

# ABSORPTION OF HYDROGEN BY VANADIUM-TITANIUM ALLOYS

by

Akio Kagawa\*

The pressure-composition isotherms for V-Ti alloys containing titanium up to 30 at% were measured and the dependence of hydriding and dehydriding characteristics on titanium content was examined in relation to their structures. V-Ti alloys show great resistance to pulverization on hydriding and dehydriding cycles and titanium as an alloy partner gives advantageous modifications, i. e., easy 'activation', rapid absorption and desorption of hydrogen and a significant increase in the enthalpy change for the formation and decomposition of the dihydride phase, while the alloys exhibit large hysteresis and sloping plateau which could be ascribed to the inherent nature of vanadium and phase separation due to monotectoid reaction possibly existing at the vanadium-rich side of the phase diagram, respectively.

## I. Introduction

Diffusivity of hydrogen in bcc metals is much greater than in fcc and hcp metals<sup>1)</sup>. Among bcc metals, vanadium has a larger diffusivity of hydrogen than niobium and tantalum. Vanadium has other suitable properties as a hydrogen storage material, i. e., proper plateau pressure (2 - 3 atm at 313K), satisfactory hydrogen storage capacity (atomic ratio of hydrogen to metal atom;  $(H/M) \approx 1$ ) of its dihydride<sup>2)</sup>, relatively low density and good workability which is expected to endow the resistance to pulverization during the hydrogen absorption/desorption cycles. However, vanadium is one of active elements and easily forms its oxides on the surface which may act as a barrier for hydrogen absorption. Therefore, activation treatment is necessary for vanadium prior to the first absorption process. Alloying with more active elements such as titanium and zirconium appears to be effective to improve the initial activation process. These alloying elements form dihydrides like vanadium and have larger values of enthalpy for the dihydride formation<sup>3)</sup>, which may result in an improved heat of formation of vanadium dihydrides by alloying with them.

The solubility of zirconium in vanadium is less than a few atomic percent, while vanadium-titanium

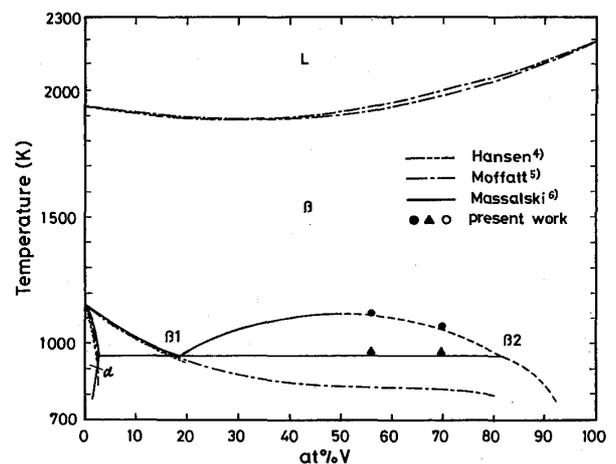


Fig. 1 Vanadium-titanium binary phase diagram.

system forms a complete solid solution at higher temperatures<sup>4 - 6)</sup>. In the V-Ti phase diagram illustrated in Fig. 1, some discrepancies are, however, seen at lower temperatures in these three phase diagrams, especially at vanadium-rich side. The latter two phase diagrams are based on the works of J. L. Murray<sup>7)</sup> and Nakano et al.<sup>8)</sup>, respectively. The  $\alpha + \beta$  two phase region at the titanium-rich side in the phase diagram given by Hansen and Anderko<sup>4)</sup> extends to 80~90 at% of vanadium in those given by Moffatt<sup>5)</sup> and by Massalski<sup>6)</sup>. A monotectoid reaction is added in the Massalski's phase diagram, while

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\*Department of Materials Science and Engineering

no monotectoid reaction in that of Moffatt.

