BEHAVIOR OF THE Ti-Zr-Ni THIN FILM CONTAINING QUASICRYSTALLINE AND APPROXIMANT PHASES UNDER RADIATIVE-THERMAL ACTION IN TRANSITION MODES

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X-ray diffraction and SEM microscopy were used to study the structural and phase changes in a thin film obtained by magnetron sputtering of a Ti52Zr30Ni18 target (at.%) on a steel substrate under the radiation-thermal influence of pulsed hydrogen plasma on an QSPA Kh-50 accelerator. A technique has been worked out for the formation of the quasicrystalline and crystal-approximant phases as a result of high-speed quenching using pulsed action with a heat load of 0.6 MJ/m^2. The changes in the contents of these phases as well as in their structure and substructure parameters were studied during isothermal vacuum annealing at a temperature of 550 °C and also as a result of irradiation with 5 plasma pulses in the range of heat load from 0.1 to 0.4 MJ/m^2. The quasicrystalline phase was found to be resistant to irradiation with hydrogen plasma.

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INTRODUCTION

Quasicrystals (QCs) are a special class of materials in the condensed state, whose structure differs from the structure of classical crystals. They have a strict long-range order in the arrangement of atoms in the absence of translational invariance and show symmetry forbidden by classical crystallography, for example, icosahedral [1]. Therefore, QCs are characterized by abnormal and unique physical properties [2]. It can be noted the following ones: corrosion resistance, high hardness, low surface energy, low thermal conductivity, hardness and increased strength at high temperatures. At low temperatures, QCs are fragile, and this makes their application difficult, but the use of thin-film technologies solves this problem [3]. So, it is known to use aluminum-based QCs thin-film coatings as heat-insulating layers on turbine blades, as well as non-stick coatings for chemical devices or household utensils [2].

In the Ti-Zr-Ni system, the formation of a quasicrystalline icosahedral phase in a 100 μm thick surface layer was first observed upon pulsed irradiation of a massive Ti41.5Zr41.5Ni17 alloy with flows of hydrogen, helium, or argon with thermal loads up to 0.6 MJ/m^2 in [4]. The features of the formation of a quasicrystalline thin-film coating are described in [5, 6].

The quasicrystals) of the Ti-Zr-Ni system are stable up to ≈ 660 °C and are distinguished by a high hydrogen absorption capacity (up to 2 H/Me) in the form of a solid solution, and therefore, increased resistance to blister formation can be expected for them [7]. It is believed that the absence of the property of translational invariance makes quasicrystals stable during operation under conditions of increased radiation [8–10]. We assume that the film coatings of Ti-Zr-Ni quasicrystals, or the Ti-Zr-Ni quasicrystal/W layered system, can serve as thermal protection and protection against hydrogen embrittlement, which is possible when operating in the ITER international fusion reactor.

In this work, the goal is to obtain a thin film of a Ti-Zr-Ni quasicrystal or its approximants on the surface of the steel by the rapid quenching method using irradiation with hydrogen plasma at the QSPA-Kh50 quasistationary accelerator. It is assumed that due to the high crystallization rate under nonequilibrium conditions, a mono- or heterophase structure can form in the exposure zone, the components of which can be a quasicrystalline phase, approximant phases, or other intermetallic phases. Also, we will study the behavior of the obtained thin film under low-energy plasma irradiation.

1. SAMPLES AND INVESTIGATION TECHNIQUE

The main idea of the experiment is to form a quasicrystalline structure in the Ti-Zr-Ni coating subjected to high-speed surface hardening. The surface of the initial Ti-Zr-Ni coating is irradiated with a powerful pulsed flow of hydrogen plasma of microsecond duration and an ion flux of up to 10^{27} m$^{-2}\cdot$s^{-1} with a surface thermal load (q) of about 0.6 MJ/m^2, which is of the order of the tungsten melting threshold.

