

NEUTRON DIFFRACTION STUDY OF ORDERING OF ATOMS AND ANTIPHASE DOMAINS IN TITANIUM CARBOHYDRIDES

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Introduction

Hydrogen effects greatly properties and structure of refractory titanium carbide which is essential in the technique described [1]. To obtain carbides with the largest concentrations of hydrogen and *Ti* carbides that have given service characteristics, structural features of these materials should be known. In the present work the *Ti* carbides of different compositions at the lower limit of homogeneity range were studied by means of X-ray and powder neutron diffraction.

Neutron diffraction patterns were obtained using the neutron diffractometer mounted at the thermal column of the atomic reactor of the INP AS RUz ($\lambda = 1.085 \text{ \AA}$). The treatment of neutron diffraction patterns was carried out by the Rietveld full-profile analysis (program of DBW 3.2) [2]. Samples of carbides TiC_xH_y were prepared by mean sintering [3]. Treatment of samples was carried out in evacuated and sealed quartz ampoules, thus preventing hydrogen escape from the samples. Concentration of carbon and hydrogen atoms in the samples was controlled by chemical and neutron diffraction analysis.

According to the results of X-ray analysis, the samples were homogeneous, mono-phasic and had the NaCl - type structure (face-centered cubic unit cell) with average lattice parameter $a_0 = 0.4301 \text{ nm}$, after quenching from $1200 \text{ }^\circ\text{C}$ temperature. Minimum values of the divergence factors (no more than 4 %) and satisfactory agreement between experimental and calculated peak intensities may be obtained only in the framework of space group Fm3m, where carbon atoms occupy statically the octahedral sites 4 (b) and hydrogen atoms the tetrahedral interstices 8 (c). After annealing from temperatures $1100 - 1000 \text{ }^\circ\text{C}$ $\text{Ti}_{0.47}\text{C}_{0.22}\text{H}$ and $\text{Ti}_{0.51}\text{C}_{0.21}\text{H}$ still had the disordered structure described in the framework of sp. gr. Fm3m, but transition of some of the

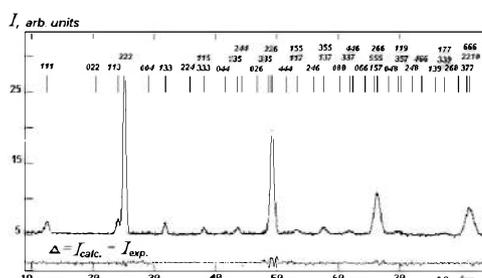


Fig 1. Neutron diffraction pattern of the sample $\text{TiC}_{0.50}\text{H}_{0.21}$ after annealing at temperature of $900\text{-}800 \text{ }^\circ\text{C}$. Solid line and dots - calculated and experimental values of diffraction intensity. Miller indices of the reflecting planes are indicated above the peaks.

hydrogen atoms from tetrahedral to octahedral interstices and exchanges with carbon atoms are observed. After the annealing of the samples at temperatures of $900 - 800 \text{ }^\circ\text{C}$ for 48 h in their neutron diffraction patterns some superstructure maxima were observed (Fig.1). The crystal structure of the ordered phase described in the framework of the sp. gr. Fd3m in which 70 % of carbon atoms arrange in an ordered configuration over the octahedral interstices 16 (c) and hydrogen atoms - over the other type of octahedral interstices 16 (d). The sizes of antiphase domains [4] in titanium carbides seems to be close and the average, is equal to $D = 115 \text{ \AA}$ after annealing at the temperature of $600 \text{ }^\circ\text{C}$.

After annealing of samples at temperatures of $750 - 600 \text{ }^\circ\text{C}$ for 48 h traces of $\alpha\text{-Ti}$ were observed in the neutron diffraction patterns in addition to the basic cubic phase. Initial samples were then annealed at $450 \text{ }^\circ\text{C}$ for 400 h, and superstructure reflections corresponding to sp. gr. Fd3m arose in the neutron diagrams. Splitting of the superstructure reflections should be noted. Fig. 2 shows the neutron diagram of $\text{TiC}_{0.50}\text{H}_{0.21}$ after annealing at $450 \text{ }^\circ\text{C}$ for 400 h. Splitting of the super-structural reflections at the Bragg angles $2\theta > 30^\circ$ into three symmetrically located reflections indicates that a long-period ordered antiphase domain (APhD) structure is formed in the sample [5]. It should be noted that at Bragg angles $2\theta > 30^\circ$ almost all superstructure reflections are splitted.