On the other hand, pressure-composition-temperature (p-c-T) relationships for the formation and decomposition of  $\gamma$  dihydride in V-Ti-H system have been reported by Ono et al.<sup>9)</sup> and Lynch et al.<sup>10)</sup>. The maximum hydrogen-to-atom ratios (H/M) measured in their work are 1.4 for V-40at%Ti alloy and 1.6 for V-20at%Ti alloy<sup>9)</sup> and 1.9 for V-10 at%Ti alloy<sup>10)</sup>. These results appear to indicate that an increase in titanium content leads to a reduction in the capacity for hydrogen storage in V-Ti alloys. In the p-c isotherm for V-40at%Ti alloy in reference 9, a severe reduction of the amount of absorbed hydrogen was seen in the absorption isotherm and no plateau was observed in the desorption process, where no evidence of the disproportionation of  $\gamma$  dihydride was detected in their X-ray analysis. The deterioration of hydrogen storage capacity by titanium addition seems to suggest that there possibly exists a certain structural change which could influence the p-c-T relationships of the vanadium-rich V-Ti alloys.

In the present work, the p-c-T relationships and other hydriding/dehydriding properties were measured for V-Ti alloys containing titanium up to 30 at% and factors affecting these properties were discussed in relation to the phase diagram.

## II. Experimental

V-Ti alloys containing 5~68at%Ti were prepared by arc-melting vanadium and titanium of 99.8% purity under argon atmosphere. The alloys were remelted several times for homogenization and some of them were subjected to further homogenization heat-treatment at 1373K for 1 week followed by furnace cooling to examine the effect of the heat-treatment on the p-c isotherm. The powder and granular samples for X-ray analysis and the measurement of p-c isotherm, respectively, were prepared by machining the button ingots. X-ray analysis was performed using  $\text{CuK}\alpha$  radiation with nickel filter and the lattice parameters were determined by the extrapolation method using the Nelson-Riley function. In the measurement of the p-c isotherm, about 1 g of the granular sample was put into a stainless steel container in the Sieverts apparatus. The sample was

degassed under vacuum less than  $1 \times 10^{-4}$  Pa at 723 K for 3 h prior to the introduction of hydrogen to the container. After degassing, the sample was exposed to hydrogen at 4 MPa and cooled to 273K until no pressure change was detected over a period of 1 h. The desorption isotherm was measured during the phase transformation from  $\gamma$  dihydride to  $\beta$  monohydride and then the absorption isotherm was measured up to a hydrogen pressure of 4 MPa. Electrical resistance measurement was carried out to examine the presence of phase separation at the vanadium-rich side of V-Ti system. For the measurement of electrical resistance, a thin plate 0.2mm thick was prepared from a part of the button ingot by cold-rolling and the ribbon sample 0.2mm thick, 1 mm wide and 60mm long was cut from the plate. The electrical resistance was measured by the four-probe method on heating at a constant rate of 4 K/h in the temperature range from room temperature to 1173K.

## III. Results

In the X-ray diffraction patterns of the as-cast alloys only a bcc phase was observed. The lattice parameters are given as a function of titanium con-

