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Kinetics of Interaction of ПТ-4 Grade Ti with VN and Graphite during Mechanical Alloying

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A detailed x-ray diffraction study of test samples selected after each hour of the mechanochemical processing of two equimolar (ПТ-4 Ti)–VN and (ПТ-4 Ti)–VN–C blends in a high-energy planetary ball mill is carried out. Initial mixtures contain individual VN and C_{Gr} (graphite), as well as TiH_2 and α-Ti phases in ПТ-4 grade titanium powder. Because of the crystal-structure refinement of each phase existing in the mixtures milled, it is shown that the interaction between the charge components occurs in two stages during 10 hours of processing. Namely, the formation of vacancies in VN phase dominates at the first stage, which is accompanied by embedding of released V atoms into the tetrahedral voids of the TiH_2 structure and dehydrogenating of TiH_2. The second stage is characterized by embedding of Ti atoms forming because of α-Ti destruction into VN crystal lattice with a concurrent embedding of carbon atoms into the TiH_2 structure. The final products of the mechanochemical synthesis, in addition to α-Ti, contain the following compounds: $\cong TiV_{0.33}H_{0.66}$ ((ПТ-4 Ti)–VN blend) and $\cong TiV_{0.33}H_{0.66}C_{0.22}$ ((ПТ-4 Ti)–VN–C blend) on the base of TiH_2 hydride, as well as $\cong V_{0.67}Ti_{0.33}N_{0.93}$ (both blends) solid solution on the base of VN. Nanoscale final products (crystallite size of up to 20 nm) of the mechanical alloying will be compacted to determine the stability of the new phases formed and to study the properties of compacts prepared in order to find out prospects of their further application.

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Key words: mechanochemical synthesis, hydride, nitride, crystal structure, x-ray diffractometry.

Проведено докладне рентґенівське дослідження тестових проб, відібраних через кожну годину механохемічного оброблення у високоенергетичному планетарному млині двох еквімолярних сумішей (ПТ-4 Ti)–VN і (ПТ-4 Ti)–VN–C, які містять VN і C_{Gr} (графіт), а також TiH_2 й α-Ti в порошку титану марки ПТ-4. В результаті уточнення кристалічних структур фазових складових, наявних в оброблених сумішах, показано, що за час проведення експерименту (10 годин оброблення) взаємодія між компонентами шихти проходить у два етапи. А саме, на першому етапі синтези домінує процес формування вакансій у нітриді VN з подальшим втіленням атомів Ванадію, які через це утворилися, до тетраедричних пор структури TiH_2, а також перебігає процес дегідрування TiH_2. На другому етапі відбувається втілення до структури нітриду VN атомів Титану, які утворюються в результаті руйнування структури α-Ti, а також втілення атомів Карбону до структури TiH_2. Показано, що фінальні продукти механохемічної синтези, окрім α-Ti, містять такі сполуки: $\cong TiV_{0,33}H_{0,66}$ (в суміші (ПТ-4 Ti)–VN) і $\cong TiV_{0,33}H_{0,66}C_{0,22}$ (в суміші (ПТ-4 Ti)–VN–C) на основі гідриду TiH_2, а також твердий розчин $\cong V_{0,67}Ti_{0,33}N_{0,93}$ (в обох сумішах) на основі нітриду VN. Одержані нанорозмірні матеріяли будуть компактовані для вивчення властивостей і визначення подальших перспектив їхнього використання.

Ключові слова: механохемічна синтеза, гідрид, нітрид, кристалічна структура, рентґенівська дифракція.

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1. INTRODUCTION

Titanium and its alloys are widely used in medical device industry due to such characteristics as low Young's modulus, excellent corrosion resistance and increased biocompatibility [1–3]. Therefore, such titanium alloys as T6Al4V, T6Al4V (ELI) (so-called medical titanium alloys) are widely used in the manufacture of surgical instruments, external and internal prostheses, implants, *etc*. [4, 5].

Usually the sponge titanium (99.1–99.7% Ti) with Al, V and other alloying elements are used to produce titanium alloys (including T6Al4V (ELI) alloys). However, as mentioned in Refs. [6, 7] the addition of TiH_2 to initial charge of Ti alloy has a positive effect on mechanical properties of the material manufactured due to compaction of its microstructure and an increase in plasticity. Thus, the introducing of TiH_2 as an alloying element with a pore-forming ability and as an active agent in the synthesis of medical titanium Ti6Al4V made it possible to obtain a biocompatible material with a Young's modulus of 5.8–9.5 GPa, similar to human cancellous bone, which alleviates the prob-

lem of mechanical mismatch between bone and metallic titanium implant [8]. The titanium raw material that contains its hydride is industrial titanium powder of grade ПТ-4, which is specifically used for the manufacture of medical implants.

