STRUCTURAL-PHASE CHANGES IN THIN FILMS AND SURFACE LAYERS OF Ti41.5Zr41.5Ni17 ALLOY, STIMULATED BY RADIATION-THERMAL IMPACT OF HYDROGEN PLASMA

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X-ray diffraction and SEM microscopy were used to study structural and phase changes in the surface layers of a Ti41.5Zr41.5Ni17 alloy bulk sample (target) and a thin film (deposited by magnetron sputtering of the target) under radiation-thermal action of pulsed hydrogen plasma with a thermal load of 0.6 MJ/m^2 in QSPA Kh-50 installation. It is established that the irradiation results in the formation of a two-phase state: the icosahedral quasicrystalline phase together with the phase of the 1/1 approximant crystal (W-phase). As a result of isothermal (550°C) annealing, the content of the quasicrystalline phase increases.

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INTRODUCTION

Quasicrystals (QCs) are a special class of materials with an unusual crystals structure. The unusual structure causes a number of unique properties. This is, for example, low thermal conductivity, successfully used to prevent condensation of superheated steam on the surface of turbine blades coated with a layer of Al-Cu-Fe or Al-Co-Cr-Fe quasicrystals. Low surface energy, high hardness, and resistance to corrosion determine the use of Al-Cu-Fe-Cr quasicrystalline coatings as a non-sticking coating both for chemical reactors and kitchen utensils [1]. In comparison with crystals, quasicrystals show anomalous properties of plastic deformation, accumulation of elastic strain energy, and, possibly, cracking [2, 3]. Ti-Zr-Ni and Ti-Hf-Ni quasicrystals are characterized by high (up to 2H/Me) absorption of hydrogen in the form of a solid solution; therefore, they can be expected to have increased resistance to blister formation [4]. Due to the lack of the structure translational invariance, quasicrystals are considered as a promising radiation-resistant material [5]. QC formation is perspective for practical application in the form of thin layers or films on substrates [6-9]. Thus, though the QC properties are not fully understood they are interesting and useful due to high hardness, reduced wetting, a low friction coefficient, eminent corrosion resistance and hydrogen storage [10]. Ti-Zr-Ni quasicrystals could be incorporated into hydrogen storage materials. The quasicrystals have been used as a catalytic for hydrogen production and storage recently [11]. Icosahedral quasicrystal, such as Ti41.5Zr41.5Ni17, can be a promising candidate for hydrogen loader [12].

The first results on the formation of a quasicrystalline icosahedral phase under pulsed plasma treatment were presented in [13]. Polished bulk massive samples of Ti41.5Zr41.5Ni17 obtained after solidification from the melt was irradiated by pulsed hydrogen, helium or argon plasma fluxes with heat loads up to 0.6 MJ/m^2. The quasicrystalline icosahedral phase appeared as a thick surface layer of 100 μm.

It should be noted, that thin Ti-Ni-Zr films could also be promising materials for applications in micro-electromechanical systems with three-dimensional microstructures [14]. Therefore, the aim of this paper was to form a quasicrystalline phase and closely related crystalline phases in a thin surface layer of bulk and film targets using irradiation of the surface with powerful pulsed plasma fluxes of microsecond duration with a simultaneous influence of ion fluence up to 10^{27} $cm^{-2}\cdot s^{-1}$. The second task was to study the stability of these phases during repeated plasma impacts.

1. SAMPLES AND INVESTIGATION TECHNIQUE

We studied the behavior of the bulk and film samples of the Ti41.5Zr41.5Ni17 alloy (wt. %) irradiated with hydrogen plasma and annealed in vacuum. It should be noted, that such alloy can form a stable (up to ≈ 660°C) quasicrystalline icosahedral phase with a set of unique physical properties, which makes it promising for use in next step plasma devices. Bulk samples were obtained by vacuum fusion of ultrapure components in ultrapure conditions. Film samples were fabricated by sputtering of a bulk sample (target) with DC magnetron discharge in an argon atmosphere at a pressure of $2\cdot10^{-3}$mm Hg. The QC films with a thickness of h = 14.8 μm were deposited on Eurofer (9 Cr) steel. The distance between the target and the substrate was 30 mm.

Heat flux tests of the samples were performed with hydrogen plasma fluxes produced by the quasi-steady-state plasma accelerator QSPA Kh-50 [15]. The main parameters of QSPA plasma fluxes were as follows: ion impact energy is about 0.4 keV, the maximum plasma pressure is 0.32 MPa, and the flux diameter is about 18 cm. The surface energy loads measured with a calorimeter achieved 0.6 MJ/m^2. The plasma pulse duration was 0.25 ms.

