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Entropy-Enthalpy Compensation in Ti-V-Mn-Cr BCC Alloys Used as Hydrogen Storage Materials

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Abstract: In this paper, we report the effect of the Cr/Mn ratio on the thermodynamic properties of $\text{Ti}_{30}\text{V}_{60}\text{Mn}_{(10-x)}\text{Cr}_x$ ($x = 0, 3.3, 6.6$ and 10) + 4 wt.% Zr alloys. It was found that the enthalpy and entropy change with the Cr/MN ratio and that the entropy and entropy variation is coupled in an enthalpy-entropy compensation fashion. Using a compensation quality factor, it was established that the enthalpy-entropy compensation is not due to a statistical origin, with a confidence of more than 95%.

Keywords: metal hydrides; BCC alloys; enthalpy-entropy compensation

1. Introduction

With increased interest in renewable energies, hydrogen has gained significant attention as a clean energy vector. Therefore, the development of a safe and efficient hydrogen storage method is of paramount importance. Metal hydrides have emerged as one of the most promising hydrogen storage materials due to their high volumetric capacity.

Amongst the many types of metal hydrides, Ti-V-based Body Centered Cubic (BCC) solid solution alloys stand out, featuring a hydrogen storage capacity of over 3.8 wt.% at room temperature and moderate pressure [1]. However, a major challenge associated with this system is the poor hydrogen desorption performance at room temperature, limiting its practical use [2,3].

It has been shown that Ti-V alloys exhibit two distinct plateaus in the pressure-composition isotherms (PCI), leading to the formation of two distinct hydrides [4,5]. At room temperature, the first plateau is usually situated far below atmospheric pressure (around 0.1 Pa) and is the transformation of the BCC solid solution into a monohydride. The second plateau emerges at higher pressures (around 0.1 MPa), leading to the transformation of the monohydride into a dihydride [6]. Notably, in hydrogen storage applications, only the dihydride contributes to the reversible hydrogen storage capacity, while the monohydride remains too stable and necessitates high temperatures for hydrogen release. This is the reason why the reversible hydrogen storage capacity of BCC solid solutions is smaller than their total hydrogen storage capacity.

To overcome this issue and enhance hydrogen storage capacities, researchers have explored the addition of 3d elements with similar radii to vanadium, such as Mn, Cr, Fe, Co, and Ni [7,8]. Mn addition to Ti-V alloys alters the microstructure of the alloy, leading to improved PCI properties [9–14]. The Ti-V-Mn alloy consisting of BCC and C14 laves phase was first reported by Akiba and Iba [15]. In this paper, they showed that the hydrogen capacity is a linear combination of capacities of individual phases.

Another important finding in Ti-V-M alloys was that varying Ti, V and M content had a significant effect on the lattice parameter of the as-cast alloys, which leads to an increased or decreased equilibrium plateau pressure due to the different sizes of constituent elements [16–18]. Nakamura and Akiba reported that the plateau pressure of $\text{Ti}_x\text{V}_{1.0}\text{Mn}_{(2-x)}$ ($x = 1.0, 1.1$ and 1.2) alloys decreased with increasing lattice parameters [19]. Okada et al.



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found that an increase in the Cr content in Ti-V-Cr alloys leads to a shift of the equilibrium plateau pressure to higher values due to a decrease in the lattice parameter [20].

Ternary and quaternary Ti-V-M samples have been extensively studied, with Ti-V-M ($M = \text{Mn, Cr, Fe, Co}$) [9,21–23] and Ti-V-Cr-M ($M = \text{Mn, Fe}$) [17,24] alloys exhibiting favorable hydrogen storage properties. Bibienne and Huot studied the effect of the alloy composition on the hydrogen storage properties of $\text{TiV}_{2-x}\text{Mn}_x$ [25]. Their study showed that the plateau pressure in desorption increases when decreasing the lattice parameter associated with a higher Mn content. The composition $\text{TiV}_{1.8}\text{Mn}_{0.2}$ shows a maximum hydrogen storage capacity of 3.4 wt.% of hydrogen at 373 K.

Modifications in plateau pressures imply a change in the enthalpy (ΔH) and entropy (ΔS) of the hydrogenation/dehydrogenation reaction. Entropy (ΔS) is generally considered relatively constant among different metal hydrides ($-130 \text{ J} \cdot (\text{mol H}_2)^{-1} \cdot \text{K}^{-1}$) and is mainly due to the entropy loss of hydrogen from a gaseous state to a metal hydride state. A simultaneous linear decrease or increase of ΔH and ΔS may be an indication of an enthalpy-entropy compensation effect (EEC) [26], also called isokinetic relationship according to IUPAC nomenclature [27]. This compensation effect has been reported in various systems in biology with protein ligand–receptor interactions [28–30] and in chemistry with the adsorption of molecules into microporous materials [31,32]. This phenomenon was also observed in various metal hydride systems as $\text{MSi}/\alpha\text{-MSiH}_3$ ($M = \text{K, Rb, and Cs}$) [33], in the hydrogenation/dehydrogenation properties of Mg-Ti nanocomposites [34,35] and Pd-H nanocubes [35,36], and for H_2 permeation kinetics in PdAg membranes [37]. Anastasopol et al. did not identify an exact mechanism for their results on Mg-Ti nanocomposites but tentatively explained it as being possibly due to lattice strains, the presence of interfaces between coherent Mg and TiH_2 nanodomains, the presence of hydrogen vacancies, and the formation of excess free volume due to local deformations of the material [34]. For isokinetics reactions, it has been related to the Meyer–Neldel rule [38–40].

