

## Neutron Diffraction Study of Ordered Structures and Phase Transitions in Vanadium Subcarbide

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The results of neutron diffraction study of VC<sub>0.47</sub> are presented and discussed. It is established scheme of the phase transitions. A low temperature orthorhombic ordered phase (space group Pbcn) and high temperature hexagonal ordered phase (space group P6<sub>3</sub>22) exists in VC<sub>0.47</sub>. The kinetic of the transition is described by Kolmogorov – Johnson – Mehl – Avrami law.

**Keywords:** Neutron diffraction, VC<sub>0.47</sub>, Hexagonal phase, Time and temperature dependencies.

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### 1. INTRODUCTION

Carbides of V<sup>th</sup> group transition metals with cubic and hexagonal close packed crystalline lattice have a wide homogeneity region. Almost half of the nonmetal octahedral positions can be vacant in these systems and ordering of interstitial atoms occurs at specified conditions (temperature, pressure) and effects of the ordering can be used for purposive change of material properties.

The vanadium carbide is one of the V<sup>th</sup> transition metal group's carbide which forms several compounds - V<sub>8</sub>C<sub>7</sub>, V<sub>6</sub>C<sub>5</sub>, V<sub>2</sub>C<sub>z</sub> and in which the different ordered structures exists [1-7]. The initial structure of V<sub>8</sub>C<sub>7</sub> and V<sub>6</sub>C<sub>5</sub> monocarbides is the NaCl type cubic disordered structure. The cubic ordered structure with space group (sp.gr.) P4<sub>3</sub>32 [8-10] exists in V<sub>8</sub>C<sub>7</sub>, a low temperature monoclinic (sp.gr.C2/m) and a high temperature trigonal (sp.gr.P3<sub>1</sub>) ordered phases are detected [3, 4, 11] in V<sub>6</sub>C<sub>5</sub>.

More a half of octahedral positions is unoccupied in V<sub>2</sub>C<sub>z</sub> vanadium subcarbide with the L/3 type initial hexagonal close-packed structure. A low temperature orthorhombic (sp. gr. Pbcn) and high temperature hexagonal (sp. gr. P6<sub>3</sub>22) ordered structures are found out [12, 13]. The schemes of phase transitions are differ proposed in [12] and in [13].

On [12], a low temperature orthorhombic ordered phase (pr. gr. Pbcn) transfer to high temperature hexagonal ordered phase (sp. gr. P6<sub>3</sub>22), which in turn, moves over to hexagonal disordered phase L/3. The order-disorder phase transition is the first type. Existence at VC<sub>0.47</sub> of a low temperature ordered phase ( $\beta_p$ ) with the  $\xi$ -Fe<sub>2</sub>N type orthorhombic structure (sp. gr. Pbcn) and high temperature ordered phase ( $\beta$ ) with the  $\varepsilon$ -Fe<sub>2</sub>N type hexagonal structure (sp. gr. P6<sub>3</sub>22) is reported [13].

VC<sub>0.47</sub> is two-phase ( $\beta_p + \beta$ ) in 1363-1413 K temperature region but the sample consists only –  $\beta$  – phase at  $T \geq 1413$  K. The orthorhombic phase ( $\beta_p$ ) vanish

step-by-step with increasing of temperature, expression the share of hexagonal ordered phase increases and the order-order type phase transition occurs which occurs through two-phase area.

But the two-phase ordered area is absent in vanadium subcarbide on [12]. Ordered structures formation temperatures and phase transition temperatures in vanadium subcarbide adduced in [12] and in [13] are differing. The distinction [12, 13] is that high temperature studies are executed in narrow interval of Bragg angles:  $2\Theta_B = 16^\circ \div 27^\circ$  [13] and  $2\Theta_B = 16^\circ \div 40^\circ$  [12]. A little number of reflexes are measured in [12, 13] that obstructs the production of an high-precision lattice parameter values and a long range parameter of ordered phases.

Also, information are absent about study of the phase transition kinetics with the exception of [12] where investigated VC<sub>0.455</sub>O<sub>0.009</sub>N<sub>0.002</sub>. While the study of transition kinetics in VC<sub>0.47</sub> one would give of information about mechanism generation of phases and transition in vanadium subcarbide.

Thereby, the purpose this work is the investigation of ordered structures, phase transitions and phase transition kinetics in VC<sub>0.47</sub>.

