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Structure of $Ti_{1-y}V_yH_x$ Alloys Studied by X-Ray Diffraction and by ^1H and ^{51}V NMR

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The structure of the Ti–V–H system is studied by X-ray diffraction and ^1H and ^{51}V NMR measurements. It is shown that the solid solution of Ti–V is separated into a few phases by hydrogenation. They are α-Ti–V–H, β-Ti–V–H, γ-Ti–V–H, and γ-Ti–H phases, which are assumed to have their origins either in TiH_x or in VH_x. The concentration of each phase can be estimated by NMR, which is dependent on the composition of the system. The phase separation caused by hydrogenation is due to the large stability of the γ-Ti–H phase.

Introduction

Metal hydrides have recently attracted much attention because they can be used as hydrogen-storage materials. It is well known that the transition metals of IVa and Va groups form stable hydrides by reacting with hydrogen. Titanium and vanadium make a solid solution in a wide range of composition and temperature. The hydrides of titanium–vanadium alloys are expected to vary continuously in properties depending on their composition.

Nagel and Perkins (*1*) reported that the structure of $Ti_{1-y}V_yH_x$ ($0 \leqq y \leqq 0.5$, $1.6 \leqq x \leqq 1.92$) is face-centered cubic (fcc) or tetragonal (fct). Ono *et al.* (*2*) also reported on the fcc structure of $Ti_{1-y}V_yH_x$ ($0.2 \leqq y \leqq 0.8$, $x \sim 2$) and the body-centered tetragonal (bct) structure of $Ti_{0.2}V_{0.8}H_{0.90}$.

In the present work we study the structure of $Ti_{1-y}V_yH_x$ ($0.4 \leqq y \leqq 0.8$) mainly in the region of $x \sim 1$ by measuring the X-ray diffraction patterns and ^{51}V and ^1H NMR spectra; it is shown that the ^{51}V and ^1H NMR spectra can be usefully applied to study the structure of vanadium-containing hydrides, when combined with the X-ray diffraction measurements.

Experimental

Materials

The Ti–V alloys were supplied by the Central Research Laboratory of the Mitsubishi Metal Corporation. They had been prepared by the method described in (*2*). The hydrides of the Ti–V alloys, vanadium metal, and titanium metal were synthesized by reaction with hydrogen gas in a manner similar to that described previously (*3*).

The hydrogen content of the hydrides was determined from the volumes of hydrogen gas evolved at higher temperatures. The hydrides containing titanium were heated up to 1000°C and those without titanium up to 600°C.

Powder X-Ray Diffraction Measurements

The powder X-ray diffraction patterns of

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the hydrides were measured at room temperature, using Rigaku RU-200PL (Rotaflex) and Rigaku Geiger-flex diffractometers with Cu$K\alpha$ irradiation. The lattice parameters were calculated by a least-squares method, using the RSLC-3 computer program (*4*).

NMR Measurements

The hydrides were pulverized into 200-mesh powder, and then sealed in Pyrex glass ampoules under vacuum.

^{51}V and ^1H wide line spectra were measured at room temperature by a Varian wide line spectrometer equipped with a Varian V-7570 field dial regulator Mark II. The spectra of ^{51}V and ^1H nuclei were measured at 15 and 35 MHz, respectively, by sweeping the magnetic field. By using a Bruker CXP-100 pulsed spectrometer, Fourier-transformed (FT) spectra of ^1H nucleus were determined at resonance frequency of 55 MHz. The FT spectra were obtained by the Fourier-transformation of free induction decay (FID), solid echo (*5*), and spin-echo signals (*6*).

Results and Discussion

X-Ray Diffraction Patterns

Figure 1 shows the X-ray diffraction patterns of the Ti–V hydrides; Table I summarizes the results, together with those of TiH_x and VH_x.

