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LATTICE EXPANSION OF TITANIUM DUE TO DISSOLVED HYDROGEN

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The lattice parameter change of polycrystalline titanium due to interstitially dissolved hydrogen at room temperature has been determined by means of X-ray Bragg scattering. In the region of high concentrations ($1.5 < x < 2.0$) $\Delta a/a = (2.14 \pm \pm 0.27) \times 10^{-2}$ per at. % (H/Ti). In this region a small f. c. c. to f. c. t. structure distortion was observed as a consequence of the peak of the density of states arising from the states along $\Gamma - \Delta - L$ (points of the first Brillouin zone) near the Fermi level.

1. Introduction

The possible use of hydrogen as a fuel in future energy systems has focused the attention on metal hydrides as a convenient means of storing hydrogen[1]. Therefore the need for a basic understanding of the interaction between hydrogen and metals has become apparent. In all known metal-hydrogen systems the dissolved hydrogen expands the crystal lattice of the host metal. This expansion leads to lattice distortions (described as strain or stress fields) which give rise to a series of physical property changes[2-4].

The solid solution Ti-H is a system which presents an unexpected amount of hydrogen absorption at room temperature. The current interest in this system is due to the phase transitions observed and the differences in the phase-limits of the different proposed phase diagrams[5,6]. According to the phase diagram of TiH_x[6] at room temperature there is a two-phase region $\alpha + \gamma$ for $0.01 < x < 1.5$; α being the solid solution of hydrogen in h. c. p. Ti and γ the solid solution of hydrogen in f. c. c. Ti with fluorite structure. For $1.5 < x < 2{,}0$ a cubic γ-phase

is found while for $x > 1.8$ up to the strictly stoichiometric composition at $x \cong 2.0$ the tetragonal δ-phase is observed. The value of the tetragonal distortion and the temperature of the transition depend on hydrogen content[7].

Hydrogen in titanium as in many other metal-hydrogen systems is preferentially situated on interstitial sites within the lattice. An atom on such an interstitial site displaces the surrounding atoms from their original sites and a long-range displacement field will be formed around each interstitial. The strength and symmetry of the displacement field can be described by the elactis double force tensor[8-12]. Dissolved hydrogen atoms are located on tetrahedral interstitial sites in titanium[13]. The local tetragonal symmetry of the interstitial site is not transmitted to the strain field which shows cubic symmetry. It is therefore sufficient to measure the volume change in order to determine the elastic double force tensor of the defect completely[14]. Furthermore, it is interesting to study the f. c. c. to f. c. t. distortion that is observed in the region of high hydrogen concentrations in titanium[3,15], due to contradictory information on this distortion. In the present paper high precision X-ray measurements of the lattice parameter change in titanium due to dissolved hydrogen are reported.

2. *Experimental*

The lattice parameter change of TiH_x system was studied from the shift of the angle X-ray Bragg peaks (2Θ: 30°—80°) CuKα radiation[14]. The intensities of the Bragg peaks are attenuated by a static Debye-Waller factor and a diffuse intensity distribution close to the Bragg peaks (Huang scattering) and between the Bragg peaks occurs[16]. Surface effects were negligible and the relative lattice parameter change could be determined with an accuracy of $\Delta a/a > 2 \times 10^4$. The samples were Ti powder with a purity of 99.96% according to the manufacturer's (Metals Research Corp.) specification and were heated to 1500 °C in vacuum to remove the light interstitial impurities N, H, C and O. They were charged with hydrogen at a temperature of about 650 °C and then cooled rapidly down to room temperature. The samples were weighted before and after loading and the mass of the adsorbed hydrogen was calculated. In the present experiment the samples under study had the following concentration of hydrogen in titanium x: 0.22, 0.30, 0.38, 0.46, 0.56, 0.63, 0.75, 0.94, 1.05, 1.25, 1.40, 1.56, 1.65, 1.75, 1.86 and 1.98 (x = H/Ti) estimated with an accuracy of $\Delta x > 0.5\%$.

