6 MJ/m^2 on the change of morphology, structure and phase composition of Ti41.5Zr41.5Ni17 alloy are investigated. The initial state of such alloy is characterized by presence of a crystal- approximant 1/1 phase (W-phase) with lattice constant a_W = 1.428 ±0.0003 nm, Laves phase (L phase) with the lattice period a = 0.6043 ± 0.0003 nm and an icosahedral quasi-crystalline phase (*i*-phase) with quasi-crystalline parameter a_q= 0.5175 ±0.0003 nm. Plasma irradiation causes formation of the icosahedral quasi-crystalline phase in re-solidified layer with depth up to 100 μm. The substructure parameters: size of the coherence area, the value of micro-strain, phason defect concentration and the value of residual macro-stresses are determined by the plasma parameters.

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INTRODUCTION

The structure of quasicrystals (QC) is characterized by long-range order in the atomic arrangement and symmetry, which is forbidden by the classical crystallography of crystals [1, 2]. QCs show unusual physical properties [3]. QC formation is perspective for practical application in the form of thin layers or films on substrates [4, 5]. The superficial layers of the micron thickness consisting of micro-sized particles, nano-crystals and quasi-crystals are formed by methods of thermal, plasma sputtering, and by ultrasonic impact machining of surface [6, 7]. Surface processing with powerful pulsed plasma streams of microsecond duration leads to creation of extremely high values of temperature gradient in surface layer with simultaneous influence of significant ion fluence up to 10^{27} cm$^{-2}\cdot$c^{-1}. Therefore it could be also considered as effective method for modification of material properties and creation of fine structures in surface layer of several tens μm in thickness [8-10].

Due to the low thermal conductivity, QCs based on Ti, Zr and Ni can be used, for example, as a thermal barrier for blades of aviation and other turbines, generators, pistons and cylinder engines, catalytic coatings of chemical reactors, or as a reinforcing coatings on the instruments and non-stick coating of cookware and other. Based their relatively high-melting points QCs are considered to be radiation-resistant materials. QCs are also able to store hydrogen in a volume without significant structural changes to the 2 H/at.

In previous paper [11] the QC alloy irradiation by hydrogen plasma with surface energy load of 0.6 MJ/m^2 has been resulted in the formation of modified surface layer of thickness up to 50 μm. In such surface layer the phase transformation occurs from crystal approximant 1/1 to QCs phase. However, the nature of this transformation requires the comprehensive studies. According to the theory of phase transitions [12], the formation of the intermediate phase in metallic alloys is determined by the action of chemical, electronic, dimensional factors, or by its combination. In this work the mechanisms of QCs formation and appeared changes of its structure were studied in surface layer exposed by plasmas of different gases. Active light (hydrogen) and inert massive gases (helium and argon) have been chosen as working gases.

1. SAMPLES AND EXPERIMENTAL EQUIPMENT

Polished bulk massive samples of Ti41.5Zr41.5Ni17 obtained after solidification from the melt were used for the plasma load tests. Heat flux tests of the samples have been performed with hydrogen plasma streams produced by the quasi-steady-state plasma accelerator QSPA Kh-50 [13]. Argon and helium plasma was generated by MPC [14]. The main parameters of QSPA plasma streams were as follows: ion impact energy about 0.4 keV, the maximum plasma pressure 3.2 bars, and the stream diameter about 18 cm. The surface energy loads measured with a calorimeter achieved 0.6 MJ/m^2 (near the tungsten melting threshold). The plasma pulse shape was approximately triangular, and the pulse duration was 0.25 ms. The MPC plasma streams with density up to 10^{18} cm^{-3} and surface energy load 0.48 MJ/m^2 (Ar) and 0.57 MJ/m^2 (He) have triangular pulse shape with pulse duration of about 0.02 ms.

A surface analysis was carried out with an MMR-4 optical microscope equipped with a CCD camera and Scanning Electron Microscopy (SEM) of the JEOL JSM-6390 type. To study a micro-structural evolution of the exposed targets, the X-ray diffraction technique (XRD) has been used. Quasi-crystalline phase identification was carried out in conformity with the Cahn´s methodology using indices N and M [15].

To characterize the structure of the icosahedral quasi-crystalline phase and its degree of perfection we used quasi-crystalline parameter a_q, whose value is determined by (1)

$$a_q = \frac{\lambda}{4\sin\vartheta}\cdot\sqrt{\frac{N+M\tau}{1+\tau^2}} = \frac{d}{2}\cdot\sqrt{\frac{N+M\tau}{1+\tau^2}}, \qquad (1)$$

where N, M – index reflections; d – the distance between planes; τ = 1.618034 – "golden ratio."

