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Peculiarities of structural state and hydrogen storage properties of Ti–Zr–Ni based intermetallic compounds

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Abstract

Structural states of the Ti–Zr–Ni based melt-spun ribbons have been investigated by means of the X-ray diffraction analysis. The ribbon structural state was found to be strongly affected by the production conditions. A small amount of Si (0.2–0.3 at.%) in the Ti–Zr–Ni alloy leads to the formation of an amorphous or a mixed amorphous-quasicrystalline state in the ribbons produced at the different hardening rates. The amorphous-quasicrystalline structural state of the ribbons is stable during annealing up to temperatures of 400 °C but some changes in its parameters take place. The uncoated by Pd amorphous and amorphous-quasicrystalline Ti–Zr–Ni ribbons have the property of absorbing a large amount of hydrogen. Changes in the amorphous and quasicrystalline subsystems have a reversible character: the structural states of the ribbons after natural dehydrogenation practically fully returns to the initial one.

Keywords: Amorphous materials; Liquid quenching; Crystal structure and symmetry; X-ray diffraction

1. Introduction

It is known that Ti–Zr–Ni compounds have the property of accumulating a large amount of hydrogen (up to 1.6 H/M) [1–3]. But this ability is restricted by the existence of surface barrier due to oxidation, which is inherent to the compounds in the both crystalline and quasicrystalline states [1]. As a rule surface etching with subsequent coating by Pd use to remove this barrier. But it results in the essential complication in technological process and the rising in price for these materials as candidates for a commercial utilization. Therefore the palladium-free methods of hydrogen loading such as electrolytic or ball milling ones should be studied in more detail as well as the behavior of the Ti–Zr–Ni compounds at elevated temperatures, which take place during hydrogenation-dehydrogenation processes. From the other hand the hydrogen sorption property is extensively determined by the peculiarities of their structural states. The Ti–Zr–Ni compounds have a number of structural states depending on the chemical composition: from complex Laves phases to the quasicrystals and amorphous states [1,4–6]. As it was shown in [7] the production conditions have a very strong effect on the $Ti_{37.1}Zr_{38.8}Ni_{23.9}Si_{0.2}$ ribbon structural state. For instance, the melt-spun ribbons produced at the linear wheel velocity of 44 m/s have an amorphous state on the both contact and free sides, instead of the mixed amorphous-quasicrystalline one for the free side and amorphous one for the contact side in case of velocity of 30 m/s. At the same time the amorphous state was observed for a silicon concentration of one order of magnitude less than that, given in [1]. Therefore, the study of the stability of amorphous and amorphous-quasicrystalline structural state of the Pd-uncoated ribbons in process of annealing and electrolytic hydrogenation is of a special interest.

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2. Procedure

Alloy ingot with the composition of $Ti_{37.2}Zr_{38.9}Ni_{23.9}$ at.% was prepared from pure elements (99.9%) by induction melting in Ar gas atmosphere at the G.V. Kurdyumov Institute for Metal Physics. The ribbons having a cross section of 10 mm × 50 μm were produced at the Martin Luther University by the melt-spinning technology using quenching of the melt at 1400 °C on a copper wheel with a surface velocity of 44 and 30 m/s. Chemical analysis revealed the presence of a small amount of Si in the ribbons. The final composition of the ribbons is $Ti_{37.1}Zr_{38.8}Ni_{23.9}Si_{0.2}$ at.%. The most likely origin of Si in the ribbons is the quartz quenching tube used during the melt-spun procedure, as it is pointed out in [8].

X-ray diffraction (XRD) investigations were performed by means of a standard powder HZG-4 diffractometer using Cu Kα radiation (β-filter) and monochromatic Mo Kα radiation (primer pirographite monochromator). Structural parameters of the amorphous state were calculated by the procedure described in the previous papers [9–12]. Corrections for incoherent scattering, polarization, absorption and fluorescent scattering were also taken into account.

Annealing of the ribbons was performed in a vacuum furnace. The study of the electrochemical characteristics of the alloys was performed in an electrolytic cell with nickel oxide electrode. A working electrolyte of the composition 7 M KOH + 1.5 M LiOH was used.

3. Results and discussion

XRD study of the 3 years natural aged $Ti_{37.1}Zr_{38.8}Ni_{23.9}Si_{0.2}$ ribbons produced at a linear wheel velocity of 44 m/s shows that both sides of the ribbons are in an amorphous state. At the same time, there is a large difference in the diffraction diagrams from the contact and free sides for the ribbons produced at the velocity of 30 m/s. So, two broad diffuse maxima are observed at the contact side and additional three narrow Bragg peaks are present for the free side (Fig. 1a). It should be pointed out that the diffraction patterns for the natural aged ribbons are similar to the ones in as-prepared state [7]. Analysis of the XRD pattern for the ribbon produced at the linear velocity of 30 m/s allows the assumption that there is an amorphous state on the ribbon contact side and a mixed amorphous-quasicrystalline state on the free side, where the hardening rate is the lowest (Fig. 1a). The quasilattice parameter A_6 was calculated using the scheme proposed by Cahn et al. [13]. The first and third maxima correspond to the diffraction peaks for quasicrystalline lattice ($A_6 = 7.53$ Å) and they have the indexes 18/29 and 20/32, respectively. The second peak corresponds to the interplanar distance of $d = 2.45$ Å and it may be connected with NiZr intermetallic phase (space group *Cmcm* (63)) in the ribbon. XRD study of the $Ti_{37.1}Zr_{38.8}Ni_{23.9}Si_{0.2}$ ribbons annealed in the vacuum furnace at different temperatures during 1 h showed a stable structure up to 400 °C (Fig. 1b). Changes in the XRD pattern