3. *Results*

The relative lattice parameter change of titanium versus hydrogen concentration at room temperature is summarized in Fig. 1. In this Ti-H system the γ-phase component of the f. c. c. structure was mainly studied. In first region (low concentrations) which extends to $TiH_{0.65}$ the α-phase h. c. p. structure prevails. The slope of this structure $(1/a)\ (da/dx) = (1.98 \pm 0.15) \times 10^{-2}$ (x: atomic ratio H/Ti) is a measure of the volume change of the titanium and subsequently a measure of the elastic double force tensor of the defect[10,14]. The relative lattice para-

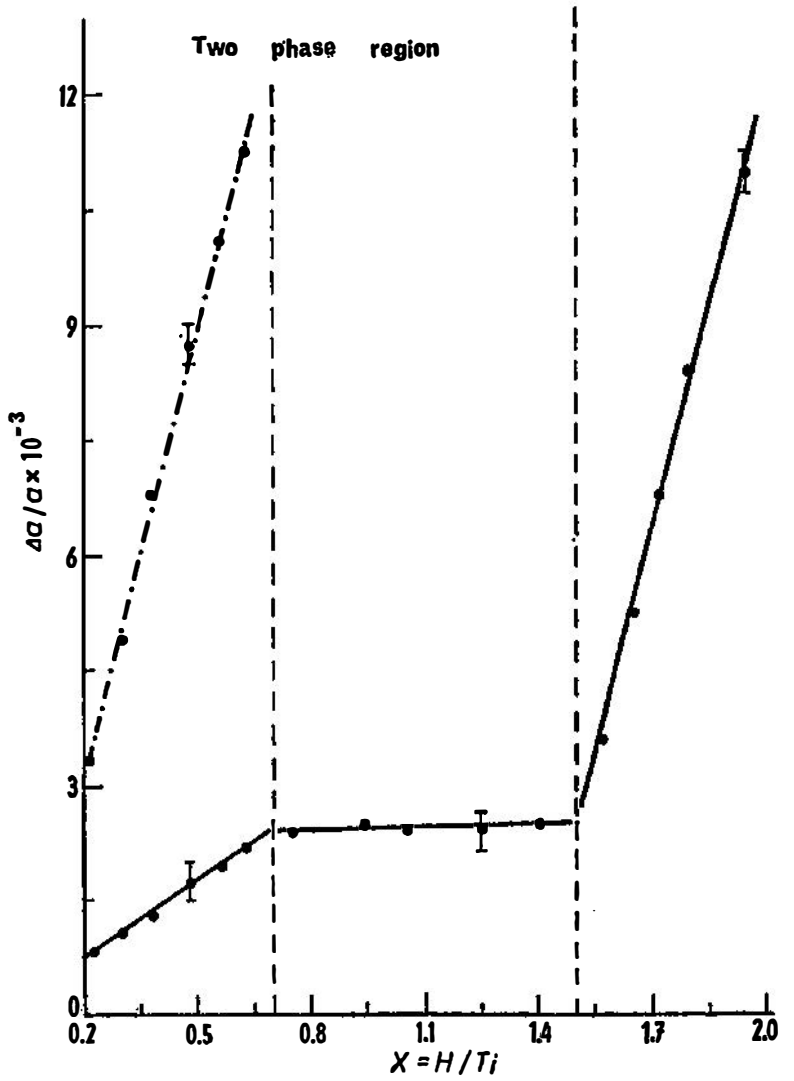

Fig. 1. Relative lattice parameter change ($\Delta a/a$) of titanium powder vs. hydrogen concentration at room temperature. (——) f. c. c. structure, (—·—·—) h. c. p. structure.

meter change ($\Delta a/a$) of the f. c. c. structure in the same region is $\Delta a/a = (2.41 \pm \pm 0.22) \times 10^{-3}$ per at % (H/Ti) and the relative volume change is $\Delta V/V = 3\,(\Delta a/a)$[12,14]. In the second region (intermediate concentrations) which extends from $TiH_{0.65}$ to $TiH_{1.5}$ the transition $\alpha \rightarrow \gamma$ phase is continued and it is very difficult to distinguish between the two phases. In the third most interesting region (high concentrations) which extends from $TiH_{1.5}$ to $TiH_{2.0}$, the γ-phase dominates and the length change of the lattice parameter is $\Delta a/a = (2.14 \pm 0.27) \times \times 10^{-2}$ per at % (H/Ti). The relative volume change ($\Delta V/V$) of the unit cell

which is determined from the slope of the curve for f. c. c. lattice is $\Delta V/V = 3(\Delta a/a) = (6.42 \pm 0.48) \times 10^{-2}$ per at % (H/Ti). This volume expansion is proportional to the trace of the elastic double force tensor of the defect[8,10,14].