The observed diffraction patterns of the hydrides of the Ti–V alloys are mixtures of three patterns of fcc, bct, and hcp (hexagonal close-packed) structures. The concentration of each phase depends on the composition of the Ti–V alloys and the hydrogen content. The hcp phase is always present in small concentration in the Ti–V hydrides studied. The fcc phase increases with the content of titanium or hydrogen. The bct phase dominates in $Ti_{0.20}V_{0.80}H_{0.77}$, while in $Ti_{0.40}V_{0.60}H_{0.79}$ and $Ti_{0.60}V_{0.40}H_{0.90}$ the bct and the fcc phases are comparable to each other. In $Ti_{0.60}V_{0.40}H_{1.78}$ the fcc phase dominates, and the lattice constant agrees with the results of Nagel and Perkins (*1*) and Ono *et al.* (*2*).

On the other hand, the hydrides of titanium or vanadium metal show single- or two-phase structures. The structures of TiH_x and VH_x are well established (*7*). For TiH_x, the α phase has a hcp structure and the γ phase has a fcc structure. The β phase of TiH_x is body-centered cubic (bcc) and is not usually observed at room temperature. For VH_x, the α phase has a bcc structure, the β phase a bct structure, and the γ phase a fcc structure.

The three structures observed in the Ti–V hydrides are assumed to have their origin either in TiH_x or in VH_x. The hcp and bct structures originate from the α phase of TiH_x and the β phase of VH_x, respectively. The lattice constants of the hcp structure in

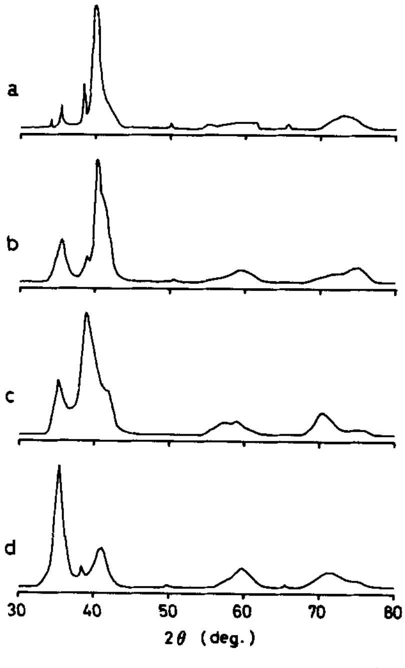

FIG. 1. Powder X-ray diffraction patterns of the Ti–V hydrides: (a) $Ti_{0.20}V_{0.80}H_{0.77}$, (b) $Ti_{0.40}V_{0.60}H_{0.79}$, (c) $Ti_{0.60}V_{0.40}H_{0.90}$, and (d) $Ti_{0.60}V_{0.40}H_{1.78}$.

TABLE I

LATTICE CONSTANTS (Å) OBTAINED FROM THE X-RAY DIFFRACTION MEASUREMENTS

Hydride	x	fcc	bct a_0	bct c_0	hcp a_0	hcp c_0
TiH_x	0				2.950[a]	4.686[a]
	0.94	4.403			2.949	4.687
	1.95	4.458				
$Ti_{0.60}V_{0.40}H_x$	0.90	4.42	3.06	3.55	[c]	
	1.78	4.39	[c]		3.05	5.10
$Ti_{0.40}V_{0.60}H_x$	0.79	4.39	3.08	3.25	3.01	5.04
$Ti_{0.20}V_{0.80}H_x$	0.77	4.37	3.07	3.32	3.03	5.09
VH_x	0.77		3.034[b]	3.410[b]		
	1.6	4.275	3.02	3.46		

[a] See p. 1416 in (*12*).

[b] S. Hayashi, K. Hayamizu, and O. Yamamoto, *J. Phy. Chem. Solids*, in press.

[c] The existence of this phase cannot be rejected.

the Ti–V hydrides are larger than those in TiH_x, and they are assumed to increase by the addition of V. The lattice constants of the bct structure of VH_x increase in the a_0 direction and decrease in the c_0 direction by Ti addition at less than 40 at.%. However, the c_0 value of $Ti_{0.60}V_{0.40}H_{0.90}$ is larger than the value of $VH_{0.77}$. In any case, the bct phase is assumed to contain both Ti and V atoms. The fcc structure can arise from both of the γ phases in TiH_x and VH_x. The increase in the fcc phase with the Ti content is explained by the increase in the γ phase which has its origin in TiH_x. The increase in the fcc phase with the hydrogen content is also observed in TiH_x and VH_x, where the γ phases of those hydrides are formed to a greater extent by addition of hydrogen. However, it is not clear from the X-ray results alone whether the fcc phase contains both Ti and V atoms.

