Effects of the Chromium Content in \((\text{TiVNb})_{100-x}\text{Cr}_x\) Body-Centered Cubic High Entropy Alloys Designed for Hydrogen Storage Applications

Renato Belli Strozi 1,2,*, Daniel Rodrigo Leiva 3, Guilherme Zepon 3, Walter José Botta 3 and Jacques Huot 1

Abstract: In this paper, we report an investigation of adding a non-hydride forming element in the multicomponent Ti-V-Nb-M system. By the Calculation of Phase Diagrams approach (CALPHAD), the thermodynamic phase stability of the TiVNBT (T = Cr, Mn, Fe, Co, and Ni) was investigated, and Cr was selected as the fourth alloying element due its fourth tendency to stabilize body-centered cubic solid solutions (BCC). The \((\text{TiVNb})_{100-x}\text{Cr}_x\) alloys (with \(x = 15, 25, \) and \(35\) at.% Cr) were synthesized by arc-melting. The structural characterization reveals that the three alloys were composed of a major BCC phase, which agrees with the thermodynamic calculations. The three alloys absorb hydrogen at room temperature without any activation treatment, achieving a hydrogen uptake of about \(H/M = 2\). The Pressure-Composition-Isotherms curves (PCI) has shown that increasing the Cr amount increases the equilibrium pressures, indicating that tunable H storage properties can be achieved by controlling the alloys’ Cr content.

Keywords: high entropy alloy; CALPHAD; BCC high entropy alloy; metal hydride; hydrogen storage; thermodynamics

1. Introduction

Currently, intensive research efforts are being made to develop renewable and non-polluting energies. In this scheme, hydrogen as an energy vector can play an important role in utilizing renewable energies. This implies that a suitable way to store hydrogen should be available. Conventional ways of storing hydrogen, such as in liquid and gaseous form, have some limitations in terms of operating temperature and high pressure. Features such as high volumetric capacity, mild temperature of operation, and low hydrogen pressure make metal hydrides attractive compared to the traditional hydrogen storage methods [1]. Metal hydrides could be used in an extensive range of applications such as off-grid renewable energy systems, fuel-cell submarines, and heavy-duty utility vehicles [2]. Additionally, hydrogen compression technology [3], electrode materials in Ni/MH rechargeable batteries [4], preparation of metal powders by a hydrogenation-dehydrogenation reaction [5] and thermal energy storage [6] are good examples of metal hydrides applications [7]. Selecting a proper alloy is crucial to control the hydride properties such as heat of reaction, kinetics, and hydrogen storage capacity.

Recently a new class of materials has attracted attention for hydrogen storage applications: the multi-principal element alloys (MPEAs) [8–11]. A formal description of the MPEAs was given by Cantor and Yeh in 2004 [12,13]. In these alloys, increasing the number of principal elements increases the configurational entropy of mixing. This can
create a favorable state to stabilize the disordered or partially ordered solid solution at high temperatures [13,14]. Thus, the MPEAs are often called high entropy alloys (HEAs).

One of the earliest investigations of HEAs-based metal hydrides reported the synthesis of several alloys of the CoFeMnTiVZr system, which crystallize in C14-type Laves phase (MgZn2 type, space group P63/mmc) [15]. These samples absorb hydrogen at room temperature, where the maximum capacity achieved was about 1.7 wt.% for the CoFeMnTiVZr2.3 alloy. According to the authors, the hydrogen capacity depends on the affinity between the alloy elements and hydrogen, whereas the sample containing more Zr can achieve higher capacity. In another work, Young et al. successfully synthesized the Zr21.5Ti12V10Cr7.5Mn6.1Co8.1Ni32.2Sn0.3Al0.4 alloy with a main C14 Laves-type phase and the Zr25Ti6.5V3.9Mn22.2Fe3.8Ni38La0.3 alloy, which crystallizes in C15 Laves phase (MgCu2 type, space group Fd-3m) [16]. Reversible capacity at 30 °C was found to be 1.32 wt.% for the C14-predominant alloy and 1.44 wt.% for the C15 alloy. Edalati et al. synthesized the equiatomic alloy TiZrCrFeMnNi HEA by arc melting [17]. They found that the alloy crystallizes in a main C14 phase with minor Ti and Ni-rich precipitates. The reversible gravimetric capacity at room temperature was 1.7 wt.%, representing a hydrogen-to-metal ratio (H/M) equal to one.