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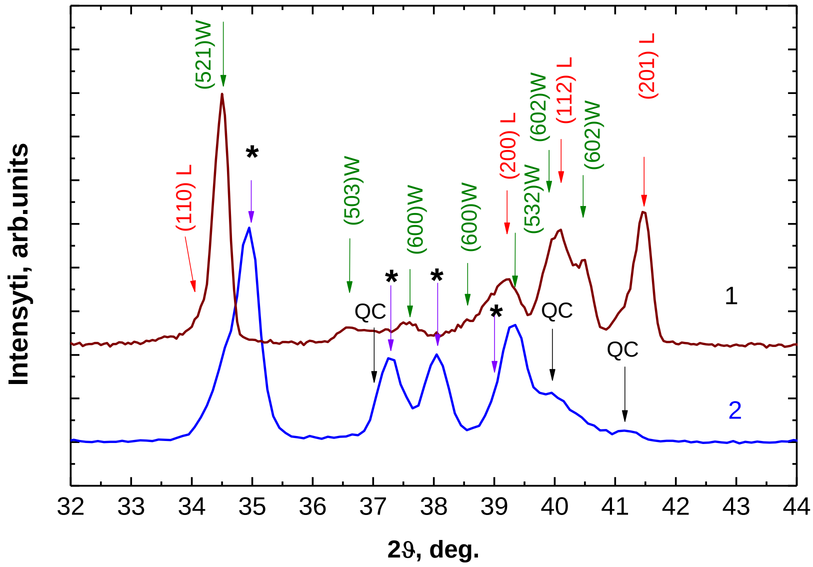

Fig. 1. X-ray diffraction patterns of Ti41.5Zr41.5Ni17 alloy bulk target in initial state (1), and after hydrogen plasma impact with 0.6 MJ/m² (2)

Surface analysis was carried out using scanning electron microscopy (SEM) in the JEOL JSM-6390 type instrument. To study a micro-structural evolution of the exposed targets, the X-ray diffraction technique (XRD) was used. ϑ…2ϑ scans were performed using monochromatic Cu-K_α radiation. Quasi-crystalline phase identification was carried out in conformity with the Cahn´s methodology using indices N and M. To simulate the diffraction pattern, the software package Powder Cell 2.1 was used. For processing of diffraction patterns, the program New_Profile 3.5 was used [13].

2. RESULTS AND DISCUSSION

X-ray diffraction patterns of an Ti41.5Zr41.5Ni17 alloy bulk sample in the initial state and after exposure to plasma are presented in Fig.1. The initial state is characterized by the presence of two crystalline phases: the crystal 1/1 approximant (W-phase) with a period of a_W = 1.42 nm and the $Ti_{2-x}Zr_xNi$ Laves phase of the C14 type. Irradiation with plasma resulted in the disappearance of the Laves phase, decreasing the lattice period of the 1/1 approximant W-phase from a_W = 1.426 nm to a_W = 1.411 nm. The reflections belonging to it are to the right of the original reflections and are marked with an asterisk. In addition, we observe the appearance of separate reflections from the quasicrystalline phase. Its reflections are weak and blurred, and the quasi-crystallinity parameter is approximately 0.5130…0.5135 nm. The obtained parameters of crystallographically related W-phases and the quasicrystalline phase are in good theoretical agreement with each other. The observed changes in the phase composition allow us to make an assumption about phase transformations by the diffusion mechanism.

SEM image of the bulk sample surface after plasma exposure is presented in Fig. 2. As it shows, the formed cracks are fairly smooth or straight, as is usually the case with glass. This fact may indirectly indicate the formation of a quasicrystalline phase.

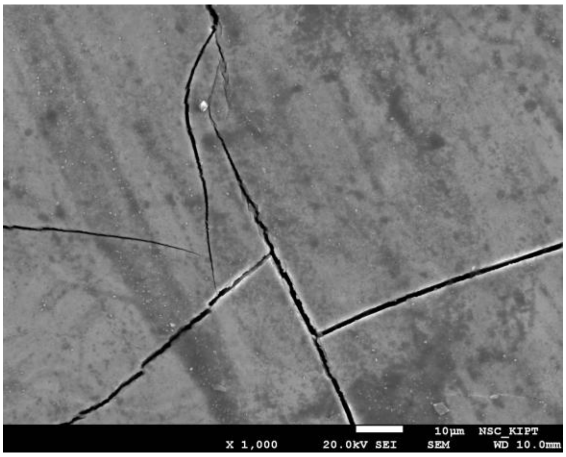

Fig. 2. SEM image of plasma irradiated surface of a Ti41.5Zr41.5Ni17 bulk sample

Fig. 3 shows diffraction patterns from a film sample with a thickness of 14.8 µm in the initial state after magnetron sputtering and deposition (1), after pulsed plasma exposure (2), and after isothermal annealing at a temperature of 550°C for 1 hour (3). The film sample was nanocrystalline in the initial state. The crystallite size calculated from the half-width of the diffraction maximum was ≈2 nm. The development of the surface relief is shown in Fig. 4. It shows that the structure consists of a conglomerate of spherical formations of micron to nanomicron sizes.

