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Structure and Phase Formation Features of Ti-Zr-Ni Quasicrystalline Films under Heating

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The paper describes the growth features of thin Ti-Zr-Ni films prepared by the method of magnetron sputtering of the targets with compositions $Ti_{53}Zr_{30}Ni_{18}$ and $Ti_{41}Zr_{38.3}Ni_{20.7}$ on the substrates at 300 K with subsequent annealing in vacuum. The formation peculiarities of phase composition, structure and thermal stability of quasicrystalline thin films were studied. It was established that in initial state the films were X-ray-amorphous or nanocrystalline with coherence lengths (according to Scherrer) near 1.6-1.8 nm independently on the element composition of the sputtered target. This structure is relatively stable up to the temperature 673 K when the formation of the quasi-crystalline phase begins. In the films with composition of $Ti_{53}Zr_{30}Ni_{18}$, the largest quantity of the quasicrystalline phase with a characteristic parameter $a_q = 0.517$ nm is observed at the annealing temperature of 673 K. It is added with an admixture of the 1/1 W-crystal approximant phase. In the films with $Ti_{41}Zr_{38.3}Ni_{20.7}$ composition, an optimal annealing temperature is between 823 K and 873 K. The quasicrystalline phase is characterized by the quasicrystallinity parameter $a_q = 0.5205$ nm. Additionally, for the first time, the data on the formation of 2/1 approximant crystal as an admixture phase in this system were obtained. Under annealing at the temperatures higher than 873 K, the decomposition of the quasi-crystalline and approximant phases into crystalline phases stable at higher temperatures according to the equilibrium phase diagram was established.

Keywords: Quasicrystals, Approximant crystals, Magnetron sputtering, Thin films, X-ray diffraction.

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1. INTRODUCTION

Scientific and technical progress is largely determined by the success in the development and creation of materials with new physical properties. In this regard, much attention was paid to quasicrystals discovered by Shechtman in 1986 [1]. The unusual atomic structure of these materials entails many anomalous and unique physical properties that are significantly different from other crystals [2].

A natural step in the study of quasicrystals was the development of the technology for producing thin films of quasicrystals and compositions based on them, since many practical applications of thin films are based on their specific properties significantly different from materials in a bulk state. In the thin film or nanostructured state, quasicrystals and nano-quasicrystals are considered as new promising materials [3]. Mastering the technology of manufacturing thin films of quasicrystals and their compositions will make it possible to create new functional materials with a combination of attractive properties.

To date, the overwhelming majority of works on quasicrystals in a thin film state refers to stable systems based on aluminum, such as Al-Cu-Fe and Al-Pd-Mn [4]. The increased interest in these coatings is primarily due to the fact that they have a set of anomalous and unique physical properties, such as high hardness and wear resistance, low friction coefficient and low electrical and thermal conductivity [5]. The use of thin coatings solves the problem of increased brittleness of bulk quasicrystals.

Interest in Ti-Zr-Ni quasicrystals is primarily due to their ability to accumulate hydrogen in the form of a solid solution in an amount up to 2H/1 at. Me [6]. One of the few papers on Ti-Zr-Ni thin quasicrystalline films [7] is devoted to the study of the possibility of retaining a significant amount of hydrogen and its isotopes to create a neutron generator. In other works, the authors stopped at the stage of amorphous coating [9]. In this work, the aim is to develop a technology for producing thin films of Ti-Zr-Ni quasicrystals, to study the structural and phase changes during annealing in vacuum, and to determine the limits of their temperature stability.

2. OBJECTS AND METHODS

The films were prepared by the method of direct-current magnetron sputtering of the target. In the experiments, Ti-Zr-Ni alloys of two compositions were used, for which the formation of icosahedral i-phase was typical for the preparation of ribbon and bulk samples [10]. The compositions were selected in order that the electron concentration $e/a = 1.25$ corresponded to the stable i-phase: $Ti_{53}Zr_{30}Ni_{18}$ ($e/a = 1.245$) and $Ti_{41}Zr_{38.3}Ni_{20.7}$ ($e/a = 1.19$, which is close to the cross section of a stable concentration $e/a = 1.20$). The theory determines that the stable i-phase is obtained at the intersection of a line of equal Ti and Zr concentrations with a line of stable electron concentration [11]. The alloys were prepared in the NSC KIPT from nickel, titanium and zirconium taken in nominal concentrations; the components were refined by the method of double electron-beam melting in an ultrahigh-vacuum not worse than 10^{-4} Pa. A detailed description of the method is given in [12]. The thickness of the $Ti_{53}Zr_{30}Ni_{18}$ films was 14.6 and 6 μm, and that of the $Ti_{41}Zr_{38.3}Ni_{20.7}$ films was 2.5 μm. Single-crystalline silicon and sapphire, glass and polished steel were used as substrates. The substrate was not specifically heated; its temperature during the deposition did not exceed 40-50 °C. Sputtering was carried out in purified argon at a pressure of $2 \cdot 10^{-1}$ Pa.