The BCC-HEAs have also been studied for hydrogen storage applications [18–21]. Zlotea et al. synthesized by arc melting the composition TiZrNbHfTa and obtained a pure BCC alloy [22]. In situ synchrotron X-ray diffraction (XRD) under hydrogen pressure showed a two-stage hydrogen absorption reaction. First, a body-centered tetragonal monohydride (BCT) was formed, followed by a second step forming a CaF2-type face-centered cubic structure (FCC) dihydride. The hydrogen sorption properties of BCC-HEAs are strongly affected by the differences in chemical composition [23]. For example, Nygard et al. synthesized by arc-melting some BCC single-phase HEAs [24]. The alloys containing only hydride-forming elements (e.g., TiVNbHf, TiVNbZr and TiVNbTa) reached a capacity of about H/M = 2. On the other hand, the alloys containing non-hydride formers elements, namely TiVCrMo, TiVNbCrMo and TiVNbMo, presented a reduced maximum capacity. In another work, Silva et al. investigated the (TiVNb)85Cr15, (TiVNb)95.3Co4.7 and (TiVNb)96.2Ni3.8 HEAs [25]. These alloys were synthesized by arc-melting and crystallized as a single BCC solid solution. Both alloys absorbed hydrogen at room temperature, undergoing the BCC to FCC phase transformation with hydrogen uptake of about H/M = 2. These results point out the importance of the balance between hydride-forming and non-hydride-forming alloying elements to control the H-sorption properties of BCC-HEAs.

In this paper, the effects on the hydrogen storage properties of adding a non-hydride forming alloying element in the Ti-V-Nb-Me system are reported. The element Me is the non-hydride forming candidate, namely Cr, Mn, Fe, Co and, Ni. Firstly, the CALPHAD method was employed to screen the non-hydride forming candidate and Cr was selected due to the higher tendency to form a BCC structure. Also, Cr could segregate at the surface and protect against oxidation without noticeably reducing the hydrogen capacity. Three alloys were investigated: (TiVNb)85Cr15, (TiVNb)75Cr25 and (TiVNb)65Cr35. The effect of chromium content on the structure and hydrogen storage properties of these alloys are compared.

2. Materials and Methods

CALPHAD simulations were performed using the Thermo-Calc® software (TCHEA3 database). The alloys were synthesized by arc melting under an inert argon atmosphere, starting from pure elements purchased from Alfa-Aesar: Ti (99.95%), V (99.7%), Cr (99%) and Nb (99.8%). To ensure the composition homogeneity, the samples were turned over and remelted five times. Scanning electron microscopy (SEM) was carried out in a FEI-Inspect S50 with an electron backscattered diffraction (EBSD) detector and an energy-dispersive spectroscopy (EDS) detector, both from EDAX®. For the EDS measurements, a compositional average was estimated by collecting at least five representative points for each microstructure contrast. For microstructural and compositional characterization by SEM,
the samples were mounted into epoxy resin, manually ground and polished with slurries of 1 and 0.5 µm alumina. Prior to hydrogenation, the ingots were crushed inside an argon-filled glovebox using a stainless-steel mortar and pestle. The crushed samples were characterized by X-ray diffraction using a Bragg–Brentano geometry diffractometer (Bruker D8 Focus) with Cu-Kα radiation. The hydrogen absorption kinetics measurements were performed at room temperature (~24 °C) and 2000 kPa of H₂ using a homemade Sievert-type apparatus. The PCI absorption/desorption isotherms were acquired at room temperature (~24 °C) using a Setaram volumetric apparatus model PCTPro (version E & E).