^{51}V *Wide Line NMR Spectra*

Figure 2 shows the ^{51}V spectra of several hydrides containing vanadium in the derivative form, and Table II summarizes the results.

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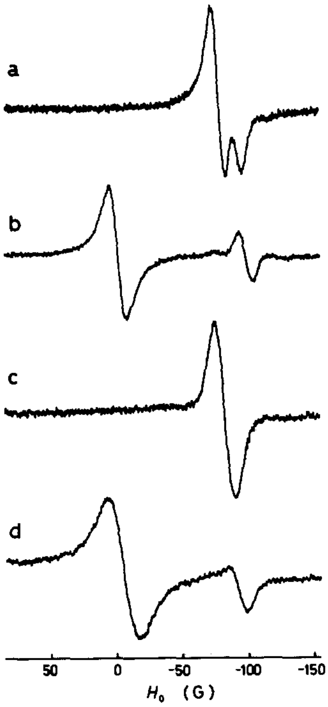

FIG. 2. ^{51}V wide line NMR spectra of the vanadium-containing hydrides at room temperature, measured at 15 MHz: (a) $VH_{0.20}$, (b) $VH_{1.6}$, (c) $Ti_{0.60}V_{0.40}H_{0.90}$, and (d) $Ti_{0.60}V_{0.40}H_{1.78}$. A NH_4VO_3 aqueous solution was used as a reference.

TABLE II

SHIFTS AND LINEWIDTHS[a] (IN PARENTHESES) OF ^{51}V AND ^1H NMR SPECTRA AT ROOM TEMPERATURE

		^{51}V [% (Gauss)][b]			^1H [Gauss][c]	
Hydride	x	α	β	γ	Narrow	Broad
TiH_x	0.94					0.7(14)
	1.95					1.7(11)
$Ti_{0.60}V_{0.40}H_x$	0.90		0.62(15)		0.6(0.5)	1.0(13)
	1.78		0.70(14)	0.04(25)	0.7(0.7)	1.3(17)
$Ti_{0.40}V_{0.60}H_x$	0.79		0.63(20)		0.6(0.6)	1.0(14)
$Ti_{0.20}V_{0.80}H_x$	0.77		0.74(11)		0.5(0.7)	
VH_x	0	0.57(13)				
	0.20	0.59(11)	0.68[d]		0.6(1.6)	
	0.41	0.59[d]	0.69(10)		0.7(1.2)	
	0.77		0.76(11)		0.7(0.8)	
	1.6		0.75(11)	0.01(13)	0.7(0.7)	2.2(24)

[a] The width between the two extrema is measured in the derivative spectra.

[b] The Knight shift relative to NH_4VO_3 aq. is calculated.

[c] The shift relative to H_2O is measured in the high-field direction in Gauss unit.

[d] This peak is a shoulder.

Shevakin (*8*) observed the ^{51}V signals of β and γ phases separately at 10.5 MHz. Däumer *et al.* (*9*) reported the separation between the signals of α and β phases at a field higher than about 30 kG (about 34 MHz). In this work we observe the ^{51}V resonance at 15 MHz and we are able to observe the signal of each phase in VH_x separately, although the separation between the α and the β phases is incomplete. The ^{51}V signals of VH_x are observed at about −80 G for the α phase, at −90 ~ −100 G for the β phase, and at about 0 G for the γ phase (referred to an aqueous solution of NH_4VO_3).