Titanium carbide TiC is an ideal strengthening dopant for titanium alloys [9]. However, a set of unique properties such as high melting point and hardness, good thermal conductivity, high chemical stability [10] and even biocompatibility [11, 12] are also inherent to VN. Since TiC easily forms strong interfacial bonds with titanium matrix [9], it is also interesting to specify the nature of interaction of VN with titanium matrix. In this research, the hydrated ПТ-4 grade titanium powder was selected as a component of the charge for studying the nature of interaction of VN nitride with a titanium matrix.

Therefore, the aim of this work was to study in detail the kinetics of interaction between components of two powder mixtures containing ПТ-4 Ti at mechanical alloying in a high-energy planetary ball mill. Results of the study of test samples of the first equimolar (ПТ-4 Ti)–VN blend, which were selected after a certain processing time, are aimed to define the nature of interaction of VN with Ti matrix. It is also assumed that TiC formed at mechanical alloying may be an additional phase in the products of mechanical alloying of the second equimolar (ПТ-4 Ti)–VN–C blend.

2. EXPERIMENTAL/THEORETICAL DETAILS

Two equimolar mixtures, namely, (ПТ-4 Ti)–VN (1:1) (marked as Blend 1) and (ПТ-4 Ti)–VN–C (1:1:1) (Blend 2) were the objects of this study. These blends as starting components contain dispersed (up to 50 μm) powders of ПТ-4 Ti (98.0% wt. of purity), VN (99.9% wt. of purity) and graphite (C, 99.99% wt. of purity). Taking into account the results of our previous research [13], 1% vol. graphite was also added to Blend 1 to prevent possible oxidation of a charge.

The prepared mixtures were placed in steel vials for further mechanical alloying in a high-energy planetary ball mill. Processing of the charges was carried out using steel balls (10 mm of diameter, the mass ratio of the balls to powder was 20:1) at a rotation speed of 1400 rpm in a cyclic mode (20 min of treatment and 10 min of cooling). Temperature of the working reactor of the mill did not exceed 100°C.

Phase transformations that the charge components undergo during mechanical processing were studied by x-ray diffraction (XRD) method on the test samples selected after each 1 hour of milling. XRD data were collected with ДРОН-3М automatic diffractometer (radiation CuK_α) in a discrete mode under the following scanning parameters: observation range $2\theta = 20°–100°$, step scan of 0.05° and counting time per step at 3 s. The original software package [14], including full com-

plex of standard Rietveld procedures, has been used for analysis and interpretation of the XRD patterns obtained. Namely, determination of both peak positions and integral intensities of the Bragg reflections by means of full profile analysis; carrying out qualitative and quantitative phase analysis using the least square method for lattice parameters refinement; testing of the structure models proposed and refining crystal structure parameters (including coordinates of atoms, atomic position filling, temperature parameter, *etc*.).

3. RESULTS AND DISCUSSION

The results XRD study of initial powders of graphite, VN and ПТ-4 Ti revealed the following: graphite and vanadium nitride powders contain C_{Gr} and $VN_{0.93}$ phases, consequently, while ПТ-4 titanium powder is a mixture of TiH_2, completely filled with nitrogen atoms, and α-Ti itself. According to the quantitative phase analysis, content of TiH_2 phase in ПТ-4 titanium powder is equal to 60% wt. (64% vol.). The diffraction patterns of the initial equimolar Blend 1 and Blend 2 mixtures are shown in Fig. 1.

The results of XRD study of the interaction kinetics of ПТ-4 Ti with VN and graphite revealed following: the phase composition of the test samples obtained from (ПТ-4 Ti)–VN mixture (Blend 1) does not change at mechanochemical processing, while the graphite phase in test samples obtained from (ПТ-4 Ti)–VN–C mixture (Blend 2) gradually disappears (Fig. 1).