The phase of cubic crystal-approximant 1/1 (W-phase) was disclosed by modeling theoretical diffraction pattern using the basis data of the lattice shown in [16]. The lattice constant of crystal- approximant 1/1 was calculated from the position of diffraction peaks. The value of the sum of main macrostresses (σ_1+σ_2) in the model of plane stress state is defined by the equation (2)

$$\sigma_1 + \sigma_2 = \frac{E}{\nu}\cdot\frac{a_q - a_{q0}}{a_{q0}}, \qquad (2)$$

where E – Young modulus; ν – Poisson ratio; a_q – quasi-crystalline parameter in surface layer according; ϑ-2ϑ – scanning by XRD studying; a_{q0}= 0.52027 nm – the average value of quasi-crystalline parameter for samples in unstressed state. The value of E is taken equal to 115 GPa, the value of Poisson ratio ν is taken equal to 0.3. To study the characteristics of the substructure in the irradiated samples the modified method of approximation is used, described in detail in [17].

2. EXPERIMENTAL RESULTS

Fig. 1 shows the diffraction patterns of the samples in the initial state and after irradiation by plasma of different composition. In the initial state crystal phases predominated, exactly a crystal phase - approximant 1/1 (W-phase) with a lattice period $a_{1/1}$= 1.428 nm and Laves phase (L, structure type C14) a = 0.6043 nm. The icosahedral quasi-crystalline phase (*i*-phase) with the quasi-crystalline parameter a_q = 0.5175 nm presents in small quantities. After five exposures with plasma heat load of 0.6 MJ/m^2 Laves-phase disappears, the number and intensity of W- phase lines decreases. The number of reflections from *i*-phase and their intensity increases significantly. For example, the intensity of reflection (52.84) from *i*-phase increases by factor 10; i-phase is strongly textured; only planes with 5-fold and 2-fold symmetry locate parallel to the surface. After irradiation the quasi-crystalline parameter increases to a_q = 0.5181 ± 0.0003 nm. Increasing the number of irradiation pulses up to 10 does not change phase composition. The decreasing of the quasi-crystalline parameter to a_q = 0.5170 ± 0.0003 nm is observed.

The similar changes of the diffraction pattern are observed in the sample irradiated by 5 pulses of argon and helium plasmas (Fig. 1). The diffraction pattern changes indicate that phase transformation occurs in the surface layer h≈50 μm which is comparable with half-value of absorption layer for X-ray irradiation.

Fig. 2 shows microstructure changes of the surface layer after plasma irradiation. The modified layer is well recognized in the cross-section views. The thicknesses of the modified layers are about 70, 50 and 20 μm after irradiation by hydrogen, helium and argon plasma, respectively. Uneven pattern of surface with dodecahedron and triacontahedron crystallite is formed in surface layer that resolidified after plasma irradiation (see Fig. 2,c). Their sizes are 30…100 μm that is typical for QCs monograins, prepared by fast quenching method [18]. According to the X-ray fluorescence analysis the composition is close to the composition Ti41.5Zr41.5Ni17 of stable icosahedral quasi-crystal.

