NEUTRON DIFFRACTION DETERMINATION OF HOMOGENEITY RANGES OF TETRAGONAL ε-Ti_2N_{1-y}-AND δ′-Ti_2N_{2x}-PHASES BY RIETVELD FULL-PROFILE ANALYSIS

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1. INTRODUCTION

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Evidently, because of unusual conditions of the δ′-Ti_2N_{2x} and ε-Ti_2N_{1-y} phases formation, they became the object of investigations in a number of works [1-5]. However information about homogeneity ranges of these phases are contradictory, and their places in the phase diagram of the system Ti-N are ambiguously determined [5]. The aim of the present work is determination of homogeneity ranges of the tetragonal ε-Ti_2N_{1-y}- and δ′-Ti_2N_{2x}– phases by neutron diffraction

Neutron diffraction method allows one to obtain reliable information about positions of light atoms in the crystal lattice of polycrystals in the presence of heavy elements [6]. The value of an amplitude of neutron coherent scattering by the nitrogen atom (b_N == 0.94 × 10^{-3} nm) allows to determine both composition and structure of the TiN_x with large reliability by analyzing the structure factors and experimental intensities of diffraction reflections. In the work the composition of the cubic δ-TiN_x– phase was determined by neutron diffraction; on the base of this phase the metastable ordered tetragonal phase δ′-Ti_2N_{2x} is formed. Also the composition of tetragonal ε- and δ′– phases was determined. The treatment and analysis of the neutron diffraction patterns were carried out by the Rietveld full-profile analysis [7].

In literature to present day it is considered that in the system Ti-N there is the strictly stoichiometric ε-Ti_2N– phase with tetragonal structure of the anti-rutile TiO_2 - type (the space group - sp. gr. $P4_2/mnm$) [5]. We have shown by neutron diffraction method that, though the structure of the given phase corresponds to formula Ti_2N, it has an homogeneity range which lies more left of stoichiometry Ti_2N. Since in literature ε-phase is described as strictly stoichiometric composition Ti_2N, we have made an attempt to obtain ε-phase nearby composition of N/Ti = 0.5. However the annealing of the samples with concentration 0.45≤ N/Ti ≤0.55 at the temperatures 1100 -900 ^{0}C during 15 days has not led to formation of pure ε-phase: the samples consisted of two phases: ε- and δ, where δ-phase has face-centered cubic (FCC) structure. At the same time after such annealing and quenching in water the samples in the range of 0.38≤ N/Ti ≤0.42 consisted only of ε-phase. The neutron diffraction pattern of ε-$Ti_2N_{0.80}$ is shown in Fig.1. The results of processing neutron diffraction patterns of the samples with concentration 0.38≤ N/Ti≤0.42 by Rietveld full-profile analysis (Tab.1) confirm the data of chemical analysis about composition of the ε- phase. As the ε-phase is nonstoichiometric, it was supposed that at long annealing it can tend to stoichiometry and then to decay. However annealing by the regime: (1000→ 900→ 800 ^{0}C) on 24 h (700 → 650→ 600→ 500 ^{0}C) on 48 h→ 450 ^{0}C during 168 h→ 400 ^{0}C during 196 h (i.e. in temperature interval of 1000-400 ^{0}C during 608 h) – has not resulted in any change of X-ray- and neutron diffraction patterns. Hence, the ε- phase refers to stable nonstoichiometric compounds within the temperature interval of 1000- 400 °C, and its homogeneity range lies much more to the left of stoichiometric composition Ti_2N, i.e. in the concentration interval of 0.38≤ N/Ti ≤0.42. So, the ε-phase should be described by the formula - Ti_2N_{1-y} where y = 0.24-0.16.

For obtaining single-phase ordered tetragonal δ′-Ti_2N_{2x} phase (sp.gr. $I4_1/amd$; Fig. 2 *b*) it is necessary to quench δ-TiN_x – phase (sp.gr. Fm3m) with concentration of 0.45≤N/Ti≤0.50 from temperature 1300-1400 °C (Fig. 2 *a*), and then to anneal it at temperatures of 550 – 500 °C during 12-24 h. Thus, in the concentration interval of 0.45≤ N/Ti ≤0.50 the high-temperature

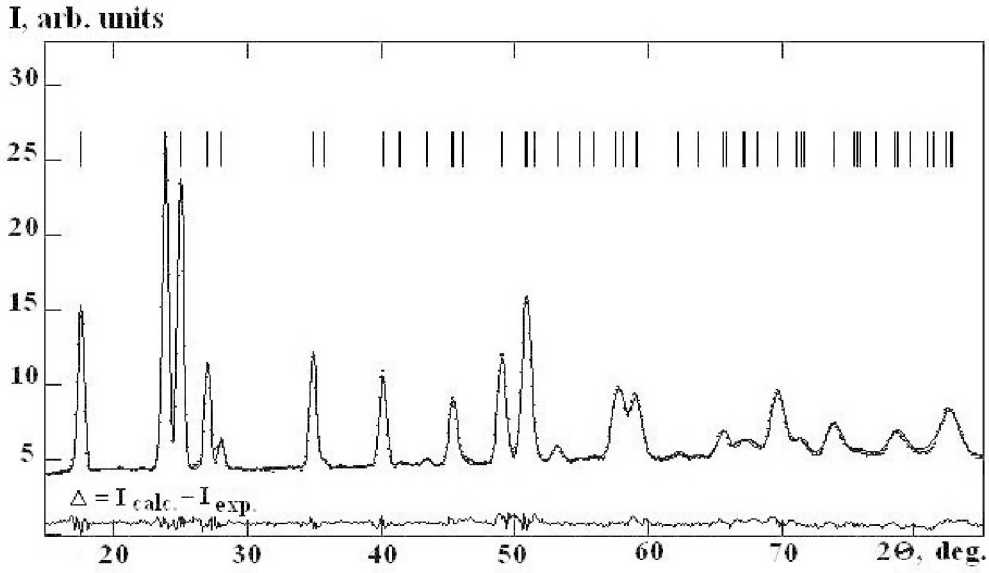

Fig. 1. Neutron diffraction pattern of ε-$Ti_2N_{0.80}$ – phase: the solid line – calculated; dots – experimental; Δ - difference curve (experimental minus calculated). Above reflexes their ideal positions are indicated within the framework of sp.gr. $P4_2/mnm$.

