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I. Bashkin, A. Kolesnikov, V. Malyshev, E. Ponyatovsky, S. Borbély, et al.. Phase separation in titanium hydrides studied by small-angle neutron scattering. Journal de Physique IV Proceedings, 1993, 03 (C8), pp.C8-287-C8-290. 10.1051/jp4:1993856 . jpa-00252287

HAL Id: jpa-00252287

<https://hal.science/jpa-00252287>

Submitted on 1 Jan 1993

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Phase separation in titanium hydrides studied by small-angle neutron scattering

I.O. BASHKIN, A.I. KOLESNIKOV, V.Yu. MALYSHEV, E.G. PONYATOVSKY, S. BORBÉLY*, L. ROSTA* and G. PÉPY**

Institute of Solid State Physics of the Russian Academy of Sciences, Chernogolovka 142432, Russia

** Research Institute for Solid State Physics, P.O. Box 49, 1525 Budapest, Hungary*

*** Laboratoire Léon Brillouin, CEN Saclay, 91191 Gif-sur-Yvette cedex, France*

Abstract

Various phases of titanium hydrides with differing hydrogen and deuterium content are studied by small-angle neutron scattering. The low temperature metastable χ phase produced by quenching under high pressure shows small, but pronounced scattering at liquid nitrogen temperature. At 140 K a very abrupt increase in the scattered intensity is detected, more than one order of magnitude for less than 30 s. The scattering from the room temperature ($\alpha+\gamma$) phase is analysed by the fractal as well as the random two-phase model. The fit does not prove fractal behaviour of the α -Ti precipitates in the γ -TiH(D)₁ matrix. A good representation is obtained in a random two-phase model, giving about 50 and 60 Å correlation lengths, independently of the deuterium or hydrogen content. For the δ phase, only the asymptotic behaviour of the scattering curves is observed in the scattering vector range covered in the experiments.

Introduction

A sequence of phase transitions can be observed on heating the TiH(D)_x ($x=0.7-0.9$) low temperature metastable phase prepared by fast cooling under high pressure[1]. Wide angle neutron diffraction experiments showed that these transformations change the distribution of H(D) atoms in the metal sublattice[2]. In the low temperature metastable χ phase, H(D) randomly occupies the octahedral interstitial sites of the *fco* metal sublattice. Above 140 K the system transforms to TiH(D)₁ (γ -phase) containing finely dispersed α -Ti. The γ phase involves H(D) atoms occupying ordered tetrahedral interstices of the subsequent {110} planes of the *fco* metal sublattice. If the γ phase is annealed above 480 K, it undergoes transformation into TiH(D)_{2-y} hydrogen(deuterium) deficient δ phase with *fcc* metal sublattice, in which H(D) is randomly distributed in the tetrahedral interstices. In the present work small-angle neutron scattering has been used to investigate the short and medium range order in TiH(D)_x samples of various phase composition.

Experimental

Samples of TiH(D)_x ($x=0.7-0.9$) were synthesized by saturating high purity titanium with hydrogen(deuterium) gas obtained from the thermal decomposition of TiH(D)₂. The hydrogen(deuterium) content was determined from the increase in weight. In order to obtain the metastable χ phase, samples were compressed to 60 kbar, heat treated at 620 K for 10 min, and rapidly quenched to liquid nitrogen temperature. The pressure was then lowered to atmospheric. All

intermediate procedures and storage involving the χ phase samples were carried out under liquid nitrogen. The measurements were also performed in a nitrogen cryostat. The γ phase was obtained by air heating of the samples to room temperature. Attempts were made to measure the intermediate steps of phase transition from χ to γ phase by slowly increasing the cryostat temperature. In order to obtain the δ phase, samples were annealed at 500 K for 2 h. The measurements were carried out using the PAXE spectrometer in LLB, Saclay, in the q -range from 0.007 to 0.08 $\text{\AA}^{-1}$. The two-dimensional spectra were treated by the commonly used procedure (circular averaging, background subtraction and normalization to the incoherent scattering of 1 mm water).

Results and Discussion

A small but pronounced scattered intensity is obtained from samples in the χ phase, as can be seen in Fig.1 where scattering curves for different phase compositions of $\text{TiD}_{0.728}$ are shown. Attempts to record the kinetics of χ - γ phase transformation were not successful. On performing 10 s expositions at about 10 K/min heating rate we observed a very abrupt increase in the scattered intensity at about 140 K in two subsequent runs; on further heating there was virtually no change. In view of this, the scattering from samples in the $(\gamma+\alpha)$ phase was measured at room temperature (Fig.1).