A film coating with a thickness of 14.8 μm was made by direct-flow magnetron sputtering of a target with the Ti52Zr30Ni18 (at.%) composition. The substrate used was Eurofer European Association base steel of the ferrite class, which is supposed to be used in ITER.

The substrate was not forced to heat; its temperature during the deposition did not exceed 40…50 °C. The samples were irradiated with hydrogen plasma flows using a QSPA Kh-50 quasistationary plasma accelerator

(NSC KIPT). The main parameters of QSPA plasma flows were as follows: ion impact energy of about 0.4 keV, maximum plasma pressure of 3.2 bar, and flow diameter of about 18 cm. The plasma pulse shape was approximately triangular, and the pulse duration was 0.25 ms. The number of pulses was 5. After irradiation, the sample was subjected to vacuum annealing at 550 °C during 1 to 8 h. Thermal-radiation resistance (the behavior of the coating under exposure) during irradiation of the sample with hydrogen plasma flows was studied using a lower heat load, namely from 0.1 to 0.4 MJ/m^2. Analysis of the structure and phase composition was performed by XRD analysis and transmission electron microscopy (TEM). X-ray measurements were carried out using a DRON-M apparatus in the filtered Cu-Kα radiation. The spectra were processed using the New_Profile3.5 software package.

The identification of the quasicrystalline phase and the determination of its quasicrystallinity parameter a_q were carried out according to J.W. Cahn [11] using the original software package. To construct nominal X-ray diffraction patterns of possible crystalline phases: the 1/1 crystal approximant (W phase), the Laves phase (Ti, Zr) 2Ni (L, structural type C14), and the α-Ti (Zr) solid solution, the PowderCell program was used taking into account data [12]. Surface morphology was studied using scanning electron microscopy (SEM) on a JEOL JSM-6390 instrument.

2. RESULTS AND DISCUSSION

2.1. CHARACTERIZATION OF THE INITIAL STATE

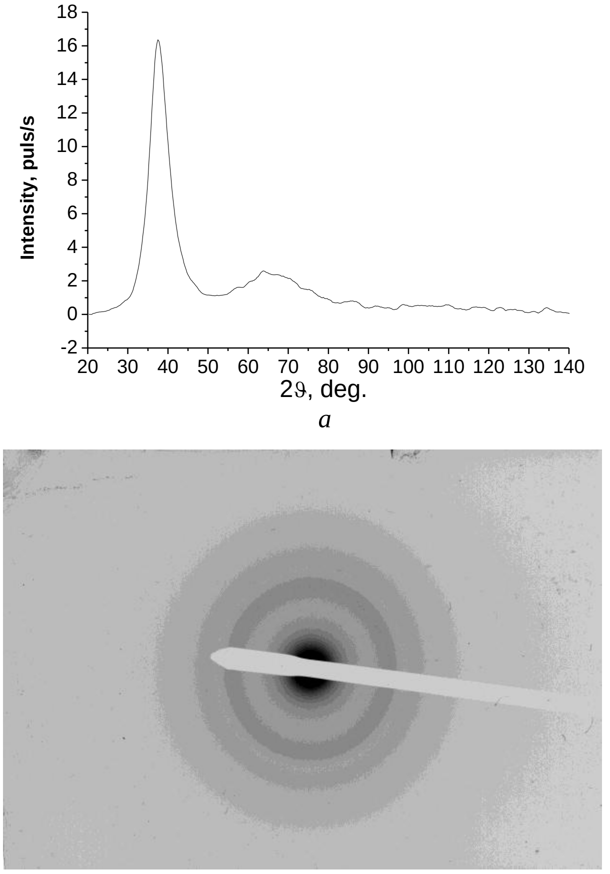
According to the results of XRD and electron diffraction (Fig. 1), the coating can be considered amorphous or nanocrystalline in the initial state after deposition, as was stated in [13], since the crystallite size calculated from the half-width of the maximum in the direction normal to the surface was about 2 nm. In the SEM patterns (Fig. 2,a,b) taken in the secondary electron mode (SEI), the surface morphology in the initial state is formed as a cluster of spherical formations ranging from micron to nanomicron size. In the figure they are marked with arrows. An increase of magnification reveals increasingly smaller formations. Similar spherical formations were observed in [6] on TEM images; note, that the contrast in the images does not change when the sample is tilted.

