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Features of the Electronic Structure of TiC and VN Phases of the Mechanically Alloyed Equimolar TiC-VN Blend

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The electronic structure of TiC and VN phases, which undergo gradual structural transformations under impact stress at mechanical alloying of the equimolar TiC-VN blend in a high-energy planetary mill, has been studied. Based on the experimental results of the study of the kinetics of phase transformations, three structural models characterizing the flow of this process were proposed and considered. Namely, Ti_4C_4 and V_4N_4 phases (TiC and VN) in the initial state; Ti_3C_4 and V_3N_4 phases, existing when the maximum fraction of structural vacancies accumulates at the second stage of mechanical alloying; solid solutions of Ti_3VC_4 and V_3TiN_4 formed in the final synthesis products. Based on the results of theoretical calculations performed using the linearized muffin-tin orbitals in the plane wave approximation (LMTO PLW) calculations of the density of electronic states (DOS) spectrum were performed and the main parameters of the electronic structure of phases were determined for each of the model proposed. It is shown that near the Fermi level, the total DOS for TiC and VN mainly consists of hybridized 3*d* states of metals (Ti or V) and 2*p* states of nonmetals (C or N), which leads to the formation of covalent bonds in the compounds. DOS profiles of the TiC and VN phases, which contain many structural vacancies, are significantly blurred (both the valence and conductivity bands) and contain additional peaks near the Fermi level. These factors indicate a high degree of structural instability, which creates preconditions for further formation of solid solutions. Density of electronic states of (Ti, V) C and (V, Ti) N solid solutions formed are somehow similar to the DOS of the initial compounds. Based on the results of theoretical calculations of the electronic structure parameters and on the data of other authors, it is shown that alloying of TiC with V generally improves its mechanical characteristics. The impact of mechanical alloying is higher on VN phase in the TiC-VN blend than on TiC phase.

Keywords: Mechanical alloying, Carbide, Nitride, Crystal structure, Electron structure.

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1. INTRODUCTION

Development of a scientific strategy for design of advanced metal-based composites and ceramics by doping these materials with nano-sized particles of refractory compounds places an important role in modern materials science. The range of such materials is quite wide and also includes those intended for the development of medical devices. Currently, medical titanium (alloys based on Ti, including the Ti-6Al-4V alloy) has found wide application as a material for surgical instruments and prostheses due to its high mechanical characteristics and corrosion resistance [1]. Meanwhile, the advanced properties of this material were obtained through reinforcing with dispersed particles of carbides, borides, etc. [2]. Titanium carbide (TiC) should be noted as the best solution among such reinforcing dopants since its ideal biocompatibility and chemical stability that contributes to the strength of Ti-TiC composites [3].

In our opinion, the formation of polycarbides (solid solutions) on the base of TiC will not only lead to the improvement of their characteristics but also impact the functional characteristics of medical instruments. Applying a combination of different refractory compounds as dopants will also improve operational characteristics of medical devices. Possibly, the biocompatible VN nitride can be tested as such dopant, since it is characterized by a set of unique physical and chemical properties [4, 5]. In addition, our detailed study of the interaction of components of ceramics of cBN-TiC-VN-Al system at high pressure (high pressure high temperature (HPHT sintering)) has revealed that the formation of stable multicomponent solid solutions (Ti, V) (C, N) and (V, Ti) N in sintering products of initial TiC and VN compounds is one of the reasons of the advanced functional characteristics of this material [6-8]. It has also been shown that titanium carbide TiC and vanadium nitride VN exhibit a tendency to form mutual solid solutions (Ti, V) C and (V, Ti) N at mechanical alloying in a planetary mill [8].

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It is well known that the main characteristics of any carbide or nitride (or their compounds) are associated with their electronic properties, e.g., the simultaneous contributions of strong covalent metal-nonmetal bonding, less important ionic bonding and not negligible metallic bonding [9]. That is, the experimental data on the parameters of the refined crystal structures of biocompatible compounds TiC and VN obtained in our previous study [8], could serve as the basis for theoretical calculations of the electronic structure of these compounds by ab initio methods, and, therefore, for a certain prediction of the physical properties of polycarbide (Ti, V) C and polynitride (V, Ti) N synthesized.

