MULTICOMPONENT METAL ALLOYS TESTED FOR HYDROGEN STORAGE

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Abstract

Hydrogen has a strong potential for use as an alternative fuel provided that it can be stored in a safe and efficient way. One possibility is to store it as a solid hydride using suitable metals or alloys. Metal hydrides have been widely studied as storage materials but most alloys are unable to fulfil the requirements of a competitive hydrogen storage unit that can be exploited in practical applications. Recently in work by Sahlberg et al. was studied absorption capacity of hydrogen in the TiVZrNbHf BCC high-entropy alloy. They report the alloy absorbs and stores extremely large amounts of hydrogen approaching hydrogen to metal ratio H/M to 2.5. This enormous stored capacity was attributed to internal lattice stresses, promoting hydrogen to occupy both tetrahedral and also octahedral interstitial positions. Such a full occupation is unique and has never been observed in transition metal hydrides before. In this article, we prepared similar TiVZrNbX alloys (X = Cr, Ni, Fe, Ag and Ta) and examined their ability to store hydrogen (in our case deuterium). The effect of lattice strains, promoting transport and storage of hydrogen (deuterium) was examined. Our comparison provides evidence that solid solutions do not have the highest storage capacity, but rather alloys composed of intermetallic compounds.

Keywords: Hydrogen storage, metalhydride, high-entropy alloy, absorbtion capacity, X-ray diffraction

1. INTRODUCTION

Hydrogen is seen as a critical component of greening Europe's energy market and becoming the first carbon-neutral continent by 2050. The bet on hydrogen seems to be logical since one kilogram of hydrogen (H_2: 33.3 kWh/kg) has approximately three times the energy content compared to conventional fuels such as petrol: 12.9 kWh/kg, compressed natural gas (CNG): 15kWh/kg and liquefied petroleum gas (LPG): 14kWh/kg, however by comparing their volume energy capacity, the ratios are opposite (H_2 - 1.6 kWh/l, petrol: 9.5 kWh/l, CNG: 2.5 kWh/l and LPG: 7.3 kWh/l) [1]. Therefore, for efficient use of hydrogen, it is critical to increase its density by compression. Today, several types of hydrogen compression are industrially applied e.g. gas compression, liquefaction of hydrogen, storage of hydrogen molecules by adsorption and hydrogen storage in metals by absorption. Among them, the most effective way to compress hydrogen is to store it in a metal lattice where a stored amount of hydrogen can significantly exceed its liquid phase, e.g. Mg_2FeH_6 shows the highest known volumetric hydrogen density of 150 kg/m^3, which is more than double that of liquid hydrogen [2].

A "Superior" step forward in this respect represents publication of M. Sahlberg, et al. entitled "Superior hydrogen storage in high entropy alloys" [3] where the authors studied the hydrogenation of the high-entropy

solid solution alloy TiVZrNbHf of bcc structure and observed, that extremely large amounts of hydrogen (2.7 wt.% of H) can be absorbed in it. The amount of hydrogen corresponds to H/M ratio of 2.5 and becomes a world record in terms of volumetric energy density 219 kg H/m^3 exceeding by far the requested 40 kg H/m^3. The authors explain these phenomena by lattice strain favouring to absorb hydrogen in both tetrahedral and octahedral interstitial sites.

In our work, we focus on deuterium absorption properties of similar TiVZrNb-X alloys, in which we replaced the most expensive and heaviest element Hf by X = Cr, Ni, Fe, Ag and Ta. The effect of lattice strains in solid solution, promoting transport and storage of hydrogen (deuterium), was examined.

2.   EXPERIMENTAL PROCEDURE

2.1.   Samples preparation and their pre-analysis

Equimolar TiVZrNb-X, (X = Cr, Ni, Fe, Ag and Ta) samples were synthesized by arc-melting in stoichiometric amounts of Ti (99.99%), V (99. 5%), Zr (99.5%), Nb (99.8%), Cr (99.99%), Ni (99.98%), Fe (99.99%), Ag (99.9) and Ta (99.9%). To ensure homogeneity, the sample were re-melted five times and turned over between each melting step. Oxygen contamination was minimized by filling the furnace two times by high purity Ar and by melting a Ti getter for 2 minutes prior to each cycle of alloy melting.

The microstructure and chemical composition was studied using the Jeol JSM 7000F scanning electron microscope (SEM) equipped with a secondary electron (SE) detector, a backscatter electron (BSE) detector and an energy dispersive X-ray spectrometer (EDS).

The density of the prepared alloys was measured at room temperature applying Archimedes principle using an analytical balance Kern ABT 120-4M with a special density determination kit ABT-A01. Measurements were performed in pure ethyl alcohol of density 0.788 g/cm^3.