The elemental composition of the targets and films was monitored by X-ray fluorescence analysis. Note that the chemical composition of the grown films corresponded to the composition of the target. Structural and phase analysis was performed by X-ray diffraction method. The measurements were carried out with a DRON-type apparatus in filtered Cu-K_α radiation. Spectra processing was performed using the New_Profile 3.5 software package. The identification of the quasicrystalline phase and the determination of its quasicrystalline parameter a_q were carried out according to Cahn J.W. [13], using the original software package.

To simulate X-ray diffraction patterns of possible crystalline phases: 1/1 approximate crystal (W-phase), Laves phases (Ti, Zr) 2Ni (L, structural type C14) and α-Ti solid solution (Zr), the PowderCell program was used. The samples were studied in the initial state and after isothermal annealing in vacuum for 1 hour at temperatures from 373 K to 1023 K with a step of 50-100 degrees.

3. RESULTS AND DISCUSSION

In the diffraction patterns from the samples obtained by sputtering the target $Ti_{53}Zr_{30}Ni_{18}$, in the initial state there are 2-3 maxima and the integral width is 5-6 degrees on the 2ϑ scale (Fig. 1). The average crystallite size along the diffraction vector (along the normal to the surface) is 1.6-1.8 nm in accordance with Scherrer calculations. According to the known data on QCs films [8], such a state of the initial structure is typical for deposition on a cold substrate and is defined as amorphous or nanocrystalline. As seen from Fig. 1, the subsequent anneals lead to a change in the character of the diffraction pattern. At annealing temperatures from 473 K to 673 K, the most noticeable changes in the intensity distribution are observed in the angular range of the extended and initially symmetrical second maximum.

Already at a temperature of 473 K, it becomes asymmetrical, and one more maximum begins to form. At temperatures $T > 623$ K, we observe the formation of several new diffraction maxima.

First, we note the formation of an additional peak to the right of the first maximum in its "tail", and at $T \approx 673$-773 K, the first maximum splits into several separate peaks. Changes in the structure of the diffraction spectra, and hence in the phase composition at higher temperatures are illustrated in Fig. 2. After annealing at a temperature of 773 K (see Fig. 2a), the coating includes two phases. These are the icosahedral

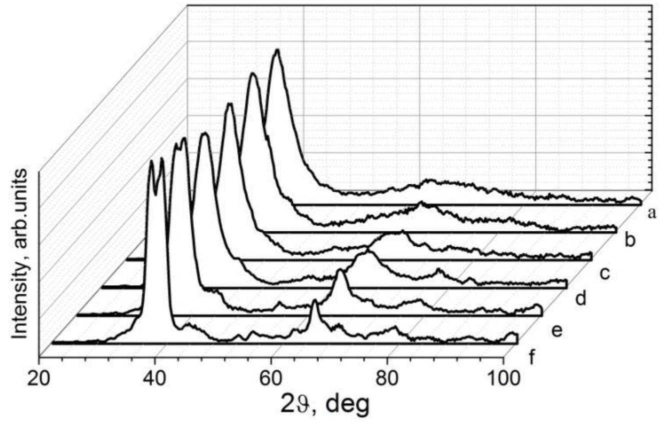

Fig. 1 – Change of the diffraction pattern from Ti-Zr-Ni thin film with a thickness of 17.8 μm after isothermal annealing for 1 hour: the initial state (a), $T = 473$°K (b), $T = 573$ K (c), $T = 623$ K (d), $T = 673$ K (e), $T = 773$ K (f). Probe radiation is Cu-K_α