2. MATERIALS AND METHODS

Parameters of electronic structure such as density of electronic states (DOS), the energy at the Fermi level (EF), the total electron charge and some other characteristics were calculated by the method of linearized muffin-tin orbitals in the plane wave approximation (LMTO PLW) using the MStudio MindLab 7.0 and MStudio MindLab 8.0 software. The calculations were based on the experimentally obtained data on the crystal structure of mechanically alloyed TiC and VN compounds of the equimolar TiC-VN blend.

Mechanical alloying (MA) of equimolar TiC-VN charge was carried out in a high-energy planetary mill [8]. Test samples were taken and examined by X-ray diffraction (XRD) after each full hour of MA processing. Diffraction spectra were collected in a discrete mode on the DRON-3M apparatus (CuK radiation). Preliminary estimation of XRD data obtained, qualitative and quantitative phase analysis with refinement of crystal lattice parameters, testing of the structural models and their refinement was provided with the original software package [10], which includes a full set of Rietveld procedures.

3. RESULT AND DISCUSSION

Crystal structure of TiC and VN phases of the mechanically alloyed equimolar TiC-VN blend. According to data of XRD phase analysis, the test samples selected contain only TiC and VN, the crystal lattice parameters of which change significantly with the duration of MA. To compare the nature of this change, the relative distortion value a_t was introduced as $\varepsilon(\%) = 100 \times (a_0 - a_t)/a_0$, where a_t is the lattice parameter at a time t of MA, and a_0 is the lattice parameter of the original blend (Fig. 1). Taking into account the data obtained, the dependencies can conditionally be divided into two separate regions (I and II), where the change of the lattice parameters of both phases is somewhat individual (Fig. 1).

The calculations performed have shown that the dominant impact of MA on TiC and VN phases is the formation of vacancies in the metal sublattices of their NaCl-type crystal structures. At the same time, the beginning of MA (region I) is characterized by a gradual accumulation of vacancies, which are formed due to the movement of a part of metal atoms into tetrahedral voids (into lattice interstices) and/or due to the movement of a part of metal atoms into the reaction zone of the mill with the formation of individual clusters. It should also be noted that certain features in non-monotonic behavior of the TiC and VN crystal lattice distortions within region I (Fig. 1), which are associated with the intensity of metal atom hopping into interstices, are not considered in this work. After the accumulation of a certain fraction of vacancies in the structures and clusters of titanium or vanadium in the reaction zone, the formation of mutual solid solutions (Ti, V)C and (V, Ti)N begins, which is accompanied by the gradual filling of the vacancies present in the structures of the phases with atoms of another metal (region II).

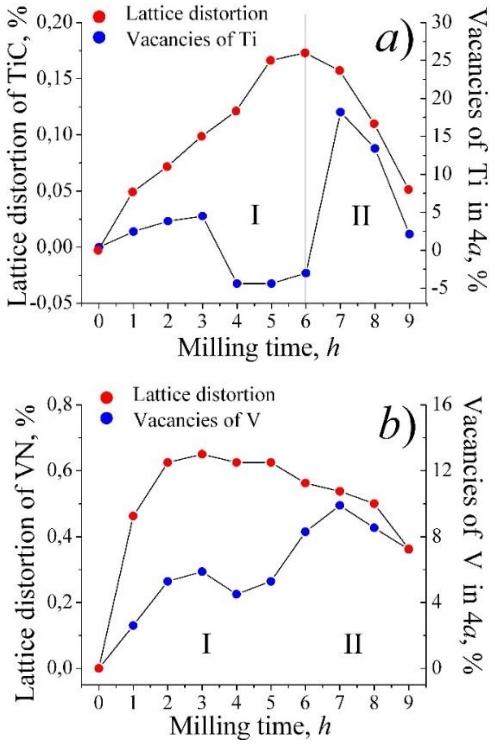


Fig. 1 – Dependences of crystal lattice distortions and the fraction of vacancies in TiC (a) and in VN (b) at MA of an equimolar TiC-VN blend

Thus, we can consider the following sequence of solid-phase processes at this MA synthesis: starting compound → movement of metal atoms with the formation of vacancies and/or individual clusters in the reaction zone of the mill → formation of mutual solid solutions. The analysis of these structural transformations, described in more detail by us in Ref. [8], made the basis for calculations of the electronic structure of these phases.