This compensation effect has never been reported in metal hydrides having Ti-V-based BCC structures. In an investigation of the BCC alloy $\text{Ti}_{52}\text{V}_{12}\text{Cr}_{36}$ with the addition of $\text{Zr}_7\text{Ni}_{10}$, Bibienne and Huot reported a formation enthalpy (ΔH) of $-60.6 \text{ kJ} \cdot (\text{mol H}_2)^{-1}$ and entropy (ΔS) of $-169 \text{ J} \cdot (\text{mol H}_2)^{-1} \cdot \text{K}^{-1}$ [41]. In a subsequent study, the same authors investigated the thermodynamic parameters of $\text{Ti}_{42}\text{V}_{21}\text{Cr}_{37}$ doped with $\text{Zr}_7\text{Ni}_{10}$ and found the values $\Delta H = -38 \text{ kJ} \cdot (\text{mol H}_2)^{-1}$ and $\Delta S = -130 \text{ J} \cdot (\text{mol H}_2)^{-1} \cdot \text{K}^{-1}$ [42]. These preliminary results indicate that BCC Ti-V alloys may exhibit a linear dependence between entropy and enthalpy.

In a subsequent investigation, the effect of Ni and Zr elements as additives was investigated, and it was found that Zr is the most effective element for enhancing the first hydrogenation of Ti-V-Cr BCC alloy [43,44]. In these alloys, a Zr-rich secondary phase is considered to be responsible for the fast kinetics.

The primary objective of this study was to further investigate the thermodynamic properties of $\text{Ti}_{30}\text{V}_{60}\text{Mn}_{(10-x)}\text{Cr}_x$ ($x = 0, 3.3, 6.6, \text{ and } 10$) + 4 wt.% Zr BCC alloys. Specifically, the objective was to explore the influence of varying Cr/Mn contents on hydrogen desorption properties and to examine the relationship between the entropy and enthalpy of the hydride formation in these BCC alloys.

2. Results and Discussion

To investigate the desorption thermodynamics of the $\text{Ti}_{30}\text{V}_{60}\text{Mn}_{(10-x)}\text{Cr}_x$ ($x = 0, 3.3, 6.6 \text{ and } 10$) + 4 wt.% Zr alloy, we conducted PCI measurements at different temperatures. It is important to note that we could only record the plateau between the dihydride and monohydride phases, as the desorption plateau of the monohydride was too low (lower than 10 kPa) to be measured with our apparatus.

Figure 1a shows the PCI desorption curves of $\text{Ti}_{30}\text{V}_{60}\text{Mn}_{10}$ + 4 wt.% Zr alloy at 423, 448, 473 and 498 K. As our study focused solely on desorption, all curves share the same high-pressure origin, as shown in the Supplementary Document. To better compare the plateaus, in this figure and all subsequent ones, the curves are vertically aligned at their

inflection point (i.e., middle of the plateau). As the temperature increases, we observed a rise in the plateau pressure, and simultaneously, the width of the higher desorption plateau decreased. This reduction in width indicates a corresponding decrease in the storage capacity. The sample desorbed 1.4 wt.% of hydrogen, which corresponds to only 41% of its total absorption after activation (3.4 wt.%), indicating the dihydride–monohydride transition.

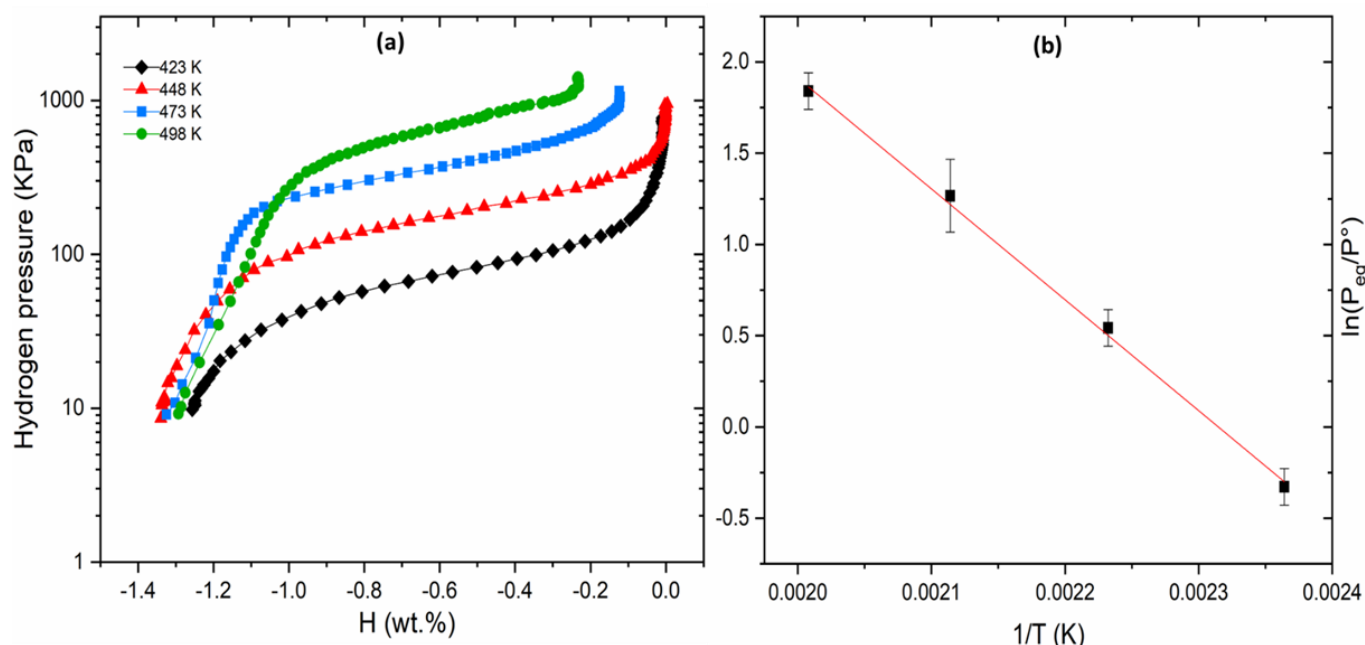


Figure 1. PCI desorption curves at 423, 448, 473 and 498 K (a) and Van't Hoff plot of $\text{Ti}_{30}\text{V}_{60}\text{Mn}_{10} + 4$ wt.% Zr alloy (b).

