The Determination of the Ratio of Two Kinds of Hydrogen in Metal Hydrides by Means of Pulsed NMR

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Synopsis. A method is proposed by which the composition of the two kinds of hydrogen with different diffusional behavior in metal hydrides can be determined accurately by means of ^{1}H NMR; using the method, it is found that the energy difference between the two sites occupied by the two kinds of hydrogen is 7.9 kJ/mol in $VH_{0.77}$.

Metal-hydrogen alloys have recently attracted much attention as hydrogen-storage materials because they can absorb and desorb large amounts of hydrogen reversibly; many studies have been performed by various methods.[1)]

A number of phases have been observed in the metal-hydrogen systems; they are called α-, β-, and γ-phases, and so on. There exist, in most of the hydrides, wide two phase regions, where at least two kinds of hydrogen are observed by means of ^{1}H NMR spectroscopy.[2)] Even if the metal lattice is in a single phase, the existence of several kinds of hydrogen is occasionally observed within a limited temperature range. It was observed by continuous-wave (cw) NMR spectroscopy that hydrogen in the hydrides of the Va group metals consists of two components in the β-phase at about 160 K;[3–5)] the same is true of hydrogen in $ZrH_{1.99}$ at about 440 K.[6)] The nature of each component is almost unknown, and, thus far, no quantitative investigations have been made of the concentration of each component. In metal-hydrogen alloys, the existence of several kinds of hydrogen is common, and it is very important to determine the composition accurately. However, in solids it is difficult to determine the true composition accurately because of instrumental limitations.

In this paper we propose a method for accurately determining the composition by means of pulsed NMR method, making use of the difference in the spin-spin relaxation times. Then, using the method, the concentrations of two kinds of hydrogen with different diffusional behavior which are observed in the β-phase of $VH_{0.77}$ are determined.

Experimental

Vanadium hydride, $VH_{0.77}$, was prepared by a reaction between vanadium metal and hydrogen gas in an autoclave. The synthesized sample was pulverized, passed through a 200-mesh screen, and sealed in a Pyrex glass ampoule.

The equipment used for the NMR measurements was a Bruker CXP-100 pulsed spectrometer whose 90° pulse width was about 1.5 μs. The measurements were performed at 55 MHz for the ^{1}H observation. The spectra were obtained by the Fourier-transformation of the free-induction decay (FID) after 90° -pulse, the solid-echo, and the spin-echo signals.

Results and Discussion

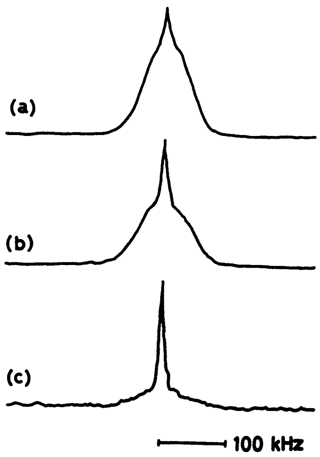

Fig. 1. FT-NMR spectra of ^{1}H in $VH_{0.77}$ at 133 K obtained by the spin-echo metod. The t_d values, which is twice the separation of the two pulses, are (a) 20 μs, (b) 30 μs, and (c) 50 μs, respectively.

Figure 1 shows the ^{1}H Fourier-transformed (FT) NMR spectra of $VH_{0.77}$ at 133 K obtained by the spin-echo method. The spectra are assumed to be superpositions of two components with different linewidths. Similar superimposed spectra are also obtained by the FID and solid-echo methods. These superimposed spectra are observed at temperatures between 120 and 180 K. Above 180 K, motional narrowing occurs, after which the spectra appears to consist of only one component.

The broader line is broadened mostly by the ^{1}H-^{51}V and ^{1}H-^{1}H dipole-dipole interaction, and then assumed to be Gaussian. The narrower line is assumed to be Lorentzian because it seems to be in the region of motional narrowing. The line separation is then carried out, assuming the above-mentioned line-shapes for each component. Thereafter, the ratio of the two components is obtained by integrating the area of each line. However, the ratio is not equal to the true ratio of the two kinds of hydrogen, for the line-shape of the spectra varies, depending on t_d, the time interval between the first 90°_x pulse and the beginning of the signal acquisition, as is shown in Fig. 1. The ratio of the narrower component (II) to the broader one (I) increases as t_d increases. The t_d dependence of the spectra can be explained by the well-known principles of pulsed NMR spectroscopy.[7)] The magnetization of the i-th component at the echo maximum, $M_i(t_d)$, is expressed as:

