

ISOTOPIC EFFECT IN HYDROGEN AND NITROGEN SOLID SOLUTIONS IN α -Ti

Khidirov I., Padurets L. N. ⁽¹⁾

Institut of Nuclear Physics, Academy of Sciences of Uzbekistan, Tashkent, 702132 Uzbekistan ⁽¹⁾
Kurnakov Institut of General and Inorganic Chemistry, Russian Academy of Sciences, Leninskiy
pr. 31, Moscow, 119991 Russia

Introduction

Hydrogen atoms strongly affect the crystal structure and properties of nitrogen and/or carbon solid solutions in α -Ti- TiN_xH_y [1]. Ordering in TiN_xH_y , nitrogen and hydrogen solid solution in α -Ti, was studied by neutron diffraction [2]. It is of interest are neutron diffraction studies of ordering in TiN_xD_y and $\text{TiN}_x\text{H}_{y/2}\text{D}_{y/2}$. The results of these studies in comparison to the results obtained from TiN_xH_y solid solutions can give valuable information about the role of hydrogen and the interaction energy of the strain between interstitial atoms and metal atoms in structure formation and phase relations for hydrogen solid solutions in α -Ti.

This study deals with ordering $\text{TiN}_{0.26}\text{H}_{0.15}$, $\text{TiN}_{0.26}\text{D}_{0.15}$ and $\text{TiN}_{0.26}\text{H}_{0.075}\text{D}_{0.075}$ solid solutions as probed by neutron diffraction.

Experiment

Neutron diffraction patterns of powder samples were taken on a neutron diffractometer ($\lambda = 1.085 \text{ \AA}$) mounted on the thermal column of a VVR-SM nuclear reactor. The DBW-3.2 program for the Rietveld neutron diffraction lineshape analysis was used in calculations and structure refinement. A DRON-3M X-ray diffractometer (CuK_α radiation) was used to measure X-ray powder diffraction patterns.

The $\text{TiN}_{0.26}\text{H}_{0.15}$ solid solution sample was prepared by self-propagating high-temperature synthesis from a PTM grade titanium powder containing 0.35 wt % H_2 [2]. $\text{TiN}_{0.26}\text{D}_{0.15}$ solid solution sample was prepared by deuteriding powdered $\text{TiN}_{0.26}$ sample at temperatures from 700 - 1000 °C by the Sieverts process. The samples were followed by 6-h homogenizing anneals in degassed and sealed silica glass ampoules at 1000 °C and by air quenches. Usually, such thermal processing does not change the hydrogen content of a sample [2]. X-ray

powder diffraction shows that the solid solutions $\text{TiN}_{0.26}\text{H}_{0.15}$ and $\text{TiN}_{0.26}\text{D}_{0.15}$ are single-phase and samples had a hexagonal unit cell with $a = 2.983 \pm 0.002$, $c = 4.805 \pm 0.003 \text{ \AA}$ and $a = 2.983 \pm 0.002$, $c = 4.805 \pm 0.003 \text{ \AA}$, accordingly [2,3]. $\text{TiN}_{0.26}\text{H}_{0.075}\text{D}_{0.075}$ solid solution are prepared in equal proportion $\text{TiN}_{0.26}\text{H}_{0.15}$ and $\text{TiN}_{0.26}\text{D}_{0.15}$ solid solutions by sintering bath in evacuated and sealed quartz ampoule was sintered under special regime selected by us. The final product was prepared after the annealing at 1000 °C (6 hours) followed by quenching in air. According to the neutron diffraction reflections pattern the sample is single-phase and that it has ordering hexagonal structure with the parameters $a = 2.987 \pm 0.007$, $c = 4.839 \pm 0.003 \text{ \AA}$. Divergence in parameters lattice in comparison with parameters lattice of the solid solutions $\text{TiN}_{0.26}\text{H}_{0.15}$ and $\text{TiN}_{0.26}\text{D}_{0.15}$ is probably conditioned different mistakes of determination parameter lattices by methods (X-ray and neutron diffraction).

Results and discussion

Processing the neutron diffraction reflections pattern for the solid solution $\text{TiN}_{0.26}\text{H}_{0.15}$ quenched from 1000 °C showed that all nitrogen atoms randomly occupy octahedral interstices 2 (a) and hydrogen atoms, both octahedral interstices 2 (a) (50 %) and tetrahedral interstices 4 (f) in terms of space group $P6_3/\text{mmc}$ (the α' -phase, Fig. 1a). After quenching the sample from temperatures in the range, diffuse neutron scattering is observed in the Bragg angle range of $2\theta = 11-18^\circ$ (Fig. 1b). Long-range ordering corresponding becomes noticeable at 650 - 550 °C (12 h, Fig 1c). The simulation of the neutron diffraction for a sample shows that at this temperatures hydrogen atoms occupy only one type of tetrahedron 2 (d) and that nitrogen