We considered the inflection points (midpoint) of each plateau as the equilibrium pressure (P_{eq}). From these pressures, a Van't Hoff plot was obtained and is shown in Figure 1b.

In the case of $\text{Ti}_{30}\text{V}_{60}\text{Mn}_{6.6}\text{Cr}_{3.3} + 4$ wt.% Zr alloy, Figure 2 illustrates the PCI desorption curves and the corresponding Van't Hoff plot. A comparison with the ternary alloy $\text{Ti}_{30}\text{V}_{60}\text{Mn}_{10}$ reveals that the addition of 3.3 at % Cr results in a drop in plateau pressure, although the sample desorbed 1.6 wt.% of hydrogen. It should be noted that some plateaus are broader than others. The reason for this is that there is some drop of capacity with cycling and that the isotherms were taken on the same sample.

At 473 K, the first isotherm displayed a wider plateau pressure, as observed in Figure 2a. This was due to the lattice strain inherent to the material at its initial state, which slightly affected the plateau pressure. As the material underwent cycling, the lattice strain was relieved, resulting in subsequent isotherms with narrower plateau pressures. As seen in Figure 2b, the data point corresponding to the 473 K isotherm is somewhat off from the Van't Hoff line. This indicates that cycling has a minimal effect on the plateau pressure and also that the effect is concentrated on the first cycle.

Similarly, Figure 3 represents the PCI desorption curves of $\text{Ti}_{30}\text{V}_{60}\text{Mn}_{3.3}\text{Cr}_{6.6} + 4$ wt.% Zr and its Van't Hoff plot. Here, a further replacement of Mn by Cr (6.6 at % Cr) leads to a rise in desorption plateau pressure, while the desorption capacity remains unchanged.

Figure 4 presents the PCI desorption curves of $\text{Ti}_{30}\text{V}_{60}\text{Cr}_{10} + 4$ wt.% Zr alloy and the corresponding Van't Hoff plot. Even with a total substitution of Mn by Cr, the dehydrogenation plateau pressure continues to increase.

Notably, the plateau pressure of alloys (with x from 3.3 to 10) increases with an increasing Cr/Mn ratio. Table 1 shows that the equilibrium pressure (P_{eq}) values are significantly influenced by the chromium proportion. As observed in our previous work,

XRD analyses confirmed that $\text{Ti}_{30}\text{V}_{60}\text{Mn}_{(10-x)}\text{Cr}_x$ ($x = 3.3, 6.6$ and 10) + 4 wt.% Zr alloys exhibit a BCC crystal structure, with their lattice parameters decreasing as the Cr content increases [45]. This is because the atomic radius of Cr (1.25 Å) is smaller than that of Mn (1.35 Å). This result confirms that the plateau pressure can indeed be controlled by adjusting the Cr/Mn ratio.

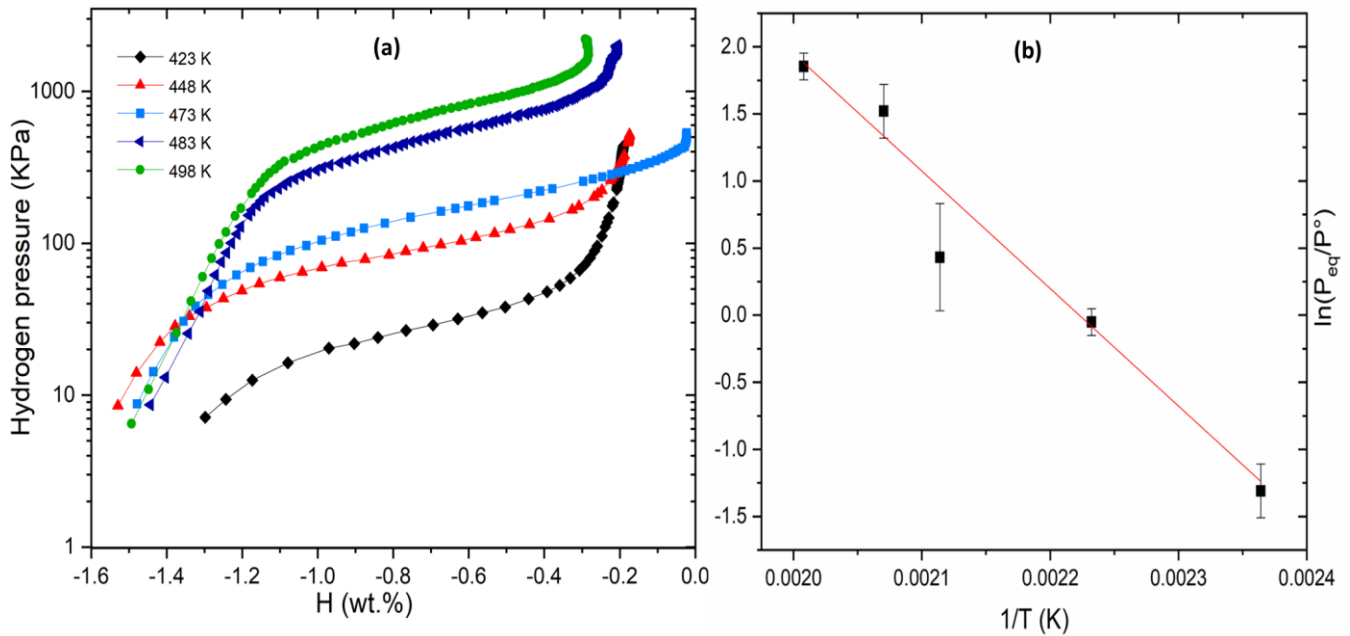


Figure 2. PCI desorption curves at 423, 448, 473, 483 and 498 K (a) and Van't Hoff plot of $\text{Ti}_{30}\text{V}_{60}\text{Mn}_{6.6}\text{Cr}_{3.3}$ + 4 wt.% Zr alloy (b).