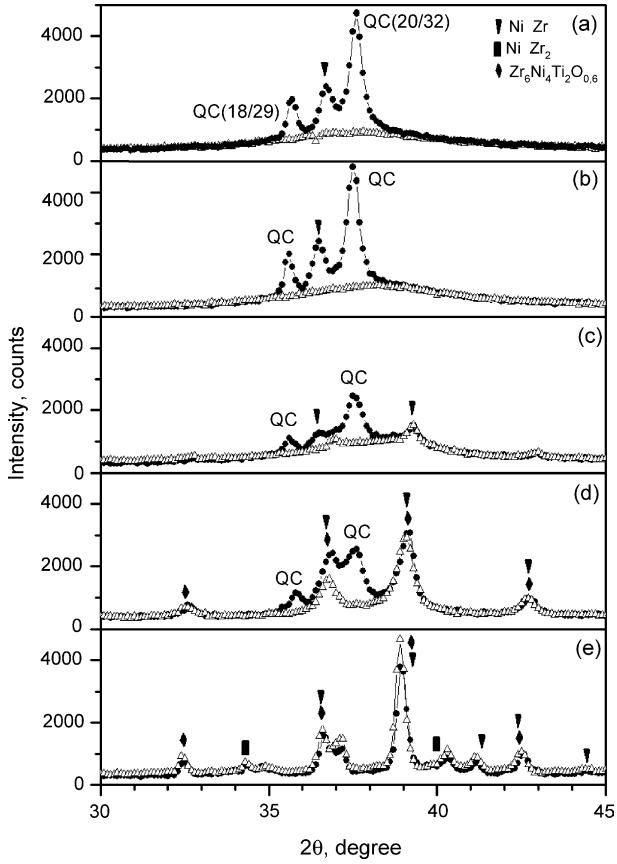

Fig. 1. Fragments of XRD patterns of the 3 years naturally aged $Ti_{37.1}Zr_{38.8}Ni_{23.9}Si_{0.2}$ ribbon produced at the linear wheel velocity of 30 m/s, Cu K_α radiation (△, contact side; •, free side): (a) initial state, (b), (c), (d), (e) – annealed state at the temperatures of 400 °C, 450 °C, 500 °C, 600 °C, accordingly. Indexation of quasicrystalline peaks is given using Cahn scheme [13].

appear only after 450 °C: the intensity of the quasicrystalline peaks at the free side of the produced ribbon at velocity of 30 m/s essentially decreases and the features of new maxima, connected with NiZr phase (Fig. 1c), arise. These phenomena become clearly defined (Fig. 1d) at 500 °C. No the quasicrystalline peaks and the difference between the XRD patterns of contact and free sides were observed at 600 °C. There are peaks of NiZr, $NiZr_2$ (space group *I4/mcm* (140)) and complex $Zr_6Ni_4Ti_2O_{0.6}$ (space group *Fd3m* (227)) phases peaks in the XRD pattern (Fig. 1e). The possible influence of oxygen impurities on the ribbon crystallization process should be noted.

The question arises about the influence of the hydrogenating process on the ribbon structure state. In our case, the hydrogenating was performed for the 3 years natural aged $Ti_{37.1}Zr_{38.8}Ni_{23.9}Si_{0.2}$ ribbons, produced at the linear wheel velocity of 30 and 44 m/s, in the electrolytic cell during 8 h at the current density of 5 mA/cm^2 and voltage of 1.68 V. The ribbon surface has been neither etched nor coated by Pd. At this treatment, a hydrogen concentration of 0.5 H/M was achieved. XRD study of the freshly hydrogenated samples testifies amorphous state for the 44 m/s velocity ribbon. At the