2.2.   Deuterium storage measurements

Deuterium storage capacity of the alloys was determined by gravimetric method. High pressure absorption uptakes of 99.9% pure deuterium were measured by magnetic suspension balance (Rubotherm, Germany) [4] which can be operated up to 50 MPa. The temperature control during measurement was done externally by a temperature control unit consisting of a heating device controlled by using a thermostat Eurotherm 2408.

For the experiment the alloys in bulk form were powdered by vibration mill and sieved to particle size $< 45\mu m$. In the experiment, a stainless steel sample holder was filled by 1g of powder sample and the balance was evacuated for 0.5 h at 298 K and 0.3 Pa until constant mass was achieved. For measuring the absorption capacity, the gas was dosed into the balance chamber to 0.1 MPa and equilibrium was achieved in 30 min. The temperature was increased to 393 K (heating rate 5 K min^{-1}) with final accuracy of ±1 K for each measurement. After temperature reached equilibrium at 393 K the reaction chamber was filled by deuterium gas to 5 MPa and absorption uptake was measured for 24 h.

2.3.   X-ray diffraction measurements

The hard XRD experiment was performed in transmission (Debye-Scherrer) geometry at the P21.1 undulator beamline located at the electron storage ring PETRA III (storing electron of energy: 6.0 GeV and current: 100 mA, operated in top-up mode) at DESY (Hamburg, Germany). The following setup was applied: transmission (Debye-Scherrer) geometry; monochromatized high energy X-ray beam of photon energy ~ 103.06 keV (λ=0.1203 Å) to obtain high quality diffraction patterns up to the magnitude of the scattering vector $Qmax = 4\pi sin(\theta)/\lambda = 8$ Å^{-1}; beam cross-section on the sample was ~ 0.5 mm × 0.5 mm; fast 2D image plate detector Perkin Elmer XRD 1621 (2048 pixels × 2048 pixels, size of a pixel: 200 μm × 200 μm) to record diffracted X-rays [5].

The recorded 2D XRD patterns were then radially integrated to *I(Q)* space from which the X-ray total structure factors *S(Q)* was obtained, based on the Faber-Ziman approach [6]. The total pair distribution function *G(r)* was calculated from the total structure factor *S(Q)* by the following equation:

$$G(r) = \frac{2}{\pi} \int_{Q_{min}}^{Q_{max}} Q(S(Q) - 1) \sin(Q\,r)\, dQ \qquad (1)$$

3.   RESULTS AND DISCUSSION

3.1.   High-entropy alloy (HEA) prediction

In the first step, we verify whether our assumed alloys TiVZrNb-X, (X = Cr, Ni, Fe, Ag and Ta) fall into the area of solid solutions stability (High-Entropic Alloys).

Conventionally, HEAs solid solution is defined as alloys comprised of 5 or more elements with concentrations between 5 and 35 atom percent forming simple phase solid solutions [7]. Zhang et al. [8] proposed the use of two parameters for the design of HEAs, namely, the atomic size difference δ and the mixing enthalpy ΔH_{mix} [10]:

$$\delta = \sqrt{\sum_{i=1}^{n} c_i \left(1 - \frac{r_i}{\sum_{j=1}^{n} c_j r_j}\right)^2} \qquad (2)$$

where c_i and r_i denote the atomic fraction and atomic radius of the ith element, respectively,

$$\Delta H_{mix} = \sum_{i=1, i \neq j}^{n} \Omega_{ij} c_i c_j = \sum_{i=1, i \neq j}^{n} 4 \Delta H_{ij}^{mix} c_i c_j \qquad (3)$$

where ΔH_{ij}^{mix} is the enthalpy of mixing of the binary liquid between the ith and jth elements at an equiatomic composition.

HEAs generally tend to form single-phase solid solutions in the case of low mixing enthalpy and atomic size difference. In general, the formation of a single-phase solid solution corresponds to the region0 $\Delta H_{mix} > -12$ kJ/mol and $\delta \leq 6.6\%$.
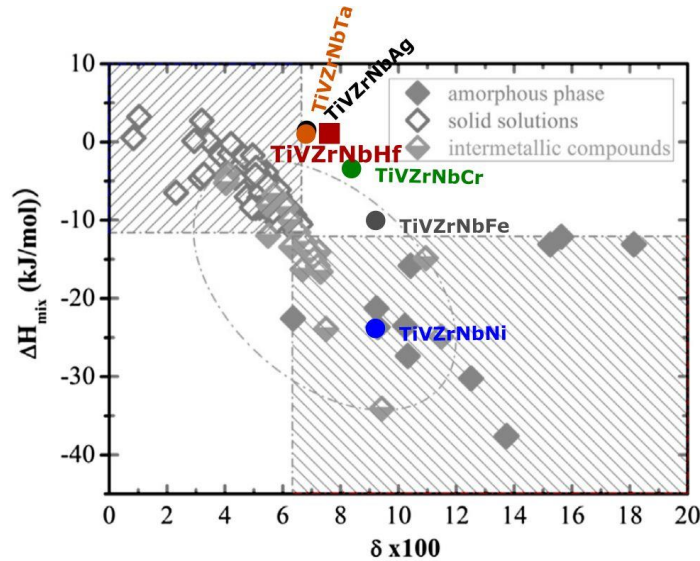

