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HYDROGEN ABSORPTION BY Ti–Zr–Ni-BASED ALLOYS

ABSORPCIJA VODIKA V ZLITINAH Ti–Zr–Ni

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Some transition metals and their alloys have the ability to reversibly absorb considerable amounts of hydrogen. The amount of absorbed hydrogen and the absorption kinetics depend on interactions between the hydrogen atoms and the alloy. Titanium and zirconium show a high affinity for hydrogen, and Ti–Zr–Ni alloys with either amorphous or quasicrystalline structures have proved to be excellent absorbers of hydrogen. In this study we have focused on processing Ti–Zr–Ni ribbons with four different compositions and investigating their hydrogenation behaviour. A melt-spinning process was used as the alloy-preparation technique, and samples from each composition were examined before and after the hydrogenation process. The ribbons were analysed by X-ray diffraction (XRD) and examined with a scanning electron microscope (SEM) equipped with an energy-dispersive X-ray spectrometer (EDS). Only the sample with the lowest nickel concentration was found to absorb any significant quantity of hydrogen under the applied experimental conditions.

Keywords: Quasicrystals, Ti–Zr–Ni alloys, Hydrogenation

Nekatere kovine prehoda in njihove zlitine imajo sposobnost reverzibilne absorpcije vodika. Količina absorbiranega vodika in kinetika absorpcije sta odvisni od interakcij med atomi vodika in atomi zlitine. Titan in cirkonij imata visoko afiniteto do vodika in zato zlitina Ti–Zr–Ni z amorfno ali kvazikristalno strukturo odlično absorbira vodik. V tem delu smo se osredinili na postopek izdelave trakov Ti–Zr–Ni s štirimi različnimi sestavami in preučili postopek hidrogenacije. Kot postopek izdelave trakov smo uporabili litje taline na vrteči se valj. Hitrostrjene trakove različnih sestav smo preučili pred hidrogenacijo in po njej. Trakove smo analizirali z rentgensko spektroskopijo (XRD) in vrstičnim elektronskim mikroskopom (SEM) z energijsko disperzijo rentgenskih žarkov (EDS). Le vzorec z najnižjo vsebnostjo niklja je pri danih pogojih absorbiral znatnejše količine vodika.

Ključne besede: kvazikristali, zlitine Ti–Zr–Ni, hidrogenacija

1 INTRODUCTION

Amorphous and quasicrystalline alloys have recently attracted a lot of attention for hydrogen-storage applications. Much of the research has concentrated on Ti- and Zr-based alloys and related materials. These alloys mostly contain an *i*-phase, which has an icosahedral quasicrystalline structure. These quasicrystals are able to absorb/desorb considerable amounts of hydrogen[1, 2, 3, 4]. Containing more tetrahedral sites in their structure than other crystals, and with Ti and Zr having high affinities for hydrogen, makes these alloys potentially excellent hydrogen-storage materials [5]. The *i*-type quasicrystal is formed either by rapid quenching or solid-state transformation at 500–600 °C, generally leading to a microstructure of quasicrystal and crystal phases with a grain size of several microns [1]. The melt-spinning process is a technique used for the rapid cooling of molten metals and alloys. It is used to develop materials that require extremely high cooling rates in order to form, for example, metallic glasses. The cooling rates achieved are of the order of 10^4–10^7 K/s. Therefore, the process can be successfully used for the preparation of amorphous and quasicrystalline samples through the rapid solidification of a molten alloy on a cold spinning wheel made of copper. The cooling rate of the process has also been defined for this type of alloy with additions of silicon [6]. The hydrogenation of these alloys was successful at high temperatures and low pressures. However, only 10 % of the absorbed hydrogen can be evolved from the alloy during the heat treatment [7]. The aim of this study was to optimise the melt-spinning process for the production of ribbons with amorphous and quasicrystalline structures.

