

# HYDROGEN DISTRIBUTION IN THE $\text{Mo}_{0.5}\text{Ti}_{0.5}\text{H}_x$ ALLOY AS PROBED BY NMR

**Tarasov V.P., Privalov V.I., Kirakosyan G.A., Padurets L.N., and Shilov A.L.**  
Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences,  
Leninskii pr. 31, Moscow, 119991 Russia  
*E-mail: tarasov@igic.ras.ru*

## Introduction

Hydriding of binary alloys of transition metals leads to the introduction of hydrogen atoms into tetrahedral and/or octahedral interstices of the metal matrix. The number of interstices suitable for accommodation of hydrogen atoms is determined by the type of lattice, the H–H blocking radius (2.15–2.25 Å), and the "activity for hydriding." In molybdenum hydride MoH with an hcp lattice obtained at the hydrogen pressure  $P_{\text{H}_2} \sim 30\text{--}50$  thousand atmospheres, hydrogen occupies only octahedral positions. In titanium hydrides  $\text{TiH}_x$  with an fcc lattice obtained at  $P_{\text{H}_2} = 1$ , hydrogen atoms occupy only tetrahedral interstices. The  $\text{Mo}_x\text{Ti}_{1-x}$  alloy has a bcc lattice. This alloy absorbs hydrogen at  $P_{\text{H}_2} = 1$  atm to form a hydride with an fcc lattice. Here, we report the results of the  $^1\text{H}$  and  $^{95}\text{Mo}$  NMR study of the compositions  $\text{Mo}_{0.5}\text{Ti}_{0.5}\text{H}_{1.94}$  (**I**) and  $\text{Mo}_{0.5}\text{Ti}_{0.5}\text{H}_{2.0}$  (**II**) aimed at determining the hydrogen distribution over interstices and the hydrogen mobility in the binary alloy.

## Experimental

The  $\text{Mo}_{0.5}\text{Ti}_{0.5}$  alloy was hydrided at  $P_{\text{H}_2} = 1$  atm as described in [1]. The X-ray powder diffraction patterns of **I** and **II** showed that the major phase has an fcc lattice. The second phase was not identified. The  $^{95}\text{Mo}$  NMR spectra were recorded in a magnetic field of 7.5 T. The  $^1\text{H}$  NMR spectra were recorded in magnetic fields of 0.55, 7.05, and 14.1 T in a temperature range of 210–390 K. The  $T_1$  and  $T_2$  times of protons were measured in the magnetic field  $H_0 = 0.55$  T at a frequency of 23.5 MHz in the range 210–390 K.  $T_1$  was measured by the magnetization inversion–recovery method using the two-pulse sequence  $\{\pi-\tau-\pi/2\}_n$ ; the  $\pi/2$  pulse width was 7  $\mu\text{s}$ . In  $T_1$  measurements, the magnetization recovery was described by a single-exponential function. The spin–spin relaxation time ( $T_2$ ) was measured using the Carr–Purcell–Meiboom–Gill (CPMG) multipulse sequence  $\{\pi/2-\tau/2-\pi-\tau(\text{echo})-\pi-\tau(\text{echo})-\pi-\dots\}_n$ . Echo signals were recorded. The number of echo signals was  $n = 1024$ , the time interval between  $\pi$  pulses was  $\tau = 40$   $\mu\text{s}$ , and the repetition time was

2 s. The decay of the echo signal amplitude  $M(t)$  was approximated by a sum of two exponents  $M(t) = M_A \exp(-t/T_2^{\text{long}}) + M_B \exp(-t/T_2^{\text{short}})$  using the WINFIT software (Fig. 1). Data processing gave the relative hydrogen contents  $M_A$  and  $M_B$  and relaxation times  $T_2^{\text{long}}$  and  $T_2^{\text{short}}$ .

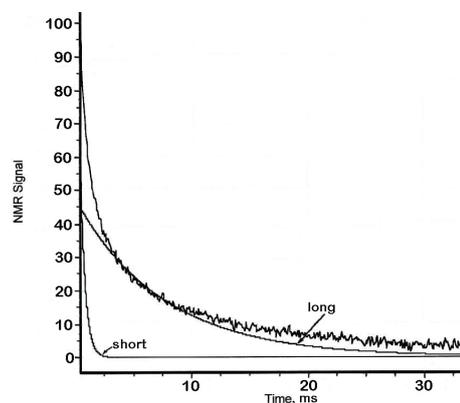


Fig. 1.  $^1\text{H}$  NMR echo decay curve (the CPMG sequence) for sample **II** at 313 K and the result of its decomposition into two exponents with  $T_2^{\text{long}}$  и  $T_2^{\text{short}}$ .

## Results and discussion

For samples **I** and **II**, two spin–spin lattice relaxation times were determined, which differ by an order of magnitude:  $T_2^{\text{long}} \sim 3$  ms and  $T_2^{\text{short}} \sim 0.3$  ms. This is evidence of the existence of two states of hydrogen in **I** and **II**. The relative hydrogen content in each state changes with temperature: as  $T$  increases from 250 to 340 K,  $M_A$  decreases from 21 to 19% in **I** and from 12 to 7% in **II** (Fig. 2).

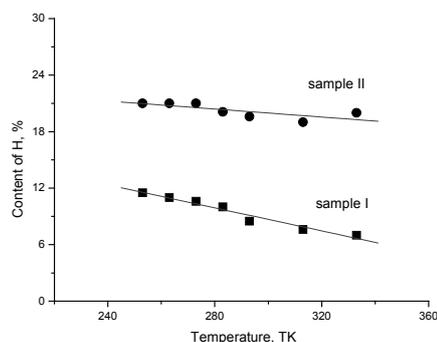


Fig. 2. Hydrogen content in the phase with  $T_2^{\text{long}}$  in **I** and **II** versus temperature.