^{51}V NMR was applied to the Ti–V hydrides in order to examine the existence of the phases corresponding to the three phases in VH_x. Only the β phase is observed in $Ti_{0.60}V_{0.40}H_{0.90}$, while the X-ray results indicates the existence of two or three phases. The spectra of $Ti_{0.40}V_{0.60}H_{0.79}$ and of $Ti_{0.20}V_{0.80}H_{0.77}$ are similar to that of $Ti_{0.60}V_{0.40}H_{0.90}$. These results suggest that the vanadium atoms in the Ti–V–H system exist only in the β phase, i.e., the bct phase, at a hydrogen concentration of $x \sim 0.8$. The hcp structure is present in small concentration and thus it may not be observed by ^{51}V NMR, even if vanadium atoms exist in this phase. The fcc phase in these hydrides contain no vanadium atoms, and, therefore, it is assumed to be the γ phase of TiH_x. The lattice constants of the fcc phase agree well with the value of the fcc phase in $TiH_{0.94}$.

On the other hand, the vanadium atoms in $Ti_{0.60}V_{0.40}H_{1.78}$ exist both in the β and in the γ phases. The existence of the β (bct) phase is confirmed by ^{51}V NMR, although it is not clearly present in the X-ray diffraction patterns. The γ phase observed is assumed to be the fcc phase of VH_x modified by titanium atoms. It is not clear whether the γ phase of TiH_x exists or not.

^1H *Wide Line NMR Spectra*

Figure 3 shows the ^1H NMR spectra of several hydrides in the derivative form at room temperature, and Table II summarizes the results. Two components with different linewidths are observed.

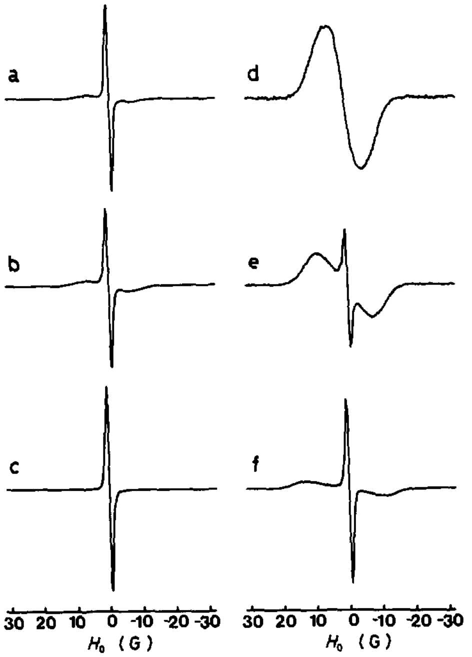

FIG. 3. ^{1}H wide line NMR spectra of the hydrides at room temperature, measured at 35 MHz: (a) $Ti_{0.60}V_{0.40}H_{0.90}$, (b) $Ti_{0.40}V_{0.60}H_{0.79}$, (c) $Ti_{0.20}V_{0.80}H_{0.77}$, (d) $TiH_{1.95}$, (e) $Ti_{0.60}V_{0.40}H_{1.78}$, and (f) $VH_{1.6}$. A $CuSO_4$ aqueous solution was used as a reference.

Only the broad component is observed in TiH_x, which is the ^{1}H atoms in the γ phase. For VH_x, the ^{1}H atoms in the β phase form the narrower component and those in the γ phase the broader component. The linewidth of the γ phase is broader in VH_x than in TiH_x. Only the narrow component is observed in $Ti_{0.20}V_{0.80}H_{0.77}$, which is assumed to be the bct phase. The spectra of $Ti_{0.60}V_{0.40}H_{0.90}$ and $Ti_{0.40}V_{0.60}H_{0.79}$ consist of two components, where the narrower is the bct phase of Ti–V–H and the broader is the γ phase of Ti–H. In $Ti_{0.60}V_{0.40}H_{1.78}$, the two components observed are the bct and the fcc phases. The hydrogen in the hcp phase should be observed in the narrower component, but it cannot be observed separately.