2 EXPERIMENTAL DETAILS

Samples with the compositions in Table 1 were prepared from $Ti_{78.6}Ni_{21.4}$, $Zr_{65.9}Ni_{34.1}$ and $Ti_{60}Zr_{40}$ binary-alloy ingots. The starting alloys were crushed into smaller lumps (≈3 cm), and suitable amounts of each composition were put in to a melting crucible in an induction furnace. The crucible we used was made of graphite, coated with a zirconia-water suspension that was dried before use. The coating was used to prevent the formation of carbides. Induction melting in a vacuum was used to prepare the pre-alloy with the desired composition. The homogenous pre-alloys were then re-melted and spun to obtain the ribbons. The melt-spinning process was carried out with a 25.2 m/s wheel speed, and the size of the crucible's nozzle was

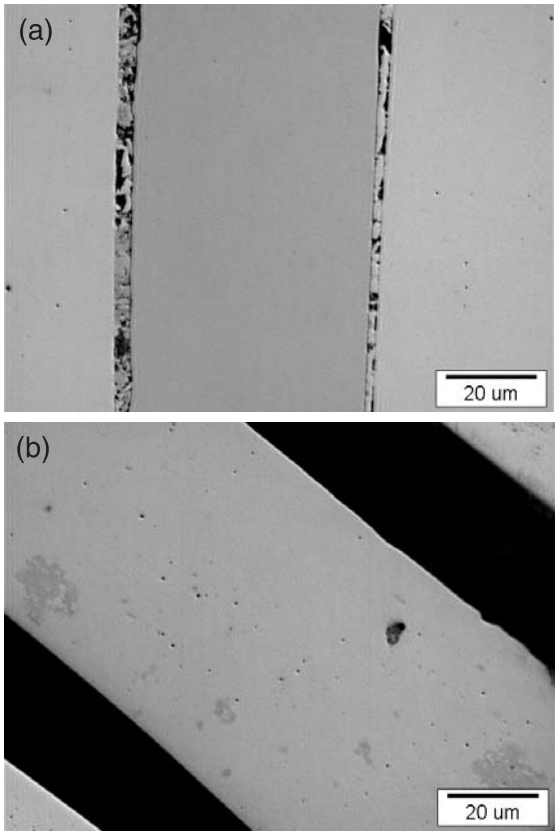

Figure 1: Cross-sectional view of the ribbon with the most (a) and the least (b) amount of Ni present in the microstructure
Slika 1: Prečni prerez traku z največjo (a) in najmanjšo (b) vsebnostjo Ni v mikrostrukturi

2.2 mm (ϕ). To obtain melt-spun ribbons with the desired structure it was necessary to choose a suitable wheel speed and the correct size of nozzle. The process was carried out in a slight under-pressure of argon. Some of the prepared ribbons were examined and others were hydrogenated. The hydrogenation process was carried out in a furnace in a hydrogen atmosphere. First, the ribbons were put in to the furnace and the furnace was sealed. The furnace was then evacuated and refilled with an 8-bar over-pressure of hydrogen. The furnace was heated up to 350 °C, and the temperature was maintained at this temperature. When the absorption was complete the furnace was allowed to cool down and the remaining hydrogen was released from the system.

All the ribbons, as-melt-spun and hydrogenated, were investigated with an X-ray diffractometer (XRD) and examined with a scanning electron microscope (SEM) equipped with an energy-dispersive spectrometer (EDS). The samples for the SEM examinations and the EDS analyses were ground and polished prior to the examination.

3 RESULTS AND DISCUSSION

The cross-sections of the samples obtained using an optical microscope can be seen in **Figure 1**. A comparison was made between sample A1, with the highest amount-of-substance fraction of Ni present in the composition (26.3 %), and sample A2, with the smallest amount-of-substance fraction of Ni present in the