3. Results and Discussion

3.1. Alloy Design

Figure 1 displays the results from thermodynamic simulation carried out using the CALPHAD method, where the amount of equilibrium phases is plotted as a function of temperature. As seen in Figure 1a, the ternary TiVNb alloy prediction exhibits a large BCC single-phase field at high temperatures and no secondary phases appear even at low temperatures. The addition of different non-hydride forming elements in this ternary system was also investigated by CALPHAD. The equilibrium phases as a function of temperature were calculated for the equiatomic quaternary TiVNbT (T = Cr, Mn, Fe, Co, Ni) alloys (Figure 1b–f). One can see that only the TiVNbCr exhibits a large BCC single-phase field. The other alloys’ equilibrium phases are composed mainly of secondary BCC phases, differing from each other by the composition and ordered phases. Therefore, the quaternary (TiVNb)₉₀₋ₓCrₓ was taken as the object of this project.

Since the goal of this work was to obtain a BCC solid solution by varying the fraction of the non-hydride forming element, the equilibrium phases as a function of temperature were calculated for three compositions: (TiVNb)₈₅Cr₁₅, (TiVNb)₇₅Cr₂₅ and (TiVNb)₆₅Cr₃₅. As can be seen in Figure 2, when Cr is added, the formation of a C15-type Laves phase at low temperature is predicted. As the Cr content increases, the temperature of formation of C15-Laves phase increases. However, the thermodynamic calculations show that a large BCC single-phase field at high temperatures is present for the three alloys. Usually, HEAs that form solid solutions at high temperature tend to keep the same structure at low temperature. Therefore, we think that these alloys are excellent candidates for this investigation.

3.2. Structural Characterization

The microstructure of the arc-melted ingots as seen from backscattered electron microscopy is shown in Figure 3. EDS measurements were carried out to investigate the chemical composition of each area. The average composition of each region is shown in Table 1. The arc melted samples are composed of a dendritic matrix. The contrast difference between the dendrite core (bright gray) and boundaries (dark gay) reveals a composition gradient. The dendrite’s center tends to be niobium rich, and the dark gray regions are Cr and Ti-rich. The composition gradient comes from Ti and Cr segregation. As seen in Table 1, the bright and dark gray phases’ chemical compositions are relatively close. For the samples containing 15 and 25 at.% Cr, a black phase is also present. As seen in Table 1, this phase is a titanium-rich precipitate.

Figure 4 shows the XRD diffraction patterns of the as-cast alloys. All patterns show a main BCC phase and a minor FCC structure (Cu-type, Fm-3m). As shown in Table 2, increasing the Cr amount decreases the BCC lattice parameter. The average atomic radius for each composition was also calculated and displayed in Table 2. Considering the atomic radii of the elements (Ti = 1.46 Å, V = 1.32 Å, Nb = 1.43 Å and Cr = 1.25 Å), one can see that the variation of the lattice parameter is directly proportional to the variation of the average atomic radius and decreases by increasing the Cr content due to the smaller atomic radius of Cr compared to the other elements. The ratio of the lattice parameter over the average radius is not constant within the experimental error. This may indicate that other factors beside the average atomic radius play a role in the formation of BCC alloy.
Figure 1. Thermodynamic calculation of the TiVNbT (T = Cr, Mn, Fe, Co and Ni) system. Amount of equilibrium phases against temperature. TiVNb (a), TiVNbCr (b), TiVNbFe (c), TiVNbMn (d), TiVNbCo (e) and TiVNbNi (f). The phase indicated by Mu is a topologically close pack (TCP) phase; \( W_6Fe_7 \) prototype (space group R-3m).
Figure 2. CALPHAD thermodynamic calculation of (TiVNb)$_{100-x}$Cr$_x$ alloys. Amount of equilibrium phases as a function of temperature. $x = 15$ (a), $x = 25$ (b) and $x = 35$ at.% Cr (c).