^{1}H Pulsed NMR Spectra

The pulsed NMR method has many advantages over the wide line (continuous wave) NMR method. Concerning the FT spectra, different types of spectra can be obtained by changing the pulse sequence, i.e., the measuring mode. Usually the FID signal after a single pulse is observed. The solid echo method (*5*) is useful for observing the very broad component whose lineshape cannot be obtained exactly from the FID signal due to the dead time of the receiver. In the spin-echo method no signal is obtained from a component which is broadened only by the homonuclear dipole–dipole interaction (*5*).

Figure 4 shows the variation of the lineshape of $Ti_{0.60}V_{0.40}H_{0.90}$ due to the change of the measuring mode. The ratio of the broader to the narrower components decreases in the order of solid-echo (b), FID (a), and spin-echo (c) spectra. In the spin-echo spectra the broader component disappears, which suggests that the broader component is due to a rigid lattice with only

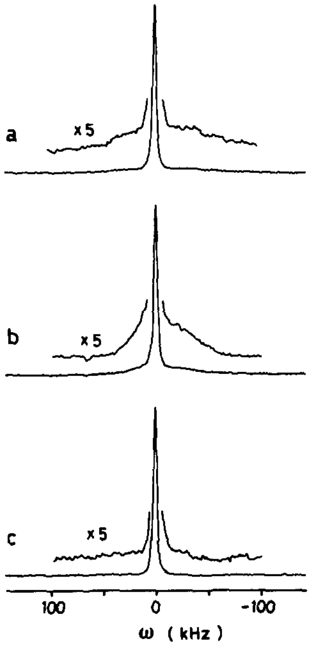

FIG. 4. ^{1}H FT NMR spectra of $Ti_{0.60}V_{0.40}H_{0.90}$ at 296 K, measured at 55 MHz. The pulse sequences used are (a) single 90° pulse (FID), (b) 90°_x–90°_y (solid echo), and (c) 90°_x–180°_y (spin echo).

the homonuclear dipole–dipole interaction (5). For titanium, although ^{47}Ti and ^{49}Ti nuclei have nuclear spins, their natural abundances and resonance frequencies are very low compared to ^{1}H nucleus. Therefore, the ^{1}H–Ti dipolar interaction is negligible. On the other hand, for vanadium, the ^{1}H–^{51}V dipolar interaction should be taken into consideration since the natural abundance of the ^{51}V nucleus is about 100%. It is proved conclusively that the broader component does not arise from the Ti–V–H system but from the Ti–H system, which is consistent with the results of the wide line NMR.

For $Ti_{0.40}V_{0.60}H_{0.79}$, spectra similar to that in Fig. 4 are observed, and the existence of the Ti–H phase is also ascertained. The hydrogen content is estimated from the area of each component. The hydrogen in the Ti–H phase is about 30% of the total hydrogen for $Ti_{0.60}V_{0.40}H_{0.90}$ and about 50% for $Ti_{0.40}V_{0.60}H_{0.79}$. For $Ti_{0.20}V_{0.80}H_{0.77}$, the broader component cannot be detected by NMR.

Figure 5 shows the spectra of $Ti_{0.60}V_{0.40}H_{1.78}$. A broader component is observed in the spin-echo spectra, which suggests that the component is in the phase containing vanadium. The area of the broader component in the solid-echo as well as in the FID spectra is much larger than in the spin-echo spectra. In the solid-echo and the FID spectra the broader component is about 90%, and in the spin-echo spectra it is about 60%. This suggests that the broader component is a mixture of two phases with and without vanadium. Thus, the fcc phase in $Ti_{0.60}V_{0.40}H_{1.78}$ consists of Ti–V–H and Ti–H. The narrower component is assigned to the bct-Ti–V–H phase. The composition can be estimated as follows: bct-Ti–V–H 10%, fcc–Ti–V–H 15%, and fcc-Ti–H 75%.

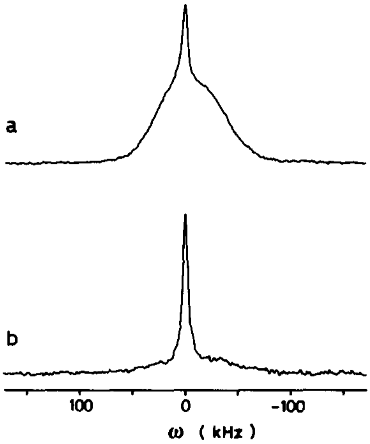

FIG. 5. ^{1}H FT NMR spectra of $Ti_{0.60}V_{0.40}H_{1.78}$ at 296 K, measured at 55 MHz: (a) solid echo, and (b) spin echo.

