Hydrogen absorbing properties of a Ti–Zr–Mn eutectic alloy

V. IVANCHENKO[1]*, T. PRYADKO[1], V. DEKHTYARENKO[1], T. KOSORUKOVA[1]

[1] *Department of Phase Equilibria, G.V. Kurdyumov Institute for Metal Physics of NAS of Ukraine,*
acad. Vernadsky av. 36, 03142 Kyyiv, Ukraine
* Corresponding author. E-mail: ivanch@imp.kiev.ua

Hydrogen storage properties of Ti-Zr-Mn eutectic alloys with the formula $Ti_{0.475}Zr_{0.3}Mn_{0.225}$ were evaluated at ambient temperature and 565 °C using a Sieverts-type device. The initial alloys were studied by means of SEM-EDS technique, X-ray diffraction and DTA. The phase compositions and the crystal structures of the hydrogenation products were determined. The hydrogenation product obtained at room temperature consisted of an ε-hydride with a tetragonal crystal structure of ThH_2 type ($a = 0.455$ nm, $c = 0.469$ nm) and a Laves phase-based hydride with $MgZn_2$-type crystal structure ($a = 0.5587\pm0.0005$ nm, $c = 0.9135\pm0.0007$ nm) and had the composition $0.634(Ti_{0.64}Zr_{0.29}Mn_{0.066})H_{1.96} + 0.366(Ti_{0.18}Zr_{0.32}Mn_{0.5})H_{1.3}$. The phase composition of the hydrogenation products obtained at 565 °C was estimated to $0.55(Ti_{0.71}Zr_{0.285}Mn_{0.005})H_{1.85} + 0.45(Ti_{0.19}Zr_{0.32}Mn_{0.5})H_{1.35}$ and consisted of a δ-hydride with a cubic crystal structure of CaF_2 type ($a = 0.4597$ nm) and a Laves phase-based hydride with $MgZn_2$-type crystal structure ($a = 0.5598\pm0.0006$ nm, $c = 0.9192\pm0.0008$ nm).

Laves phase / Ternary alloy system / Crystal structure / Hydrogen storage

Introduction

Iba and Akiba reported that if Ti-based AB_2 alloys consisted of bcc and Laves phases, every phase participates in the hydrogenation [1,2]. In particular, the bcc phase absorbed hydrogen in a favorable manner, like intermetallic compounds, and showed the same hydrogenation pressure as the other constituent phases. On the other hand, Semboshi *et al.* [3] showed that a lowering of the Mn content in the $TiMn_2$ compound leads to an increase of the hydrogen sorption properties. Taizhong *et al.* [4] studied the hydrogen absorption-desorption behavior of zirconium-substituted Ti–Mn based hydrogen storage alloys and found that the hydrogen storage capacity of Ti–Mn based alloys increases with increasing Zr content.

The aim of this study consisted in the realization of these three conditions in an alloy with eutectic structure, which consists of a Ti-base solid solution and a Laves phase, where the Mn contents in both phases are near the minimum [5,6].

Sample preparation and experimental procedure

An ingot, which had the composition 47.5Ti–30Zr–22.5Mn (at.%), was prepared by argon arc melting.

After six remelts the alloy was cast into a copper mould with a diameter of 12 mm. The starting components had purities better than 99.95 %. The chemical composition of the ingot was analyzed using X-ray spectral analysis (X-ray spectrometer VRA 30). It was close to the nominal composition. The microstructure of the alloy and the composition of the constituent phases were studied using SEM-EDS technique (JSM 840 equipped with an X-ray microanalyzer Link with wave spectrometer Ortec). The crystal structures of the phases were studied by X-ray diffraction (DRON-3M). The melting temperature and the temperature of the beta transus of the alloy were measured using DTA technique (high temperature differential thermal analyzer VDTA-3M). An Y_2O_3 crucible was used for the measurement of the melting temperature. The heating and cooling rates were the same and equal to 0.7 °C/s. Before the measurement of the beta-transus temperature the specimen was annealed at 500 °C for 1 h. For a better accuracy of the measurement a crucible was not used, but the specimen was placed directly on the hot thermojunction.

The absorbing properties were studied by the Sieverts method at room temperature and at 565 °C. The specimens used for the measurement of the hydrogen sorption properties were pellets that had been prepared by electro-charged cutting from an as-

cast ingot. Both surfaces of the pellets were thoroughly polished and cleansed with dry acetone. The final size of the pellets was 11.8 mm in diameter and 3 mm in height. The hydrogen capacity was calculated based on the decrease of the hydrogen pressure in a reactor of known volume.