Table 1. Average EDS measured composition. The error on the last significant digit is indicated in parentheses.

| Alloy Composition for Each Alloy in the As-Cast Condition (at.%) | Composition for Each Alloy in the As-Cast Condition (at.%) |
|---------------------------------------------------------------|---------------------------------------------------------------|
| Alloy | Contrast | Ti | V | Nb | Cr |
| (TiVNb)$_{85}$Cr$_{15}$ | Bright Gray | 28.0 (3) | 30.6 (3) | 27.6 (7) | 13.8 (5) |
| | Dark Gray | 29.5 (8) | 30.8 (1) | 21.7 (2) | 17.2 (9) |
| | Black | 88.5 (4) | 5.0 (7) | 5.9 (7) | 0.7 (4) |
| (TiVNb)$_{75}$Cr$_{25}$ | Bright Gray | 22.9 (3) | 29.0 (6) | 28.4 (6) | 23.2 (8) |
| | Dark Gray | 24.9 (4) | 27.8 (4) | 20.3 (6) | 27.0 (8) |
| | Black | 89.0 (2) | 4.1 (5) | 5.1 (1) | 1.7 (9) |
| (TiVNb)$_{65}$Cr$_{35}$ | Bright Gray | 22.8 (5) | 21.7 (4) | 22.0 (5) | 33.4 (3) |
| | Dark Gray | 25 (1) | 19.2 (8) | 20.1 (7) | 35.2 (4) |
Figure 3. Backscattered electron micrograph of as-cast alloys: (TiVNb)$_{85}$Cr$_{15}$ (a), (TiVNb)$_{75}$Cr$_{25}$ (b) and (TiVNb)$_{65}$Cr$_{35}$ (c).

Figure 4. Indexed XRD patterns for samples in as cast condition. Alloys’ compositions are indicated on the figure.
Table 2. Lattice parameter evaluated by XRD analysis for alloys with different Cr content in the as-cast condition. Nominal average atomic radius and ratio of the lattice parameter over the average radius.

| Alloy       | Lattice Parameter (Å) | Average Atomic Radius (Å) | Ratio     |
|-------------|-----------------------|---------------------------|-----------|
| (TiVNb)₈₅Cr₁₅ | 3.158 (1)             | 1.380                     | 2.2884 (7) |
| (TiVNb)₇₅Cr₂₅ | 3.122 (1)             | 1.365                     | 2.2872 (7) |
| (TiVNb)₆₅Cr₃₅ | 3.105 (6)             | 1.350                     | 2.300 (4)  |

The XRD patterns show the presence of a small secondary phase that could be indexed as FCC. The BCC phase is associated with the bright and dark gray regions seen in Figure 3. From Table 1 these two regions have close chemical compositions, indicating that the BCC phase is a solid solution with a range of composition. The minor FCC phase is associated with the black Ti-rich precipitates. This affirmation is supported by EBSD analysis of the (TiVNb)₇₅Cr₂₅ alloy. As shown in Figure 5, while the matrix is the BCC phase, the Ti-rich precipitates are the FCC phase.

The appearance of an FCC Ti-rich has not been reported in the Ti-V-Nb-Cr system [24,25]. The exact nature of the Ti-rich FCC phase is not determined. We tentatively indexed it with space group Fd-3m but a better understanding of this precipitation phenomenon demands further investigation, which is out of this study’s scope.

![Figure 5](image_url)

**Figure 5.** FCC Ti-rich precipitates embedded in the BCC matrix in (TiVNb)₇₅Cr₂₅ multi-principal element alloy. (a) Secondary electrons SEM image. The yellow rectangle indicates the EBSD acquisition area. (b) EBSD phase map. The red and green areas were indexed respectively as BCC and FCC phase structures.

3.3. Structural Characterization

Figure 6 shows the kinetic measurements of the first hydrogen absorption for the as-cast (TiVNb)₃₀₋ₓCrₓ alloys. Even under mild conditions, i.e., room temperature and 2000 kPa of H₂, the alloys absorb hydrogen at a fast rate with a short incubation time, achieving a hydrogen-to-metal ratio of approximately 2.
patterns were taken ‘post-mortem’ in air. There is then the likelihood that the sample desorbed after being taken out of the hydrogenation apparatus because the hydride is relatively unstable. To confirm this hypothesis, the Pressure-Composition Isotherms (PCI) at room temperature were measured.