We assume that the observed spherical formations are “crystallite-nuclei” of the icosahedral phase, which, during growth, inherit the Bergman cluster or triacontahedron close to the spherical shape [1, 2].

A detailed characterization of the structure of the films we obtained in the initial state was given in [5]. There, the peculiarities of the formation of their structure and phase composition were discussed, and the temperature boundaries of the stability of the quasicrystalline phase in thin films were determined under vacuum annealing for 1 h. It was found that the quasicrystalline phase is formed in the temperature range of 500 to 550 °C. Further, we use precisely this temperature range for annealing.

2.2. THE RESULTS OF IRRADIATION WITH AN ENERGY OF 0.6 MJ/m^2 AND SUBSEQUENT ANNEALING

The XRD results for a sample irradiated with energy of 0.6 MJ/m^2 are presented in Fig. 3. It is seen that a system of diffraction peaks has formed; the most intense are located at 2ϑ angles of approximately 37.5 and 39.5 degrees. Moreover, it is noticeable that the maxima are composed of double or even triple lines.



a

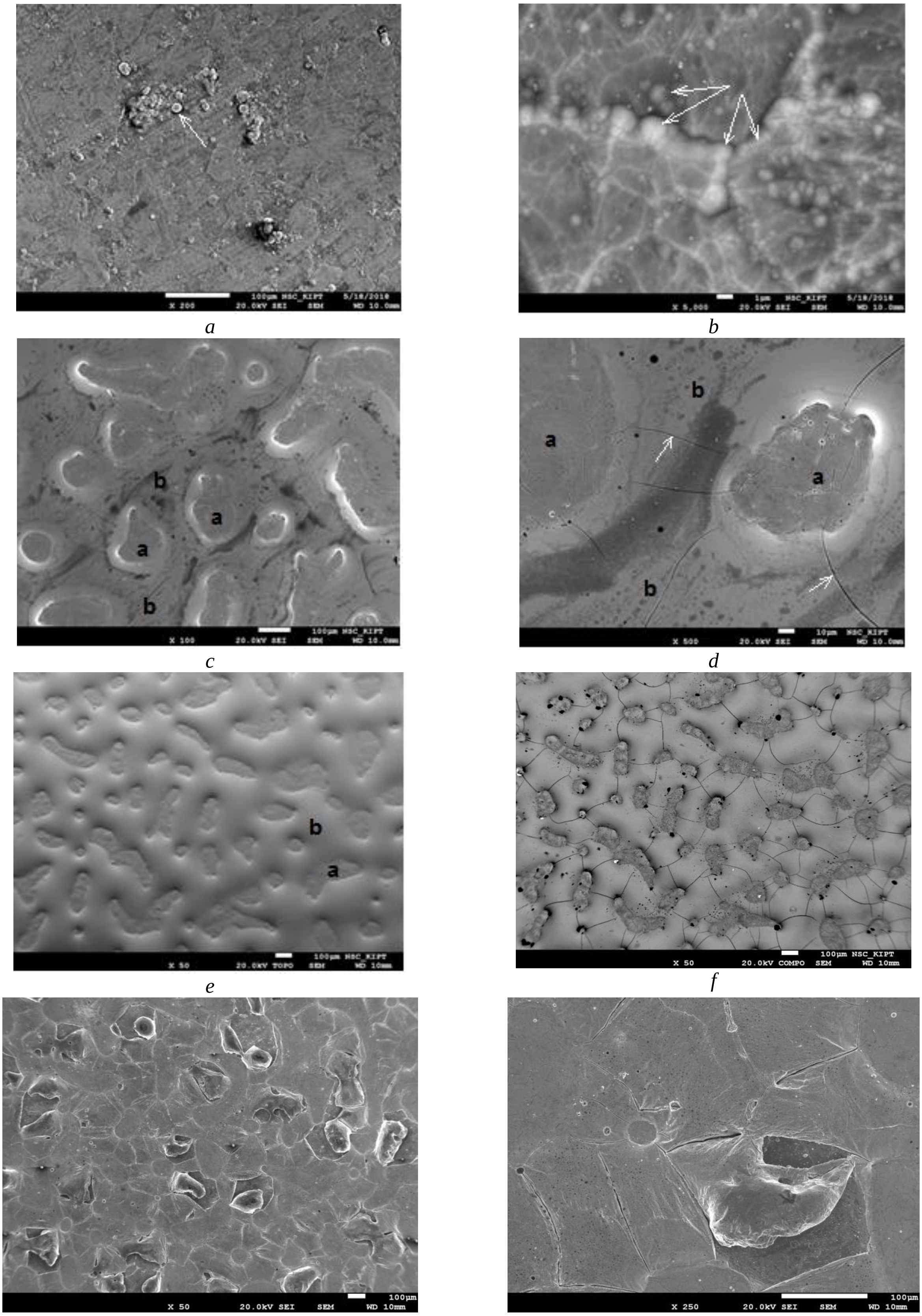
b

Fig. 1. XRD pattern in Cu-Kα (a) and electron diffraction (b) from the coating in the initial state

The separation of overlapping maxima in the New_Profile3.5 program made it possible to establish that two phases are present in the film: the icosahedral quasicrystalline phase and the 1/1 crystal-approximant phase (W phase). From the ratio of their line intensities, we conclude that these phases are contained in approximately equal proportions.

In Fig. 3, reflections from the quasicrystalline phase are indicated by double Kahn indices, and the W phase is indicated by arrows. The icosahedral phase is characterized by a quasicrystallinity parameter $a_q = 0.5100$ nm and a crystallite size about 100 nm as calculated by the Selyakov-Scherrer formula based on the half-width of the (20.32) reflection. The W crystal-approximant phase has a lattice period $a_W = 1.41$ nm consistent with a_q. It should be noted that the choice of the (20.32) reflection is not accidental.