The dependence of  $T_1$  on temperature has a flat minimum caused by diffusion motion of hydrogen:  $T_{1\min} = 100$  ms at  $\sim 275$  K and  $T_{1\min} = 58$  ms at 265 K for samples **I** and **II**, respectively. The activation energy and preexponential factor are  $E_a = 8.6$  kJ/mol,  $\tau_0 = 97 \times 10^{-12}$  s for **I** and  $E_a = 7.1$  kJ/mol,  $\tau_0 = 170 \times 10^{-12}$  s for **II**. The  $^1\text{H}$  NMR linewidth ( $\Delta\nu$ ) depends on the magnitude of the polarizing magnetic field  $H_0$ . At  $H_0 = 0.55$  T, a single line is observed; at  $H_0 = 7.05$  и 14.1 T, the spectra show two signals with the chemical shifts (referenced to H<sub>2</sub>O signal as zero)  $\sigma_A = -7.7$  ppm and  $\sigma_B = -125.9$  ppm and the integrated intensity ratio  $I_A/I_B = 1.7$  for **I** and  $\sigma_A = -1.3$  ppm,  $\sigma_B = -155.7$  ppm, and  $I_A/I_B = 4.9$  for **II**. Temperature variation is accompanied by a reversible change in the Knight shifts of signals A and B: with decreasing temperature, signal B shifts upfield by  $\sim 100$  ppm, while the shift of signal A depends only slightly on temperature (Fig. 3).

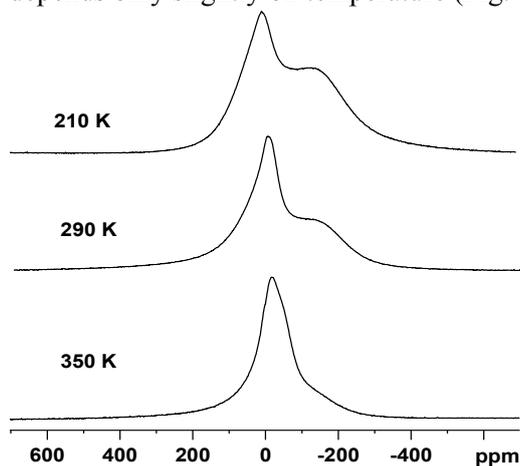


Fig. 3.  $^1\text{H}$  NMR ( $H_0 = 7.05$  T) of  $\text{Mo}_{0.5}\text{Ti}_{0.5}\text{H}_{1.94}$ .

It is worth noting that, for titanium hydrides  $\text{TiH}_x$  ( $x \geq 1.6$ ), the  $^1\text{H}$  NMR signal is also observed in high fields at  $-130 \div -160$  ppm, but the temperature behavior is opposite to the above case; i.e., the signal shifts downfield with decreasing temperature [2].

The field dependence of the linewidths  $\Delta\nu_A$  and  $\Delta\nu_B$  (Table 1) is evidence that each line is a superposition of overlapping signals of hydrogen atoms in different environments. For the fcc lattice

of the  $\text{Mo}_{0.5}\text{Ti}_{0.5}\text{H}_x$  alloy, there are five types of tetrahedral  $[\text{Mo}_x\text{Ti}_{4-x}]$  and seven types of octahedral  $[\text{Mo}_x\text{Ti}_{6-x}]$  surroundings of hydrogen with the maximal content of  $[\text{Mo}_2\text{Ti}_2]$  and  $[\text{Mo}_3\text{Ti}_3]$ , respectively. If signals A and B are taken to be due to T and O positions, respectively, the change in the spectrum shape with temperature reflects the reversible redistribution of hydrogen between the T and O positions.

Table 1.  $^1\text{H}$  NMR linewidths in various magnetic fields  $H_0$  ( $T = 300$  K).

$H_0$ (T)	$\text{Mo}_{0.5}\text{Ti}_{0.5}\text{H}_{1.94}$		$\text{Mo}_{0.5}\text{Ti}_{0.5}\text{H}_{2.0}$	
	$\Delta\nu_A$ , (kHz)	$\Delta\nu_B$ , (kHz)	$\Delta\nu_A$ , (kHz)	$\Delta\nu_B$ , (kHz)
0.55	1.57		2.8	
7.05	13	60	28	60
14.1	27	120	60	100

The  $^{95}\text{Mo}$  NMR spectra of alloys **I** and **II** at 295 K are characterized by the Knight shift  $K(^{95}\text{Mo}) = 1795$  ppm and the quadrupole coupling constant  $\chi_Q \sim 4.7$  MHz.

## Conclusions

On the basis of relaxation and spectral measurements, we demonstrated that there are two hydrogen states in  $\text{Mo}_{0.5}\text{Ti}_{0.5}\text{H}_x$  with rather different Knight shifts and spin-spin relaxation times  $T_2$ .

## References

1. Tarasov V.P., Padurets L.N., Shilov A.L., and Kirakosyan G.A. Dynamics of deuterons in the  $\gamma$  phase of titanium deuteride as probed by NMR. Russ. J. Inorg. Chem. 2009; 54(8).
2. Tarasov V.P., Muravlev Yu.B., Padurets L.N., Shilov L.N., and Kirakosyan G.A., X International Conference ICHMS "Hydrogen Materials," Sudak, Ukraine, 2007, p. 230.

This work was supported by the Russian Foundation for Basic Research, project no. 07-03-00252.