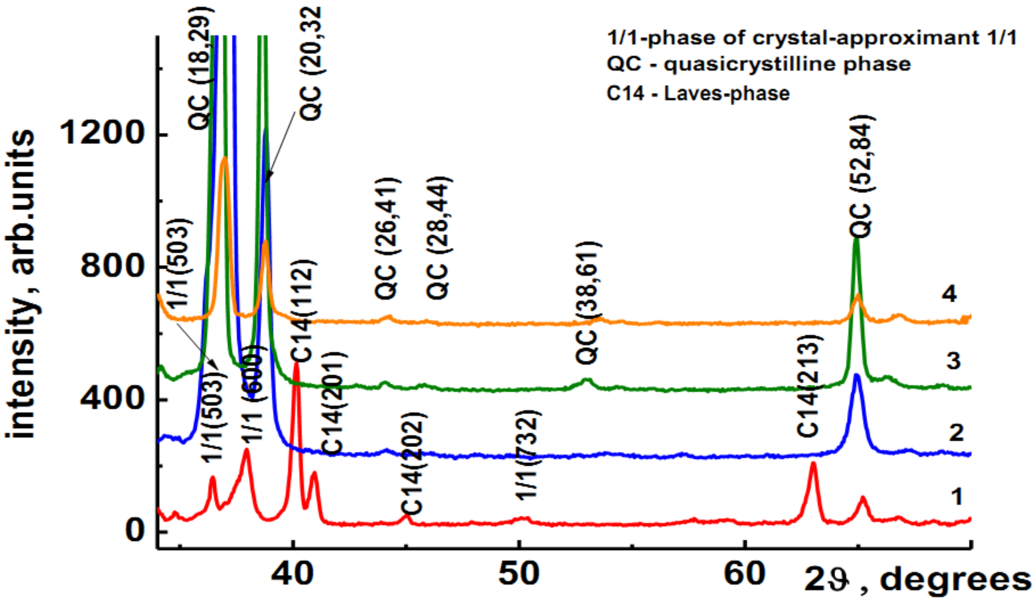

Fig. 1. Diffraction patterns of : initial state (1), areas exposed by 5 pulses of argon plasma with heat load of 0.48 MJ/m^2 (2), after 10 pulses of hydrogen plasma of 0.6 MJ/m^2 (3), after 5 pulses of helium plasma of 0.57 MJ/m^2(4), (Cu-Kα radiation)

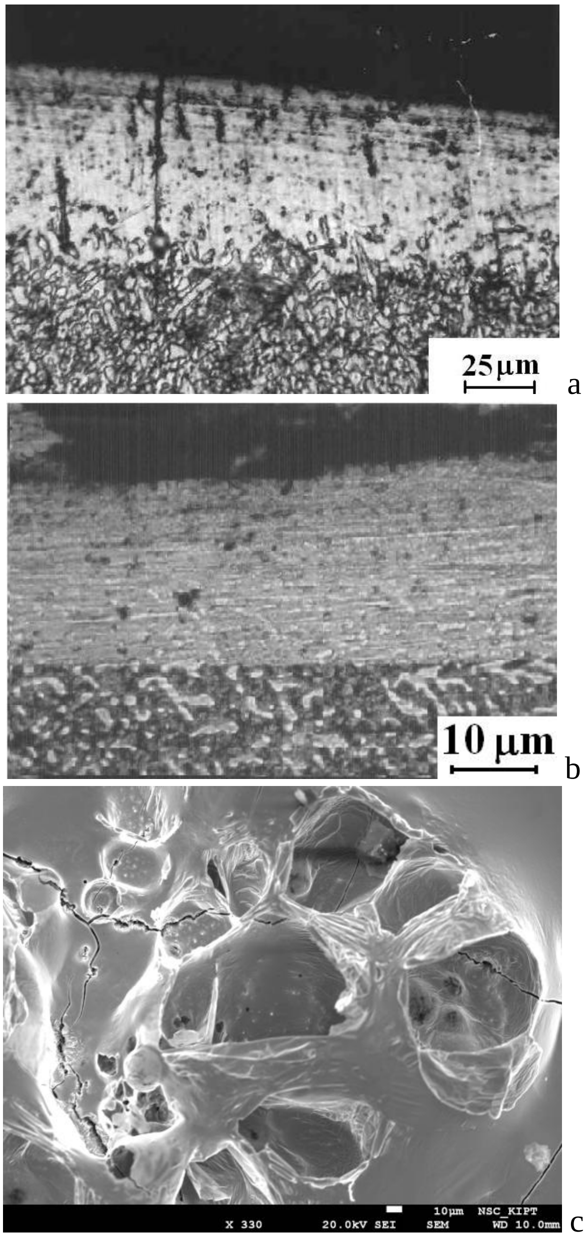

Fig. 2. Views of exposed sample: optical image of cross section after helium (a) and argon (b) plasma irradiation, SEM image of surface exposed by argon plasma (c)

The size of the bright areas of the cross section is in agreement with calculated size of half-value absorption layer for X-rays. Thus, it could be concluded that the phase transformation is occurred in this layer.

The parameters of the substructure and the internal macrostresses have been appraised for the formed quasi-crystalline phase. The values of phason defects concentration *(n)*, size of coherent area *(L)*, the value of microstrain *(ε)* that calculated by modified method of approximation are presented in Table. It also shows the sum of the main stresses.

It can be noted that in the irradiated surface layer the value of residual tensile stresses is significantly less than in a similar tungsten targets after plasma irradiation. Cracks with smooth edges are also observed on the exposed surface. Such cracks are typical for fracture of the amorphous material. The nature of these cracks differs from cracks appearing in tungsten after irradiation by hydrogen plasma.