The question is that in quasicrystals the smearing of the diffraction maximum depends not only on microdispersity and microstrains, but also on the density of phason defects [2]. The reflections with an increased value of the modulus of $Q_\perp$ (one of the components of the six-dimensional diffraction vector of the icosahedral structure) are most sensitive to the presence of phason defects [14, 15]. The (20.32) reflection is not one of such.



a *b* *c* *d* *e* *f* *g* *h*

Fig. 2. Change in the surface morphology of the film coating after irradiation with hydrogen plasma and annealing: the initial state (a, b), after irradiation with 0.6 MJ/m^2 (c, d) and subsequent annealing at 550 ℃ for 4 h (e, f) and irradiation with 0.4 MJ/m^2 (g, h)

In the SEI images taken in the secondary electron mode (see Fig. 2,c,d), one can observe a labyrinth system consisting of two regions with different contrasts. In the figure they are marked with **a** and **b** letters**.** According to microanalysis, in the (**a**) region the composition was the following: Ti – 23.8, Zr – 14.5, Ni – 8.3, as well as Fe – 45.6, Ni – 8.3, and Mn – 0.2 at.%. The presence of iron, nickel and manganese contained in the steel substrate means that the film thickness in this place is not more than 2 μm. In the (**b**) region, the composition turned out to be different: Ti – 52.6, Zr – 30.7, and Ni – 16.8 at.%. It practically coincides with the composition of the initial target. The absence of elements from the composition of the substrate means that in this place the coating thickness is more than 6 μm. Thus, we can conclude that the relief of the coating is a system of protrusions (**b**) and depressions (**a**). Annealing the samples for 8 h at 550 °C did not introduce any changes in the surface morphology; the inhomogeneity in the thickness of the sample was preserved.