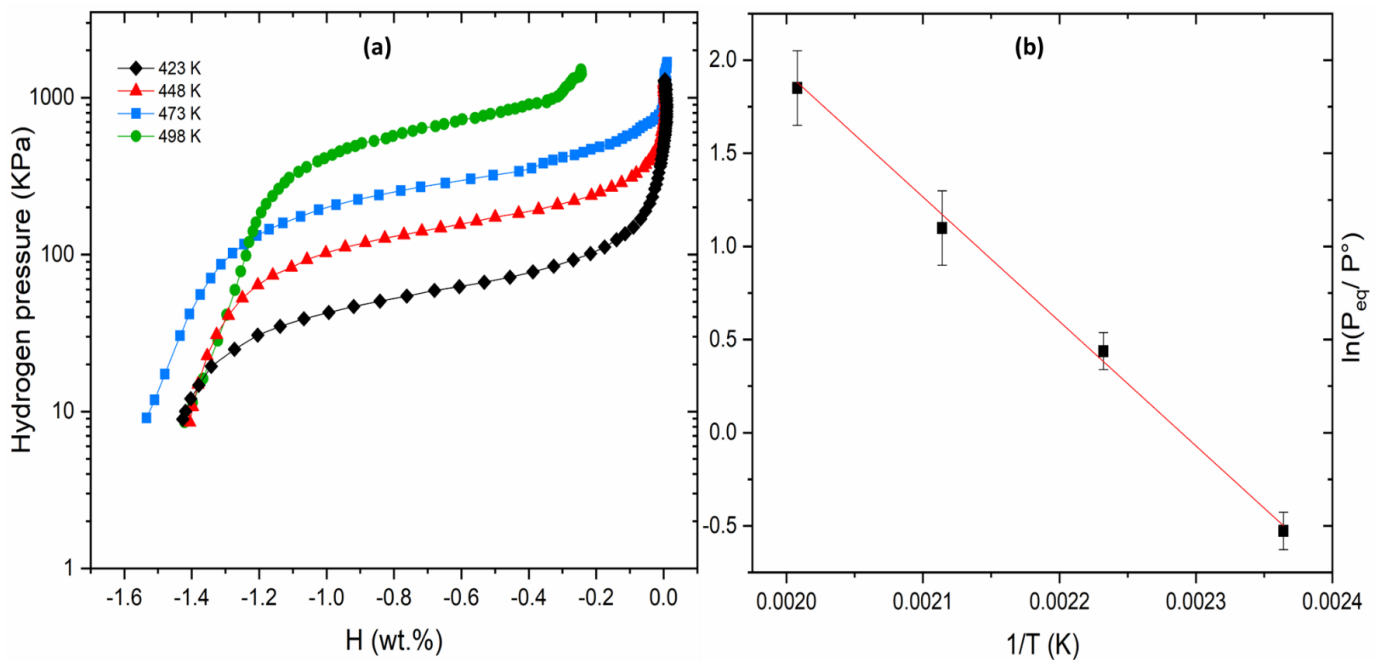


Figure 3. PCI desorption at 423, 448, 473 and 498 K (a) and Van't Hoff plot of $\text{Ti}_{30}\text{V}_{60}\text{Mn}_{3.3}\text{Cr}_{6.6}$ + 4 wt.% Zr alloy (b).

