STRUCTURE, PHASE COMPOSITION AND HYDROGEN SORPTION PROPERTIES OF EUTECTIC ALLOY $Ti_{47.5}Zr_{30.2}Mn_{22.5}$ OBTAINED USING TITANIUM SPONGE

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Abstract: *The microstructure and phase composition of the eutectic alloy $Ti_{47.5}Zr_{30.2}Mn_{22.5}$ obtained using titanium sponge, as well as the phase composition of hydrogenation product were investigated by scanning electron microscopy and X-ray phase analysis. It was found that when iodide titanium was completely replaced by titanium sponge, the alloy structure remained eutectic and consisted of bcc solid solution and Laves phase. It was shown that after a sorption-desorption cycle the alloy was in activated state and was capable to absorb hydrogen at room temperature and low pressure (0.21 MPa) starting from the first seconds of contact with hydrogen atmosphere, with hydrogen capacity of 2.61 wt.%.*

KEYWORDS: LAVES PHASE, BCC SOLID SOLUTION, EUTECTIC, TITANIUM SPONGE, SORPTION/DESORPTION, HYDROGEN CAPACITY.

1. Introduction

Previously, the prospect of using eutectic alloys of the Ti-Zr-Mn system as a material for the safe storage and transport of hydrogen in a bound state (hydride) was shown [1]. The use of eutectic alloys based on the Ti-Zr-Mn system, which consist of bcc solid solution with high hydrogen capacity and Laves phase (acceptable operating temperatures, sorption capacities ~ 1.0 H/Me and high hydrogenation rates), leads both to a significant increase in the sorption capacity and to the improvement of kinetic and thermodynamic parameters of hydrogenation and dehydrogenation processes due to combining the advantages of both phases.

According to the literature, the processes of hydrogen sorption and desorption in the alloys designed for hydrogen storage are affected by many factors: production techniques (mechanical doping or induction melting [2], arc melting or formation of thin strips from melt [3]), heat treatment parameters [3-4], structure and phase composition of the initial alloys [5-6]. The main common feature of all alloys proposed for hydrogen storage is the use of high-purity materials (not lower than 99.5%) [1-7]. These materials are quite expensive, that significantly increases the cost of the resulting hydride. The cost of the resulting hydride can be reduced by replacing the expensive components by cheaper ones.

The purpose of the present work was to assess the possibility of reducing the cost of the resulting hydride by replacing the high-purity components by cheaper ones. For this goal, previously investigated [1] alloy $Ti_{47.5}Zr_{30}Mn_{22.5}$ was melted, wherein iodide titanium ($70 for 1 kg) was replaced by cheap grades of titanium sponge (TG-110, TG-130, TG-TV, $10 for 1 kg).

2. Materials and methods

The alloy was produced by electric arc melting in a laboratory furnace with a non-consumable tungsten electrode in an atmosphere of purified argon. Titanium sponge, iodide Zr (99.975%), and electrolytic Mn (99.9%) were used as initial components. The deviation of chemical composition of the alloy from the nominal one was determined by XRF (VRA-30 unit). It coincided with the nominal one within the measurement error (0.03%).

Differential thermal analysis was performed at a VDTA-8M thermoanalyzer [8] at a heating rate of 40 °C/s in a high-purity helium atmosphere using Y_2O_3 crucibles. The solidus and liquidus were determined with accuracy ± 7 °C.

Metallographic examinations were performed with a scanning electron microscope JSM-6490 LA.

The phase composition and lattice parameters were determined by X-ray phase analysis at a Dron-3M diffractometer with a standard GUR-8 goniometer at monochromatic Cu-K_α.

The hydrogen adsorption properties were studied on the alloy in a cast solid state. The interaction of the alloy with hydrogen was studied by the Sieverts method at IVGM-2M unit [9] at room temperature and upon heating at a rate of 0.125 °C/s at absolute pressure ~ 0.6 MPa. The hydrogen desorption was studied at an automated dilatometric complex (ADC) with a mass spectrometer [10].

3. Results and discussion

As seen from DTA curves (Fig. 1), only one thermal effect is observed regardless of initial state of titanium, and the temperature of the phase transformation (melting, solidification) coincides within the measurement error. Previously we showed [1] that the structure of the alloy is close to eutectic, since there is only one thermal effect on the heating and cooling DTA curves, and the difference between the temperatures of start of melting and solidification is minimal (15 °C).