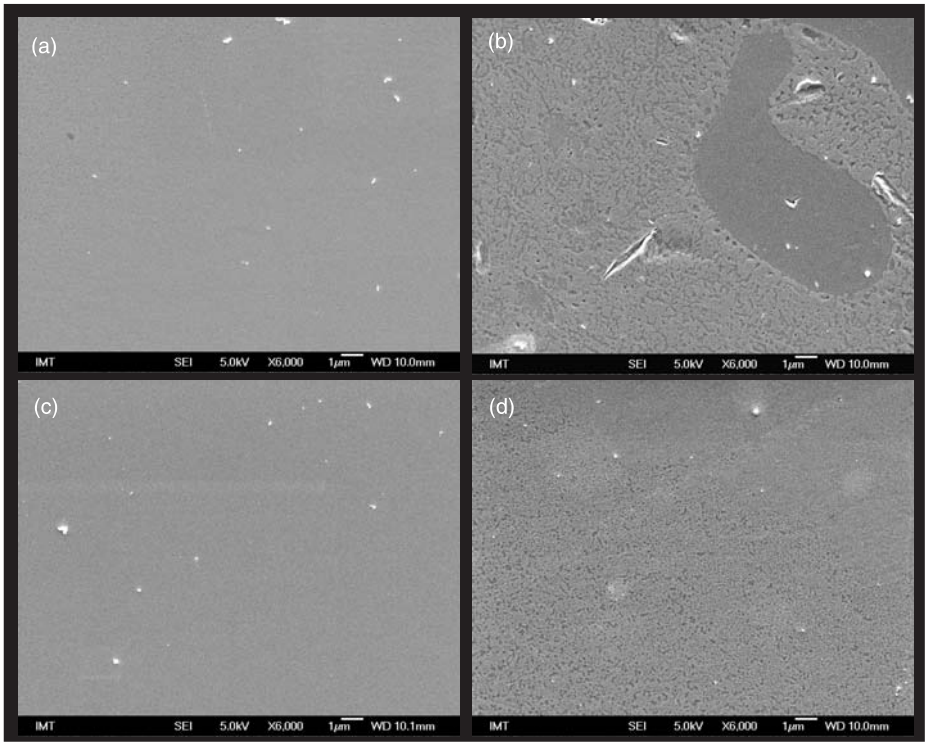

Figure 2: Cross-sectional views of the as-melt-spun ribbons with compositions A1 (a), A2 (b), A3 (c) and A4 (d)
Slika 2: Prečni prerez hitrostrjenih trakov s sestavami A1 (a), A2 (b), A3 (c) in A4 (d)

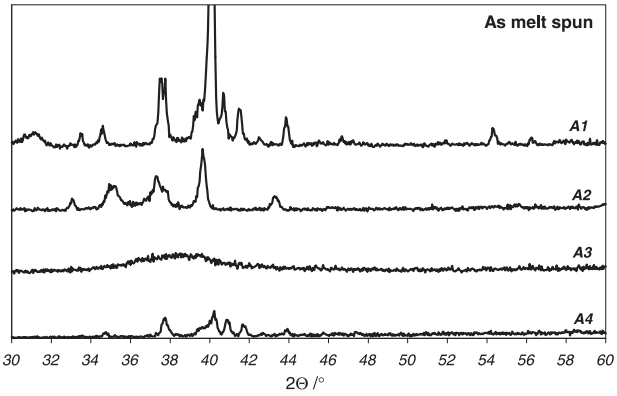

Figure 3: XRD scans of as-melt-spun Ti–Zr–Ni ribbons
Slika 3: XRD spektri hitrostrjenih trakov Ti–Zr–Ni

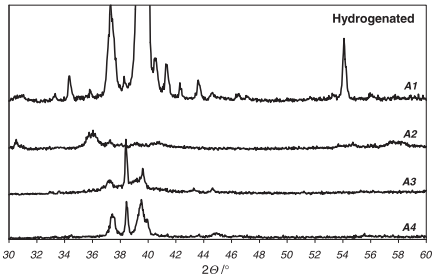

Figure 4: XRD scans of as-melt-spun Ti–Zr–Ni ribbons after hydrogenation
Slika 4: XRD spektri hitrostrjenih trakov Ti–Zr–Ni po hidrogenaciji

composition (17 %). It seems that the sample with less Ni in the overall composition forms a two-phase microstructure and the sample with more Ni forms a single-phased microstructure. The assumption was confirmed by the SEM investigation. From the images shown in **Figure 2** it is clear that sample A2 (**Figure 2b**) is the only one consisting of two phases. All the other samples, with higher Ni concentrations, have single-phase microstructures. All the samples and phases were analysed with EDS, and the results are collected in **Table 2**. All the phase compositions are in accordance with the starting compositions listed in **Table 1**. The ribbons with the A2 composition are the only samples containing Ti–Zr particles in a matrix structure, which again agrees with the original composition (**Table 1**). The particles can be seen in **Figures 1 b and 2 b**.