VN and TiH_2 are the main phase components of all test samples but

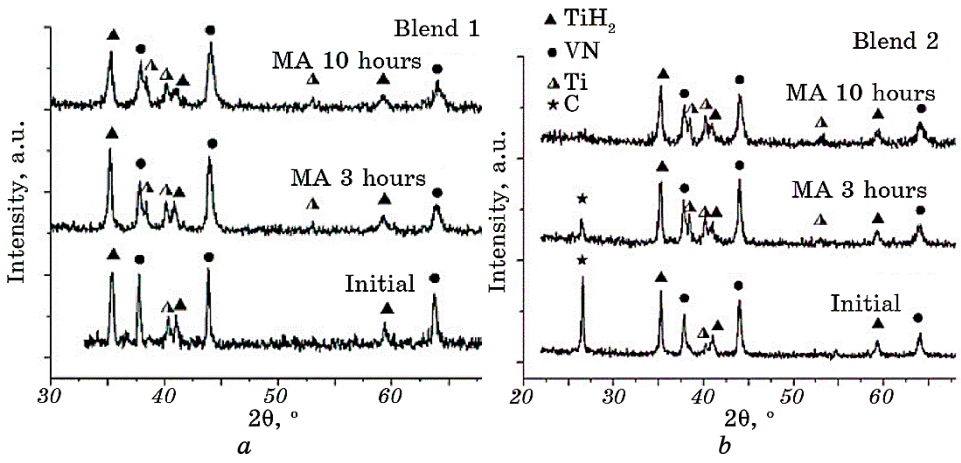

Fig. 1. Fragments of XRD patterns of the equimolar (ПТ-4 Ti)–VN (Blend 1) and (ПТ-4 Ti)–VN–C (Blend 2) mixtures: initial and after processing in a ball mill.

their crystal structure is somehow modified at mechanochemical processing. First of all, the lattice parameters of these phases gradually change (Fig. 2).

As a result of the calculations performed for refinement of the VN crystal structure, it was found that q_1—the filling degree of $4a$ position by vanadium atoms—gradually changes, resulting in the total number of atoms per lattice equal to $4q_1$ (Table 1). This undoubtedly indicates the formation of atomic vacancies in the structure, the number of which is $4(1 - q_1)$ per unit cell. Figure 3, *a* illustrates the change in the total number of atomic vacancies per VN lattice at mechanical alloying.

The crystal structure of TiH_2 phase undergoes transformations, which are more complex. At the beginning of mechanical alloying this phase keeps a cubic structure of the CaF_2 type, which transforms into rhombohedral after 2 hours of milling due to internal deformation (Table 1). However, external deformation of the crystal lattice is not observed, which allows providing the lattice parameter calculations of TiH_2 phase in the cubic syngony (Fig. 2, *b*). That is why further considerations of TiH_2 lattice parameters will be presented in the cubic aspect.

According to our model (listed in Table 1 and presented in Fig. 4 in cubic aspect), one half of the undeformed tetrahedral voids of TiH_2 gradually loses hydrogen atoms, while another half of the tetrahedral voids is partially filled with vanadium atoms, displacing hydrogen atoms at the same time. Those processes lead to a certain deformation of voids at the beginning of mechanical alloying.

Analysis of the structural calculation data revealed that at the beginning of mechanical alloying (up to 5 hours of milling) the amount of hydrogen in TiH_2 rapidly decreases (Fig. 5), while the number of va-

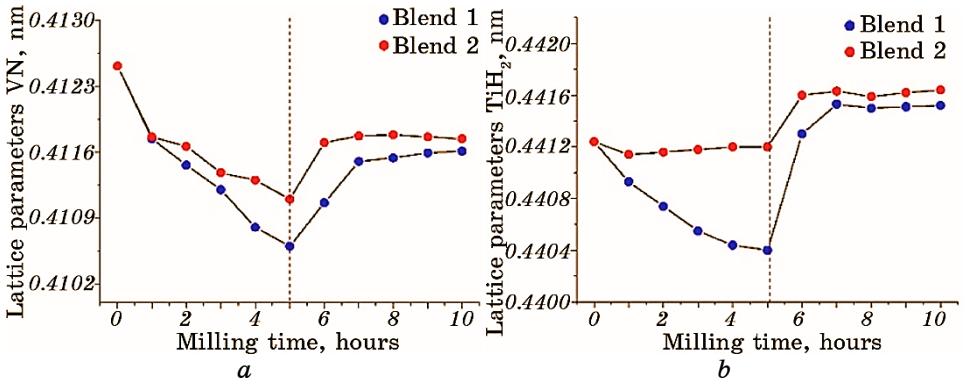

Fig. 2. Dependences of lattice parameters of VN (*a*) and TiH_2 (*b*) phases of equimolar (IIT-4 Ti)–VN (Blend 1) and (IIT-4 Ti)–VN–C (Blend 2) mixtures after their processing in a ball mill.