Experimental results

The microstructure of the alloy is presented in Fig. 1. The eutectic structure is regular and consists of Laves phase thin plates with a ~0.5 μm thick plate located in the Ti-base solid solution matrix. The Laves phase (white in the electron back scattering image) has the composition $Ti_{0.18}Zr_{0.32}Mn_{0.5}$. The crystal structure is of the $MgZn_2$ type with lattice parameters $a = 0.5215\pm0.0005$ nm and $c = 0.8581\pm0.0007$ nm. It is the leading phase under eutectic crystallization. The Ti-based solid solution consists of the bcc β-phase and a low quantity of hexagonal ω-phase. Under as-cast conditions the composition of the mixture of β-phase and ω-phase was $Ti_{0.644}Zr_{0.29}Mn_{0.066}$ with a lattice parameter of the β-phase $a = 0.3383\pm0.0003$ nm. The ω-phase has a hexagonal structure with the lattice parameters $a = 0.455\pm0.001$ nm, $c = 0.2792\pm0.0005$ nm. The ω-phase is metastable and can be regarded as a transition structure between high-temperature β-Ti and the low-temperature α-phase. It was formed upon rapid cooling of the specimen in the copper mould. After casting into the copper mould the rate of cooling of the ingot in the temperature interval 700-500 °C was about 40 °C/s. These conditions of formation of the ω-phase are in good accordance with [7], who reported that athermal or as-quenched ω-phase is formed between 2.6 and 7 at.% Mn upon quenching.
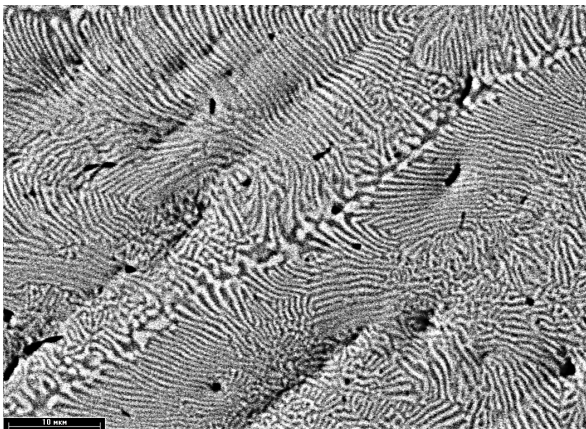

Fig. 1 Microstructure of the 47.5Ti–30Zr–22.5Mn (at.%) eutectic alloy (electron back scattering image).

The measured lattice parameter of the β-phase agrees well with the value estimated using the expression
$$a_\beta(X_{Mn}, X_{Zr}) = a_\beta^o + \partial a_\beta/\partial X_{Mn} \cdot X_{Mn} + \partial a_\beta/\partial X_{Zr} \cdot X_{Zr}$$

where $a_\beta^o = 0.33065$ nm, the cell parameter of pure Ti [7], $\partial a_\beta/\partial X_{Mn} = -0.00025$ nm/at.% Mn, calculated using data presented by [8], $\partial a_\beta/\partial X_{Zr} = 0.0003$ nm/at.% Zr, calculated using data presented by [9], X_{Mn}, X_{Zr} – at.% of Mn and Zr in the solid solution. The result of the estimation is: a_β(6.6 at.% Mn, 29 at.% Zr) = 0.3377 ± 0.0006 nm.

The melting temperature of the alloy was 1050 °C. The absence of additional heat effects on the heating and cooling curves concerned with melting or freezing of primary crystals of the β- or Laves phase (Fig. 2a) may be regarded as an evidence of the strongly eutectic composition. The melting interval was about 20 °C. The α⇒β transformation on heating began at 537 and came to an end at 645 °C (Fig. 2b). The maximum rate of phase transformation was observed at 592 °C.