Figure 6. Kinetic curves of the first hydrogen absorption of the (TiVNb)$_{100-x}$Cr$_x$ alloys. Experiments were performed at 24 °C and under 2000 kPa of H$_2$.

Figure 7 shows the XRD patterns after the first hydrogenation. The (TiVNb)$_{85}$Cr$_{15}$ and (TiVNb)$_{75}$Cr$_{25}$ patterns show structural changes due to the hydrogen uptake. They are indexed as a main FCC phase with small FCC peaks related to the Ti-rich precipitates. The main FCC phase is associated with the dihydride phase (CaF$_2$-type structure), the typical structure of the fully hydrogenated BCC phase [26,27]. A broadband was also observed around 40° that may be coming from a BCC fraction that was not hydrogenated. These patterns agree with the full hydrogenation (H/M ≈ 2) seen in Figure 6.

Figure 7. Indexed XRD patterns of (TiVNb)$_{85}$Cr$_{15}$, (TiVNb)$_{75}$Cr$_{25}$ and (TiVNb)$_{65}$Cr$_{35}$ alloys after the first hydrogen absorption.

The XRD pattern of the (TiVNb)$_{65}$Cr$_{35}$ alloy shows a BCC phase and the FCC (Ti-rich) phase. Compared to the as-cast condition, the BCC phase lattice parameter slightly increased to 3.188(1) Å. This translates to an increase of unit cell volume of 2.46 Å$^3$. From the Peisl relationship, in a metal hydride the unit cell volume varies from 2 to 2.9 Å$^3$ per hydrogen atom in the host lattice [28]. This translates to a H/M between 0.42 and 0.62, a value much smaller than the H/M ratio of 2 deduced from the capacity measured in
the first hydrogenation. The possible reason for this discrepancy is the fact that the X-ray patterns were taken 'post-mortem' in air. There is then the likelihood that the sample desorbed after being taken out of the hydrogenation apparatus because the hydride is relatively unstable. To confirm this hypothesis, the Pressure-Composition Isotherms (PCI) at room temperature were measured.

Figure 8 shows the PCI of the three compositions at 24 °C. As the samples were exposed to the air before PCI tests, prior to measurement, the samples were submitted to a dynamic vacuum for two hours at 450 °C. This removed any trace of moisture or other adsorbed gases. Upon hydrogenation, the (TiVNb)_{65}Cr_{15} alloy reached a hydrogen-to-metal ratio close to 1.9, which corresponds to a gravimetric capacity of about 3.0 wt.%. The PCI curve shows a low absorption equilibrium pressure (~1 kPa), while the desorption pressure was too low to be measured. The PCI curve of the (TiVNb)_{75}Cr_{25} alloy displayed two absorption plateaus. The first one is at very low pressure and corresponds to the monohydride while the second one is at around 20 kPa and is coming from the monohydride-dihydride transformation. The total capacity is H/M ≈ 1.7, which corresponds to a gravimetric capacity of 2.7 wt.%. Again, the desorption pressure was too low to be measured. The PCI curve of the TiVNb_{65}Cr_{35} alloy showed a maximum H/M capacity of 1.7 which corresponds to a gravimetric capacity of about 2.8 wt.%. This agrees with the measured capacity of the first hydrogenation. This composition also shows two plateaus on absorption but the one at low pressure is very short and the high-pressure plateau ranges from H/M ≈ 0.4 to 1.79. It seems that on absorption there is no clear boundary between the monohydride and the dihydride. However, such distinction seems to be present in desorption as we see a high plateau that reaches down to H/M = 0.8. The lower plateau is at a pressure too low to be measured by the apparatus. A diffraction pattern was recorded on the sample after the PCI isotherm. The pattern was identical to the one shown in Figure 7. The H/M estimated from this pattern was between 0.42 and 0.62. These values are smaller than the H/M of 0.8 registered on the PCI curve but the X-ray pattern is registered in air and some further desorption may have occurred. Therefore, we consider that the diffraction pattern agrees with the PCI results.

