



DSC Study of $\text{Zr}_{18}\text{Ti}_{23}\text{V}_{18}\text{Nb}_{25}\text{Ta}_{16}$ Hydrogenated Alloy

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Abstract

In this work, the behavior of absorbed hydrogen in the high entropy alloy ZrTiVNbTa is investigated. The latter was obtained by remelting the corresponding pure metals in an argon-arc furnace in an environment of pure argon (99.9999). SEM, EDS and XRD analyzes were performed on the thus obtained alloy. Differential scanning calorimetry shows that the amount of absorbed hydrogen is retained for days and the hydrogen leaves the investigated alloy in the process of the DSC analysis, being released in at least two well-defined peaks. From the kinetic measurements, the activation energies of the corresponding desorbed hydrogen peaks were determined.

Keywords: high entropy alloy, hydrogen, DSC analysis

1. Introduction

Recently, new types of alloys, known as (HEA) multicomponent alloys, have expanded the number of systems and compositions for applications such as hydrogen storage. Solid-state hydrogen storage using metal hydrides is a relatively safer option given the lower risk of leakage and potential explosions [1,2]. In addition, metal hydrides offer high volumetric efficiencies at low operating pressures [3–5]. Unfortunately, most of the known conventional metal hydrides have limitations such as low gravimetric storage, slow absorption/desorption kinetics, or undesirable thermodynamic properties limiting operating temperature and/or pressure conditions [4,6]. These alloys contain at least three elements with significant atomic fractions in their composition and often form single-phase solid solutions with atoms randomly organized in their crystal structure [7]. Although these new types of alloys have been extensively analyzed in terms of mechanical behavior, evaluation of the hydrogen-storage properties of multicomponent alloys is relatively scarce. Hydrogen storage in HEAs has been proposed as an application, since many of the elements commonly found in alloys [8] form binary metal hydrides [9]. In general, the development of efficient hydrogen storage systems is considered crucial for the widespread use of hydrogen as an energy carrier. Metal hydrides are attractive materials for such applications because they can achieve higher bulk hydrogen densities than even liquid H_2 [10].

The aim of the present work is to synthesize a $\text{Zr}_{18}\text{Ti}_{23}\text{V}_{18}\text{Nb}_{25}\text{Ta}_{16}$ alloy and to investigate the behavior of hydrogen in it.

2. Materials and Methods

Alloy ingots of nominal composition Zr-Ti-V-Nb-Ta are prepared by vacuum argon-arc melting in a water-cooled copper crucible under an argon atmosphere. The furnace is shown in fig. 1 below and is capable of synthesizing four ingots at one furnace charge, each ingot ~8g.

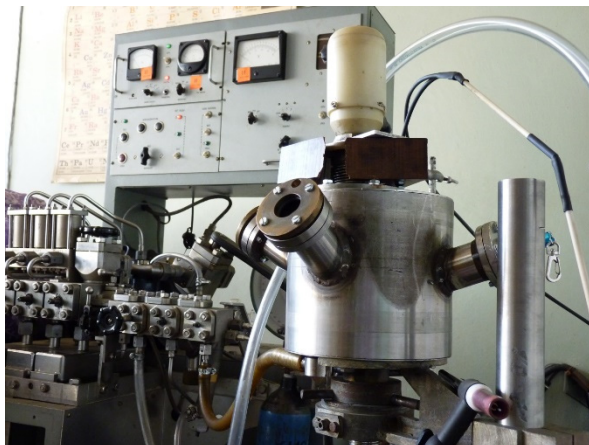


Fig. 1 General view of a laboratory argon arc furnace

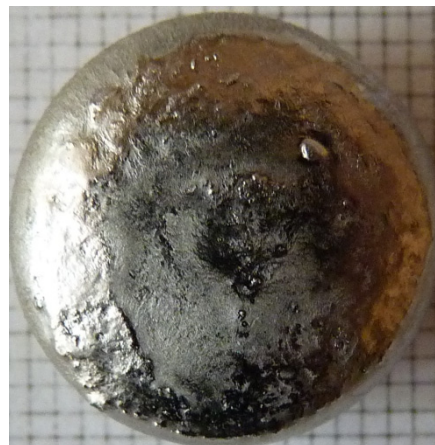


Fig. 2 Photograph of an ingot of **Zr₁₈Ti₂₃V₁₈Nb₂₅ alloy - 8 g.**

The rods and lumps of the pure metals (Zr- 99.8 wt.%, Ti - 99.99 wt.%, V - 99.7 wt.%, Nb- 99.8 wt.% and Ta- 99.95 wt.%) were weighed, for to obtain the desired composition presented in Table 1 for ~ .8 grams of ingot.