In the same region for concentrations near $x = 2.0$ a distortion of f. c. c. to f. c. t. structure is observed. The extent of the distortion is evaluated from ratio c/a ($c = 0.4445 \pm 0.0005$ nm, $a = 0.4470 \pm 0.0005$ nm) of the f. c. t. lattice which is 0.994. This distortion is explained theoretically in Ref. 17 by means of the TiH_2 energy bands that are derived from self-consistent band structure calculations of the hydride. The origin of this distortion is believed due to the peak of the density of states arising from the states along $\Gamma - \Lambda - L$ (points of the first Brillouin zone) near the Fermi level. The presence of 66.4 at % hydrogen in TiH_2 that leads to an appreciable increase in the lattice parameter affects the electron momentum distribution of titanium valence electrons. However, because the distortion of the f. c. c. to f. c. t. structure is small, we can accept that, in first approximation the TiH_2 system has the f. c. c. structure and study theoretically[17-19] and/or experimentally[20,21] the electron momentum distribution.

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References

1) R. Wiswall, in Hydrogen in Metals II, Topics in Applied Physics, vol. **29**, Springer, Berlin 1978 (p. 201);
2) H. Pfeiffer and H. Peisl, Phys. Lett. **60A** (1977) 363;
3) J. H. Weaver, D. J. Peterman, D. T. Peterson and A. Franciosi, Phys. Rev. B **23** (1981) 1692;
4) R. G. Leisure, T. Kanashiro, P. C. Riedi and D. K. Hsu, Phys. Rev. B **27** (1983) 4872;
5) W. M. Mueller, J. P. Blackledge and G. G. Libowitz, in Metal Hydrides, Academic Press, New York/London 1968 (p. 336);
6) B. L. Beek, U. S. A. EC Rep. LAR 10 Denver Res. Inst. **77** (1966);
7) E. Debowska, Phys. Stat. Sol. (b) **117** (1983) 699;
8) J. D. Eshelby, in Solid State Physics **3** New York, Academic Press 1956 (p. 79);
9) H. Wagner and H. Horner, Adv. Phys. **23** (1974) 587;
10) B. Baranowski, S. Majchrzak and T. B. Flanagan, J. Phys. F. **1** (1971) 258;
11) H. Sugimoto and Y. Fukai, J. Less-Common Met. **89** (1983) 307;
12) M. A. Pick and R. Bausch, J. Phys. F **6** (1976) 1751;
13) R. Khoda-Bakhsh and D. K. Ross, J. Phys. F **12** (1982) 15;
14) H. Preisl, in Hydrogen in Metals I, Topics in Applied Physics, vol. 28, Springer, Berlin 1978 (p. 53);
15) K. Kandasamy and N. A. Surplice, Phys. Lett. **101A** (1984) 35;
16) H. Peisl, Proc. Yamada Conf. V, Kyoto, Japan. Point Defects and Defect Interactions in Metals. Amsterdam, Netherlands: North Holland 1982 (p. 41);
17) D. A. Papaconstantopoulos and A. C. Switendick, J. Less-Common Met. **103** (1984) 317;

18) N. I. Kulikov, V. N. Borzunov and A. D. Zvonkov, Phys. Stat. Sol. (b) **86** (1978) 83;
19) D. A. Papaconstantopoulos, N. C. Bacalis and N. Papanikolaou (1985), to be published;
20) G. D. Boulakis, The Experimental Compton Profile of Hydrogen in $TiH_{1.98}$ (1985), to be published;
21) G. D. Boulakis, Phys. Stat. Sol. (b) **130** (1985) K127.

ŠIRENJE KRISTALNE REŠETKE TITANIJA USLIJED OTOPLJENOG VODIKA

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Promjena parametra kristalne rešetke polikristalićnog titanija zbog intersticijalno otopljenog vodika izmjerena je na sobnoj temperaturi pomoću Braggovog raspršenja X-zraka. U području visokih koncentracija ($1.5 < x < 2.0$) $\frac{\Delta a}{a} = (2.14 \pm \pm 0.27) \times 10^{-2}$ po at % (H/Ti). U ovom području opažena je mala distorzija strukture od f.c.c. prema f.c.t. kao rezultat maksimuma u gustoći stanja nastala od stanja u smjeru $\Gamma - \Lambda - L$ (točke prve Brillouinove zone) u blizini Fermi nivoa.