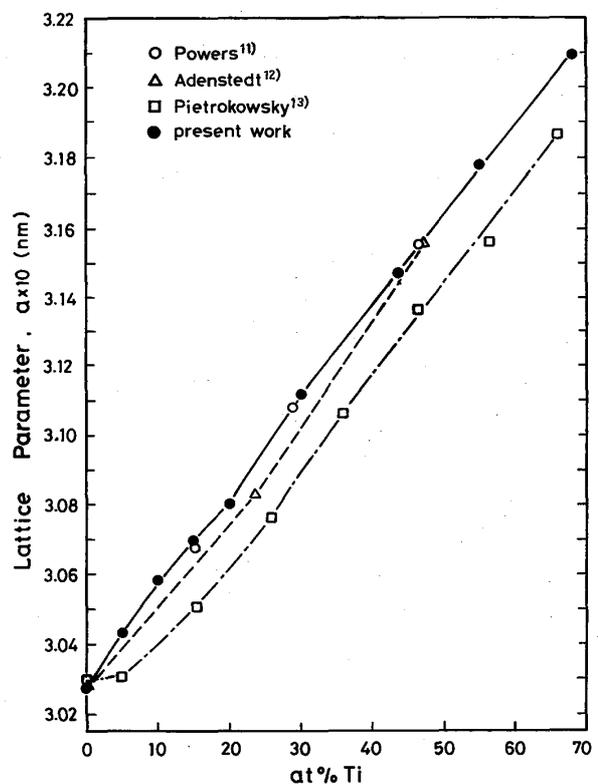


Fig. 2 Lattice parameters of V-Ti alloys as a function of titanium content.

tent in Fig. 2. A small concave seems to exist around 20at%Ti and similar tendency is seen in the results given by Powers and Whilheim<sup>11)</sup>, Adenstedt et al.<sup>12)</sup> and Pietrokowsky and Duwez<sup>13)</sup>.

The p-c-T relationships of V- 5, 10, 15, 20 and 30at%Ti alloys are shown in Figs. 3 and 4. The maximum hydrogen contents in the alloys containing 5 ~20at%Ti were 1.85~1.90 H/M, irrespective of titanium content. The heat-treatment at 1373K for 1

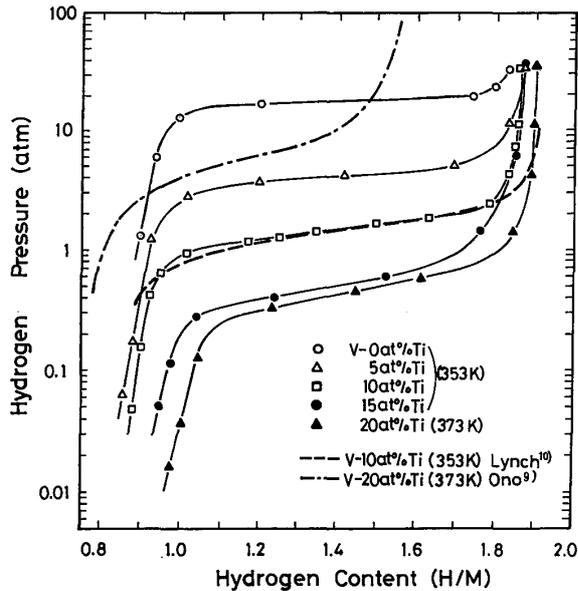


Fig. 3 The p-c desorption isotherms of V-Ti alloys containing 5 - 20at%Ti.

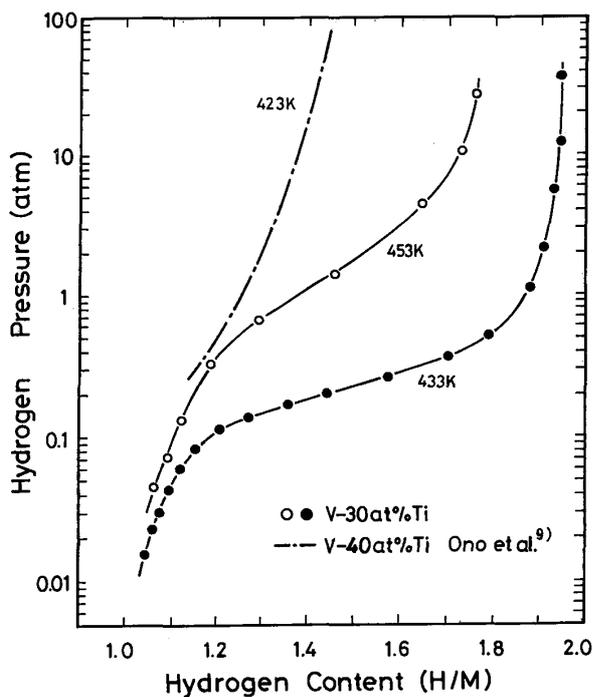


Fig. 4 The p-c desorption isotherms of V-30at%Ti alloy.