$$M_i(t_d) = M_i^\circ \exp(-t_d/T_{2i}), \qquad (1)$$

where M_i° is the magnetization at $t_d=0$ and where T_{2i} is the spin-spin relaxation time of the i-th component. The observed magnetization is the sum of that of each component. Component I has a shorter T_2 than Component II, so $M_I(t_d)$ decreases faster than $M_{II}(t_d)$ as t_d increases. If we could make t_d equal to zero, the true ratio of the two kinds of hydrogen, M_{II}°/M_I°, could be determined. This is generally impossible, however, because of instrumental limitations. The receiver cannot work for a short period, which is called "dead time," after a transmission of the radiofrequency pulse. For our equipment it is about 8 μs. The observed linewidth of the broader component in $VH_{0.77}$ is about 50 kHz, and the T_2 value is estimated to be 6 μs, which is comparable to the "dead time." However, $M_{II}°/M_I°$ can be determined by the extrapolation of $M_{II}(t_d)/M_I(t_d)$ to $t_d=0$, as is shown in Fig. 2. A very good linearity is obtained, and the slope is defined as a function of the two T_{2i} values.

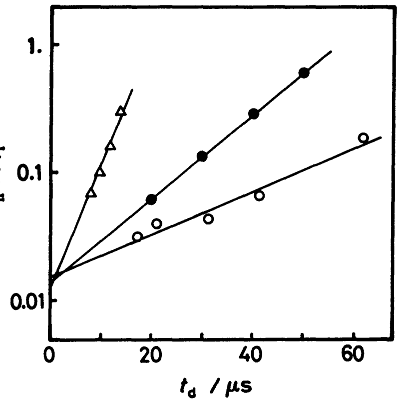

Fig. 2. The t_d dependence of the apparent ratio of the two components in $VH_{0.77}$ at 133 K.
○: Solid echo, ●: spin echo, and △: FID.

Similar t_d dependences of the line-shapes are observed by the other two methods, the solid-echo and the FID methods, as is shown in Fig. 2. The M_{II}/M_I values change exponentially with t_d, the slope being different in the three methods. In the solid-echo method, the magnetization of each component at the echo maximum decays with a time constant longer than T_2. The FID curve falls faster than the other two methods. If the line-shape of the FT spectra is of a Lorentzian type, the FID curve shows an exponential decay whose time constant is expressed as:

$$1/T_{2i}^* = 1/T_{2i} + (\text{magnetic inhomogeneity term}). \quad (2)$$

While the broader component seems to be a Gaussian type in the present case of $VH_{0.77}$, it can be assumed to be approximately a Lorentzian type, as is shown in Fig. 2, for the linear extrapolation is possible and the extrapolated value, M°_{II}/M°_I, in this method is in excellent agreement with the values in the other two methods.

The agreement of the extrapolated values in the three methods, within the limits of experimental error, proves the validity of this extrapolation method for determining the ratios of each hydrogen. The first 90°_x pulse width should be taken into consideration if it is not negligible compared to t_d. It is about 1.5 μs for our equipment, though, and is negligible, considering the experimental error. The accuracy of the extrapolated value becomes higher as the difference of T_{2i} decreases, due to the nature of the extrapolation method. However, a component with an extremely low concentration and a long spin-spin relaxation time will be observed by a good choice of t_d values, and then the approximate concentration of the component can be obtained by the extrapolation method described above.

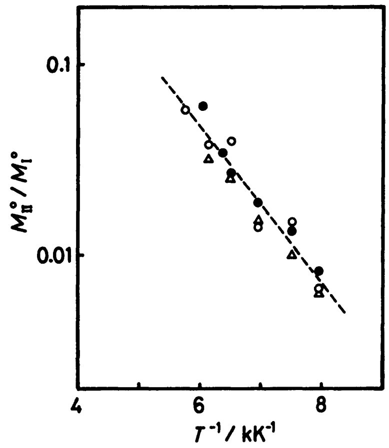

Fig. 3. The temperature dependence of the ratio of the two kinds hydrogen in $VH_{0.77}$.
○: Solid echo, ●: spin echo, and △: FID.

Figure 3 shows the temperature dependence of the ratio of the two kinds of hydrogen in $VH_{0.77}$. The Arrhenius relation is satisfied in the temperature range from 120 to 170 K, and from its slope, the apparent energy difference of the two components is calculated to be 7.9 kJ/mol. Hydrogen atoms of Component I occupy more stable sites than those of Component II, and the exchange of hydrogen atoms between the two sites is slow. "Motional narrowing" has already occurred in Component II in the temperature range studied, but not in Component I; *i.e.*, hydrogen of Component II diffuses faster than that of Component I. Thus, we can determine the composition of different kinds of hydrogen with different diffusional behavior in metal hydrides by means of pulsed NMR spectroscopy.

References

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