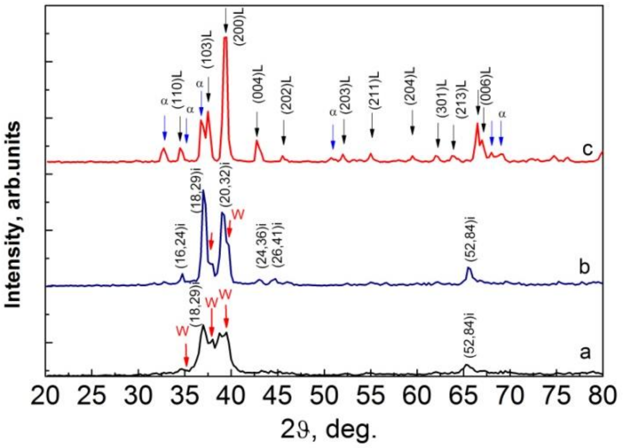

Fig. 2 – Diffraction patterns from a Ti-Zr-Ni thin film after isothermal annealing at temperatures $T = 723$ K (a), $T = 873$ K (b) and $T = 1023$ K (c)

quasicrystalline phase and the crystal-approximant *W*-phase with an approximately equal intensity ratio. An increase in the annealing temperature to 873 K (Fig. 2b) contributes to a noticeable increase in the intensity of QC reflections and a decrease in the intensity of *W*-phase peaks.

In this case, the quasicrystallinity parameter a_q increases from 0.5128 nm to 0.517 nm, and the coherent length increases from 7 to 30 nm. The approximant crystal phase has a lattice period $a_w = 1.428$ nm and a crystallite size from17 to 20 nm. The structure parameters a_q and a_w are in good theoretical agreement and are determined by the expression:

$$a_{q/p} = \frac{2\left(p+q\tau\right)}{\left(2+\tau\right)^{1/2}} a_q ,$$

where *q*/*p* is the approximant rank – 1/1.Annealing at temperatures above 923 K leads to a weakening and then disappearance of the above phases. So, on the diffraction pattern shown in Fig. 2c, one can only see reflections from the Laves phase and the phase of the zirconium based solid solution *α*-Zr (Ti). Note that in the films prepared by deposition and then annealed, the quasicrystallinity parameter of the icosahedral quasicrystalline phase turned out to be slightly less than that observed earlier in single-phase rapidly quenched ribbon samples [14].

We corrected the composition of the target and carried out the deposition and annealing at 600 °C of films obtained from the target with the composition $Ti_{41}Zr_{38.3}Ni_{20.7}$. The film thickness was 2.5 μm; the substrate was polished austenitic steel. The corresponding diffraction pattern is shown in Fig. 3. The diffraction pattern contains a large number of sharp and intense maxima. It was found that the icosahedral quasicrystalline phase is present in the film. It shows most intense reflections. In Fig. 3, they are marked using two J.W. Cahn's indices.

The quasicrystalline parameter is $a_q = 0.5205$ nm and the crystallite size is about 30 nm. The reflections marked in Fig. 3 with an arrow do not belong to the QC phase. It can be assumed that they belong to the approximant phase. The calculation showed that the structure of 1/1 approximant (*W*-phase) with the lattice period equal to $a_w = 1.4327$ nm cannot fully determine the positions and indices of all reflections. More than five strong reflections are not indexed as *W*-phase. For these, the sum of squared indices turns out to be odd; and since the *W*-phase has a bcc lattice, they cannot belong to it by the extinction rule. We assumed that these reflections belong to the 2/1 approximant with the calculated lattice period $a_{2/1} = 2.31815$ nm; so, we carried out a standard indexing procedure for the crystals. The result turned out to be amazing (maybe less emotionally – positive) – we succeed to assign indices to all reflections without exception, without some significant rounding. This clearly indicates that a 2/1 approximant crystal phase is present in the sample.

All the described changes in the phase composition and the revealed transition temperatures are in good agreement with the polythermal section of the phase diagram for the Ti-Zr-Ni system given in [15], as well as with the data from [7] on the deposition of films on heated substrates. According to this diagram at temperatures below 873 K, with equal concentrations of titanium and zirconium, and nickel concentration of 16 at %, the W-phase is stable, while at 17 at % of Ni, the quasicrystalline *i*-phase is stable. Heating above 873 K should lead to a reverse peritectoid transformation and decomposition of these phases into the Laves phase and the *β*-solid solution of Ti and Zr. We really observe this process, taking into account the fact that when cooled, the *β*-solution turns into the α-solution. It should be noted that for the films with different elemental composition annealed at the optimal temperature of 823-873 K, their phase compositions and structure parameters turned out to be close to the data from [19, 20] for bulk samples. A feature of film samples was the fact that, with the composition $Ti_{53}Zr_{30}Ni_{18}$ and *e*/*a* = 1.245, we observed, in addition to the *W*-phase, the *i*-phase with a small value of the quasicrystallinity parameter, which was called a low-temperature quasicrystalline phase in [16].