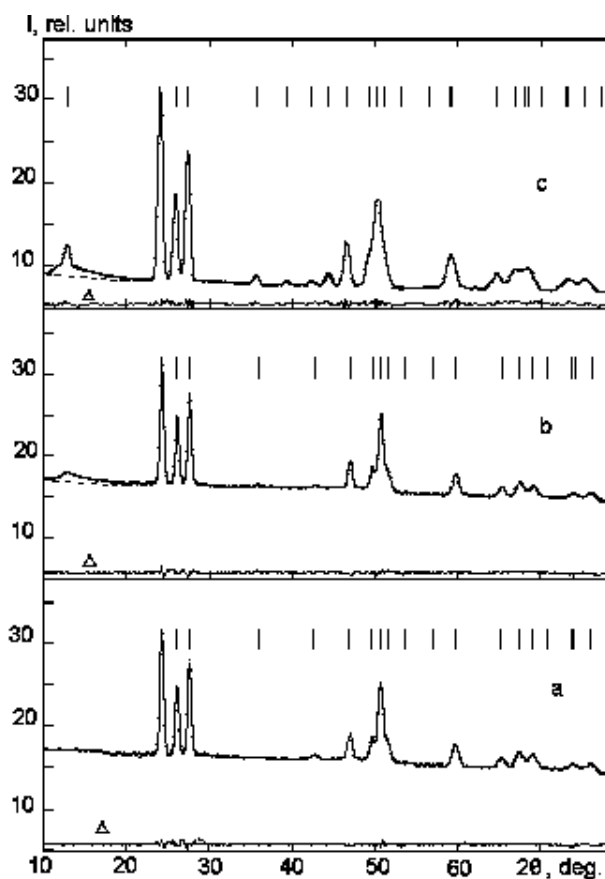


Fig.1. Neutron diffraction patterns of $\text{TiN}_{0.26}\text{H}_{0.15}$ solid solution samples quenched from 900 °C (a); 800 °C (b) and 620 °C (c) (points show data points, the solid line is the fitted curve, and $\Delta = I_{\text{exp}} - I_{\text{calc}}$).

atoms are partially disordered, preferring to occupy octahedral positions 1 (a) in terms of space group $P\bar{3}m1$ (α' -phase). Longer exposures of up to 28 h at 580 °C cause the complete demixing of the solid solution into a pair of phases, one with a lower and the other with a higher nitrogen percentage than that in $\text{TiN}_{0.26}\text{H}_{0.15}$. One phase is the ordered α' -phase, and the other is the ordered γ -phase (space group $C2/m$). Thus, the partially ordered α' phase in the $\text{TiN}_{0.26}\text{H}_{0.15}$ solid solution is metastable. Neutron diffraction study of the solid solutions $\text{TiN}_{0.26}\text{D}_{0.15}$, $\text{TiN}_{0.26}\text{H}_{0.075}\text{D}_{0.075}$ and comparison the results with results of investigation of the $\text{TiN}_{0.26}\text{H}_{0.15}$ allowed to reveal isotopic effect, revealing in following.

1. Nitrogen ordering in $\text{TiN}_{0.26}\text{D}_{0.15}$, $\text{TiN}_{0.26}\text{H}_{0.075}\text{D}_{0.075}$ in terms space group $P\bar{3}m1$ starts at higher temperatures (~ 1000 °C and ~ 900 °C, accordingly) than in $\text{TiN}_{0.26}\text{H}_{0.15}$ (~ 750 °C).

2. Unlike $\text{TiN}_{0.26}\text{H}_{0.15}$, in $\text{TiN}_{0.26}\text{D}_{0.15}$, the appearance of superstructural reflections in the neutron diffraction patterns is not preceded by diffuse scattering.

3. The low-nitrogen homogeneity boundary of the monoclinic ordering phase with space group $C2/m$ in the Ti-N-D system lies at lower nitrogen concentrations than in the Ti-N-H system; the $\text{TiN}_{0.26}\text{D}_{0.15}$ sample is the single monoclinic phase at temperature of 630 °C.

4. Hydrogen atoms in ordered $\text{TiN}_{0.26}\text{H}_{0.15}$ reside only in tetrahedral positions; in ordered $\text{TiN}_{0.26}\text{H}_{0.075}\text{D}_{0.075}$ and $\text{TiN}_{0.26}\text{D}_{0.15}$ some deuterium atoms also occupy the octahedral positions unoccupied by nitrogen atoms.

The higher onset temperature of ordering in the Ti-N-D system than in the Ti-N-H system can be interpreted as follows. In highly imperfect solid solutions, an essential role is played by strain, long-range interactions [4]. It can be therefore suggested that the replacement of H by D atoms in the solid solution changes the lattice strain field and, in all probability, enhances the stability of the ordered state of the solid solution. The disordering temperature becomes higher in association. The results of study $\text{TiN}_{0.26}\text{H}_{0.075}\text{D}_{0.075}$ show that heterogeneity lattice field of the interstitial atoms else intensifies the strain interaction.

As regards the location of part of the D atoms in $(0,0,\frac{1}{2})$ octahedral of ordered α' - and γ -phases, it may be presumed that the blocking effect caused by repulsion forces between a nitrogen atom N in a octahedron $(0,0,0)$ and a deuterium atom D in a tetrahedral is stronger than between N and H atoms. As a result, part of the D arrears at longer distances (in 1(a)).

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