![Figure 8. PCI absorption/desorption isotherms carried out at 24 °C. The compositions are indicated in the figure.](image-url)

We see that increasing the Cr/(TiVNb) ratio had the effect of increasing the absorption plateau pressure. However, the desorption plateaus pressures are still too low for any practical applications. One important observation is that changing the Cr/(TiVNb) ratio
had an effect on the thermodynamics but only minimal change in the maximum capacities. Thus, further increasing the Cr/(TiVNb) ratio may lead to a hydride that could have practical reversibility while keeping good hydrogen capacity. However, the concern is that, because of the large hysteresis, the absorption will have to be performed at higher pressure than 1000 kPa. Nevertheless, investigation of a higher Cr/(TiVNb) ratio should be undertaken. Another path would be to modify the TiVNb composition. One more point that deserves special attention is the fast first hydrogenation at room temperature, which has a significant impact for practical applications. Usually, metal hydrides have sluggish first hydrogenation due to the presence of stable and dense surface oxides and hydroxides. Unfortunately, our experimental set-up did not have the means to measure oxygen content. As this is a crucial parameter, we intend to perform a dedicated experiment in the near future.

4. Conclusions

The thermodynamic phase stability of the TiVNbT (T = Cr, Mn, Fe, Co and Ni) alloys was investigated using the CALPHAD approach. The (TiVNb)\(_{100-x}\)Cr\(_x\) alloy system was selected, with \(x = 15, 25\) and 35 at. % CALPHAD predictions indicate single BCC alloys formation in this range of composition, which was confirmed experimentally. Increasing the Cr/(TiVNb) ratio leads to significant increases in the equilibrium plateau pressure of the (TiVNb)\(_{100-x}\)Cr\(_x\) alloys without significant loss of maximum capacity. It was thus shown that the proportion of non-hydride forming element (Cr) could be increased in a HEA without substantial loss of capacity. The only drawback seems to be the important hysteresis. Having a rapid first hydrogenation without any prior heat treatment means that the hydrogen storage tank could be directly filled with the as-cast alloy [29].

Author Contributions: Conceptualization, R.B.S. and J.H.; methodology, R.B.S. and J.H.; software, R.B.S. and G.Z.; validation, J.H. and D.R.L.; formal analysis, R.B.S., J.H., D.R.L., G.Z. and W.J.B.; investigation, R.B.S. and J.H.; resources, J.H. and G.Z.; data curation, J.H.; writing—original draft preparation, R.B.S. and J.H.; writing—review and editing, R.B.S., J.H., D.R.L., G.Z. and W.J.B.; visualization, R.B.S. and J.H.; supervision, J.H., D.R.L. and G.Z.; project administration, J.H.; funding acquisition, J.H. and G.Z. All authors have read and agreed to the published version of the manuscript.

Funding: This work was supported in part by a Discovery Grant from the Natural Sciences and Engineering Research Council of Canada (NSERC). This study was financed in part by the Coordenação de Aperfeiçoamento de Pessoal de Nível Superior—Brasil (CAPES)—Finance Code 001. Additionally, this work was financially supported by the Serrapilheira Institute (grant number Serra-1709-17362).

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: The data presented in this study are available on request from the corresponding author.

Acknowledgments: The authors are grateful to the Laboratory of Structural Characterization (LCE) of the Department of Materials Engineering at Federal University of São Carlos (DEMa/UFSCar) for the electron microscopy facilities.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Wei, T.Y.; Lim, K.L.; Tseng, Y.S.; Chan, S.L.I. A review on the characterization of hydrogen in hydrogen storage materials. Renew. Sustain. Energy Rev. 2017, 79, 1122–1133. [CrossRef]
2. Bellosta von Colbe, J.; Ares, J.R.; Barale, J.; Baricco, M.; Buckley, C.; Capurso, G.; Gallandat, N.; Grant, D.M.; Guzik, M.N.; Jacob, I.; et al. Application of hydrides in hydrogen storage and compression: Achievements, outlook and perspectives. Int. J. Hydrogen Energy 2019, 44, 7780–7808. [CrossRef]
3. Lototskyy, M.V.; Yartys, V.A.; Pollet, B.G.; Bowman, R.C.B., Jr. Metal hydride hydrogen compressors: A review. Int. J. Hydrogen Energy 2014, 39, 5818–5851. [CrossRef]
4. Liu, Y.; Pan, H.; Gao, M.; Wang, Q. Advanced hydrogen storage alloys for Ni/MH rechargeable batteries. J. Mater. Chem. 2011, 21, 4743–4755. [CrossRef]
5. Na, T.W.; Park, K.B.; Lee, S.Y.; Yang, S.M.; Kang, J.W.; Lee, T.W.; Park, J.M.; Park, K.; Park, H.K. Preparation of spherical TaNbHfZrTi high-entropy alloy powders by a hydrogenation–dehydrogenation reaction and thermal plasma treatment. *J. Alloys Compd.* **2020**, *817*, 152757. [CrossRef]