With the composition $Ti_{41}Zr_{38.3}Ni_{20.7}$, the quasicrystallinity parameter a_q turned out to be higher and close

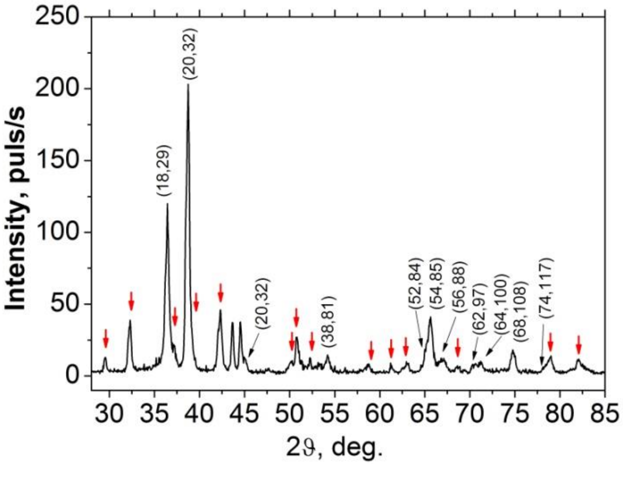

Fig. 3 – Diffraction pattern for a thin film with composition $Ti_{41}Zr_{38.3}Ni_{20.7}$ after isothermal annealing at $T = 873$ K for 1 hour. Red arrows indicate reflections from a 2/1 approximant crystal

to what we previously observed in ribbon samples of the optimal composition $Ti_{41.5}Zr_{41.5}Ni_{17}$ [17]. In addition, in films of this composition we found the presence of a 2/1 approximant W-phase, which was not previously mentioned in the literature on this system. Taking into account the fact that the structures of all three mentio-ned phases (*i*, 1/1 and 2/1) can be constructed on the base of the same multi-shell atomic cluster (triacontahedron), we assume that the phases obtained after an-nealing have different ordering character for both the clusters themselves and the atoms inside the cluster.

4. CONCLUSIONS

A technology has been developed for growing Ti-Zr-Ni thin films containing the icosahedral quasicrystalline phase using the method of magnetron sputtering of the target and subsequent annealing in vacuum. The features of the phase composition, structure, and thermal stability of Ti-Zr-Ni thin films containing the quasicrystalline phase were studied. The data on the formation of a 2/1 approximant crystal in this system were obtained for the first time.

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Структурні і фазові особливості формування квазікристалічних плівок Ti-Zr-Ni при нагріванні

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У роботі описуються особливості вирощування тонких плівок Ti-Zr-Ni методом магнетронного розпилення мішеней складу $Ti_{53}Zr_{30}Ni_{18}$ та $Ti_{41}Zr_{38.3}Ni_{20.7}$ на підкладки при $T = 300$ K з наступним відпалом у вакуумі. Вивчено особливості формування фазового складу, структури та термічної стабільності тонких плівок квазікристалів. Встановлено, що плівки у вихідному стані є рентгено-аморфними, або нанокристалічними з розміром областей розсіювання згідно Шерреру близько 1.6-1.8 нм незалежно від елементного складу мішені, яка розпилювалась. Ця структура є відносно стабільною до температури 673 K, при якій починається формування квазікристалічної фази. В плівках складу $Ti_{53}Zr_{30}Ni_{18}$ найбільша кількість квазікристалічної фази, яка характеризується параметром квазікристалічності $a_q = 0.517$ нм, спостерігається при температурі відпалу 673 K. Вона доповнюється домішкою W-фази кристала-апроксиманта 1/1. В плівках складу $Ti_{41}Zr_{38.3}Ni_{20.7}$ оптимальна температура відпалу знаходиться між 823 K та 873 K. Квазікристалічна фаза характеризується параметром квазікристалічності $a_q = 0.5205$ нм. Крім того, вперше отримані дані про формування 2/1 кристалічного апроксиманту як фази домішки. При відпалу за температур понад 873 K встановлено розпад фаз квазікристала та апроксиманта на стабільні при високих температурах кристалічні фази згідно діаграмою рівноваги.

Ключові слова: Квазікристали, Кристали апроксиманти, Магнетронне розпилення, Тонкі плівки, Рентгенівська дифрактометрія.