week gave no detectable influence on the p-c isotherms of these alloys. An excellent accordance of the p-c isotherm for V-10at%Ti alloy in the present work is seen with that given by Lynch et al.<sup>10)</sup>. On the other hand, the V-20at%Ti alloy in the work of Ono et al.<sup>9)</sup> shows a lower hydrogen content of about 1.6 H/M and a higher plateau pressure than in the present work. In Fig. 4, the alloy containing 30 at%Ti show degenerated p-c-T characteristics, i. e., a significantly sloping plateau, reduced capacity of hydrogen storage at elevated temperatures and poor reproducibility of p-c isotherm.

From the results of p-c isotherm measurement, it was revealed that alloying with titanium endowed vanadium with some modified properties; i) very easy 'activation' (only degassing at 723K in vacuum makes alloys absorb a considerable amount of hydrogen with a bursting evolution of heat) ii) the alloys show no traces of pulverization after hydriding and dehydriding cycles. The appearance of the samples before and after 100 cycles is shown in Fig. 5 together with the result of LaNi<sub>5</sub> alloy. No serious reduction in its hydrogen absorption capacity and no significant change in the plateau pressure were observed in the

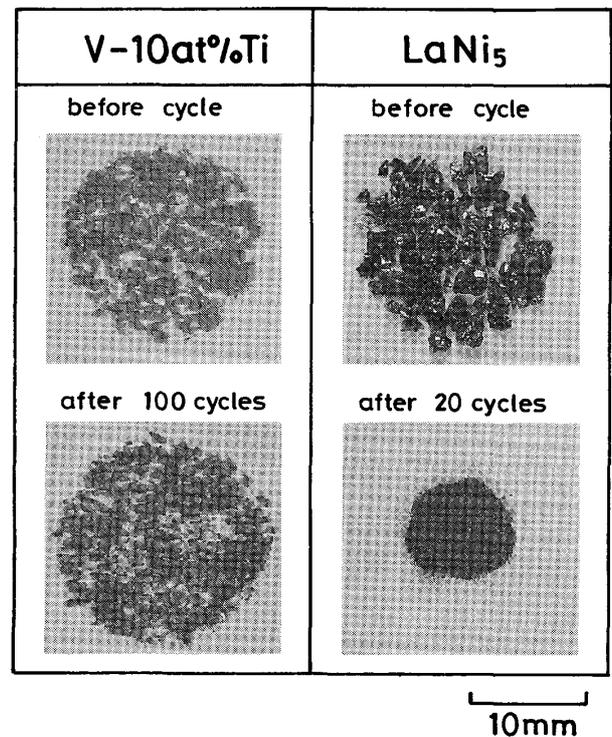


Fig. 5 The appearance of V-10at%Ti alloy and La Ni<sub>5</sub> alloy before and after hydriding and dehydriding cycles.

p-c isotherm of V-10at%Ti alloy after 100 cycles of  $\beta$  monohydride  $\leftrightarrow$   $\gamma$  dihydride transformation. iii) the rate of hydrogen absorption and desorption increases prominently with increasing titanium content. In V-10, 20 and 30at%Ti alloys with initial particle size shown in Fig. 5, the time need for completion of 80% reaction at room temperature was 12min, 3 min and 1 min, respectively.