In the backscattered electron images taken with a semiconductor detector in the topo mode (see Fig. 2,e) and in the compo mode (see Fig. 2,f), the system of depressions (**a**) and protrusions (**b**) is manifested even more clearly. In Fig. 2,f, the (**a**) areas, as expected, have a darker contrast. In the SEI images, a crack system can also be seen. Each of these areas has its own different crack system. Upon transition from one region to another, cracks break off (see Fig. 2,d). In the (**a**) region, the cracks are smooth (marked by arrows in Fig. 2,d), and in the other one – they are fractured and branched.

Smooth cracks are usually characteristic of amorphous glasses; in quasicrystals, they were first observed in [4]. We assume that the (**a**) region corresponds to the quasicrystalline region, and the (**b**) region corresponds to the crystal-approximant phase.

Vacuum annealing for up to 8 h resulted in the shift of quasicrystal reflections to smaller 2θ angles, and, accordingly, to the increase of the a_q parameter to 0.513 nm. The lattice period of the W phase also changed to a_W = 1.4151 nm. Reflections from the approximant and the quasicrystal are more clearly separated.

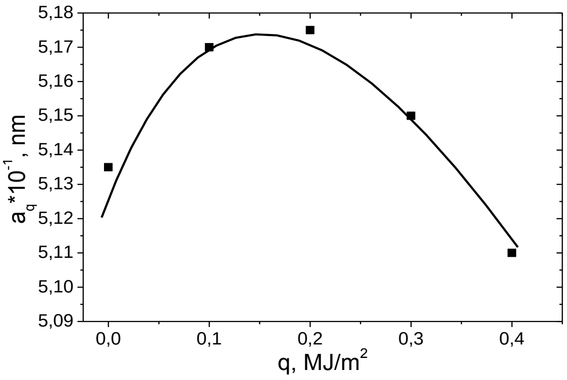


Fig. 5. Change in the quasicrystallinity parameter as a function of thermal load (q) for a thin film irradiated by pulsed plasma flows

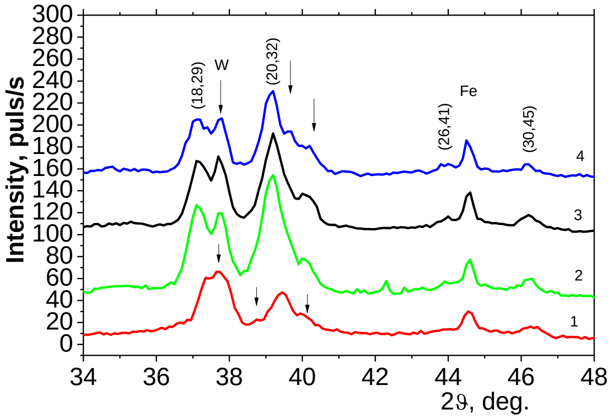


Fig. 3. A fragment of the diffraction pattern from a film irradiated with 5 pulses with a load of 0.6 MJ/m² (1) and vacuum annealing at 550 °C for 1 h (2), 4 h (3), and 8 h (4)

We assume that upon annealing, a partial diffusion phase transformation of the crystal-approximant W phase into a quasicrystal occurs. The change in the diffraction pattern as a result of sequential irradiation with 5 pulses with thermal loads of 0.1; 0.2; 0.3, and 0.4 MJ/m^2 are shown in Fig. 4.