Table 1. Structural characteristics and divergence factors of structure determination of ε-Ti_2N_{1-y}-phase within the framework of sp. gr. $P4_2/mnm$.

Atom	Position	Atom coordinates x y z	B, Å^2 ΔB, Å^2	n Δn
Ti	2 (*d*)	0,2961±0,0004 0,2961±0,0004 0	0,79 0,08	4 0
N	1 (*a*)	0 0 0	0,53 0,04	1,6 0,02
a = 4.989±0.001; c =3.0637 ±0.0005 Å^2; R_n = 2,9; R_{wn} = 3,9; R_{Bn} = 5,1 %				

Notice. B – individual thermal factor; n – positions occupancy phase is FCC one, from which at slow cooling within temperatures interval of 550° C <T≤1000° C the ε-phase is precipitated. At T≤ 500° C this phenomenon is not practically observed because decay process is strongly delayed. In the same concentration interval at T = 550 - 500°C the ordered tetragonal δ'-Ti_2N_{2x}- phase is formed on base of the "frozen" metastable high-temperature FCC - phase. In the Tab.2 the results of processing the neutron diagram of δ'-Ti_2N - phase are given.

Thus, neutron diffraction analysis by means of the Rietveld full-profile technique makes possible to establish unambiguously the homogeneity ranges of tetragonal ε-Ti_2N_{1-y} and δ'-Ti_2N_{2x}- phases: the ranges lie wihtin the concentration interval of 0.38≤ N/Ti≤ 0.42 and 0.45≤ N/Ti≤ 0.50, accordingly.

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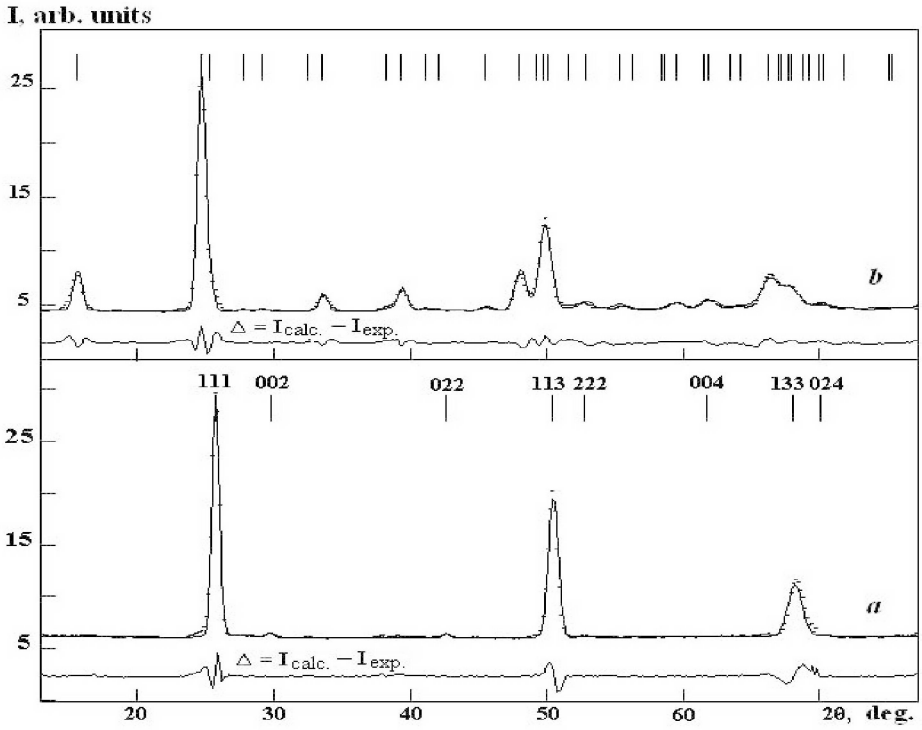

Fig. 2. Neutron diffraction patterns: of δ-$TiN_{0.50}$ – phase (*a*) (above the reflexes the Miller indices of reflecting planes are indicated within the framework of sp.gr. Fm3m); of the ordered tetragonal δ'-Ti_2N – phase(*b*) (above the reflexes their ideal positions are indicated within the framework of sp.gr. $I4_1/amd$); the remaining notation are the same as in Fig. 1.

Table 2. Structural characteristics and divergence factors of structure determination of δ'-Ti_2N – phase within the framework of sp. gr. $I4_1/amd$

Atoms	Positions	Atom coordinates x y z Δz	B, Å^2 ΔB, Å^2	n Δn
Ti	8 (*d*)	0 0, 25 0,1110 0,001	0,40 0,20	8 0
N	4 (*a*)	0 0,75 0,125	0,79 0,10	3,44 0,02
H	4 (*d*)	0 0.25 0,375	0,79 0,10	0,56 0,02
a = 4,187±0,002 Å^2; *c* = 8.773 ±0,004 Å^2; R_p = 5,4; R_{wp} = 7,2; $R_{Бр}$ = 6,9 %				

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