The formation of fractal-like precipitates of TiH_2 on heating of the hydrogenated amorphous TiCu matrix was reported by Mangin et.al.[3]. Therefore we also checked the applicability of the fractal approach for the α -Ti "particles" embedded in the γ - $\text{TiH}(\text{D})_1$ matrix. The following formula was fitted to the scattering curves[4]:

$$I(q) = A\xi^3 \frac{\Gamma(D+1)}{[1+q^2\xi^2]^{\frac{(D-1)}{2}}} \frac{\sin[(D-1)\arctan(q\xi)]}{(D-1)q\xi} + B \quad (1)$$

with adjustable parameters ξ , D and A . Here q , ξ , D , A and B denote the magnitude of the scattering vector, the correlation length, the fractal dimension, a scaling constant, and an internal incoherent background respectively. The last parameter was used to take into account the high internal incoherent background of hydrogenated samples. This value was determined from an Iq^4 versus q^4 plot (Fig.2) where the slope of the straight region directly gives the background correction B . The experimental scattering curves and the fractal fit for hydrogen-containing samples are shown in Fig.3. The results of the fit are presented in Table 1b. One can see, that the fractal dimension D is somewhat larger than 3, but not smaller than is expected for fractal behaviour. The larger than 3 values of D may be due to the gradual transition from the hydrogen-free regions to the perfectly ordered and fully occupied $\text{TiH}(\text{D})_1$ matrix. Actually, from the diffraction experiments an occupation probability of 0.94 was obtained, which can also be explained by the above phenomenon. Considering the fact, that in the γ phase $\text{TiH}(\text{D})_1$ is formed, while the remaining Ti is finely dispersed in it, the scattered intensity must decrease with increasing $H(\text{D})$ content. This can be well seen in Fig.4, where the scattering curves are drawn for deuterated samples, giving high contrast between the TiD_1 and α -Ti phases.

Not finding fractals in the samples, we described the scattering curves by a random two-phase model[5],

$$I(q) = \frac{A\xi^3}{(1+q^2\xi^2)^2} + B \quad (2)$$

with adjustable parameters A and ξ . The meaning of q , A , ξ and B is the same as in eq.1. The best fit correlation lengths are shown in Table 1a. It is worthy of note that hydrogenated samples give a larger correlation length than the deuterated ones, revealing marked isotope effect.

In the phase transition from $(\alpha+\gamma)$ to $(\alpha+\delta)$ the amount of α -Ti increases compared to the

Figure 1: Scattering curves for various phases of $\text{TiD}_{0.728}$

Figure 2: Porod plot for $\text{TiH}_{0.809}$ sample, $(\alpha+\gamma)$ phase

Figure 3: Scattering curves and fractal fit for different TiH_x samples, $(\alpha+\gamma)$ phase

Figure 4: Scattering curves of different TiD_x samples, $(\alpha+\gamma)$ phase

hydrogen(deuterium)-containing phase mostly because of the increase in the dimension of H(D) deficient "particles". Consequently, an increase in the scattered intensity is expected. In reality, only the asymptotic behaviour of the scattering curves (q^{-4}) could be observed in the q range covered in the experiments, indicating a significant increase in the amount of α -Ti.

Table 1.

The best fit parameters of the random two phase(a) and fractal(b) model for samples in $(\alpha+\gamma)$ phase

a/			b/		
X	$\xi(\text{\AA})$	χ	$\xi(\text{\AA})$	D	χ
TiD _x			TiD _x		
0.728	51.43±0.34	2.74	41.75±0.42	3.17±0.01	1.33
0.832	50.51±0.35	1.61	44.38±0.43	3.10±0.01	0.93
0.917	47.78±0.33	1.48	42.90±0.40	3.09±0.01	1.05
TiH _x			TiH _x		
0.738	56.91±0.56	1.68	47.80±0.62	3.14±0.02	1.03
0.809	59.20±0.66	2.16	56.51±0.83	3.03±0.02	0.65
0.892	59.94±0.68	1.11	53.10±0.78	3.09±0.02	0.69

In Table 1 χ denotes the following:

$$\chi = [\Sigma(y_{i,exp} - y_{i,fit})^2 / \sigma_i^2]^{1/2} / (N - N_p + 1) \quad (3)$$

where $y_{i,exp}$, $y_{i,fit}$, σ_i , N and N_p are the measured and fitted intensity, the experimental error, the number of experimental points and the number of parameters respectively.

Conclusions

The metastable χ phase of TiH(D)_x shows weak SANS signals, which indicate a relatively homogeneous distribution of H(D) atoms. At about 140 K a very rapid transformation takes place. In contrast to the findings in a similar system, the results do not reveal fractal behaviour of the room temperature two-phase samples. The random two phase model yields a correlation length of 50-60 $\text{\AA}^{-1}$ for these samples. In the high temperature δ phase, a significant increase in the dimension of α -Ti precipitates is detected.

Acknowledgement: This work was supported in part by the Hungarian National Scientific Research Fund OTKA No. 2951 grant.

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