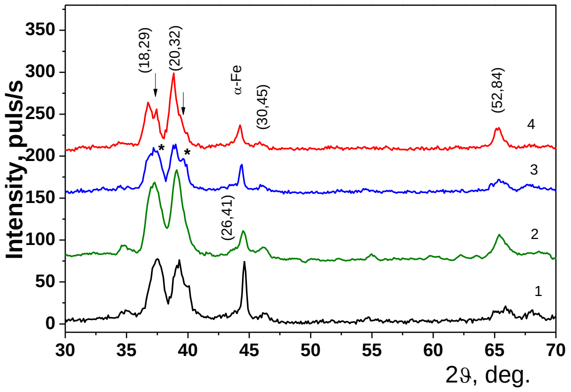


Fig. 4. A fragment of the diffraction pattern from a film subjected to subsequent irradiation with 5 pulses with a load of 0.1 (4), 0.2 (3), 0.3 (2), and 0.4 MJ/m² and vacuum annealing at 550 °C for 1 h (1)

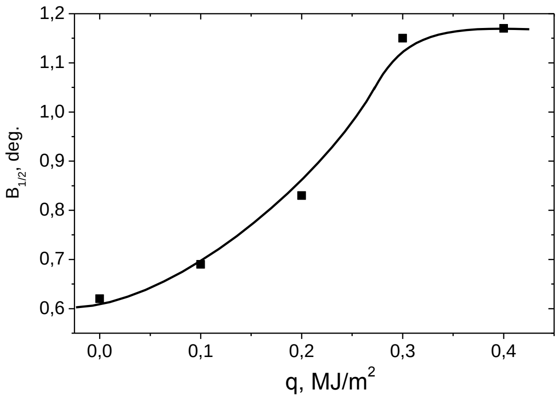


Fig. 6. Change in the half-width of the (20.32) diffraction maximum of the quasicrystalline phase as a function of the heat load (q) for a thin film irradiated by pulsed plasma flow

2.3. RESULTS OF PLASMA COATING IRRADIATION

Indicing and interpretation of the diffraction patterns indicates that after the first two irradiations, the reflections from the W phase gradually disappear and the reflections from the quasicrystalline phase increase. They shift toward smaller angles and the of reflections from the 2/1 approximant appear. When the load increases to 0.3 MJ/m^2, all reflections present are indiced as belonging to the quasicrystalline phase. After irradiation with 0.4 MJ/m^2, the reflections from QC are strongly shifted to the right, and reflections from the W phase reappear. Additionally, the morphology of the coating surface changes significantly (see Fig. 2,g,h). It can be seen from the figure that the coating experienced recrystallization. This fact is not surprising, since during the irradiation, the coating surface can briefly heat up to 1800 °C [16], and according to [17], eutectic melting in the alloy should occur at about 810 °C. Thus, the surface layers had the ability to melt and solidify again. As a result, the system almost returned to the state of the structure, as after exposure to a load of 0.6 MJ/m^2. A change in the quasicrystallinity parameter correlates with these data; it is presented in Fig. 5. It can be seen that the change in a_q is nonmonotonic. After the first and second loadings, the parameter a_q increases and then begins to decrease, and ultimately reaches a value such as after exposure to a load of 0.6 MJ/m^2. It is noteworthy that the total (annealing + the first two irradiations) increase in the quasicrystallinity parameter Δa_q amounted to a significant value of $0.75\cdot10^{-2}$ nm. There is an opinion [2, 18–20] that the higher the perfection of the icosahedral phase, the numerically higher the value of the corresponding quasicrystallinity parameter. It can be concluded that when heated to relatively low temperatures (not higher than about 1000 °C), we have a manifestation of an improvement in the regular structure of the quasicrystalline phase. When irradiated with 0.3 MJ/m^2 (short-term heating of the surface to about 1350 °C) we obtained a single-phase quasicrystalline coating, but with a reduced value of the parameter a_q. Further exposure further reduces it. It is known that the quasicrystallinity parameter linearly increases with increasing average weighted atom size of the icosahedral structure [21–24]. We believe that the decrease in the quasicrystallinity parameter can be explained by the predominance of the titanium content over zirconium, which has a larger atom radius than titanium. The authors [25] have a similar opinion.

The change in the half-width of the diffraction maximum $\Delta(2\vartheta) = B_{1/2}$ of the quasicrystalline phase (Fig. 6) has somewhat different character. The width $B_{1/2}$ monotonously increases with increasing q to 0.3 MJ/m^2, and then reaches saturation. According to the calculation, the change in the half-width (indicated in Fig. 6), may be due to a decrease in the size of the coherent scattering length from 15 to 8 nm along the normal to the film surface.