In Fig. 6, the values of enthalpy and entropy changes for the formation and dissociation of  $\gamma$  dihydride, the slope of plateau,  $d(\ln P)/d(H/M)$ , and the hysteresis factor,  $\ln(P_a/P_d)$ , are shown as a function of titanium content. In determining plateau pressure for a sloping plateau, an average pressure in the plateau region was adopted. In Fig. 6 a, the absolute values of enthalpy changes for the formation and dissociation of  $\gamma$  dihydride increased with increasing titanium content and the alloy containing 20 at%Ti had a value of enthalpy change approximately

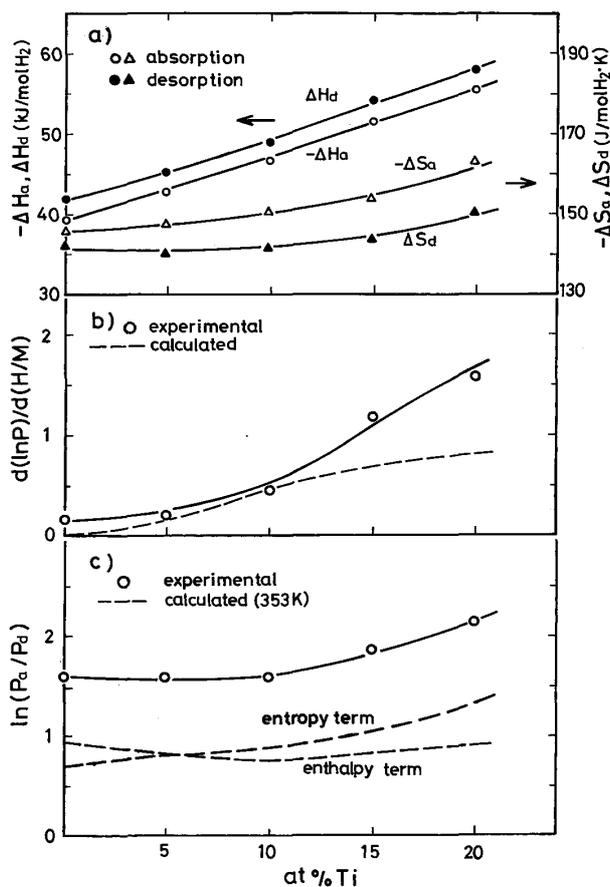


Fig. 6 The enthalpy and entropy changes for the formation and dissociation of  $\gamma$  dihydride(a), the slope of plateau(b) and hysteresis factor(c) for V-Ti alloys as a function of titanium content.

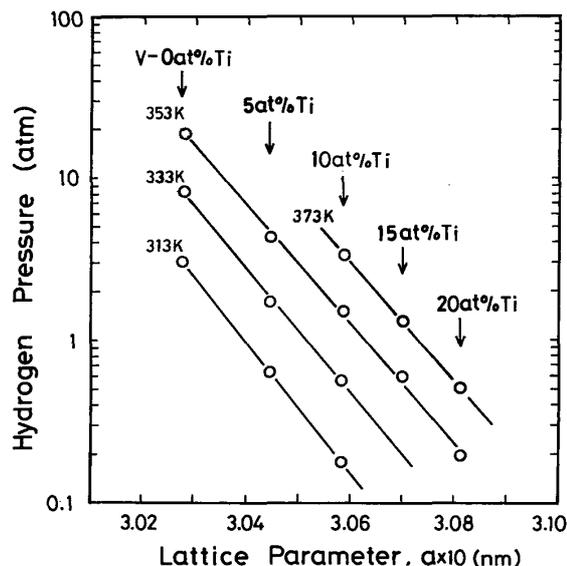


Fig. 7 Relationship between desorption plateau pressure and lattice parameter of V-Ti alloys.

twice of that for LaNi<sub>5</sub>.<sup>3)</sup> The absolute values of entropy change increases gently with increasing titanium content. Since the lattice parameter vs titanium content relationship shown in Fig. 2 is approximately given by a linear function up to 20at%Ti, a linear relationship is observed between the logarithmic plateau pressure and the lattice parameter as illustrated in Fig. 7. On the other hand, the slope of plateau increases gradually with titanium content up to 10at% and steeply at higher Ti content (Fig. 6 b). Hysteresis factor shows a similar dependence on titanium content in Fig. 6 c.