Performed calculations have shown that after hydrogen plasma irradiation size of coherent area size is greater by order of magnitude than after argon and helium plasma irradiation. The value of micro-deformations is also the largest – $2.2\cdot10^{-3}$. The concentration of phason defects *(n)* varies depending on the kind of plasma (ion composition). These differences can be explained by insignificant distinction of the exposure parameters. In the surface layers the parameters of the quasicrystals substructure and the parameters of rapidly quenched ribbons are found to be rather comparable [17]. It can be concluded that the heating and rapid quenching are the main factors influencing on the quasicrystalline phase formation. Most likely the radiation factor does not play a significant role, because the layer of the projected range is 20…30 monolayers. It is smaller than the thickness of the modified layer. The role of electron-chemical factor is also negligible because of the phase transformation is observed both for chemically active (hydrogen) and inert (argon) gases irradiation.

The parameters of the substructure, structure and residual stresses for investigated samples

Type of irradiation	*L, nm*	$\varepsilon\cdot10^3$	$n\cdot10^{12}$, cm^{-2}	$a_q\cdot10$, *nm*	$\sigma_1+\sigma_2$, *MPa*
Hydrogen plasma	200	2.2	3.3	5.1700	550
Helium plasma	24	0.5	0.001	5.1678	590
Argon plasma	35	1.1	5.7	5.1730	500

CONCLUSIONS

1. The irradiation of the alloy Ti41.5Zr41.5Ni17 by hydrogen, helium or argon plasma flows with heat loads up to 0.6 MJ/m^2, causes the formation of quasicrystalline icosahedral phase in the surface layer of 100 µm in thickness.
2. The substructure parameters: size of the coherence area, the value of micro-strain, phason defect concentration and the value of residual stresses are determined by the parameters of the impacting plasma.
3. Temperature gradient in plasma affected layer is the main factor influencing on the formation of quasicrystalline structure.

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МОДИФИКАЦИЯ Ti-Zr-Ni-СПЛАВОВ ПОД ВЛИЯНИЕМ ОБЛУЧЕНИЯ ПЛАЗМОЙ РАЗЛИЧНЫХ ГАЗОВ

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Исследовано влияние облучения водородными, гелиевыми, аргоновыми плазменными потоками с тепловыми нагрузками 0,4…0,6 МДж/м^2 на изменение морфологии, структуры и фазового состава сплава Ti41,5Zr41,5Ni17. Исходное состояние такого сплава характеризуется присутствием фазы кристалла-аппроксиманта 1/1 (W-фазы) с периодом решетки a_W = 1,428 ±0,0003 нм, фазы Лавеса (L-фаза) с периодом решётки a = 0,6043±0,0003 нм и икосаэдрической квазикристаллической фазы (*i*-фаза) с параметром квазикристалличности a_q = 0,5175±0,0003 нм. Установлено, что плазменное облучение вызывает в поверхностном слое до 100 мкм формирование квазикристаллической икосаэдрической фазы. Установлено, что параметры субструктуры фазы: размер области когерентности, величина микронапряжений и плотность фазонов, а также уровень остаточных напряжений, определяются параметрами плазменного потока.

МОДИФІКАЦІЯ Ti-Zr-Ni-СПЛАВІВ ПІД ВПЛИВОМ ОПРОМІНЕННЯ ПЛАЗМОЮ РІЗНИХ ГАЗІВ

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Досліджено вплив опромінення водневими, гелієвими, аргонними плазмовими потоками з тепловими навантаженнями 0,4…0,6 МДж/м^2 на зміну морфології, структури і фазового складу сплаву Ti41,5Zr41,5Ni17. Початковий стан такого сплаву характеризується присутністю фази кристала-апроксиманта 1/1 (W-фази) з періодом решітки a_w = 1,428 ± 0,0003 нм, фази Лавеса (*L*-фаза) з періодом решітки a = 0,6043 ± 0,0003 нм і ікосаедричної квазікристалічної фази (*i*-фаза) з параметром квазікристалічності a_q = 0,5175 ± 0,0003 нм. Встановлено, що опромінення плазмою викликає в поверхневому шарі до 100 мкм формування квазікристалічної ікосаедричної фази. Показано, що параметри субструктури фази: розмір області когерентності, величина мікронапружень, а також рівень залишкових макронапружень, визначаються параметрами плазми в потоці.