Table 1. Chemical composition of investigate alloy in gr.

Zr, gr	Ti, gr	V, gr	Nb, gr	Ta, gr
1.5618	0.8258	0.8712	1.6448	3.3181

To ensure the stability of the electric arc between the W-Th electrode and the metal workpiece, the furnace chamber was evacuated to a pressure of 5×10^{-3} mbar, followed by argon purging for 20 min. In order to achieve a homogeneous distribution of the elements, each ingot of the alloy is remelted several times. In the manner thus described two ingots with approximately the same composition were obtained. The resulting ingots have a lenticular shape, a photograph of such an ingot is shown in Fig. 2. These alloys will serve as starting points for studying their behavior in a hydrogen environment. The resulting specimens were broken into small pieces and loaded for hydrogenation in a system consisting of an electric resistance canthal furnace and a vacuum-tight stainless steel chamber equipped with vacuum bellows valves, at temperatures up to 530°C for 120 minutes. shown in the figure 3 below. In the hydrogenation process, a portion of the test bodies are further crushed. For TG/DSC measurements, only a small fraction is used, after sieving with a 0.10 laboratory sieve. The temperature regime of the hydrogenation process is shown in fig. 4. Hydrogenation takes place at a hydrogen pressure of 1.5 atm, set at room temperature.

The X-ray structural analysis was carried out with a powder X-ray diffractometer Bruker D8 Advance with CuK α radiation (Ni filter) and LynxEye registration in a solid-state position sensitive detector. Qualitative phase analysis was conducted using the International Center for Diffraction Data (ICDD) PDF-2 (2009) database using the DiffracPlusEVA software package.

X-ray microanalysis was performed using a Carl Zeiss EVO 10 scanning electron microscope with a Bruker microanalyzer. The chemical composition of the phases was determined by ten-fold EDS analyzes of each of the phases under the same conditions, performed with a Bruker spectrum analyzer with an energy dispersive silicon drift detector XFlash (SSD), resolution 126 eV (MnK α).



Fig. 3 General view of a laboratory chamber for hydrogenation

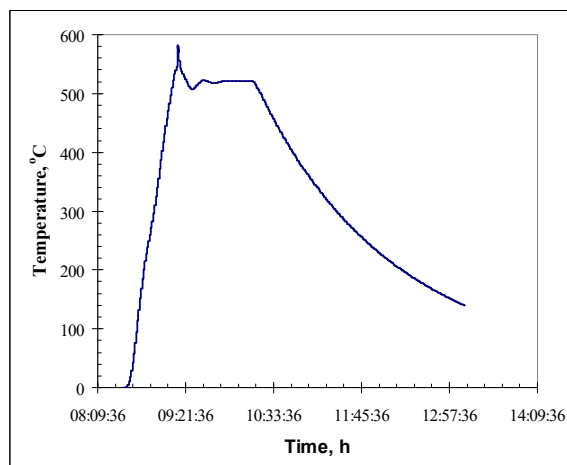


Fig.4 Temperature mode of hydrogenation

The phase changes during heating of the test bodies from the investigated alloys were followed by F3 Jupiter STA / TG / DTA / DSC (NETZSCH, Selb, Germany), with a heating rate (from 20 to 50) K/min in an atmosphere of argon (6N), to a maximum temperature of 1023 K, and data processing was performed using NETZSCH Proteus Analysis software (v. 5.2.1/2011, Netzsch, Selb, Germany). Instrument calibration is performed before each.

3. Results and Discussion

Figure 5 is an XRD phase analysis of the resulting $\text{Zr}_{18}\text{Ti}_{23}\text{V}_{18}\text{Nb}_{25}\text{Ta}_{16}$ alloy crystallized in the water-cooled crucible of the arc furnace. The structure of this alloy consists of a solid solution with a **bcc** lattice $a = 3.3\text{\AA}$. The crystallite size is determined according to the Scherrer equation and is $\sim 18\text{ nm}$.