The eutectic alloy was exposed at room temperature to a hydrogen atmosphere of 0.4 MPa for 24 h without any previous heating in vacuum leading to activation of the specimen surface. Absorption of hydrogen began after exposure for ~3 h, continued for ~1 h, and gave a hydrogen capacity of 2.62 mass% H (62.6 at.%). No sorption was registered during additional exposure for ~20 h. The hydrogenation products consisted of an ε-hydride with a tetragonal crystal structure of ThH_2 type ($a = 0.455$ nm, $c = 0.449$ nm) and a Laves phase-based hydride with $MgZn_2$ type crystal structure ($a = 0.5587\pm0.0005$ nm, $c = 0.9135\pm0.0007$ nm). To estimate the hydrogen capacities of the Ti-based solid solution and the Laves phase, the ratio of the molar fractions of the (β+ω)-solid solution and the Laves phase in the starting specimen was calculated in accordance with the lever rule based on the composition of the ingot and the compositions of the constituents of the eutectic. It is equal to $n_{(\beta+\omega)}/n_\lambda = 0.634/0.366$. Since no decomposition of the eutectic constituents under hydrogenation was observed, it was supposed that the content of metal atoms in the metal sublattices of the hydrides was the same as in the starting phases. This means that the ratio of molar fractions of the hydrides in the hydrogenation product is the same as the ratio estimated for the starting material. The hydrogen capacity of the Laves phase was calculated in accordance with the rule formulated by [9], which states that for almost all metal hydrides the increase in cell volume is approximately $2.9\cdot10^{-3}$ nm^3 per H/M unit. The measured increase of the cell volume of the Laves phase per metallic atom after hydrogenation at room temperature was $3.73\cdot10^{-3}$ nm^3 per H/M unit, which gives a composition of the Laves phase-based hydride of $(Ti_{0.18}Zr_{0.32}Mn_{0.5})H_{1.3}$ and a hydrogen capacity of 56.33 at.%. Since the mole fraction of the Laves phase is 0.366 and the mole fraction of the Ti-base solid solution is 0.634, the composition of the ε-hydride was estimated to $(Ti_{0.64}Zr_{0.29}Mn_{0.066})H_{1.96}$. These results give a phase composition after hydrogenation at room temperature as follows: $0.634(Ti_{0.64}Zr_{0.29}Mn_{0.066})H_{1.96} + 0.366(Ti_{0.18}Zr_{0.32}Mn_{0.5})H_{1.3}$.
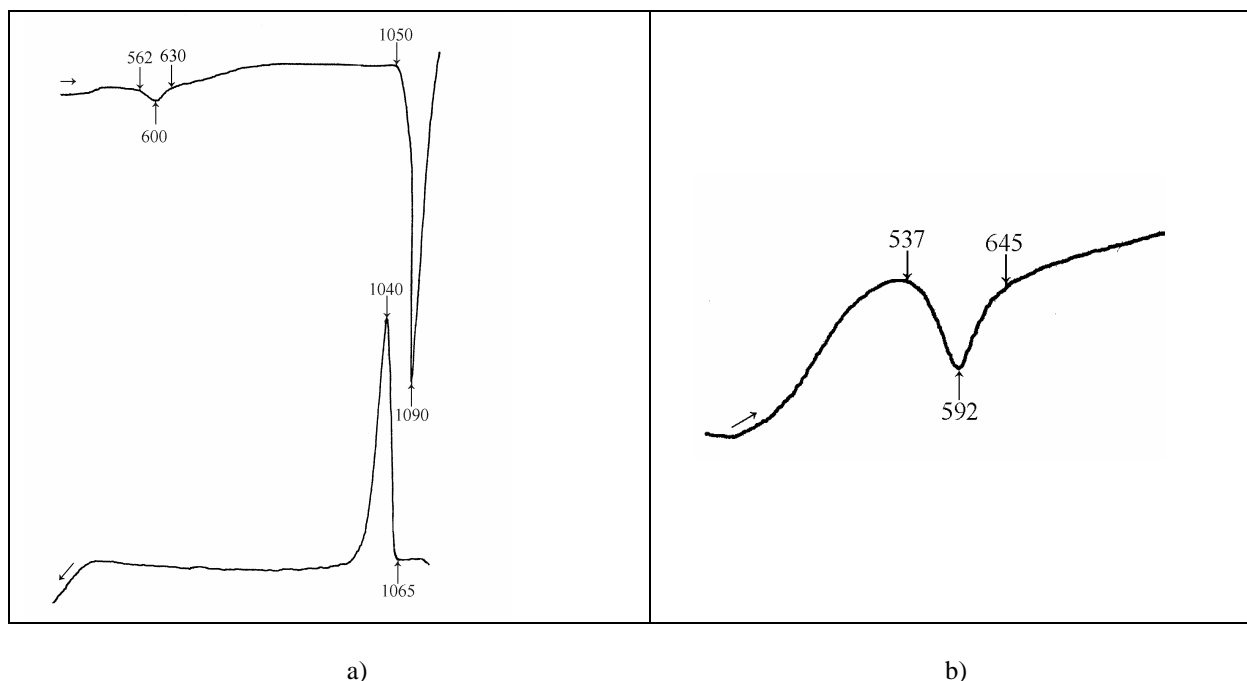
a)   b)

Fig. 2 Results of DTA of the 47.5Ti-30Zr-22.5Mn (at.%) alloy: a) in an Y_2O_3 crucible, b) without crucible.