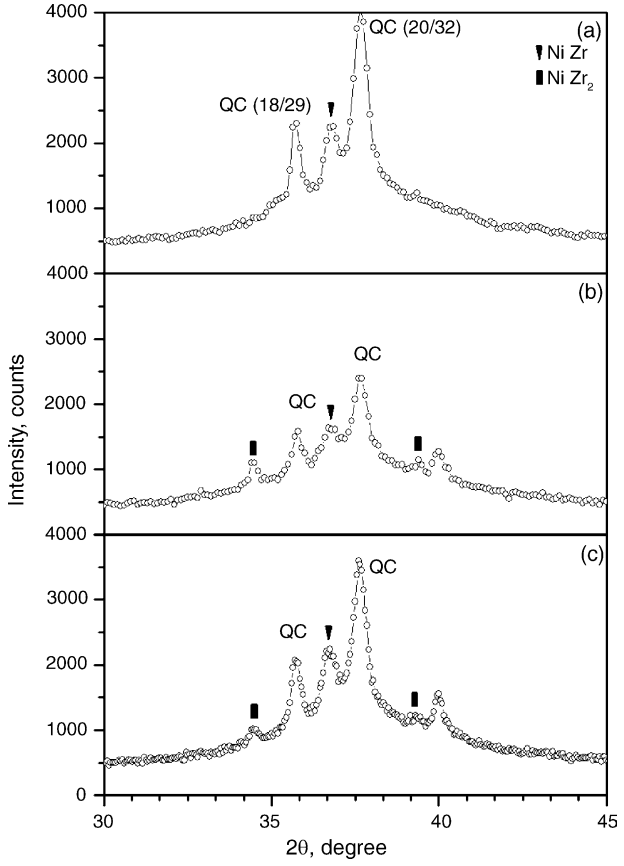

Fig. 2. Fragments of XRD patterns of the $Ti_{37.1}Zr_{38.8}Ni_{23.9}Si_{0.2}$ ribbon produced at the linear wheel velocity of 30 m/s, Cu K_α radiation, free side (Indexation of peaks is similar to Fig. 1): (a) initial state, (b) in a day after hydrogenation, (c) in a week after hydrogenation.

same time, there are essential changes in the structure states of the free side of 30 m/s velocity ribbon (Fig. 2a, b): namely, the intensity of the quasicrystalline peaks decreased, but their positions did not change, which is in an agreement with [2]. At that additional peaks from Laves phases appeared.

To study the changes in a structure of the amorphous subsystem of hydrogenated ribbons, the XRD investigation using Mo Kα radiation was conducted. The structural factor $i(s)$ and the radial distribution function (RDF) were calculated for the both types of ribbons in the initial and hydrogenated states using the set of programs, developed by A.G. Ilinskii [14]. The parameters of the amorphous structure calculated from the X-ray data are shown in Table 1.

Obviously, the changes in the structural state of the amorphous subsystem take place during hydrogenation for both ribbon types: the position of the 1st diffuse maxima shifts towards the smaller angle values and its intensity decreases. The position of the first maximum s_1 of a structure factor is connected with the most probable interatomic distance r_1 on a RDF diagram. As a rule, it is associated with the structure component having the largest volume fraction. In other words, an increase of the interatomic distances and a decrease of the degree of short range order take place in an amorphous subsystem during hydrogenation.

The study of the stability of the hydrogenated ribbon structural state is of a special interest. The conducted XRD study reveals that the relaxation processes in the ribbons appear during the 1st day after hydrogenation. The fragments of the XRD patterns for the cases of the initial state, in a day after hydrogenation and in a week after hydrogenation are presented in Fig. 2 for ribbons with hardening velocity of 30 m/s. As it is seen from Fig. 2, the intensity of quasicrystalline peaks practically amounts to the initial value in a week after hydrogenation. It seems to be a result of an interaction between amorphous and quasicrystalline subsystems.

4. Conclusions

(i) $Ti_{37.1}Zr_{38.8}Ni_{23.9}Si_{0.2}$ ribbons with a small amount of Si have been produced by the melt-spinning technology in different nanostructural states. The ribbon structural state depends on the production conditions: reducing of the hardening rate leads to the formation of the mixed amorphous-quasicrystalline structure on the free ribbon side in contrast to the amorphous one on the contact side.

(ii) The amorphous-quasicrystalline structure state of the ribbons is stable during annealing up to temperature of 400 °C but some changes in its parameters take place. A further increase of the annealing temperature leads to the formation of a mixed amorphous-quasicrystalline-crystalline state, which transforms into a crystalline one after 600 °C.

(iii) The hydrogen concentration of 0.5 H/M was achieved by means of the electrochemical method in the uncoated by Pd, 3 years naturally aged $Ti_{37.1}Zr_{38.8}Ni_{23.9}Si_{0.2}$ ribbons. The structural changes are observed in both the amorphous and quasicrystalline subsystems. This

Table 1
Parameters of an amorphous state of $Ti_{37.1}Zr_{38.8}Ni_{23.9}Si_{0.2}$ ribbons produced at the linear velocity of 30 and 44 m/s in the initial (3 years of natural aging) and hydrogenated states (s_1 and s_2 are the positions of the first and second diffraction maxima, $i(s_1)$ is the height of the first maximum on the $i(s)$ diagram, r_1 is the position of the first maximum on the RDF diagram)

No.	State of samples	s_1 (Å^{-1})	s_2 (Å^{-1})	$i(s_1)$ (e.u.)	r_1 (Å)
1	Linear velocity of 30 m/s, initial state, free side	2.62	4.43	3.83	3.09
2	Linear velocity of 30 m/s, hydrogenated state, free side	2.57	4.45	3.72	3.12
3	Linear velocity of 44 m/s, initial state, free side	2.64	4.41	3.49	3.13
4	Linear velocity of 44 m/s, hydrogenated state, free side	2.62	4.43	3.19	3.09

phenomenon has a reversible character: the ribbon structure state reverts almost entirely to the initial state after natural dehydrogenation.

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