Taking into account the experimentally determined values of the fraction of vacancies accumulated after 6 hours of MA of TiC-VN mixtures, as well as data on the compositions of solid solutions formed after 9 hours of MA (the solubility of the second metal is about 6-9 at. %), in our opinion, it is correct to consider three different models of the arrangement of atoms in the crystal

structures of TiC and VN phases (Fig. 2) for the calculations of electronic structure. Namely, Model 1 corresponds to TiC and VN in the initial state (completely filled NaCl-type crystal lattices); in Model 2, the metallic sublattices of the phases contain one vacancy per four titanium or vanadium atoms; in Model 3, the vacancies present in TiC and VN are occupied by atoms of a different type (vanadium and titanium, respectively).

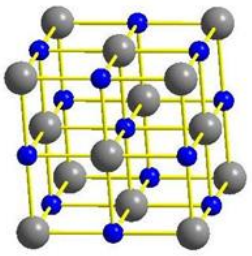
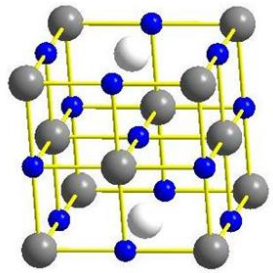
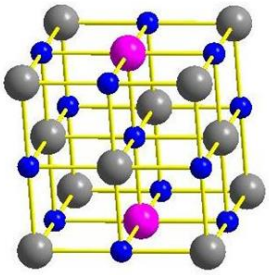
Model 1 Initial phases of TiC or VN Space group *Fm3m* 4Ti or 4V in 4*a* 0 0 0; 4C or 4N in 4*b* 0.5 0.5 0.5. Ti or V – gray circles, C or N – blue circles.	
	Model 2 TiC or VN phases after 3-6 hours of MA (vacancies are present) Space group *Fm3m* 3Ti or 3V in 4*a* 0 0 0; 4C або 4N в 4*b* 0.5 0.5 0.5. Ti or V – large gray circles, C or N – blue circles, Vacancy – white circle.
Model 3 TiC or VN after 9 hours of MA (the presence of interstitial atom) Space group *Fm3m* 3Ti or 3V in 4*a* 0 0 0; 1V or 1Ti in 4*a* 0 0 0; C or N in 4*b* 0.5 0.5 0.5. Ti or V of the main lattice – gray circles, V or Ti, which are embedded in a lattice – violet circles, C or N – blue circles.	

Fig. 2 – Patterns of models of mechanically alloyed TiC and VN phase structures, which were used for calculation the electron density of these phases

Electronic structure of mechanically alloyed TiC and VN phases of an equimolar TiC-VN blend. The electronic structure calculations of TiC carbide, provided within the framework of this work were compared with the available literature data for DOS spectra of TiC (Fig. 3). Fig. 3 shows complete coincidence of the results obtained both in terms of the DOS spectrum profile, and in terms of energy ranges and values of the density of states. Thus, all the results obtained can be considered as quite correct.