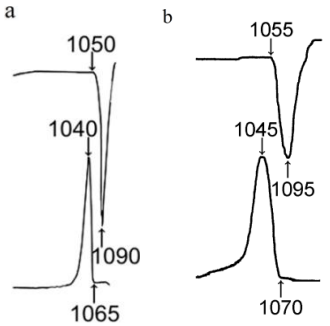

Fig. 1. *DTA curves of $Ti_{47.5}Zr_{30}Mn_{22.5}$ alloys: a – iodide titanium [1]; b – titanium sponge.*

The data of scanning electron microscopy confirmed the conclusion drawn from DTA studies: the complete replacement of iodide titanium by titanium sponge does not change the structure of the alloy (Figs. 2a, b).

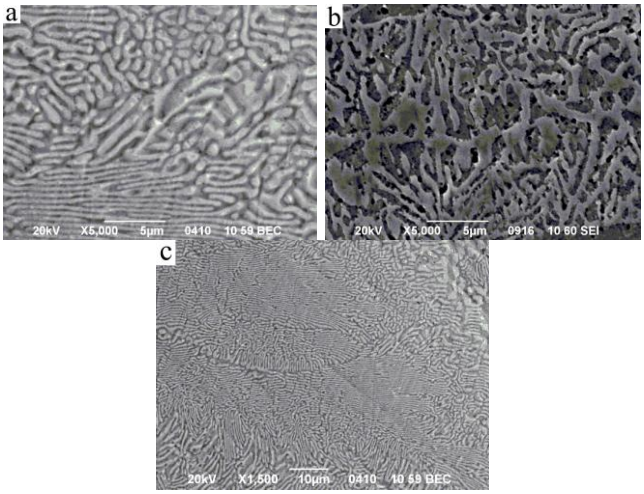

Fig. 2. *Microstructure of $Ti_{47.5}Zr_{30}Mn_{22.5}$ alloys: a – iodide titanium [1]; b – titanium sponge; c – a typical eutectic structure.*

The eutectic consists of bcc solid solution and Laves phase and has a skeletal structure in which the Laves phase plays role of a nucleating phase that initiates eutectic solidification. It grows in the

form of a branched backbone and forms a framework of colony; it has bright color on back-scattered electron images (Fig. 2c). The fact that the Laves phase initiates solidification is clearly seen from the rounding of its fibers in the joints of eutectic colonies. As the eutectic colonies grow towards one another, heat is released, and the cooling rate drops sharply, therefore the transition from the fibrous structure to the formation of globules at the end of the fibers is observed. The guided phase is bcc solid solution which forms a colony matrix. Thus, as in most metal-intermetallic systems, the phase that initiates and leads the eutectic solidification is the phase with a higher melting enthalpy and a higher anisotropy of interatomic bonds due to directed bonds between atoms of different types. The formation of the framework of eutectic colony and its subsequent growth are typical for the eutectic polyhedron-dendrite.

The results of X-ray phase analysis confirmed the data of scanning electron microscopy on the consistency of the alloy phase composition (Fig. 3). As expected, there is hexagonal Laves phase of C14 type and space group *P6₃/mmc* (structural type $MgZn_2$) with lattice parameters *a*=0.5200 ± 0.0009 (nm) *c*=0.8542 ± 0.0009 (nm) (for previously investigated alloy *a*=0.5215 ± 0.0009 (nm) *c*=0.8581 ± 0.0009 (nm) were obtained), and β(Ti,Zr,Mn) solid solution with space group *1m-3m* (structural type W) with lattice parameters *a*=0.3374 ± 0.0009 (nm) (for previously investigated alloy *a*=0.3383 ± 0.0009 (nm) were obtained) [1], and traces of ω-phase.