The next experiment was conducted upon heating at a rate of 0.125 °C/s in a hydrogen atmosphere with a starting pressure of 0.5 MPa. The heating was stopped when hydrogen sorption started. The effect of temperature on the hydrogen sorption is presented in Fig. 3. The hydrogen sorption began at ~540 °C and continued for ~18 min. The maximal rate of sorption was registered at 565 °C. The main quantity of hydrogen was absorbed by the specimen over ~12 min at this temperature. The total hydrogen capacity was measured as 2.576 mass% H (62.16 at.% H). The hydrogenation product consisted of a δ-hydride with a cubic crystal structure of CaF_2 type ($a = 0.4597$ nm) and a Laves phase-based hydride with $MgZn_2$ type crystal structure ($a = 0.5598\pm0.0006$ nm, $c = 0.9192\pm0.0008$ nm).

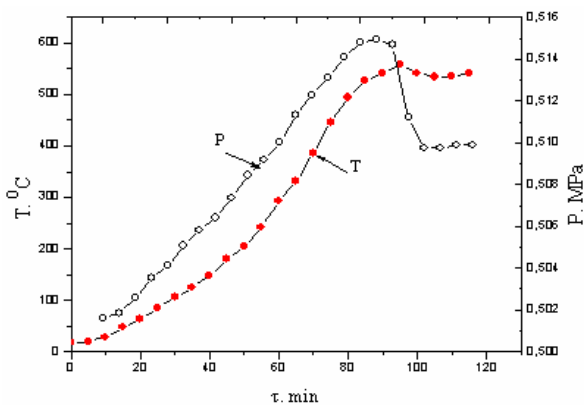Upon heating, the β+ω-phase mixture present in the Ti-base solid solution transforms into an α+λ mixture and the molar ratio of the constituent phases before the start of the α⇒β transformation was equal to $n_\alpha/n_\lambda = 0.55/0.45$. Using the method of calculation presented above, the phase composition of hydrogenation products was estimated to $0.55(Ti_{0.71}Zr_{0.285}Mn_{0.005})H_{1.85}+0.45(Ti_{0.19}Zr_{0.32}Mn_{0.5})H_{1.35}$.

Discussion

The processes of hydrogen absorption by monolithic specimens at room temperature and at 565 °C have some common features. In both cases the processes of hydrogen absorption have an explosive character, when, after activation, the absorption has not finished immediately but after a short time. The Ti-base solid solutions absorb hydrogen in a favorable manner, like an intermetallic compound, and achieve a high level of hydrogen capacity in a short time. These peculiarities are related to the high surface area of the interphase boundaries typical for a eutectic structure, where the coefficient of hydrogen diffusion is about 10^3 times higher than for a bulk material. But the processes of surface activation at room temperature and 540 °C have different nature. At 540 °C the activation of the specimen begins on the Ti-based solid solution matrix. It is the result of the α⇒β phase transformation that occurs with an expansion of the atomic volume, which in turn leads to the destruction of the thin surface oxide film and provokes the absorption process. At ambient temperature the sorption process begins from activation at points located at the interphase

Fig. 3 Effect of temperature on the hydrogen sorption.

boundaries. In both cases, once the process of hydride formation has begun, it continues with high rate due to the high brittleness of the Laves phase, resulting in fast chipping and formation of fresh surfaces that are ready to absorb hydrogen.