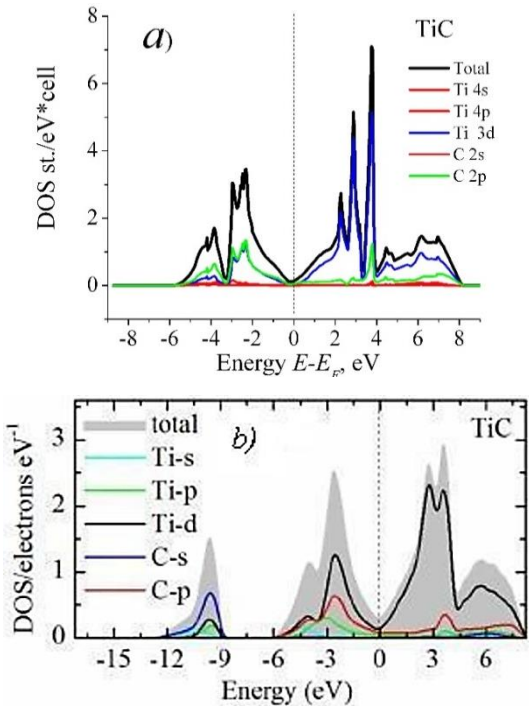


Fig. 3 – DOS spectra for TiC phase in the initial state based on the results of our calculations (a) and according to the Ref. [11] (b)

To assess the changes that occur in TiC and VN during the accumulation of structural vacancies, which are formed because of metal atoms are displaced from their positions, and during the formation of mutual solid solutions, the calculations of the electronic structure of these phases were carried out. Calculating the parameters of electronic structure, the models presented in Fig. 2 were used. DOS spectra for MA TiC and VN are shown in Fig. 4, 5.

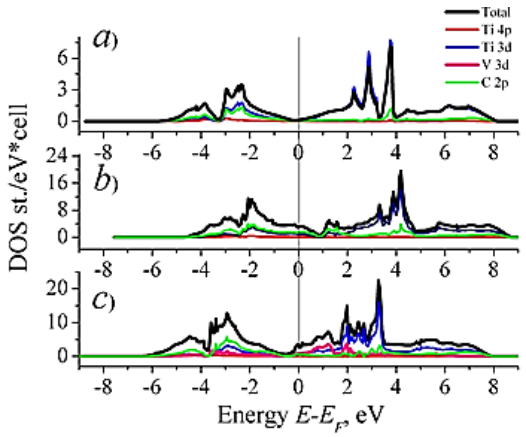


Fig. 4 – DOS spectra calculated for TiC phase in the initial state (model 1) (a), after 6 h of MA (model 2) (b) and after 9 h of MA (model 3) (c)

The spectra (Fig. 4, 5) calculated illustrate the change in DOS of TiC and VN phases, which occurs when those phases accumulate maximal number of structural defects

in the form of vacancies (after 3-6 h of MA), and during the subsequent formation of mutual solid solutions, which are formed as a result of filling these vacancies with atoms of another metal present in the reaction zone of the mill in the form of separate clusters (after 9 h of MA). It is clearly seen that the presence of these structural transformations leads to certain changes in the electronic structure of the compounds, especially near the Fermi level.

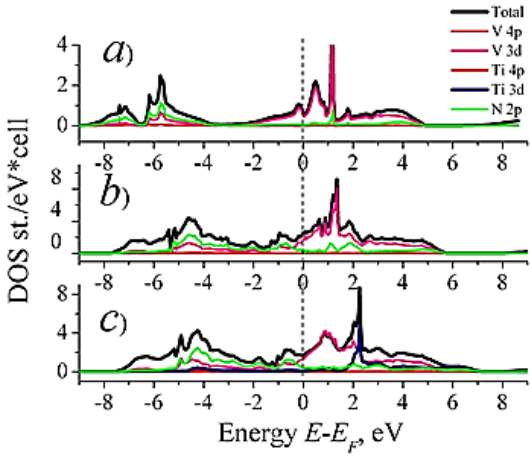


Fig. 5 – DOS spectra calculated for VN phase in the initial state (model 1) (a), after 3 h of MA (model 2) (b) and after 9 h of MA (model 3) (c)

First of all, it should be noted that the conductivity band of DOS of both TiC and VN phases is mainly formed by the 3d states of titanium or vanadium atoms, while its valence band is significantly contributed by the 2*p* states of carbon or nitrogen with an admixture of 3*d* states of metals (Fig. 4, 5). It should also be noted that the s states of metals and metalloids practically do not participate in the formation of the DOS spectrum.