### 2. METHODS AND MATERIALS

Sample VC<sub>0.47</sub> was prepared by sintering of cold-pressed of vanadium metal and graphite at 1773 K in the high-temperature vacuum furnace (vacuum  $1.5 \times 10^{-6}$  Torr). Chemical analysis showed that the content of oxygen in sample was less than 0.2 wt %.

High resolution powder neutron diffraction [14] investigation was carried out for determination of ordered structures and scheme of phase transitions. High resolution powder diffractometer (HRPD) ( $d/d = 2 \times 10^{-3}$ ) is installed at reactor "HANARO" of the Korea Atomic Energy Research Institute (KAERI) [15].

High temperature measurements were carried out on vacuum ( $10^{-5}$  Torr) graphite furnace [15] directly on

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neutron beam. Take to account of results [13], furnace is used with minimal temperature gradient on height and on width that is important when temperature interval of coexistence of ordered phases is a very narrow.

The phase transition kinetics was study at neutron diffractometer with positional-sensitive detector (PSD) [15, 16]. Using PSD is associated with that the phase transition kinetics occurs a very speed and for its studies are necessary the short time measurements. Herewith experimental data must be processed and informative.

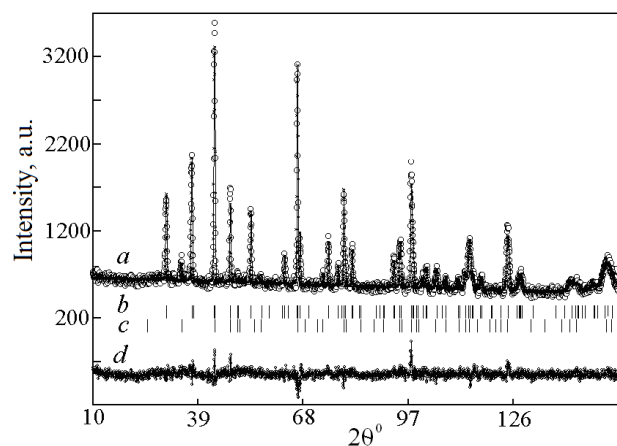
The integral intensity of separate peak measured at PSD in 12 times over than measured at HRPD, but the ratio of effect to background at PSD in 1.5 times over than at HRPD. Therefore diffractometer with position-sensitive detector was used to study of phase transition kinetics in vanadium subcarbide. PSD has active area (window) sizes  $20 \times 10 \text{ cm}^2$ , which filled by mixture of  $\text{He}^3$  (3.1 bar) and  $\text{CF}_4$  (2 bar) gas, the detector space resolution is 2.6 mm. Detector efficiency is about 60 % for hot neutrons with 0.1834 nm wavelength.

PSD was installed at antiparallel position in all measurements. The conditions of experiment realization were defined depending from tasks and, for example, phase transition kinetic was defined (after temperature assignment) at measurements with two minutes temporary step during two hours. The measurements were conducted in 20 minutes for determine of phase transition temperature, moreover the measurements were conducted five-six times repeatedly at same temperature. These results were summarized at carrying out of calculation.

Rietveld method [17, 18] was used for determine of crystalline structure and parameters.

### 3. EXPERIMENTAL RESULTS AND DISCUSSION

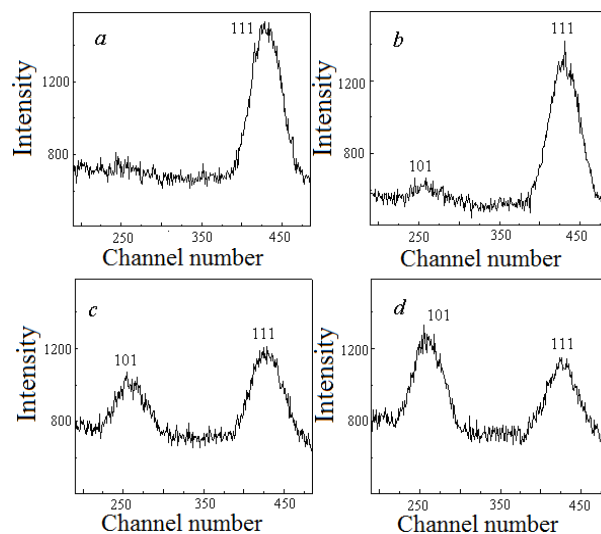
The room temperature neutron diffraction studies of initial  $\text{VC}_{0.47}$  at HRPD have shown (Fig. 1.) that sample consists from two ordered phases: orthorhombic ( $\beta$ - phase; sp. gr. Pbcn) and hexagonal ( $\beta'$ -phase; sp. gr.  $\text{P6}_322$ ). The orthorhombic phase (sp. gr. Pbcn) with lattice parameters:  $a = 0.45677 \text{ nm}$ ;  $b = 0.57678 \text{ nm}$  and  $c = 0.50189 \text{ nm}$  dominates in  $\text{VC}_{0.47}$  on neutron diffraction data.