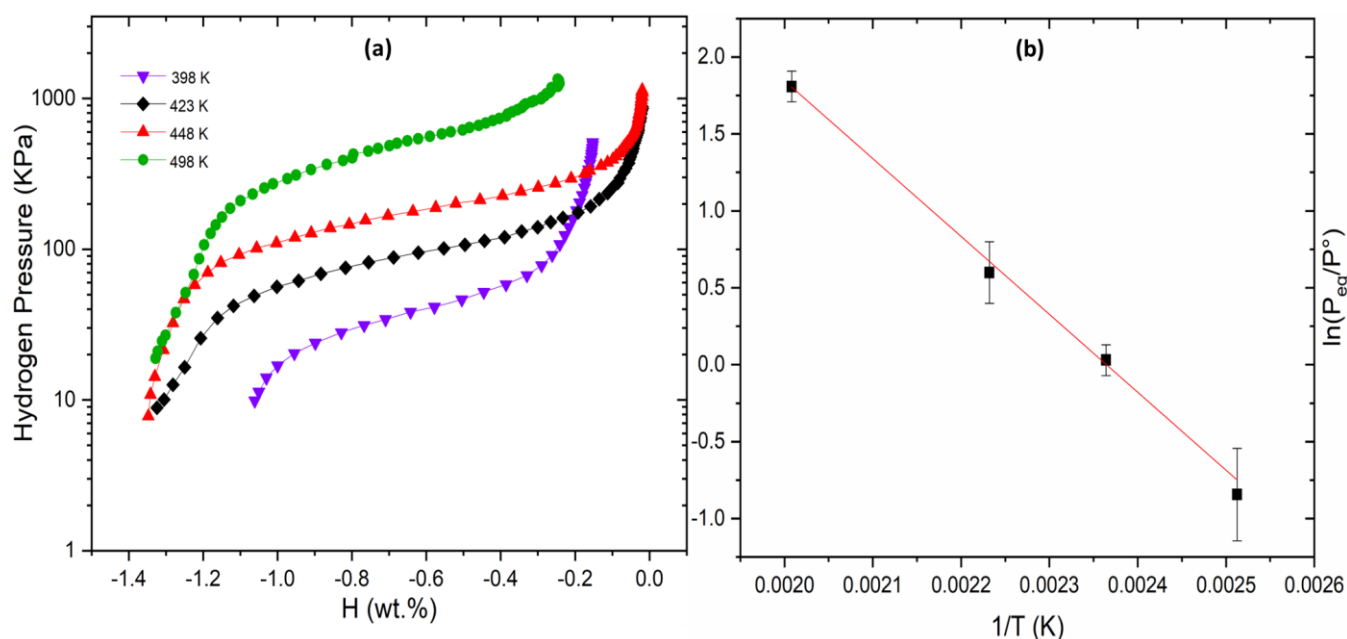


Figure 4. PCI desorption at 398, 423, 448 and 498 K (a) and Van't plot of $\text{Ti}_{30}\text{V}_{60}\text{Cr}_{10} + 4 \text{ wt.}\% \text{ Zr}$ alloy (b).

Table 1. The equilibrium pressure (P_{eq}) data given at different temperatures of PCI curves. Thermodynamic parameters of $\text{Ti}_{30}\text{V}_{60}\text{Mn}_{(10-x)}\text{Cr}_x$ ($x = 0, 3.3, 6.6$ and 10) + 4 wt.% Zr alloy determined from Van't Hoff plots.

Sample	Desorption						Enthalpy kJ/mol H ₂	Entropy J/K·mol H ₂
	Plateau Pressure (kPa)							
	398 K	423 K	448 K	473 K	483 K	498 K		
Ti ₃₀ V ₆₀ Mn ₁₀ + 4 wt.% Zr	-	72 (1)	172 (1)	355 (2)	-	630 (1)	−50 (2)	−117 (1)
Ti ₃₀ V ₆₀ Mn _{6.6} Cr _{3.3} + 4 wt.% Zr	-	27 (2)	95 (1)	154 (4)	457 (2)	638 (1)	−72 (9)	−160 (9)
Ti ₃₀ V ₆₀ Mn _{3.3} Cr _{6.6} + 4 wt.% Zr	-	59 (1)	155 (1)	300 (2)	-	629 (2)	−54 (3)	−124 (5)
Ti ₃₀ V ₆₀ Cr ₁₀ + 4 wt.%	42 (3)	103 (1)	182 (2)	-	-	610 (1)	−43 (2)	−102 (4)

The ΔH_{des} and ΔS_{des} values calculated from the slope and intercept of the Van't Hoff equation [$\ln(P_{\text{eq}}/P^\circ) = (\Delta H/RT) - (\Delta S/R)$] are reported in Table 1. The ΔH_{des} of $\text{Ti}_{30}\text{V}_{60}\text{Cr}_{10}$ is significantly lower than the ΔH_{des} of $\text{Ti}_{30}\text{V}_{60}\text{Mn}_{10}$. Therefore, the stability of the dihydride phase is reduced with a higher Cr content.

Figure 5 illustrates the correlation between the enthalpy and entropy values and the Cr proportion. Notably, our observations indicate the absence of a linear relationship between these thermodynamic parameters and the variation in x . However, there seems to be a correlation between the thermodynamic parameters themselves.

The Van't Hoff plots for the four alloys are displayed in Figure 6. Notably, the lines of $\ln(P_{\text{eq}}/P^\circ)$ as a function of the inverse of the temperature demonstrate a convergence at around 500 K. Therefore, an entropy–enthalpy compensation (EEC) may be expected.

Figure 7 shows the plot of ΔH versus ΔS , revealing a clear linear relationship between these two parameters, indicative of EEC behavior. The linear regression line has a high R square value of 0.99989. The slope of this line defines the so-called compensation temperature $T_c = \Delta H/\Delta S = 499.9 \text{ K}$, where all compositions have the same equilibrium pressure. This is very close to the convergence temperature seen in Figure 6.

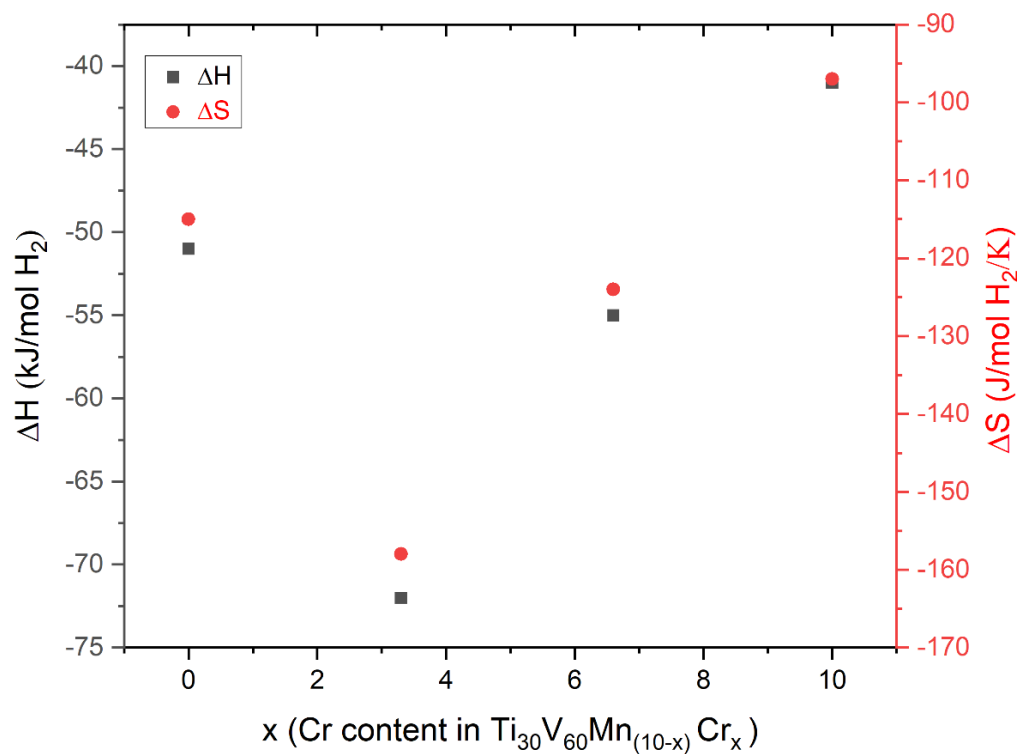


Figure 5. The variation of ΔH and ΔS as a function of x .