After plasma irradiation of a film sample with energy loads above the alloy melting threshold, a quasicrystalline phase is formed as the main phase with the quasicrystalline parameter of a_q = 0.5135 nm. The crystallite size is ≈100 nm. In addition, there is the W-phase in an amount of up to 20…30 % with a period of a_W = 1.410 nm.

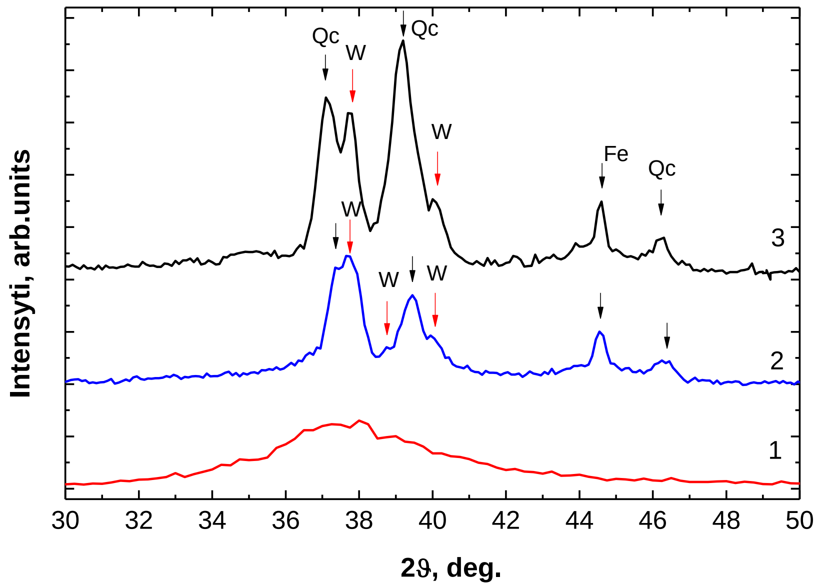

Fig. 3. Diffraction patterns of a Ti41.5Zr41.5Ni17 film sample in initial state after deposition (1), after plasma pulsed impact (2), and after subsequent isothermal annealing at 550 ℃ for 1 h (3)

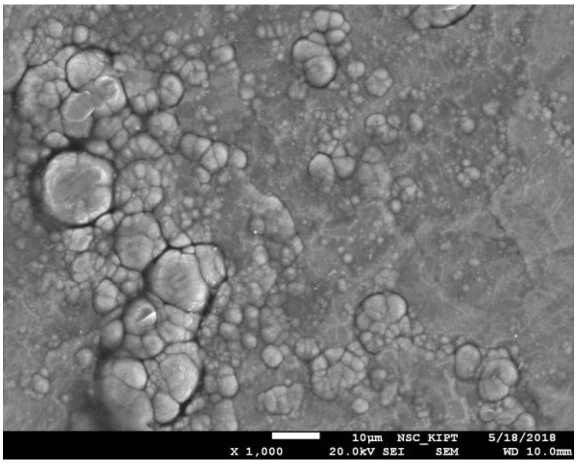

Fig. 4. SEM image of film sample initial surface

This practically corresponds to the theoretical crystallographic relationship between the icosahedral and related crystal structures with a_{Wteor} = 1.413 nm.

According to the SEM data (Fig. 5), after plasma exposure, a system of spot-islands surrounded by bright areas located in a homogeneous gray mass is observed on the surface of the film sample. Taking into account that the SEM images were obtained in the mode of secondary electrons, and their contrast is partly due to conductivity, it can be assumed that the observed regions belong to two different phases. According to X-ray phase analysis, these are the quasicrystalline icosahedral phase and the phase of the 1/1 approximant crystal (W-phase). Characteristic linear smooth cracks are found in SEM images. Moreover, the cracks located in one of the phases do not have their continuation in the other phase. They are interrupted in the bounder zone. Each phase has its own system of cracks.

Annealing of the sample irradiated at 550°C leads to a decrease in the W-phase content. All diffraction lines are slightly shifted towards smaller angles. The quasicrystalline parameter of the icosahedral phase became a_q = 0.5141 nm, and the lattice period of the W-phase, respectively, a_W = 1.4151 nm. We assume that diffusion phase transformation occurs during annealing.