#### IV. Discussion

To elucidate the existence of phase separation at vanadium-rich side of the system, electrical resistance was measured for the alloys containing titanium up to 44at%. In Fig. 8, the electrical resistance is shown as a function of temperature. The ordinate in the figure are given by the normalized resistance of  $R/R_0$  where  $R_0$  is the electrical resistance at room temperature. In V-30at%Ti and V-44at%Ti alloys, two inflection points were observed at about 970K and around 1100K. Decreasing titanium content, the higher inflection point decreases and the lower one appears to remain constant. No significant changes were seen in the alloys containing less than 20at%Ti. However, their resistance curves

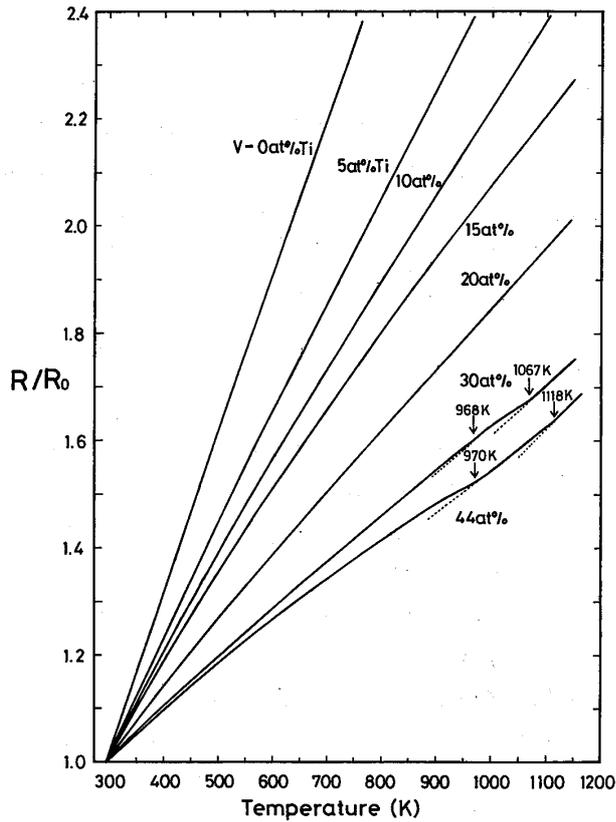


Fig. 8 Variation in electrical resistance of V-Ti alloys with temperature.

show a gentle convex shape and the tendency becomes more distinct with increasing titanium content. The results of electrical resistance measurement are plotted on the phase diagram shown in Fig. 1. It was suggested from the figure that the higher and lower inflection temperatures corresponded to the miscibility gap of  $\beta_1 + \beta_2$ , and the monotectoid temperature in the phase diagram given by Massalski, respectively. A concavity observed around 20at%Ti in the lattice parameter vs titanium content relationship in Fig. 2 appears to support the existence of solubility limit suggested in the Massalski's phase diagram. The presence of the concavity can be explained as a result of the depletion of titanium in the matrix due to the precipitation of a Ti-rich phase from the  $\beta_2$  matrix. On the basis of the solubility limit possibly existing at the vanadium-rich side of the phase diagram, convex-shaped resistance curves observed in the alloys containing less than 20at%Ti in Fig. 8 can be regarded as a result of the dissolution of Ti-rich phase into the  $\beta_2$  matrix, which may be in an intermediate stage because of the limited heating rate employed in

the present work.

The origins of sloping plateau and hysteresis have been discussed by many workers (Ref. 14 - 18 for sloping plateau, Ref. 19 - 22 for hysteresis). In the present results shown in Fig. 6 b, chemical heterogeneity introduced both on solidification and by phase separation on the subsequent cooling was believed to be one of origins for the sloping plateau. On melting raw materials and subsequent solidification, continuous local fluctuation of alloy composition should be introduced in the as-cast alloys, and such chemical heterogeneity could affect on the slope of plateau. From the liquidus and solidus in the phase diagram given by Moffatt<sup>5)</sup> in Fig. 1, it is indicated that the degree of chemical heterogeneity is small at lower titanium concentration and increases with titanium concentration up to about 30at%. This effect gives partly a possible explanation for an increase in the slope of plateau with titanium content. In Fig. 6 b, the calculated slopes of plateau due to chemical heterogeneity introduced on solidification are shown by a broken curve. In the calculation, the distribution profile of titanium was evaluated by Scheil equation<sup>23)</sup> given by the following equation.