TABLE 1. Crystal structure data for VN and TiH_2 phases of (ПТ-4 Ti)–VN–C mixture (Blend 2) at the beginning of its processing in a ball mill (3 hour of milling).

Atom	Site	Site occ.	x	y	z
		VN			
V	4*a*	0.770(4)	0	0	0
N	4*b*	0.935	0.5	0.5	0.5
Space group			F–43m (No. 216)		
Lattice parameter a, nm			0.41138(6)		
Total isotropic B factor, nm^2			$B = 1.82(3)\cdot10^{-2}$		
Phase			$V_{0.77}N_{0.93}$		
Reliability factor			$R_B = 0.006$		
Atom	Site	Site occ.	x	y	z
		Rhombohedrally distorted TiH_2			
Ti	3*a*	1.00(1)	0	0	0
V	3*a*	0.28(1)	0	0	0.327(2)
H(1)	3*a*	0.72(1)	0	0	0.327(2)
H(2)	3*a*	0.55(2)	0	0	0.666(2)
C	3*a*	0.04(2)	0	0	0.666(2)
Space group			$R3m$ (No. 160)		
Lattice parameter a, c, nm			$a = 0{,}3121(2)$, $c = 0{,}7647(3)$		
Total isotropic B factor, nm^2			$B = 1.72(3)\cdot10^{-2}$		
Calculated phase content, at.%			$TiV_{0.3}H_{1.3}C_{0.04}$		
Reliability factor			$R_B = 0.02$		

cancies formed in the VN corresponds to the number of V atoms embedded in the tetrahedral voids of TiH_2 structure (Fig. 3). At the same stage, the carbon atoms from the graphite of (ПТ-4 Ti)–VN–C mixture (Blend 2) start to displace the hydrogen atoms in undeformed tetrahedral voids (Figs. 4, 5). This leads to a decrease in the amount of graphite phase in Blend 2 mixture (Fig. 1).

Certain stabilization of TiH_2 structure is achieved after 5 hours of mechanochemical processing, when the undeformed tetrahedral voids become empty: filling of the position with H(2) atoms is zero for Blend 1, while in the case of Blend 2 these empty voids are gradually filled with carbon atoms (Tables 1, 2, Fig. 4). Moreover, the number of additional vanadium atoms in TiH_2 structure practically does not change (Fig. 3, *b*). However, at this stage, other processes dominate, in which the number of vacancies in VN structure gradually decreases (Fig. 3,

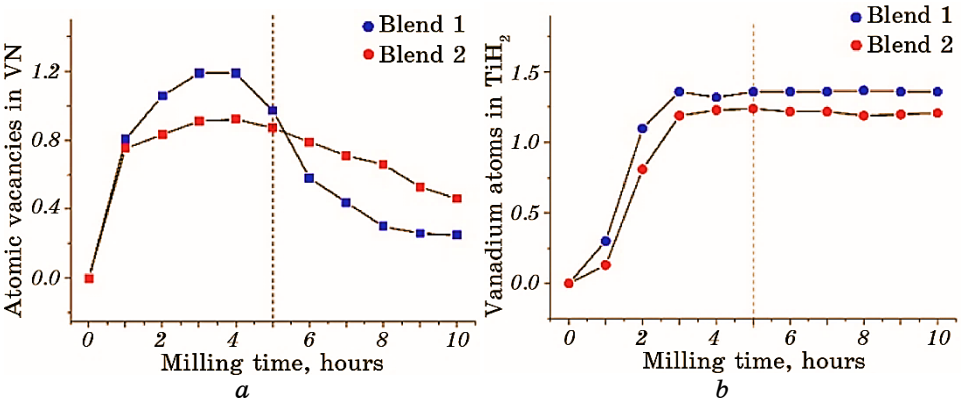

Fig. 3. Dependences of atomic vacancies number in VN (*a*) and additional V atoms in TiH_2 phases of equimolar (ПТ-4 Ti)–VN (Blend 1) and (ПТ-4 Ti)–VN–C (Blend 2) mixtures after their processing in a ball mill.

a). The crystal data for VN and TiH_2 phases of the final product of the mechanochemical synthesis of (ПТ-4 Ti)–VN–C mixture (Blend 2) are listed in Table 2.