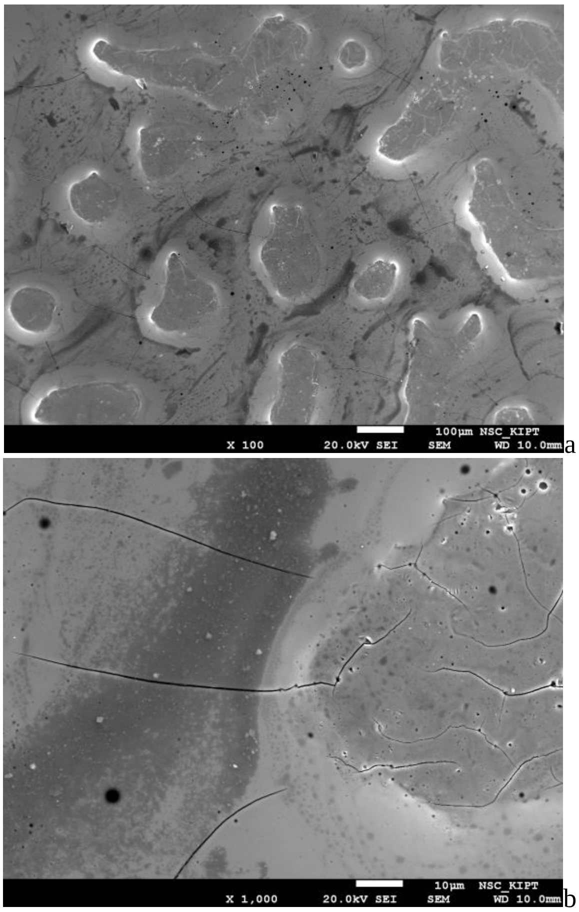

Fig. 5. SEM images a Ti41.5Zr41.5Ni17 film sample after plasma irradiation: a and b were obtained with different magnifications

CONCLUSIONS

Samples of Ti41.5Zr41.5Ni17 bulk alloy, as well as films with a thickness of h = 14.8 μm deposited on a Eurofer steel substrate, were irradiated by hydrogen QSPA Kh-50 plasma streams of 0.6 MJ/m^2. As a result of the plasma treatment, a two-phase state as the icosahedral quasicrystalline phase together with the 1/1 approximate crystal phase (W-phase) was formed in the surface layer comparable to the half-absorption layer of Cu radiation (≈7 μm). Also, after isothermal (550°C) annealing, the content of the quasicrystalline phase increased.

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СТРУКТУРНО-ФАЗОВЫЕ ИЗМЕНЕНИЯ В ТОНКИХ ПЛЕНКАХ И ПОВЕРХНОСТНЫХ СЛОЯХ Ti41.5Zr41.5Ni17-СПЛАВА, СТИМУЛИРОВАННЫЕ РАДИАЦИОННО-ТЕРМИЧЕСКИМ ВОЗДЕЙСТВИЕМ ВОДОРОДНОЙ ПЛАЗМЫ

С.В. Малыхин, В.А. Махлай, С.В. Суровицкий, С.С. Борисова, С.С. Геращенко, В.В. Кондратенко, И.А. Копылец, А.А. Батурин, D. Terentyev

Методами рентгеновской дифракции и SEM-микроскопии изучены структурные и фазовые изменения в поверхностных слоях массивного образца (мишени) сплава Ti41.5Zr41.5Ni17 и тонкой пленки, полученной магнетронным распылением мишени, при радиационно-термическом воздействии импульсной водородной плазмой с тепловой нагрузкой 0,6 $МДж/м^2$ на КСПУ Х-50. Установлено, что в результате облучения формируется двухфазное состояние: икосаэдрическая квазикристаллическая фаза совместно с фазой кристалла-аппроксиманта 1/1 (W-фаза). В результате изотермического (550°С) отжига содержание квазикристаллической фазы увеличивается.

СТРУКТУРНО-ФАЗОВІ ЗМІНИ В ТОНКИХ ПЛІВКАХ І ПОВЕРХНЕВИХ ШАРАХ Ti41.5Zr41.5Ni17-СПЛАВУ, СТИМУЛЬОВАНІ РАДІАЦІЙНО-ТЕРМІЧНОЮ ДІЄЮ ВОДНЕВОЇ ПЛАЗМИ

С.В. Малихін, В.О. Махлай, С.В. Суровицький, С.С. Борисова, С.С. Геращенко, В.В. Кондратенко, І.А. Копилець, О.А. Батурін, D. Terentyev

Методами рентгенівської дифракції та SEM-мікроскопії вивчені структурні і фазові зміни в поверхневих шарах масивного зразка (мішені) сплаву Ti41.5Zr41.5Ni17 і тонкої плівки, отриманої магнетронним розпиленням мішені, при радіаційно-термічному впливі імпульсною водневою плазмою з тепловим навантаженням 0,6 $МДж/м^2$ на КСПП Х-50. Встановлено, що в результаті опромінення формується двофазний стан: ікосаедрична квазікристалічна фаза спільно з фазою кристала-апроксиманта 1/1 (W-фаза). В результаті ізотермічного (550°С) відпалу зміст квазікристалічної фази збільшується.