Breaking of certain atomic bonds, which undoubtedly accompanies the formation of vacancies (Model 2, Fig. 2), leads to the formation of a transition zone between the valence and conductivity bands (Fig. 4b, 5b), since the absence of overlapping between them in the initial TiC and VN phases (Fig. 4a, 5a). Besides, a certain smoothing of DOS profiles is observed.

When TiC ((Ti, V) C)-based solid solution is formed by filling existing vacancies with vanadium (Model 3, Fig. 2), the DOS profile (Fig. 4c) is very similar to the DOS profile of the initial titanium carbide, although the transition region between the valence and conductivity band becomes somewhat blurred (Fig. 4a).

The profile of the density of electronic states spectrum of (V, Ti)N solid solution is also similar to DOS profile of the initial nitride VN (Fig. 5a, c), it is also has a blurred transition region between the valence and conductivity band, where an additional peak is present (Fig. 5c).

The parameters of initial models for DOS calculations and the obtained parameters of the electronic structure of the MA phases are listed in Table 1.

It should be noted that the results of the calculations indicate that the formation of vacancies in TiC and VN phases studied causes the same changes in their DOS profiles. Thus, in Fig. 4b, 5b, the formation of an additional separate peak near the Fermi level, which mainly consists of 2*p* states of non-metals (N or C), is clearly visible. At the same time, in VN nitride this additional peak is located slightly below the Fermi level, while in TiC carbide it is located above the Fermi level.

The formation of a similar additional asymmetric peak, which in the highest occupied state exists slightly above the Fermi level, was shown by the authors of Ref. [12] when studying the electronic structure of $ScMeN_2$ polynitrides (Me-V, Nb, Ta) in the initial state and in the presence of defects in the form of vacancies and atoms C, O, F embedded in the lattice. According to the authors of [12], such a local maximum of the DOS near the Fermi level often correlates to a first approximation with the degree of structural instability, since the formation of a vacancy corresponds to the separation between the binding and anti-binding states of the compound.

Table 1 – Parameters of the electronic structure of mechanically alloyed TiC and VN phases of the TiC-VN charge

Phase	MA	Lattice parameter, a.u	Model	MT radius		Fermi energy		Electron charge per lattice
				Me	C/N	Ry	eV	
TiC	initial	8.1733	1-Ti_4C_4	2.206	1.879	1.0095	13.73	9.461
TiC	6 h	8.1722	2-Ti_3C_4	1.769	1.769	1.5022	20.43	14.265
TiC	9 h	8.1685	3-$Ti_3V_1C_4$	2.205	1.878	1.0287	14.00	9.526
VN	initial	7.7967	1-V_4N_4	2.144	1.754	1.2008	16.34	9.328
VN	3 h	7.7683	2-V_3N_4	1.683	1.683	1.6991	23.11	14.235
VN	9 h	7.7752	3-$V_3Ti_1N_4$	2.136	1.747	1.2177	16.56	9.478

Discussion. Kinetics of the interaction of TiC and VN phases established on the basis of the results of the crystal structures refinement at their XRD study, completely correspond to the existing provisions of the theory mechanochemical synthesis. Namely, the applied mechanical stresses activate the formation of point defects, which results in the partial destroying of the crystal structure and the creation of active centers for subsequent chemical reactions. It is precisely such processes that occur in titanium carbide and vanadium nitride during processing of the TiC-VN blend in a high-energy planetary mill.

The influence of vacancies present in TiC on its electronic structure was previously studied in Refs. [13-15]. However, in these works, the options for placing vacancies only in its carbon sublattice (compositions TiC_x $x < 1$) were considered. Thus, based on theoretical calculations the authors of Refs. [13-15] have shown that the presence of vacancies in the carbon sublattice leads to the formation of new types of bonds that are not present in stoichiometric TiC. Analysis of DOS spectrum has revealed the strengthening of covalent Ti-Ti bonds caused by Ti atoms that are not directly adjacent to the vacancy, as well as an increase in the ionic nature of C-Ti bonds. In addition, carbon vacancies induce two additional peaks in the DOS profile [13-15].