Figure 1 The δ-ΔH_{mix} plot delineating the phase selection in HEAs. The dashed regions highlight the individual region to form simple solid solutions, and amorphous phases. Intermetallic region is within the dotted ellipse. Position of the TiVZrNb-X, X = Cr, Ni, Fe, Ag and Ta alloys are highlighted in colour. The TiVZrNbHf alloy published in [5] was also added to this plot for comparison (red)

Figure 1 taken from [9] shows in the upper left corner a stability region of multicomponent HEA solid solutions. The TiVZrNb-X, X = Cr, Ni, Fe, Ag and Ta alloys are shown in the plot in colour together with the TiVZrNbHf alloy (in red) previously published in [3]. From this graphical comparison, it is clear that none of the alloys falls within the stability range of HEA solid solutions. The closest are the TiVZrNbTa and TiVZrNbAg alloys, where in fact simple cubic phases have been identified, see **Table 1**.

Table 1 Chemical and phase composition, deuterium absorbtion/desorbtion properties and calculated parameters ΔH_{mix}, δ of the TiVZrNb-X, X = Cr, Ni, Fe, Ag and Ta alloys. IM stands for intermetallic compounds and SS for solid solution

| Sample	EDX composition	Phase	Density [g/cm^3]	Absorbed deuterium [wt. %]	Absorbed D/M	Deuterium desorbed up to 873K [wt. %]	ΔH_{mix} [kJ/mol]	δ x 100 [%]
TiVZrNbCr	$Ti_{17}V_{19}Zr_{19}Nb_{22}Cr_{23}$	IM	6.59	3.28	1.1	2.28	-4.99	8.8
TiVZrNbNi	$Ti_{20}V_{20}Zr_{22}Nb_{16}Ni_{22}$	IM	6.93	2.94	1	-	-23.37	9.1
TiVZrNbFe	$Ti_{19}V_{19}Zr_{20}Nb_{21}Fe_{21}$	IM	6.79	2.94	1	-	-10.92	8.9
TiVZrNbAg	$Ti_{20}V_{20}Zr_{21}Nb_{19}Ag_{20}$	SS	7.18	2.44	0.95	-	+1.27	6.4
TiVZrNbTa	$Ti_{20}V_{20}Zr_{19}Nb_{22}Ta_{19}$	2xSS	9.03	2.07	0.94	-	+0.35	6.3

3.2. Deuterium absorption
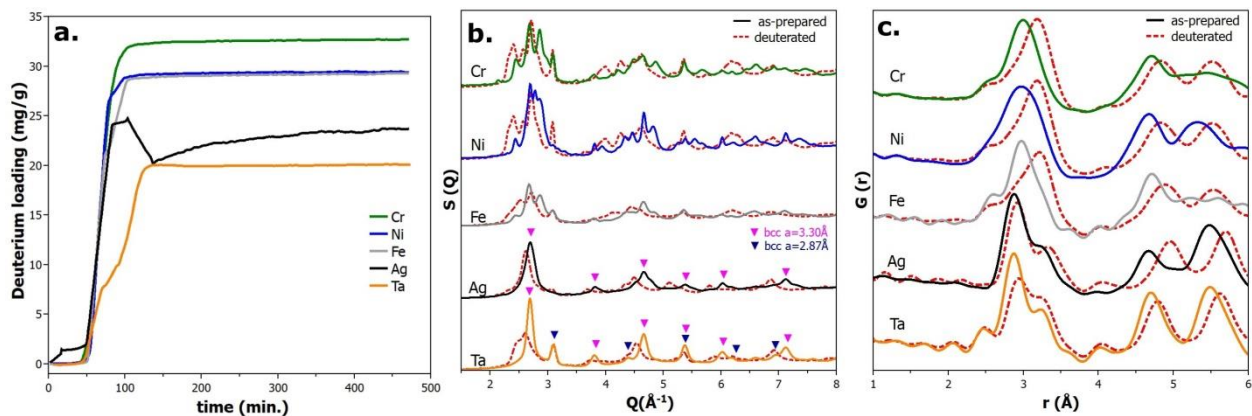
Figure 2 a. deuterium absorption uptakes of the TiVZrNb-X, X = Cr, Ni, Fe, Ag and Ta alloys, **b**. deuterium induced phase transformations documented by change of diffraction patterns, **c**. corresponding total pair distribution function G(r)