6. Manickam, K.; Mistry, P.; Walker, G.; Grant, D.; Buckley, C.E.; Humphries, T.D.; Paskevicius, M.; Jensen, T.; Albert, R.; Peinecke, K.; et al. Future perspectives of thermal energy storage with metal hydrides. *Int. J. Hydrogen Energy* **2019**, *44*, 7738–7745. [CrossRef]

7. Huot, J. Metal Hydrides. In *Handbook of Hydrogen Storage: New Materials for Future Energy Storage*; Hirscher, M., Ed.; Wiley-VCH Verlag GmbH & Co. KGaA: Weinheim, Germany, 2010; pp. 81–116, ISBN 9783527629800.

8. Zhang, C.; Song, A.; Yuan, Y.; Wu, Y.; Zhang, P.; Lu, Z.; Song, X. Study on the hydrogen storage properties of a TiZrNbTa high entropy alloy. *Int. J. Hydrogen Energy* **2019**, *44*, 8956–8964. [CrossRef]

9. Sahlberg, M.; Karlsson, D.; Zlotea, C.; Jansson, U. Superior hydrogen storage in high entropy alloys. *Sci. Rep.* **2016**, *6*, 36770. [CrossRef] [PubMed]

10. Zepon, G.; Leiva, D.R.; Strozi, R.B.; Bedoch, A.; Figueroa, S.J.A.; Ishikawa, T.T.; Botta, W.J. Hydrogen-induced phase transition of MgZrTiFe0.5Co0.5Ni0.5 high entropy alloy. *Int. J. Hydrogen Energy* **2018**, *43*, 1702–1708. [CrossRef]

11. Kunce, I.; Polanski, M.; Bystrzycki, J. Microstructure and hydrogen storage properties of a TiZrNbMoV high entropy alloy synthesized using Laser Engineered Net Shaping (LENS). *Int. J. Hydrogen Energy* **2014**, *39*, 9904–9910. [CrossRef]

12. Cantor, B.; Chang, I.T.H.; Knight, P.; Vincent, A.J.B. Microstructural development in equiatomic multicomponent alloys. *Mater. Sci. Eng. A* **2004**, *375–377*, 213–218. [CrossRef]

13. Yeh, J.W.; Chen, S.K.; Lin, S.J.; Gan, J.Y.; Chin, T.S.; Shun, T.T.; Tsau, C.H.; Chang, S.Y. Nanostructured high-entropy alloys with varying degree of local lattice strain. *Materials Science and Engineering: A* **2019**, *775*, 375–377, 152757. [CrossRef]

14. Ye, Y.F.; Wang, Q.; Lu, J.; Liu, C.T.; Yang, Y. High-entropy alloy: Challenges and prospects. *Mater. Today* **2016**, *19*, 349–362. [CrossRef]

15. Kao, Y.-F.; Chen, S.-K.; Sheu, J.-H.; Lin, J.-T.; Lin, W.-E.; Yeh, J.-W.; Lin, S.-J.; Liou, T.-H.; Wang, C.-W. Hydrogen storage properties of multi-principal-component CoFeMnTiXVYzR alloys. *Int. J. Hydrogen Energy* **2010**, *35*, 9046–9059. [CrossRef]