Hence, in the carbohydrides APhD ordering occurs in different directions. Using the distances between satellites of superstructure reflections the period of the ordered APhD structures P has been determined according to [5]. The values of APhD structures P determined by of superstructural reflections were within the interval of ~ 10 -12. Reflexes 133 and 024 of X-ray patterns (indices for initial Fm3m structure) indicate

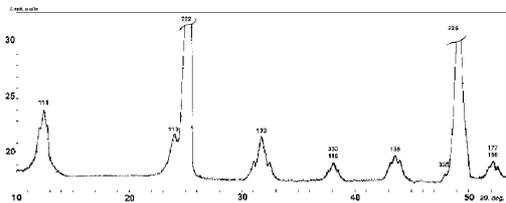


Fig 2. Neutron diffraction of $\text{TiC}_{0.50}\text{H}_{0.21}$ annealed at temperature $450\text{ }^\circ\text{C}$ for 400 h.

some distinctions in structure of the initial and annealed samples. For these reflexes of all samples a noticeable shift of 2θ towards smaller angles is observed after heat treatment. Fig. 3 shows a fragment of X-ray pattern corresponding to reflection (133) for $\text{TiC}_{0.50}\text{H}_{0.21}$ initial (a) and annealed at $450\text{ }^\circ\text{C}$ for 400 h, after the appearance of periodic APhD structures (b). The lattice parameter of carbohydrides having the ordered APhD structure increases markedly ($\Delta a \approx 0.009\text{ \AA}$). Additionally, after low-temperature annealing of $\text{TiC}_{0.47}\text{H}_{0.22}$ and $\text{TiC}_{0.50}\text{H}_{0.21}$, some fuzziness of $K_{\alpha 1} - K_{\alpha 2}$ doublet is observed.

It is known that change in cell dimensions and appearance of microdistortions, resulting in degradation of the doublet, is a result of formation of the long-period APhD structure. Absence of APhD ordering in samples annealed at higher temperatures ($T \leq 600\text{ }^\circ\text{C}$) may be explained by the formation of ordered and randomly oriented APhD. At lower temperatures a slow formation of fine and oriented (ordered) APhD is observed. As the APhD size at temperature of $600\text{ }^\circ\text{C}$ is $\sim 115\text{ \AA}$, one can assume that sizes of the ordered domains are considerably smaller than 100 \AA . Thus, at the lower limit of the carbon homogeneity region five temperature ranges for structural change are found.

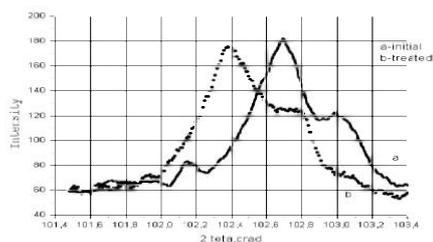


Fig 3. Fragments of the X-ray diffraction pattern of reflection 133.

1) $T \geq 1200\text{ }^\circ\text{C}$, at which titanium carbohydrides have disordered cubic structure, is described within the framework of sp. gr. Fd3m, where the carbon atoms occupy octahedral interstices and the hydrogen atoms - tetrahedral ones.

2) $1000\text{ }^\circ\text{C} \leq T \leq 1100\text{ }^\circ\text{C}$: the disordered cubic structure is still observed in which the hydrogen atoms are arranged statistically on both octahedral and tetrahedral interstices. It should be noted that filling up tetrahedral interstices by hydrogen atoms in the disordered titanium carbohydride is observed for the first time.

3) $800\text{ }^\circ\text{C} \leq T < 1000\text{ }^\circ\text{C}$: formation of long-range order is observed. Crystal structure of the ordered phase is described within the framework of sp. gr. Fd3m, where the carbon atoms occupy one type of octahedral interstices 16 (c) and the hydrogen atoms the other type of octahedral interstices 16 (d).

4) $600\text{ }^\circ\text{C} \leq T < 800\text{ }^\circ\text{C}$: decay of ordered cubic phase with segregation of $\alpha\text{-Ti}$ is observed.

5) $T \leq 475\text{ }^\circ\text{C}$: formation of metastable ordered cubic phase with the formation of periodic antiphase domains is observed. At these temperatures the process of decay is hindered. It should be noted that the formation of ordered periodic antiphase domains (long-period structure) in the interstitial phase is observed for the first time. This work was supported by the Center of Science and Technology of Uzbekistan (contract № $\Phi - 2.1.2$).

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