Figure 2a shows deuterium absorption uptakes of the TiVZrNb-X, X = Cr, Ni, Fe, Ag and Ta alloys under deuterium gas pressure of 5 MPa and temperature 393 K. From the comparison it is clear that the highest deuterium uptake has the TiVZrNbCr intermetallic alloy 3.28 wt.% corresponding to deuterium to metal ratio D/M 1.1. The lowest uptakes, on the other hand, show the two HEA solid solutions 2.44 and 2.07 wt.% corresponding to D/M ~ 0.95. The X-ray diffraction patterns of the alloys in as-prepared (full line) and deuterated state (red dashed line) are shown in **Figure 2b**. The sample containing Ag has a single body centred cubic (bcc) structure; the one with Ta is composed of two bcc phases different just by lattice constants, while the other samples show multiple intermetallic compounds composition. The total pair distribution functions, **Figure 2c**, clearly demonstrate influence of deuterium on the first metallic atomic neighbours. In all

cases, the presence of deuterium increases distances between the metallic atoms. In the case of Cr, Ni and Fe the increase is significant - by more than 0.2Å, while for the HEA it is less pronounced ~ 0.1Å.

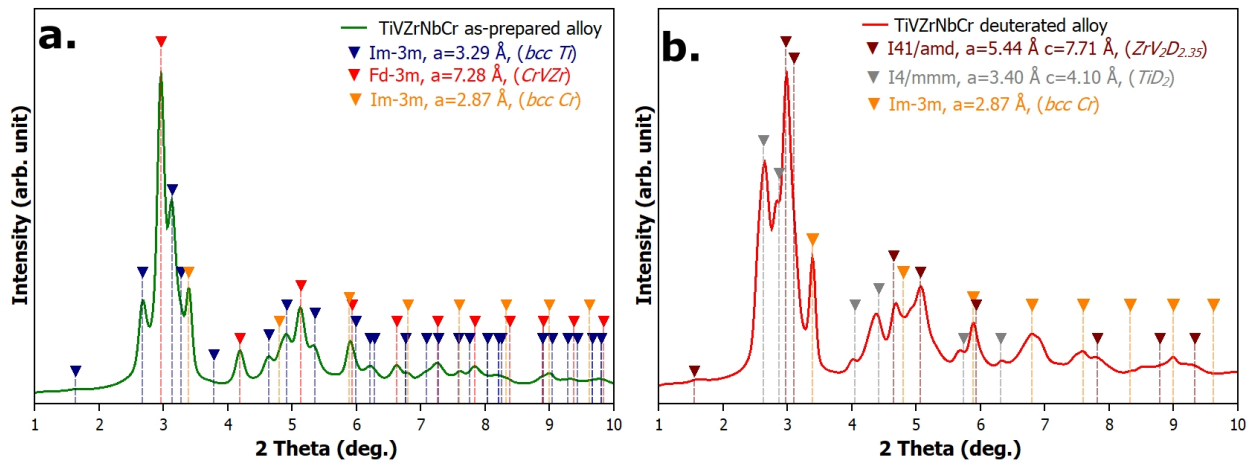### 3.3. Phase composition of the TiVZrNbCr alloy

Figure 3 a. XRD pattern of the TiVZrNbCr alloy with marked Bragg's peaks of the three identified cubic phases, **b.** XRD pattern of the alloy after deuteration with marked peaks of corresponding phases

The XRD pattern of the TiVZrNbCr alloy in the as-prepared state is shown in **Figure 3a.** The alloy consists of three cubic phases, whose space groups and lattice parameters are shown in the figure. This confirms the alloy has multiphase intermetallic compound composition. The alloy after deuterium saturation shows a completely different XRD pattern (for comparison see **Figure 3b**, top patterns), the peaks of which can be assigned to two known hydride phases ($ZrV_2D_{2.35}$ COD ID: 1531582 [7], TiD_2 COD ID:2310984 [8]) and one cubic Cr-like bcc phase.

4. CONCLUSIONS

In this article we report our preparation, and measurement of deuterium storage in the TiVZrNb-X, (X = Cr, Ni, Fe, Ag and Ta) alloys.

- the alloy containing Ag consist of single bcc phase high-entropy solid solution, the alloy with Ta is composed of 2 bcc solid solutions, while the others form multiple intermetallic phases,

- the highest deuterium storage capacity was measured for the TiVZrNbCr alloy containing 3.25 wt.% of deuterium which corresponds to D/M ratio 1.1. On the other hand the lowest capacity is had by the SS alloys TiVZrNbAg and TiVZrNbTa,

- the TiVZrNbCr alloy in the as-prepared state consists of three cubic phases and by deuteration its phase composition changed to two tetragonal hydrides and one cubic, likely metallic phase,

The results of our analysis suggest that these alloys are not suitable for hydrogen storage due to the relatively low absorption capacity D/M ~1 and relatively high hysteresis of deuterium remaining in the alloy.

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