The higher temperature of hydrogenation leads to higher hydrogen solubility in the Laves phase. The increase of the saturation temperature from ambient to 565 °C produces a slow increase of the hydrogen capacity of the Laves phase from $H/M = 1.3$ to $H/M = 1.35$. At the same time the hydrogen capacity of the Ti-base solid solution is decreased from $H/M = 1.96$ to $H/M = 1.85$. This fact may be explained by different diffusion rates of hydrogen in the constituent phases of the alloy. The hydrogen diffusion coefficient in β-Ti is equal to $2.4 \cdot 10^{-7}$ m^2/s and that of α-Ti at 565 °C to $6.8 \cdot 10^{-8}$ m^2/s, that is ~3.5 times lower [10]. At 565 °C the Ti-base matrix consists of an $\alpha + \beta$ mixture where the β-phase fraction is about 10 %. For this reason the time required for full saturation of the matrix with hydrogen must be longer than the time used in the present experiment.

Conclusions

A eutectic 47.5Ti–30Zr–22.5Mn (at.%) alloy in monolithic state could react with hydrogen after 3 h exposure at room temperature to a pressure of 0.4 MPa hydrogen. The hydrogen capacity was measured as 2.62 mass% H (62.6 at.%). The hydrogenation product obtained under these conditions consisted of an ε-hydride with tetragonal crystal structure of ThH$_2$ type ($a = 0.455$ nm, $c = 0.469$ nm) and a Laves phase-based hydride with MgZn$_2$-type crystal structure ($a = 0.5587 \pm 0.0005$ nm, $c = 0.9135 \pm 0.0007$ nm), and had the composition $0.634(Ti_{0.64}Zr_{0.29}Mn_{0.066})H_{1.96} +$ $0.366(Ti_{0.18}Zr_{0.32}Mn_{0.5})H_{1.3}$.

Upon heating in a hydrogen atmosphere with a pressure of 0.5 MPa the activation of the specimen in monolithic state begins at a temperature somewhat higher than the temperature of the start of the $\alpha \Rightarrow \beta$ phase transformation, which may be related to the destruction of the thin oxide layer on the surface of specimen due to the difference between the atomic volumes in the α and β phases. The alloy reacts with

hydrogen quickly under the conditions of 565 °C and 0.5 MPa hydrogen. The hydrogen capacity was measured as 2.576 mass% H (62.16 at.% H). The hydrogenation product consisted of a δ-hydride with a cubic crystal structure of CaF$_2$ type ($a = 0.4597$ nm) and a Laves phase-based hydride with MgZn$_2$ type crystal structure ($a = 0.5598 \pm 0.0006$ nm, $c = 0.9525 \pm 0.0008$ nm). The phase composition was estimated to $0.55(Ti_{0.71}Zr_{0.285}Mn_{0.005})H_{1.85} +$ $0.45(Ti_{0.19}Zr_{0.32}Mn_{0.5})H_{1.35}$.

References

[1] H. Iba, E. Akiba, *J. Alloys Compd.* 231 (1995) 508-512.

[2] H. Iba, E. Akiba, *J. Alloys Compd.* 253-254 (1997) 21-24.

[3] S. Semboshi, N. Masahashi, S. Hanada, *J. Alloys Compd.* 352 (2003) 210-217.

[4] H. Taizhong, W. Zhu, Y. Xuebin, C. Jinshou, X. Baojia, H. Tiesheng, X. Naixin, *Intermetallics* 12 (2004) 91-96.

[5] V.G. Ivanchenko, T.V. Pryadko, I.S. Gavrylenko, V.V. Pogorelaya, *Chem. Met. Alloys* 1 (2008) 67-72.

[6] V. Ivanchenko, T. Pryadko, in: G. Effenberg, S. Ilyenko (Eds.), Landold-Boernstein, New Series, Group IV, Vol. 11, *Ternary Alloy Systems, Subvolume C, Non-Ferrous Systems*, Part 3, Springer-Verlag, Berlin-Heidelberg, 2007, pp. 475-485.

[7] J.L. Murray, *Bull. Alloy Phase Diagrams* 2 (1981) 334-343.

[8] V.G. Ivanchenko, I.S. Gavrylenko, V.I. Nychyporenko, T.V. Pryadko, V.V. Pogorelaya, *Metaloznavstvo i Obrobka Metaliv* (Metallurgy and Treatment of Metals) 4 (2004) 16-20 (in Ukrainian).

[9] R. Pucci, G. Piccito (Eds.), *Molecular Systems under High Pressure*, Elsevier, Amsterdam, 1991, pp. 139-156.

[10] E. Fromm, E. Gebhardt (Eds.), *Gase und Kohlenstoff in Metallen* (Gases and Carbon in Metals), Springer-Verlag, Berlin-Heidelberg, 1976 (in German).