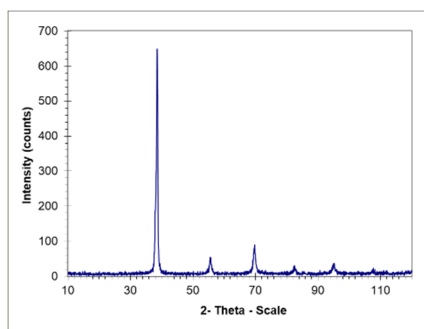
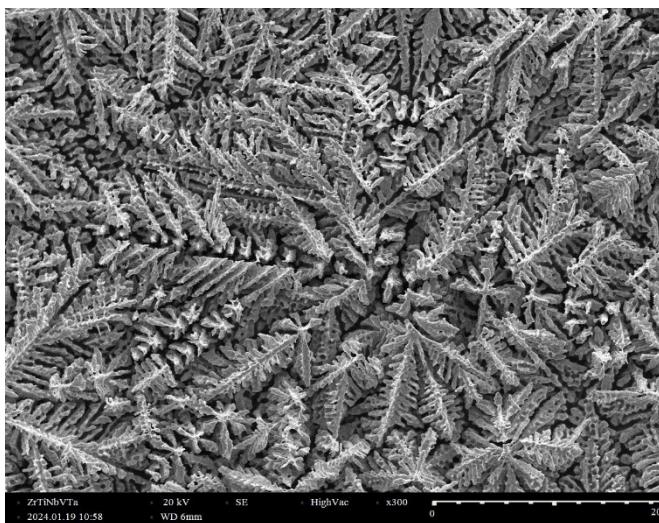


Fig. 5 XRD phase analysis of the obtained crystal alloy $\text{Zr}_{18}\text{Ti}_{23}\text{V}_{18}\text{Nb}_{25}$

Figure 6 shows SEM (dendritic structure) and EDS analyzes of the alloy. The results of the EDS analysis are average values taken from three different locations on the alloy.



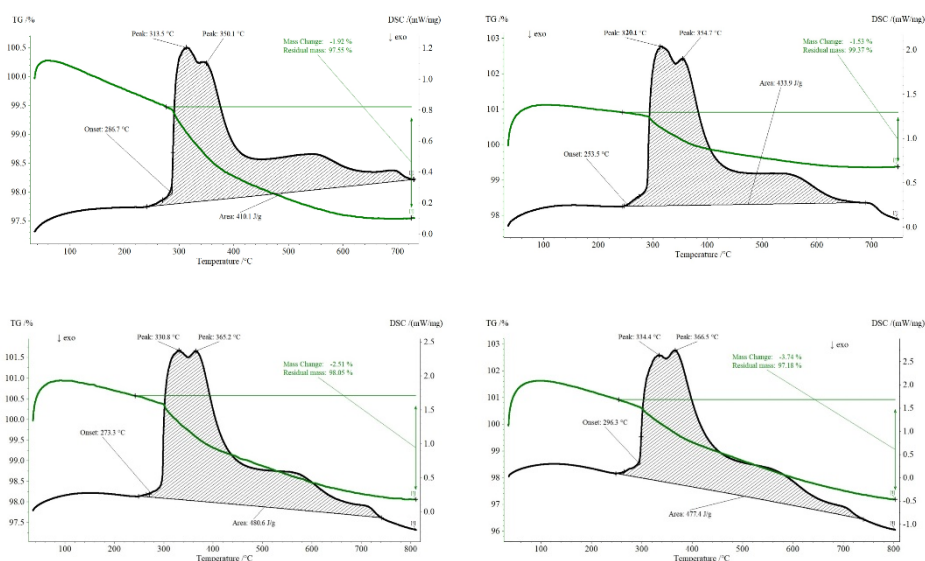
3670							
Element	At. No.	Netto	Mass [%]	Mass Norm. [%]	Atom [%]	abs. error [% (1 sigma)]	rel. error [% (1 sigma)]
Ta	73	2313	31.99	34.65	17.28	1.17	3.67
Nb	41	2345	23.90	25.88	25.14	1.11	4.63
Zr	40	1461	16.11	17.44	17.25	0.84	5.24
Ti	22	1564	10.74	11.63	21.91	0.45	4.22
V	23	1496	9.60	10.40	18.42	0.41	4.24
		Sum	92.33	100.00	100.00		
3671							
Element	At. No.	Netto	Mass [%]	Mass Norm. [%]	Atom [%]	abs. error [% (1 sigma)]	rel. error [% (1 sigma)]
Ta	73	2085	25.89	28.94	13.74	0.98	3.67
Nb	41	2570	23.34	26.09	24.13	1.07	4.63
Zr	40	1814	18.21	20.35	19.17	0.91	5.24
Ti	22	2084	11.96	13.36	23.98	0.47	3.67
V	23	1888	10.07	11.26	18.99	0.40	4.22
		Sum	89.48	100.00	100.00		
3672							
Element	At. No.	Netto	Mass [%]	Mass Norm. [%]	Atom [%]	abs. error [% (1 sigma)]	rel. error [% (1 sigma)]
Ta	73	2243	31.41	32.49	15.89	1.16	3.67
Nb	41	2412	24.72	25.57	24.35	1.14	4.63
Zr	40	1610	18.28	18.91	18.34	0.94	5.24
Ti	22	1774	12.36	12.78	23.62	0.50	4.07
V	23	1625	9.91	10.25	17.81	0.41	4.15
		Sum	96.69	100.00	100.00		