$$C_s = kC_o(1 - f_s)^{(k-1)} \quad (1)$$

where  $C_s$  and  $C_o$  are titanium concentrations in the solid and in the alloy, respectively,  $k$  is the coefficient for equilibrium partition of titanium between solid and liquid and  $f_s$  is a fraction solidified. The value of  $k$  for titanium was read from the phase diagram given by Moffatt<sup>5)</sup>. The maximum and minimum titanium concentrations at  $f_s = 0$  and  $f_s = 0.8$  where a subsequent solidification ( $f_s > 0.8$ ) was considered to progress in an instant were converted to corresponding plateau pressures through the results given in Figs. 2 and 7. The calculated change in plateau pressure represents well the experimental results up to 10at%Ti but a deviation is seen at higher titanium content. This discrepancy can be ascribed to the existence of solubility limit, and the precipitation of Ti-rich second phase could cause an enhanced chemical inhomogeneity. In the case of V-30at%Ti, the additional phase separation due to the monotectoid reaction is considered to cause an additional chemical

heterogeneity which led to the intensively sloping plateau.

The cause of hysteresis is not fully clarified, although several explanations have been demonstrated<sup>19-22</sup>. Flanagan and Clewley<sup>24</sup> have discussed the mechanism and have related their model to Wagner's explanation<sup>20</sup>. They introduced an additional enthalpy term  $\Delta H_{\text{disl}}$  for dislocation production in the chemical potential equations for hydride formation and decomposition. The hysteresis factor is given,

$$\ln(P_a/P_d) = 2 \Delta H_{\text{disl}}/RT \quad (2)$$

where  $P_a$  and  $P_d$  denote absorption and desorption plateau pressures, respectively.

For pure vanadium, using the enthalpy values given in Fig. 6 a, we obtain  $\Delta H_{\text{disl}} = 2.35 \text{ kJ/molH}_2$  for its dihydride formation. The value of  $\Delta H_{\text{disl}}$  for vanadium is much greater than that of  $0.8 \text{ kJ/molH}_2$  for  $\text{LaNi}_5$  alloy<sup>25</sup>. This may be attributable to the difference in lattice stiffness of  $\text{LaNi}_5$  alloy and vanadium monohydride because vanadium monohydride is expected to be much stiffer than non-hydrided  $\text{LaNi}_5$  alloy. The contributions of enthalpy and entropy terms to the hysteresis factor were evaluated from the von't Hoff equation and are given in Fig. 6 c. Both the terms are of the same magnitude. Since the enthalpy term is roughly constant, the dependence of entropy term on titanium content reflects itself in that of the hysteresis factor. The accordance of the increase in hysteresis factor at titanium content higher than 10at% with the large deviation of the slope of plateau from the calculated curve may imply that the dependence of hysteresis factor on titanium content could be related to the phase separation possibly occurred in the alloys with higher titanium contents.

## V. Conclusion

From the measurement of p-c isotherms for V-5~30at%Ti alloys, it was revealed that on the application for metal hydride heat-pump, V-Ti alloys have excellent characteristics such as rapid absorption and desorption of hydrogen, easy activation, a large heat evolution on the formation of the dihydride

and a superior resistance to pulverization on hydriding and dehydriding cycles. However, the alloys inherit a large hysteresis of pure vanadium and the alloys containing more than 30at%Ti display intensively sloping plateau due to phase separation resulting from monotectoid reaction and solubility limit indicated at vanadium-rich side of the phase diagram given by Massalski.

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