**Fig. 1** – Neutron diffraction pattern of  $\text{VC}_{0.47}$ , measured at room temperature. *a* – experimental points and calculated profile; *b* – reflections appropriate to an orthorhombic ordered phase (sp. gr. Pbcn); *c* – reflections appropriate to a hexagonal ordered phase (sp. gr.  $\text{P6}_322$ ); *d* – difference curve

The stable state of  $\text{VC}_{0.47}$  at room temperature may be two-phase or one of these phases is a metastable. For improvement the high temperature neutron diffraction measurements were carried out up 1203 K to 1423 K (Fig. 2). The finding at HRPD and PSD has shown that orthorhombic ordered phase is a low temperature phase (Fig. 2) and hexagonal ordered phase is a high temperature phase.

The presence at low temperature of the hexagonal ordered phase (sp. gr.  $\text{P6}_322$ ) is connected by high velocity cooling of sample at which high temperature phase is retained. The existence of two-phase region is one of main result of present work which unlike [12]. Also two-phase area ( $\beta + \beta'$ ) much broader and exceeds 175 K (Fig. 2) that unlike [13].



**Fig. 2** – A part of neutron diffraction pattern of  $\text{VC}_{0.47}$  measured at PSD at 1203 K (*a*); 1273 K (*b*); 1343 K (*c*) and at 1393 K (*d*). The reflection (111) appropriate to a low temperature orthorhombic (sp. gr. Pbcn), reflection (101) appropriate to high temperature a hexagonal ordered (sp. gr.  $\text{P6}_322$ ) phases

The results of PSD and HRPD measurements are indicative about step-by-step transition of a low temperature orthorhombic phase to a high temperature hexagonal ordered phase through two-phase area. Constancy of integral intensity of the reflection (101) at 1393 ÷ 1423 K temperature interval which found in our experiments is indicative about high value of transition temperature from two-phase ordered area to single-phase ordered area in  $\text{VC}_{0.47}$ .

The phase transition temperature is 1448 K which defined by extrapolation to zero of (111) reflection intensity. Because of high disordered ( $\beta' \rightarrow \beta$ ; a hexagonal ordered phase transition to a hexagonal disordered phase  $L3$ ) temperature not succeed to determine this transition by experimentally.

The temperature dependency of (111) intensities and of (101) reflexion intensities (*b*) for  $\text{VC}_{0.47}$  is brought on Fig. 3.

On the base of positional-sensitive detector results (Fig. 3) possible define of the time and temperature at which the value of both phases will be same in two-phase sample. Also the detection is possible of the phase's ratio at free time. For example, point of intersection curves (Fig. 3) indicates to  $T \approx 1374 \text{ K}$  under which the quantity of both phases equally.

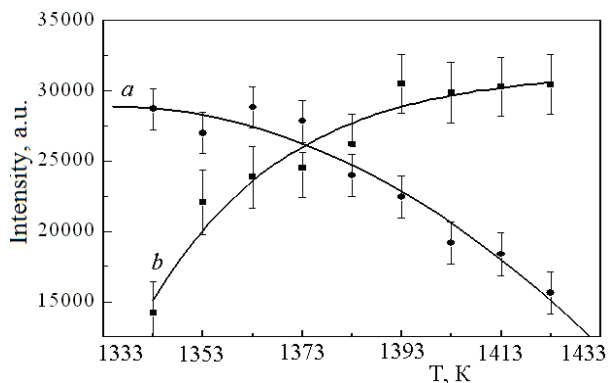


Fig. 3 – The temperature dependency of (111) orthorhombic reflexion intensities (a) and of (101) hexagonal reflexion intensities (b) for  $VC_{0.47}$