Fig. 6 SEM and EDS analyzes of $Zr_{18}Ti_{23}V_{18}Nb_{25}Ta_{16}$ alloy The EDS analysis results are average values taken from three different locations on the alloys

As can be seen from the EDS analysis, the obtained blanks are homogeneous and close in chemical composition to the assumed one.

4. DSC Analysis of $Zr_{18}Ti_{23}V_{18}Nb_{25}Ta_{16}$ Hydrogenated Alloy

Fig.7 shows four representative TG/DSC measurements carried out during hydrogen desorption from the investigated hydrogenated alloys. Hydrogen leaves the investigated alloy during the DSC analysis, being released in at least two well-defined peaks. The analyzes were performed in an argon atmosphere, up to 800°C for each investigated heating rate (20, 30, 40, 50 K/min).



Фиг.7 TG/DSC analysis of hydrogenated alloy $Zr_{18}Ti_{23}V_{18}Nb_{25}Ta_{16}$, at different heating rates; 20, 30, 40, 50 K/ min

The activation energy corresponding to the hydrogen desorption process under continuous heating can be estimated by the Kissinger equation [11]: $\ln(q/T^2) = -E/RT + C$ where q is the heating rate, R is the gas constant (8.314 J/mol), i.e. the characteristic temperature (T_p) at a certain heating rate, E is the apparent energy of activation for the relevant process. E_p is the peak desorption energy. A Kissinger plot for $Zr_{18}Ti_{23}V_{18}Nb_{25}Ta_{16}$ alloy is shown in Fig.8, from which the values for the activation energies for the corresponding peak are calculated: $E_{Ipik}=110.17\text{ kJ/mol}$, $R^2=0.9646$; $E_{IIPik}=147.88\text{ kJ/mol}$, $R^2=0.9244$.

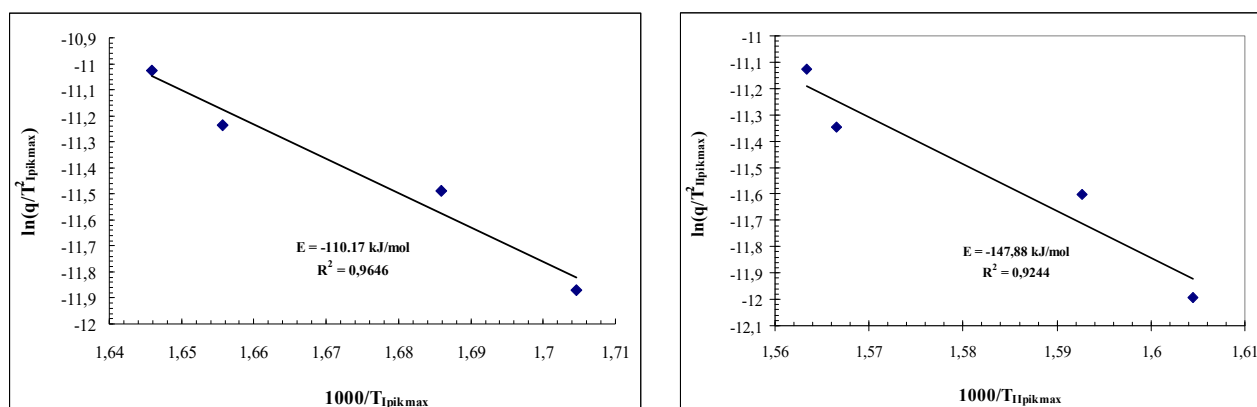


Fig.8 a,b, Kissinger plot for: a) T_{Ipik} ; b) T_{pIIPik}

5. Conclusion

A high entropy alloy $Zr_{18}Ti_{23}V_{18}Nb_{25}Ta_{16}$ was obtained, which was hydrogenated at 520oC and 1.5 atm of hydrogen.

From the TG/DSC performed it is shown that:

- the amount of absorbed hydrogen does not decrease;
- and data on the activation energy of hydrogen desorption were obtained.

Acknowledgements

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