XRD results obtained here for test samples selected after each full hour of mechanical alloying of equimolar (ПТ-4 Ti)–VN and (ПТ-4 Ti)–VN–C mixtures in a high-energy planetary ball mill provide information on the kinetics of interaction of the phases present in these blends, namely, the TiH_2 and α-Ti phases, which are the components of ПТ-4 Ti, VN and graphite. It is shown that mechanical alloying takes place in two

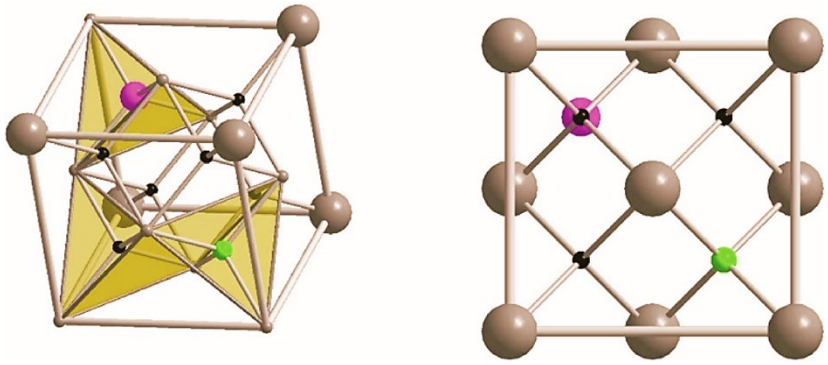

Fig. 4. Crystal structure of the rhombohedrally deformed TiH_2 phase and its projection presented in the cubic aspect. Slightly deformed VTi_4 polyhedra with V atom in the centre (Ti atoms is grey circles, V atoms is purple circles) and undeformed HTi_4 and CTi_4 polyhedra with a hydrogen or a carbon atom in the centre (hydrogen atoms is small black circles, carbon atoms is small green circles).

stages regardless of the charge composition (presence/absence of graphite). Each stage is characterized by its own mechanism.

At the first stage of mechanical alloying (up to 5 hours of milling), part of V atoms leaves the crystal structure of VN, forming individual V clusters in the reaction zone of a mill because of the applied shock load. This process is accompanied by a gradual accumulation of vacancies in VN (Fig. 3, *a*). Most of V clusters formed (probably as ions) are embedded in the tetrahedral voids of the rhombohedrally deformed structure of TiH_2, which are released during its dehydrogenation (Figs. 3, *b*, 5). At the same stage, the process of filling the released voids of TiH_2 structure with carbon atoms begins, apparently.

At the end of the first stage of mechanical alloying, both dehydration and transformation of TiH_2 structure become balanced (the number of embedded V atoms does not change (Figs. 3, *b*, 5)). Therefore, at the second stage of synthesis (after 5 hours of processing), in our opinion, the process of embedding of Ti atoms (formed during partial decomposition of α-Ti) into the crystal structure of VN prevails and leads to a gradual decrease in the fraction of vacancies (Fig. 3, *a*).

It should be noted that during experiment, TiH_2 does not show any signs of destruction (except for some dehydrogenation; Fig. 4), and its interaction with VN and carbon leads to the formation of a compound with the composition $\cong TiV_{0.33}H_{0.66}C_{0.22}$ ($Ti_3VH_2C_{0.66}$). In turn, VN accumulates a certain amount of titanium, forming $V_{0.67}Ti_{0.33}N_{0.93}$ solid solution with about 16 at.% of Ti. These results fully correspond to the data of Refs. [15, 16]. M. A. Roldán *et al.* [15] synthesized $V_{0.75}Ti_{0.25}N_{0.87}$ solid solution in a nitrogen environment from mixture of pure metals

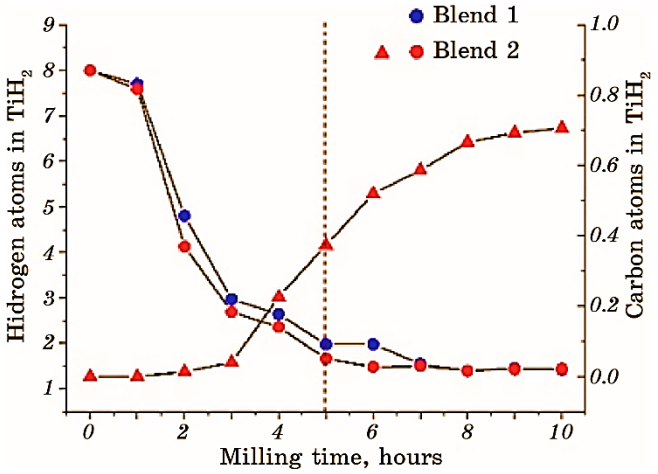

Fig. 5. Dependences of the number of hydrogen atoms (circles) and carbon atoms (triangles) in the structure of TiH_2 of equimolar (ПТ-4 Ti)–VN (Blend 1) and (ПТ-4 Ti)–VN–C (Blend 2) mixtures after their processing in a ball mill.