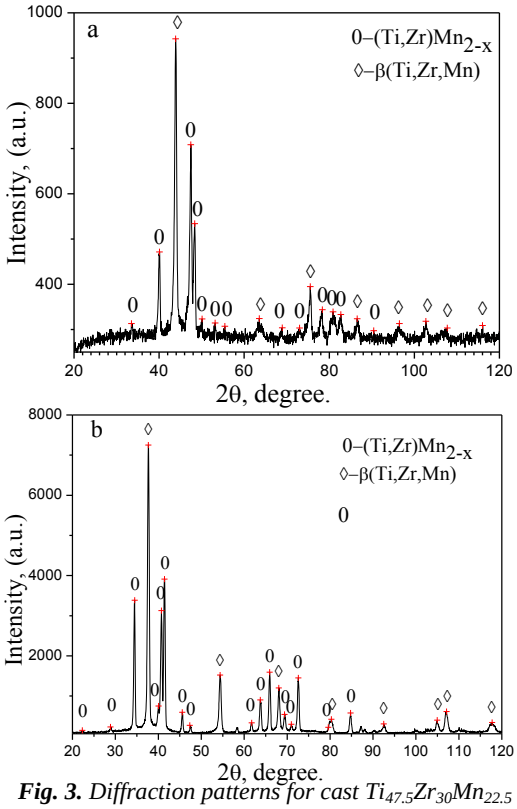

Fig. 3. *Diffraction patterns for cast $Ti_{47.5}Zr_{30}Mn_{22.5}$ alloy: a – iodide titanium [1]; b – titanium sponge.*

The alloy obtained using titanium sponge was kept at room temperature at hydrogen absolute pressure of 0.6 MPa for 24 hours; however, these hydrogenation conditions did not lead to surface activation and hydrogen absorption. Active absorption of hydrogen was observed only when the alloy was heated up to 565 °C. The start of intense hydrogen absorption during the first hydrogenation was estimated by deviation of the curve "pressure change vs. temperature" from straight line. For the present and previously investigated alloys intense hydrogen absorption started at ~ 525 °C and at ~ 540 °C, respectively (Fig. 4). The maximum rate of hydrogen absorption for both alloys was observed at 565 °C. A major amount of hydrogen at 565 °C was absorbed by the present and previously investigated alloys in ~ 7 min and ~ 12 min [1], respectively. When two alloys reached the maximum absorption rate, a substantial (by 30 °C) increase of the reactor temperature was observed, which indicated the exothermic nature of the reaction of hydride formation. The total hydrogen content for the present alloy was 2.61 wt.% (H/Me=1.66), while for the previously investigated alloy it was 2.58 wt.% (H/Me=1.64) [1].

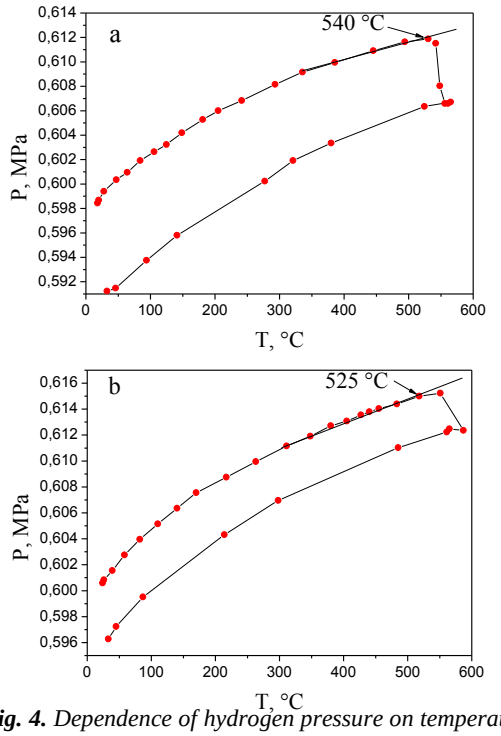

Fig. 4. *Dependence of hydrogen pressure on temperature: a – iodide titanium [1]; b – titanium sponge.*

Basing on the temperature of the start of active absorption, it can be suggested that the process of hydrogen absorption by both alloys starts in the β solid solution [11]. Regardless of the initial state of titanium, the interaction with hydrogen leads to complete destruction of solid samples to powder due to large internal stresses caused by hydrogen dissolution (Fig. 5).