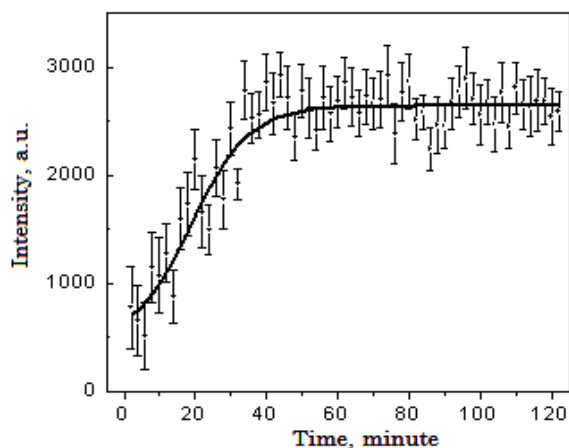


Fig. 4 – Time dependence of (111) reflection intensities for  $VC_{0.47}$  at 1203 K

For study of the transition kinetics the sample temperature maximal quickly was lowered with high (from 1423 K) to 1203 K and measurements were conducted at this temperature (1203 K). The study of the kinetics at 1203 K (low temperature phase) have shown that the maximum intensity (111) superstructure reflection is fixed at endurance for 40 minutes (Fig. 4).

Considering that at ordering maximum long range order parameter is maximal ( $\eta = 1$ ) [6] and given value is reached after anneal for 40 minutes, possible define of the law which describes the dependency of quantity of the growing phase from anneal time at constant anneal temperature (kinetic of the transition). The realized calculations have shown that kinetic of the transition (anneal at 1203 K) is described by Kolmogorov – Johnson – Mehl – Avrami law [19, 20]:

$$\beta = 1 - \exp[-kt^n]$$

where,  $\beta$  – quantity of the increasing phase;  $k$  – constant to transition speed, being function of the temperature;  $t$  – growth time;  $n$  – a factor, which informs on mechanism of the transformation. The realized calculations have shown that  $n = 1.05$  which evidence that nucleation occurs on heterogenic mechanism, but transformation proceeds through nucleation of bidimensional domens (Kolmogorov – Johnson – Mehl – Avrami law).

#### 4. CONCLUSION

By neutron diffraction method is determined that in  $VC_{0.47}$  a orthorhombic ordered phase (sp. gr. Pbcn) is a low temperature phase and high temperature ordered phase is hexagonal phase (sp. gr. P6<sub>3</sub>22) with lattice parameters:  $a = b = 0.50124$  nm,  $c = 0.45696$  nm.

Scheme of the phase transitions in  $VC_{0.47}$  looks as follows:

$$T_1 = 1273 \text{ K} \quad T_2 = 448 \text{ K} \quad T_3$$

$$\beta \text{ (sp gr. Pbcn)} \rightarrow (\beta + \beta') \rightarrow \beta' \text{ (sp. gr. P6}_3\text{22)} \rightarrow \beta \text{ (L'3)}$$

The order-order phase transition is second type phase transition.

It is determined that in  $VC_{0.47}$  the kinetic of transition is described by a Kolmogorov – Johnson – Mehl – Avrami law.

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### Изучение упорядоченных структур и фазовых переходов субкарбида ванадия методом дифракции нейтронов

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Представлены и проанализированы результаты дифракции нейтронов на образцах  $VC_{0.47}$ . Установлены схемы реализации фазовых переходов. Обнаружено существование низкотемпературной ромбической упорядоченной фазы пространственной группы Pbcn и высокотемпературной упорядоченной гексагональной фазы пространственной группы P6<sub>3</sub>22. Показано, что кинетический переход описывается законом Колмогорова-Джонсона-Мель-Аврами.

**Ключевые слова:** Дифракция нейтронов,  $VC_{0.47}$ , Гексагональная фаза, Временные и температурные зависимости.

## Вивчення впорядкованих структур і фазових переходів субкарбіда ванадію методом дифракції нейтронів

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Подані та проаналізовані результати дифракції нейтронів на зразках  $VC_{0.47}$ . Установлені схеми реалізації фазових переходів. Виявлено існування низькотемпературної ромбічної впорядкованої фази просторової групи  $Pbcn$  і високотемпературної впорядкованої гексагональної фази просторової групи  $R\bar{3}m2$ . Показано, що кінетичний перехід описується законом Колмогорова-Джонсона-Мель-Аврамі.

**Ключові слова:** Дифракція нейтронів,  $VC_{0.47}$ , гексагональна фаза, Тимчасові і температурні залежності.

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