CONCLUSIONS

We experimentally worked out the possibility of the formation of a quasicrystalline icosahedral phase and a crystal-approximant phase in a film sample with a thickness of h = 14.8 μm deposited on an Eurofer steel substrate by dc-magnetron sputtering of a target with the composition Ti52Zr30Ni18 (at%); the QC and W phases were formed as a result of pulsed irradiation with hydrogen plasma with a heat load of 0.6 MJ/m^2. It was found that after isothermal vacuum annealing at a temperature of 550 °C, both the content of the quasicrystalline phase and the perfection of its structure increased; this manifests itself in an increase of the quasicrystallinity parameter from 0.510 to 0.5137 nm. The quasicrystalline phase turned out to be resistant to pulsed irradiation with hydrogen plasma. An increase in the heat load from 0.1 to 0.3 MJ/m^2 for five pulses with a duration of 250 μs contributes to an increase in the content of the quasicrystalline phase and an increase in the quasicrystallinity parameter to 0.5175 nm. Pulse thermal exposure increases the microdispersion of the QC phase.

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ПОВЕДЕНИЕ ТОНКОЙ ПЛЕНКИ КВАЗИКРИСТАЛЛОВ И АППРОКСИМАНТНЫХ ФАЗ СИСТЕМЫ Ti-Zr-Ni ПРИ РАДИАЦИОННО-ТЕРМИЧЕСКОМ ВОЗДЕЙСТВИИ В РЕЖИМАХ ПЕРЕХОДНЫХ ПРОЦЕССОВ

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Методами рентгеновской дифракции и СЭМ изучены структурные и фазовые изменения в тонкой пленке, полученной магнетронным распылением мишени состава Ti52Zr30Ni18 (ат.%) на подложке из стали, при радиационно-термическом воздействии импульсной водородной плазмы на ускорителе КСПУ Х-50. Отработана методика формирования квазикристаллической фазы и фазы кристалла-аппроксиманта в результате скоростной закалки с помощью импульсного воздействия с тепловой нагрузкой 0,6 МДж/м^2. Изучены изменение параметров структуры и субструктуры, а также содержания указанных фаз при изотермическом вакуумном отжиге при температуре 550 °С, а также в результате облучения 5 импульсами плазмы в интервале тепловой нагрузки 0,1…0,4 МДж/м^2. Квазикристаллическая фаза оказалась устойчивой к облучению водородной плазмой.

ПОВЕДІНКА ТОНКОЇ ПЛІВКИ КВАЗІКРИСТАЛІВ І АПРОКСИМАТИВНИХ ФАЗ СИСТЕМИ Ti-Zr-Ni ПРИ РАДІАЦІЙНО-ТЕПЛОВОМУ ВПЛИВІ В РЕЖИМАХ ПЕРЕХІДНИХ ПРОЦЕСІВ

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Методами рентгенівської дифракції та СЄМ вивчені структурні і фазові зміни в тонкій плівці, отриманої магнетронним розпиленням мішені складу Ti52Zr30Ni18 (ат.%) на підкладці зі сталі, при радіаційно-термічному впливі імпульсної водневої плазми на прискорювачі КСПП Х-50. Відпрацьована методика формування квазікристалічної фази і фази кристала-апроксиманта в результаті швидкісного загартування за допомогою імпульсного впливу з тепловим навантаженням 0,6 МДж/м^2. Вивчено зміну параметрів структури і субструктури, а також вмісту зазначених фаз при ізотермічному вакуумному відпалі при температурі 550 °С, а також в результаті опромінення 5 імпульсами плазми в інтервалі теплового навантаження від 0,1 до 0,4 МДж/м^2. Квазікристалічна фаза виявилася стійкою до опромінення водневою плазмою.