XRD scans belonging to the as-melt-spun samples are collected in **Figure 3**. It is clear that sample A3 was the only sample that had an amorphous structure. All other samples, A1, A2 and A4, show patterns that indicate the presence of crystalline phases. From this we can conclude that the solidification resulting from melt spinning at 25.2 m/s with a 2.2 mm nozzle was insufficiently rapid to form an amorphous structure except in the sample with the lowest amount of Ni. The samples with compositions A1, A2 and A4 cooled down

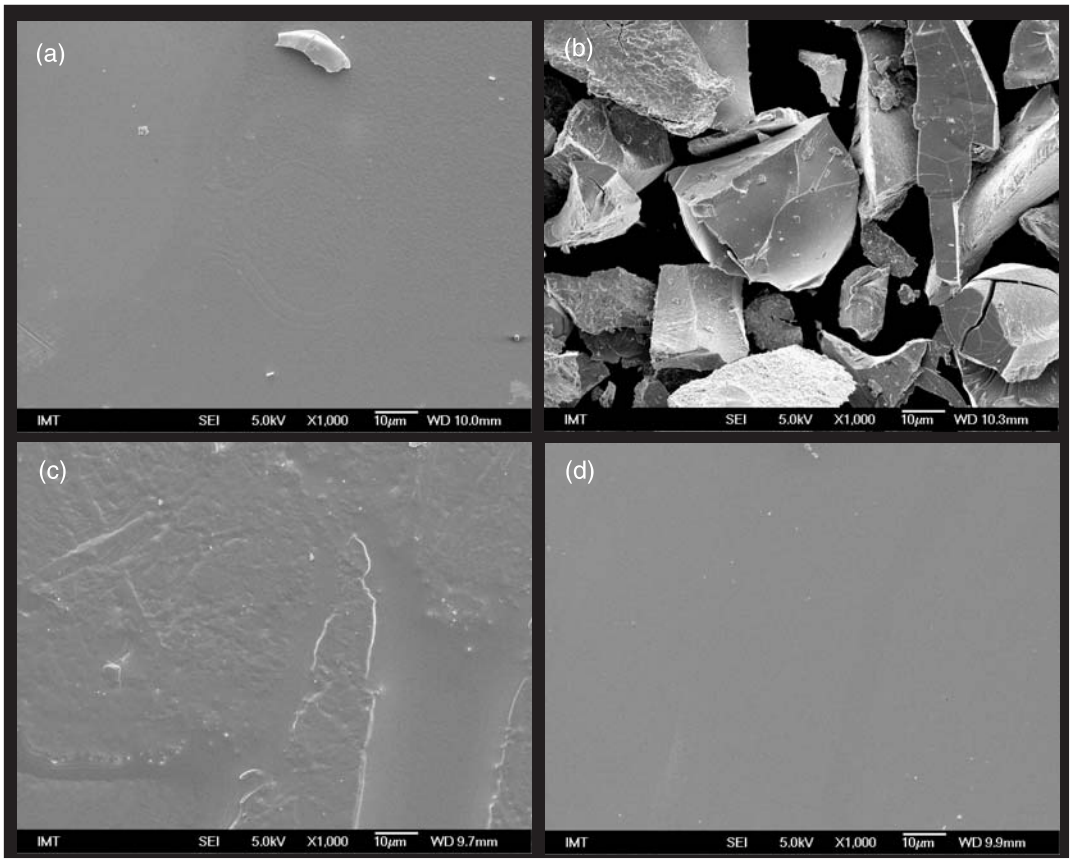

Figure 5: Ribbons with compositions A1 (a), A2 (b), A3 (c) and A4 (d) after hydrogenation
Slika 5: Trakovi s setavo A1 (a), A2 (b), A3 (c) in A4 (d) po hidrogenaciji