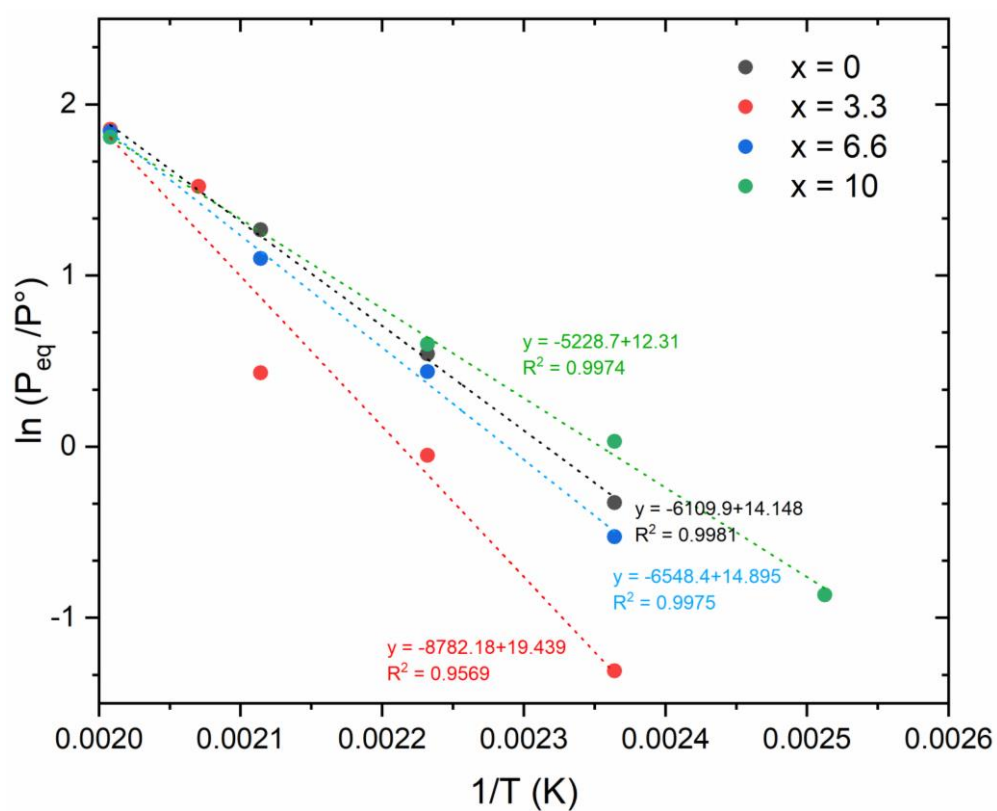


Figure 6. Van't Hoff plot of $\text{Ti}_{30}\text{V}_{60}\text{Mn}_{(10-x)}\text{Cr}_x$ ($x = 0, 3.3, 6.6$ and 10) + 4 wt.% Zr alloy.

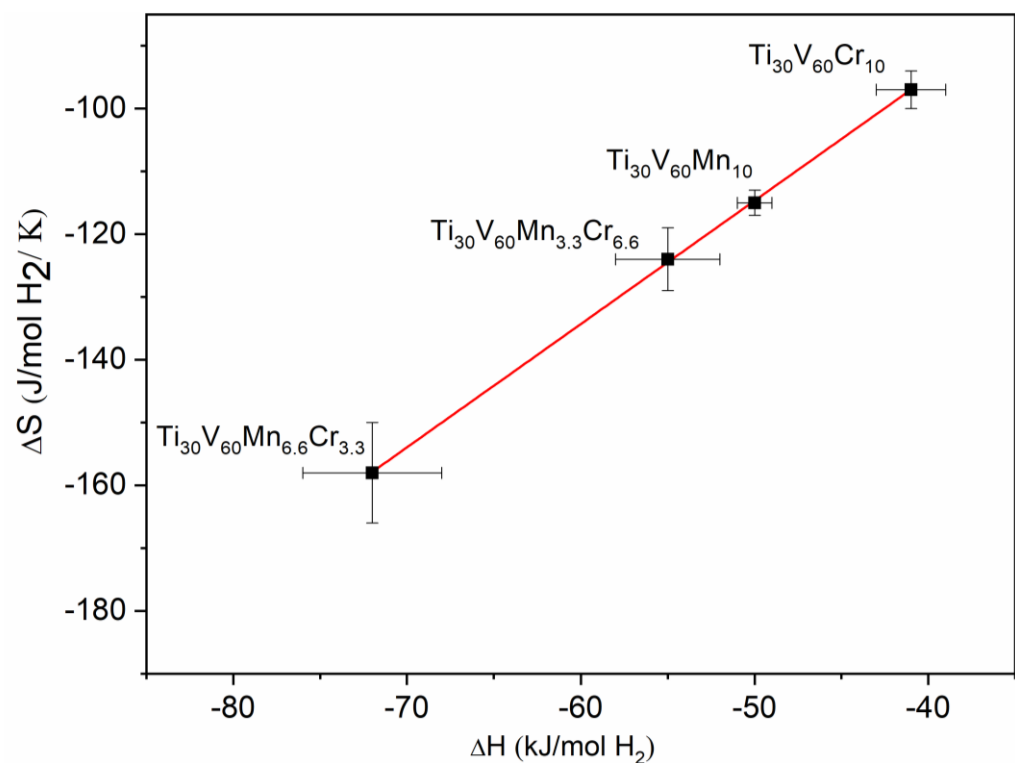


Figure 7. ΔH variation as a function of ΔS .