TABLE III

THE HYDROGEN RATIO IN THE THREE PHASES, ESTIMATED FROM THE RESULTS OF THE ^{1}H PULSED NMR

Hydride	x	Hydrogen ratios (%) bct-Ti–V–H	fcc-Ti–V–H	fcc-Ti–H
$Ti_{0.60}V_{0.40}H_x$	0.90	70	0	30
	1.78	10	15	75
$Ti_{0.40}V_{0.60}H_x$	0.79	50	0	50
$Ti_{0.20}V_{0.80}H_x$	0.77	100	0	0

Table III summarizes the hydrogen ratio in the three phases, obtained from the ^{1}H pulsed NMR spectra. The hydrogen distribution over the phases is dependent on the composition of the Ti–V–H system.

Structure of the Ti–V–H Alloys

Titanium and vanadium metals form a solid solution, called as β-Ti–V phase, over all the composition range above 900°C (*10*) At lower temperatures a small amount of α-Ti precipitates. Ono *et al.* (*2*) reported the structure of the Ti–V alloys, and they detected the α-Ti phase in the sample containing 80 at.% Ti. Thus, the Ti–V alloys are mixtures of the β-Ti–V phase and a small amount of the α-Ti phase.

The Ti–V alloys are separated into several phases by hydrogenation. We name the Ti–V–H phases according to their origin as follows: the hcp phase is the α phase, the bct phase is the β phase, and the fcc phase is the γ phase. From the above discussion the hydriding process is expressed as

$$\beta\text{-Ti–V} + \alpha\text{-Ti(small amount)} \xrightarrow{H_2} \alpha\text{-Ti–V–H} + \beta\text{-Ti–V–H} + \gamma\text{-Ti–V–H} + \gamma\text{-Ti–H}.$$

The α-Ti and the α-Ti–V–H phases are present in small concentration. The α-Ti–V–H phase can be detected only by X-ray diffraction measurements. The lattice parameter of the phase is larger than that of the α-TiH_x phase. The α-Ti–V–H phase exists in a wide range of hydrogen concentration, although the hcp structure is observed in a range of smaller hydrogen concentration in TiH_x.

The β-Ti–V phase has a bcc structure (*2*) and the β-Ti–V–H phase has a bct structure. The situation is similar to the relation between vanadium metal and β-VH_x.

The γ-Ti–H phase has a fcc structure and increases with the increase in titanium or hydrogen. Although a small amount of this phase may be produced from the α-Ti phase, most of the γ-Ti–H phase is produced from the β-Ti–V phase.

At higher hydrogen concentration, the β-Ti–V–H phase changes to the γ-Ti–V–H phase which has a fcc structure. Nagel and Perkins (*1*) and Ono *et al.* (*2*) reported on the structure of the γ-Ti–V–H phase. They did not discuss the γ-Ti–V–H and the γ-Ti–H phases separately, because the two phases both have fcc structures and cannot be separated by the X-ray diffraction measurement.

The separation of the β-Ti–V phase into a few phases, α-, β-, and γ-Ti–V–H and γ-Ti–H, is considered to result from the great stability of TiH_x. The enthalpy of formation of γ-TiH_x from Ti metal is about −30 kcal/mole (*7*), while the value for $VH_{0.500}$ is about −4 kcal/mole (*7*), and the value for $VH_{2.00}$ produced from $VH_{0.95}$ is about −5 kcal/mole (*11*). The enthalpy of mixing of two metals is usually less than a few kilocalories per mole (*12*). Thus γ-TiH_x is much more stable than the others, and, therefore, the γ-Ti–H phase precipitates upon hydrogenation of Ti–V alloys.

Acknowledgments

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