Table 1: Compositions
Tabela 1: Sestava

A1	$Ti_{48}Zr_{26}Ni_{26}$
A2	$Ti_{50}Zr_{33}Ni_{17}$
A3	$Ti_{44}Zr_{33}Ni_{23}$
A4	$Ti_{50}Zr_{29}Ni_{21}$

Table 2: Compositions of phases forming the microstructure of melt-spun ribbons
Tabela 2: Sestave faz, ki tvorijo mikrostrukturo hitrostrjenih trakov

	Phase	*x*(Ti)/%	*x*(Zr)/%	*x*(Ni)/%
A1	Matrix	48.3 ± 0.5	26.1 ± 0.7	25.6 ± 0.5
A2	Matrix	50.1 ± 0.5	33.7 ± 0.7	16.2 ± 0.5
	Particle	56.2 ± 0.5	43.8 ± 0.7	/
A3	Matrix	43.9 ± 0.5	33.3 ± 0.7	22.8 ± 0.5
A4	Matrix	51.4 ± 0.5	27.8 ± 0.7	20.9 ± 0.5

Table 3: Compositions of the phases forming the microstructure of the hydrogenated ribbons
Tabela 3: Sestave faz, ki tvorijo mikrostrukturo hidrogeniranih trakov

	x(Ti)/%	*x*(Zr)/%	*x*(Ni)/%
A1	48.7 ± 0.5	26.1 ± 0.7	25.2 ± 0.5
A2	49.1 ± 0.5	33.3 ± 0.7	17.6 ± 0.5
	56.3 ± 0.5	43.7 ± 0.7	/
A3	43.2 ± 0.5	33.8 ± 0.7	23.0 ± 0.5
A4	50.3 ± 0.5	28.0 ± 0.7	21.7 ± 0.5

too slowly and so had time to form a crystalline structure.

Based on these results we can state that the conditions used during the melt-spinning process were not suitable for producing ribbons with an amorphous structure. The oversized nozzle as well as a too-slow wheel speed during the melt-spinning process resulted in a relatively slow cooling rate and slow solidification, giving the material time to crystallise. At this stage it is also worth mentioning that the melting temperature of the alloy is increasing with decreasing Ni content. From the Ti–Zr–Ni phase diagram [9] it is clear that when the decreasing Ni content exceeds the amount-of-substance fraction ≈22 % the solidus-liquidus area starts widening. A consequence of this is the presence of solid particles in the melt that could cause difficulties during melt-spinning.

The images in **Figure 5** and the XRD scans in **Figure 4** were obtained from ribbons after hydrogenation. Comparing the scans for A1, A3 and A4 before and after the hydrogenation it is clear that the scans are the same, proving that no hydrides were formed during the hydrogenation process. The compositions in **Tables 2 and 3** also confirm that the samples did not absorb any hydrogen. Sample A2 was the only affected sample. When exposed to hydrogen the hydrogen penetrated via grain boundaries through the ribbons and forced the grains to decrepitate [9]. Consequence of the process was the formation of a powder with an unaffected composition.

It can also be concluded that the hydrogenation conditions were not sufficient for the hydrogenation to proceed. It is most likely that the hydrogen pressure applied to the sample was insufficient. Unfortunately, the existing equipment used for the hydrogenation is not capable of supporting higher pressures.

4 CONCLUSIONS

From a range of samples with different amounts of Ni in their compositions only the sample with smallest amount-of-substance fraction Ni (17 %) content forms a two-phase structure. Some Ti–Zr particles are present in the microstructure. All the other compositions formed a single-phase microstructure.

The cooling rate of the melt-spun samples was not fast enough to provide the conditions for fast solidification and, consequently, ribbons with an amorphous structure, except for the sample with least amount of Ti.

The conditions under which the hydrogenation process was carried out were found to be insufficient to initiate the formation of hydrides for three of the four samples.

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