16. Young, K.H.; Nei, J.; Wan, C.; Denys, R.V.; Yartys, V.A. Comparison of C14-and C15-predomiated AB2 metal hydride alloys for electrochemical applications. *Batteries* **2017**, *3*, 22. [CrossRef]

17. Edalati, P.; Floriano, R.; Mohammadi, A.; Li, Y.; Zepon, G.; Li, H.W.; Edalati, K. Reversible room temperature hydrogen storage in high-entropy alloy TiZrCrMnFeNi. *Scr. Mater.* **2020**, *178*, 387–390. [CrossRef]

18. Karlsson, D.; Ek, G.; Cedervall, J.; Zlotea, C.; Møller, K.T.; Hansen, T.C.; Bednarčik, J.; Paskevicius, M.; Sørby, M.H.; Jensen, T.R.; et al. Structure and Hydrogenation Properties of a HfNbTiVZr High-Entropy Alloy. *Inorg. Chem.* **2018**, *57*, 2103–2110. [CrossRef]

19. Dewangan, S.K.; Sharma, V.K.; Sahu, P.; Kumar, V. Synthesis and characterization of hydrogenated novel AlCrFeMnNiW high entropy alloy. *Int. J. Hydrogen Energy* **2019**, *44*, 22696–22704. [CrossRef]

20. Nygård, M.M.; Ek, G.; Karlsson, D.; Sahlberg, M.; Sørby, M.H.; Hauback, B.C. Hydrogen storage in high-entropy alloys with varying degree of local lattice strain. *Int. J. Hydrogen Energy* **2019**, *44*, 22696–22704. [CrossRef]

21. Montero, J.; Zlotea, C.; Ek, G.; Crivello, J.; Laversenne, L.; Sahlberg, M. TiVZrNb Multi-Principal-Element Alloy: Synthesis Optimization, Structural, and Hydrogen Sorption Properties. *Molecules* **2019**, *24*, 2799. [CrossRef]

22. Zlotea, C.; Sow, M.A.; Ek, G.; Couzinié, J.P.; Perriére, L.; Guillot, I.; Bourjon, J.; Møller, K.T.; Jensen, T.R.; Akiba, E.; et al. Hydrogen sorption in TiZrNbHfTa high entropy alloy. *J. Alloys Compd.* **2019**, *775*, 667–674. [CrossRef]

23. Strozi, R.B.; Leiva, D.R.; Huot, J.; Botta, W.J.; Zepon, G. Synthesis and hydrogen storage behavior of Mg–V–Al–Cr–Ni high entropy alloys. *Int. J. Hydrogen Energy* **2020**, *45*, 2351–2361. [CrossRef]

24. Nygård, M.M.; Ek, G.; Karlsson, D.; Sørby, M.H.; Sahlberg, M.; Hauback, B.C. Counting electrons—A new approach to tailor the hydrogen sorption properties of high-entropy alloys. *Acta Mater.* **2019**, *178*, 112–124. [CrossRef]

25. Silva, B.H.; Zlotea, C.; Champion, Y.; Botta, W.J.; Zepon, G. C and Ni high-entropy alloys. *Int. J. Hydrogen Energy* **2021**, *865*, 158767. [CrossRef]

26. Akiba, E.; Iba, H. Hydrogen absorption by Laves phase related BCC solid solution. *Intermetallics* **1999**, *9*, 439–448. [CrossRef]

27. Bau, R.; Drabmis, M.H. Structures of transition metal hydrides determined by neutron diffraction. *Inorg. Chim. Acta* **1997**, *259*, 27–50. [CrossRef]

28. Peisl, H. Lattice strains due to hydrogen in metals. In *Hydrogen in Metals I. Topics in Applied Physics*; Alefeld, G., Vökl, J., Eds.; Springer: Berlin/Heidelberg, Germany, 1978; Volume 28, pp. 53–74, ISBN 978-3-540-35892-3.

29. Sandrock, G. Panoramic overview of hydrogen storage alloys from a gas reaction point of view. *J. Alloys Compd.* **1999**, *293*, 877–888. [CrossRef]