However, to our knowledge, the electronic structure of titanium carbide with vacancies in its metal sublattice (compositions TiC_x $x > 1$) has not been considered so far, although the formation of vacancies in the titanium sublattice, according to the results of our studies, is inherent in MA TiC. Results of our calculations of the full and partial DOS spectra for MA TiC and VN phases, containing a large number of structural defects (mainly vacancies, Fig. 2), indicate a significant blurring of both their valence and conductivity bands (Fig. 4b, 5b). In our opinion, this feature of DOS profiles is caused by the loss of certain Ti-C interatomic bonds during the formation of vacancies. That is, those DOS profiles indicate structural instability of MA TiC and VN phases (regions I and II of mechanical alloying).

It should be noted that it is these unstable, transitional states that become a prerequisite for further formation of mutual solid solutions, during the formation of which the parameters of electronic structure of the phases (initial and solid solution) almost do not change (Table 1), and the DOS spectra (Fig. 4 a, c and Fig. 5 a, c) undergo changes that are especially noticeable for the (V, Ti)N solid solution (Fig. 5 a, c). Considering the data obtained at the electronic structure study, it is of interest to establish the relationship between crystal structure, parameters of the electronic structure and properties of the mechanically alloyed TiC and VN phases.

Our calculations indicate that near the Fermi level the total DOS for TiC consists of hybridized Ti-3d and C-2p states, and for VN consists of V-3d and N-2p states (Fig. 4a, 5a). According to the theory proposed by the authors of Ref. [16], such hybridization of 3d-states (or 4d-,5d-states) of the metal and 2p-states of the non-metal leads to the formation of covalent bonds in the compound, improving their hardness. This is exactly what the authors of Ref. [17] showed on the basis of theoretical calculations of the hardness of deformed TiC and TiN crystals.

Results obtained by the authors of Ref. [18] are definitely quite interesting since they predicted the mechanical properties and electronic structure of TiC and TiN compounds with different degrees of their alloying with vanadium from the first principles calculations. They have shown that $Ti_{1-x}V_xN$ solid solution has lower formation energy than $Ti_{1-x}V_xC$, which indicates its higher chemical stability (Table 2). The highest hardness among these solid solutions is shown by the $Ti_{0.25}V_{0.75}C$ phase (29.3 GPa). Simulation of the uniaxial tension of $Ti_{1-x}V_xC$ and $Ti_{1-x}V_xN$ along the [111] direction shows that the tensile strength of $Ti_{1-x}V_xN$ is stronger than that of $Ti_{1-x}V_xC$, and it increases with vanadium content increasing. Specific data on the mechanical characteristics of the hypothetical $Ti_{1-x}V_xC$ and $Ti_{1-x}V_xN$ solid solutions obtained by the authors of Ref. [18] are listed in Table 2.

Table 2 – Formation energy F (kJ·mole^{-1}), Hardness H (GPa), Young's modulus E (GPa), bulk modulus B (GPa), shear modulus G (GPa), and Poisson's ratio η для $Ti_{1-x}V_xC$ та $Ti_{1-x}V_xN$ [18]

Phase	Formation energy, F	Mechanical characteristics					
		H	E	B	G	B/G	η
TiC alloyed by V							
TiC	– 81.60	21	404.88	251.02	164.43	1.53	0.23
$Ti_{0.75}V_{0.25}C$	– 74.13	25	454.88	263.75	187.57	1.41	0.21
$Ti_{0.5}V_{0.5}C$	– 66.47	25	476.59	276.13	196.56	1.40	0.22
$Ti_{0.25}V_{0.75}C$	– 59.77	29	510.29	286.37	212.09	1.35	0.20
VC	– 53.29	23	477.90	296.75	194.02	1.53	0.23
VN alloyed by Ti							
VN	– 135.44	18	456.05	323.83	184.45	1.76	0.26
$V_{0.75}Ti_{0.25}N$	– 150.23	15	400.27	305.46	156.16	1.96	0.28
$V_{0.5}Ti_{0.5}N$	– 165.70	15	388.21	288.00	152.20	1.89	0.28
$V_{0.25}Ti_{0.75}N$	– 182.20	23	457.66	284.74	185.70	1.53	0.23
TiN	– 198.67	26	473.03	278.36	194.88	1.43	0.22