To confirm the reality of the enthalpy-entropy compensation, we applied the Combined K-CQF test designed by Griessen and Dam to verify if the enthalpy-entropy compensation had a statistical origin [36]. In this context, K denotes the position of the coalescence region within the Van't Hoff plots, while CQF quantifies the smallest dispersion among these plots. To apply this method to the $\text{Ti}_{30}\text{V}_{60}\text{Mn}_{(10-x)}\text{Cr}_x$ ($x = 0, 3.3, 6.6$ and 10) + 4 wt.% Zr alloy, we followed these steps:

1. *Temperature Calculations:* Initially, we calculated essential temperatures for our analysis:
 - i. T_{hm} , the harmonic mean of experimental temperatures, calculated as $T_{\text{hm}} = 458.80$ K using Equation (1).

$$T_{\text{hm}} = \left(\frac{1}{M} \sum_{j=1}^M \frac{1}{T_j} \right)^{-1} \quad (1)$$

T_{min} , the temperature where the spread in LnP is minimized, determined as $T_{\text{min}} = 499.99$ K via Equation (2).

$$T_{\text{min}} = \frac{T_{\text{comp}}}{R_{\text{square}}} \quad (2)$$

- ii. T^* , the temperature at which the largest LnP spread is measured is chosen so that $T^* = T_{\text{low}}$ if $1/T_{\text{min}}$ closer to $1/T_{\text{high}}$ or $T^* = T_{\text{high}}$ if $1/T_{\text{min}}$ is closer to $1/T_{\text{low}}$. Given our experimental temperature range of (423–498) K, we have $T^* = T_{\text{low}} = 423$ K.
2. *Key Parameter Calculation:* We proceeded to calculate the key parameters K and CQF using Equations (3) and (4), respectively:

$$K = \frac{\frac{1}{T_{\text{hm}}} - \frac{1}{T_{\text{min}}}}{\frac{1}{2} \left(\frac{1}{T_{\text{low}}} - \frac{1}{T_{\text{high}}} \right)} \quad (3)$$

$$CQF = 1 - \sqrt{\frac{1 - R_{\text{square}}}{\left(\frac{1}{R_{\text{square}}}\right)\left(\frac{T_{\text{comp}}}{T^*}\right)^2 - 2\left(\frac{T_{\text{comp}}}{T^*}\right) + 1}} \quad (4)$$

Using $T_{\text{comp}} = 499.93$ and $R_{\text{square}} = 0.99989$, we obtained a (K, CQF) value of (1.008679, 0.942542).

3. Position Verification:

Figure 8, taken from Griessen and Dam's research, shows the universal confidence contours derived through extensive simulations of random Van't Hoff plots [36]. These contours serve to determine the statistical origin of the EEC at a specific confidence level (CL%). The term "universal" stems from the fact that the confidence contours depend only on the number of samples N and the chosen CL%, which makes this method easily applicable. Thus, if the (K, CQF) couple lies outside the designated CL% contour, this indicates that the EEC is probably not of statistical origin at that level of confidence.

In our study, the precise position of the (K, CQF) couple (1.008679, 0.942542), characteristic of $\text{Ti}_{30}\text{V}_{60}\text{Mn}_{(10-x)}\text{Cr}_x$ ($x = 0, 3.3, 6.6$ and 10) + 4 wt.% Zr, has been distinctly marked as a star within Figure 8. However, this star lies on the border of the 95% and inside the 99% confidence contour for $N = 4$ samples. This outcome leads us to conclude that the enthalpy-entropy compensation observed in the $\text{Ti}_{30}\text{V}_{60}\text{Mn}_{(10-x)}\text{Cr}_x$ ($x = 0, 3.3, 6.6$ and 10) + 4 wt.% Zr BCC alloys is not a statistical artifact at a confidence level higher than 95% but lower than 99%.