TABLE 2. Crystal data for VN and TiH_2 of (ПТ-4 Ti)–VN–C mixture (Blend 2) at the end of its processing in a ball mill (10 hour).

Atom	Site	Site occ.	x	y	z
		VN			
V	4*a*	0.640(4)	0	0	0
Ti	4*a*	0.300(4)	0	0	0
N	4*b*	0.935	0.5	0.5	0.5
Space group			F–43m (No. 216)		
Lattice parameter a, nm			0.41178(5)		
Total isotropic B factor, nm^2			$B = 0.90(4)\cdot10^{-2}$		
Phase			$V_{0.67}Ti_{0.33}N_{0.93}$		
Reliability factor			$R_B = 0.026$		
Atom	Site	Site occ.	x	y	z
		Rhombohedrally distorted TiH_2			
Ti	3*a*	1.00(1)	0	0	0
V	3*a*	0.33(1)	0	0	0.327(2)
H(1)	3*a*	0.66(1)	0	0	0.327(2)
C	3*a*	0.22(2)	0	0	0.666(2)
Space group			$R3m$ (No. 160)		
Lattice parameters a, c, nm			$a = 0{,}3120(2)$, $c = 0{,}7649(3)$		
Total isotropic B factor, nm^2			$B = 1.58(5)\cdot10^{-2}$		
Calculated phase content, at.%			$TiV_{0.33}H_{0.66}C_{0.22}$		
Reliability factor			$R_B = 0.026$		

(Ti and V) using mechanochemical method, while according to our results [16] $V_{0.75}Ti_{0.25}N_{1.6}$ solid solution supersaturated with nitrogen was synthesized by mechanical alloying of VN and TiN mixture.

Comparison of the nature of interaction between components of (ПТ-4 Ti)–VN (Blend 1) and (ПТ-4 Ti)–VN–C (Blend 2) mixtures based on the kinetic curves shows that the processes studied here are occurring more 'softly' in the presence of graphite (Figs. 2, 3). The final products of the blend component interaction are the following compounds: $\cong TiV_{0.33}H_{0.66}$ (Blend 1) and $\cong TiV_{0.33}H_{0.66}C_{0.22}$ (Blend 2) based on the TiH_2, as well as the solid solution $\cong V_{0.67}Ti_{0.33}N_{0.93}$ (Blend 1, Blend 2) based on the VN.

4. CONCLUSION

1. A detailed XRD study of test samples selected after each hour of

mechanochemical processing in a high-energy planetary ball mill of two equimolar (ПТ-4 Ti)–VN and (ПТ-4 Ti)–VN–C mixtures, which contain VN and C_{Gr} (graphite) phases, as well as TiH_2 and α-Ti phases in ПТ-4 grade titanium was carried out.

2. Kinetics of interaction of the components was studied applying X-ray diffraction method, based on the refinement of the crystal structure of each phase present in the mixtures milled.

3. It is shown that the interaction of the components of the mixtures takes place in two stages. At the first stage, the process of formation of vacancies in VN dominates, which is accompanied by embedding of knocked out V atoms into the tetrahedral voids of TiH_2 structure and dehydrogenation of TiH_2. At the second stage, Ti clusters are embedded into the structure of VN while the carbon atoms are embedded into TiH_2 structure.

4. The final products of the interaction process at mechanical alloying of the mixtures studied are following compounds: $\cong TiV_{0.33}H_{0.66}$ (Blend 1) and $\cong TiV_{0.33}H_{0.66}C_{0.22}$ (Blend 2) on the base of TiH_2, as well as $\cong V_{0.67}Ti_{0.33}N_{0.93}$ (Blend 1, Blend 2) solid solution of the base of VN.

5. The nanocrystalline (crystalline size up to 20 nm) final products of mechanochemical synthesis, obtained in the work, will be compacted to determine the stability of the phases formed, as well as to study the properties of these materials to find out prospects of their further application.

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