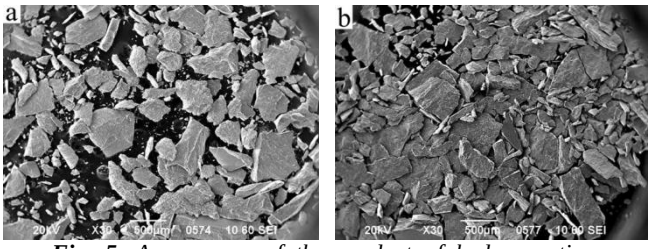

Fig. 5. *Appearance of the product of hydrogenation: a – iodide titanium [1]; b – titanium sponge.*

According to the data of X-ray phase analysis, during hydrogenation of the alloy obtained using titanium in different initial states hydrides are formed only on the basis of the original phases (Fig. 6.). The resulting hydrogenation product consists of a hydride based on the Laves phase with lattice parameters *a*=0.5590 ± 0.0009 (nm) *c*=0.9182 ± 0.0009 (nm) (for previously investigated alloy *a*=0.5598 ± 0.0009 (nm) *c*=0.9192 ± 0.0009 (nm) were obtained [1]), and δ-hydride on the basis of mixture of solid solution and ω-phase with lattice parameters *a*=0.4591 ± 0.0009 (nm) (for previously investigated alloy *a*=0.4597 ± 0.0009 (nm) were obtained, [1]). These results allow to suggest that the saturation of the alloys by hydrogen does not lead to phase decomposition.

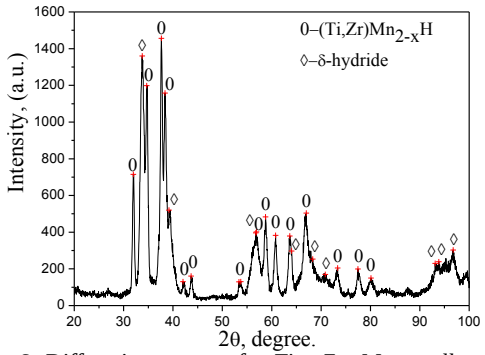

Fig. 6. *Diffraction pattern for $Ti_{47.5}Zr_{30}Mn_{22.5}$ alloy obtained using a titanium sponge after hydrogenation.*

Mass-spectrometry of hydrogenation products obtained by saturation of the alloys by hydrogen showed that hydrogen desorption at an initial pressure of $4 \cdot 10^{-3}$ Pa in both alloys started at ~ 80 °C, and at 350 °C the reverse capacity was 67% of absorbed amount (1.75 wt.%), whereas at 550 °C complete desorption of the alloys occurred (Fig. 7.).

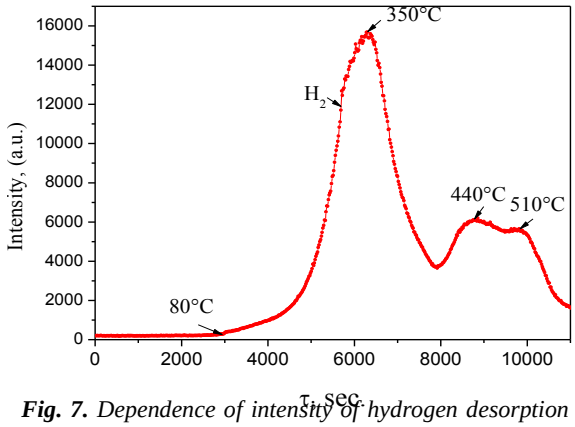

Fig. 7. *Dependence of intensity of hydrogen desorption from temperature.*

Investigation of the effect of sorption-desorption-sorption cycles on the hydrogen sorption properties of the alloys, regardless of the initial state of titanium, showed that hydrogenation in the second and subsequent cycles occurred already at room temperature and hydrogen pressure of 0.21 MPa starting from the first seconds of contact of the sample with hydrogen atmosphere. Basing on the temperature of hydrogenation, it can be suggested that after sorption-desorption cycle absorption started within the Laves phase [12]. This improvement in the hydrogen sorption properties (lowering hydrogenation temperature from 565 °C to room temperature) of the alloys, regardless of the initial state of titanium, can be explained by the destruction of solid samples to powder, as well as by the decrease in the concentration of oxygen on the surface of the particles as a result of its interaction with atomic hydrogen released.

4. Conclusion

Complete replacement of iodide titanium by titanium sponge does not affect the structure, phase composition and hydrogen sorption properties of the eutectic alloy $Ti_{47.5}Zr_{30}Mn_{22.5}$, and it allows to reduce the cost of the resulting hydride due to different costs of the source materials.

5. Acknowledgement

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6. References

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