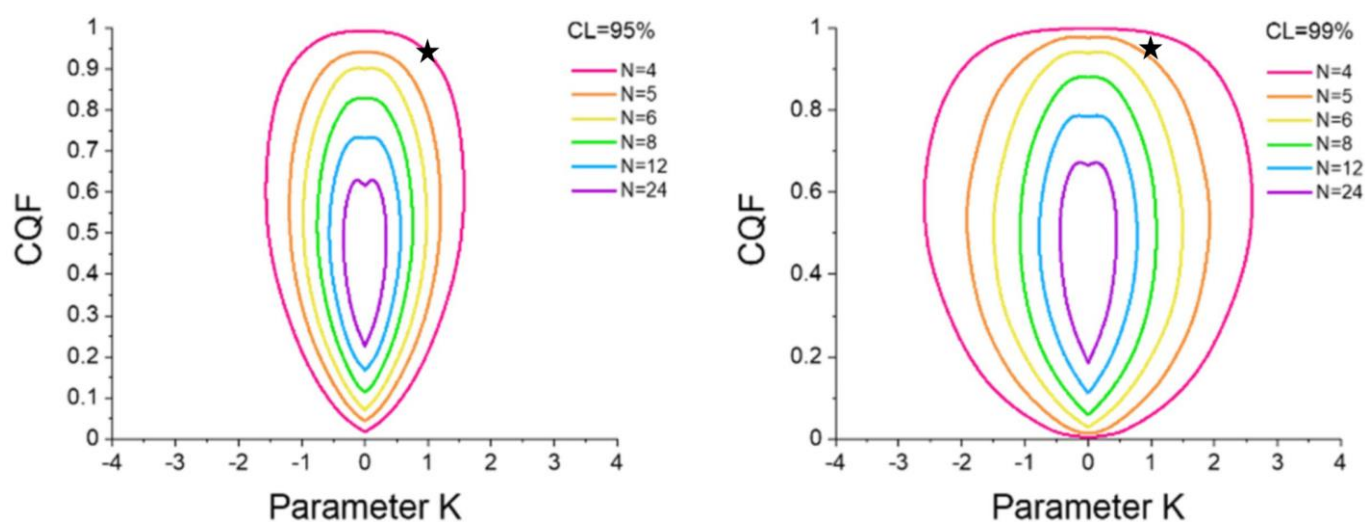


Figure 8. 95% (left panel) and 99% (right panel) confidence contours for $N = 4$ up to $N = 15$ determined from 2D-probability density surfaces. Adapted from ref. [35] with permission.

3. Materials and Methods

3.1. Alloy Synthesis

Alloys with the nominal compositions $\text{Ti}_{30}\text{V}_{60}\text{Mn}_{(10-x)}\text{Cr}_x$ ($x = 0, 3.3, 6.6$ and 10) + 4 wt.% Zr were prepared using the arc melting method under argon atmosphere. The raw materials, vanadium (irregular pieces, 99.7%), titanium (sponge, 3–19 mm, 99.95%), manganese (irregular pieces, 99.5%), chromium (irregular pieces, 99.0%) and zirconium (sponge 0.8–25.4 mm, 99.95%), were purchased from Alfa-Aesar (Ward Hill, MA, USA). Each ingot (~3 g) was remelted and turned over three times to ensure homogeneity. The obtained as-cast alloys in button shape were mechanically crushed using a mortar and pestle in an argon-filled glovebox.

3.2. Structure Analysis

The phase composition and crystal structure of the alloys were investigated by X-ray diffraction (XRD) technique using a Bruker D8 powder diffractometer (Madison, WI, USA) having Cu K α radiation. The XRD patterns were analyzed by Rietveld's method using Topas software (V6) to determine the lattice parameters, crystallite size and phase abundance [46].

3.3. Pressure-Composition-Isotherms (PCIs) Measurements

The PCI desorption curves at various temperatures were measured using a home-made Sievert-type apparatus [47]. Prior to each PCI experiment, the following sequence was repeated:

The sample was activated at 298 K under 2 MPa of hydrogen. Once complete absorption was achieved, the sample was heated up to the desired temperature under hydrogen pressure to prevent its desorption. Once the first desorption isotherm was recorded, the sample was kept under a dynamic vacuum at 573 K for 2 h to ensure complete desorption. After this process, the sample was considered fully desorbed. Subsequently, the temperature was lowered back to room temperature for the absorption process. The same process was repeated to register the PCI desorption at different temperatures. After each PCI measurement, the sample was pumped again at 573 K for one hour to ensure complete dehydrogenation. This specific temperature was chosen based on X-ray diffraction analysis performed after a similar desorption step; the recovery of the Body Centered Cubic (BCC) structure, initially present after synthesis, confirms the complete desorption of the material.

4. Conclusions

In this study, we investigated the desorption thermodynamics of $\text{Ti}_{30}\text{V}_{60}\text{Mn}_{(10-x)}\text{Cr}_x$ ($x = 0, 3.3, 6.6$ and 10) + 4 wt.% Zr alloy, building on our previous investigation of the microstructure, crystal structure, and hydrogen absorption properties of these materials.

We found that the isotherms are strongly dependent on the compositions, with a higher Cr content resulting in increased pressures.

The reversible capacities of $\text{Ti}_{30}\text{V}_{60}\text{Mn}_{(10-x)}\text{Cr}_x$ ($x = 0, 3.3, 6.6$ and 10) + 4 wt.% Zr alloy measured using PCI (between 1.4 and 1.6 wt.%) did not account for the desorption capacity of the monohydride at a very low pressure. This means that only the dihydride reaction is practically reversible.

Through Van't Hoff plots, the desorption enthalpy (ΔH_{des}) and entropy (ΔS_{des}) were obtained. A plot of the entropy vs. enthalpy shows a straight line that indicates an entropy-enthalpy compensation. The compensation temperature of 499.93 K is in agreement with the temperature where all Van't Hoff plots converge (500 K), providing crucial insights, as it represents the temperature at which all compositions exhibit the same equilibrium pressure.

The degree of confidence of the entropy-enthalpy compensation was checked using the combined K-CQF test designed by Griessen and Dam [35]. We found that the enthalpy-entropy compensation is not due to statistical origin, with a confidence of more than 95%.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/inorganics11120479/s1>, Figure S1: PCI desorption curves at 423, 448, 473 and 498 K (a) and Van't plot of $\text{Ti}_{30}\text{V}_{60}\text{Mn}_{10}$ + 4 wt.% Zr alloy (b). Figure S2: PCI desorption curves at 423, 448, 473, 483 and 498 K (a) and Van't Hoff plot of $\text{Ti}_{30}\text{V}_{60}\text{Mn}_{6.6}\text{Cr}_{3.3}$ + 4 wt.% Zr alloy (b). Figure S3: PCI desorption at 423, 448, 473 and 498 K (a) and Van't Hoff plot of $\text{Ti}_{30}\text{V}_{60}\text{Mn}_{3.3}\text{Cr}_{6.6}$ + 4 wt.% Zr alloy (b). Figure S4: PCI desorption at 398, 423, 448 and 498 K (a) and Van't plot of $\text{Ti}_{30}\text{V}_{60}\text{Cr}_{10}$ + 4 wt.% Zr alloy (b).

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

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