Thus, the electronic density calculated by models built on the basis of experimental studies can provide an explanation for such physical characteristics of the phases as hardness, Young's modulus, etc. [15-19]. Therefore, based on the data in Table 2, for the equimolar TiC-VN blend processed for 9 h in a ball mill, the following magnitudes of the main mechanical characteristics for the compacted final products could be expected considering the principle of additivity of the contributions of individual phases: $H \approx 20$ GPa, $E \approx 427$ GPa and $B \approx 284$ GPa.

4. CONCLUSION

Based on the experimental study of the kinetics of phase transformations that occur during mechanical alloying of the equimolar TiC-VN blemd, it is shown that the crystal structures of TiC and VN phases undergo certain transformations at impact stress. At the same time, those crystal lattices actively accumulate point defects in the form of structural vacancies, forming the clusters in the reaction zone of the mill at the first stage of processing since metal atoms are knocked out of their lattices. At the second stage, the vacancies in TiC and VN structures are gradually occupied by vanadium and titanium atoms, respectively, with the formation of mutual solid solutions.

Based on the quantitative assessment of the maximum fraction of vacancies in the MA TiC and VN crystal lattices and the composition of the solid solutions formed, three structural models, describing the kinetics of structural transformations at mechanical alloying were proposed. Namely, Ti_4C_4 and V_4N_4 phases (TiC and VN) in the initial state; Ti_3C_4 and V_3N_4 phases. during the accumulation of vacancies; Ti_3VC_4 and V_3TiN_4 solid solutions. For each of the model proposed the calculations of density of electronic states spectrum were performed and the parameters of electronic structure of the phases were determined. The calculations have revealed:

1. Total DOS for MA TiC and VN phases mainly consists of hybridized 3d states of metals (Ti or V) and 2p states of nonmetals (C or N) in the vicinity of the Fermi level, which leads to the formation of covalent bonds in the compounds.

2. DOS spectrum of TiC and VN phases, which contain a large number of structural vacancies, are significantly blurred (both the valence and conductivity bands) and contain additional peaks near the Fermi level. These features indicate a high degree of structural instability, which creates preconditions for further formation of solid solutions.

3. DOS profiles of (Ti, V)C and (V, Ti)N solid solutions formed are similar to the DOS of initial compounds.

4. Comprehensive analysis of the results of calculations and the data of other authors has revealed that alloying TiC with V generally improves its mechanical characteristics. At the same time, the highest hardness is inherent in polycarbide $Ti_{0.25}V_{0.75}C$.

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Особливості електронної структури карбіду TiC та нітриду VN, підданих механохімічному впливу в складі еквімолярної суміші TiC-VN

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Вивчено електронну структуру карбіду TiC та нітриду VN, які під дією ударного навантаження поетапно зазнають структурні перетворення в процесі механохімічної обробки еквімолярної суміші TiC-VN в високоенергетичному планетарному млині. Базуючись на експериментальних результатах дослідження кінетики фазових перетворень, запропоновано та розглянуто три основні структурні моделі, що характеризують перебіг цього процесу, а саме, фази Ti_4C_4 та V_4N_4 (TiC та VN) у вихідному стані; фази Ti_3C_4 та V_3N_4, які існують при накопиченні максимальної долі структурних вакансій на другому етапі механохімічної обробки; тверді розчини Ti_3VC_4 та V_3TiN_4, сформовані у фінальних продуктах синтезу. За результатами теоретичних розрахунків, виконаних методом лінеаризованих мафін-тін орбіталей у наближенні плоских хвиль (LMTO PLW), для кожної із запропонованих моделей проведено розрахунки профілів густини електронних станів DOS та визначені основні параметри електронної структури фаз. Показано, що поблизу рівня Фермі загальна DOS для TiC та VN в основному складається з гібридизованих 3d станів металів (Ti або V) та 2p станів неметалів (C або N), яка призводить до формування в сполуках ковалентних зв'язків. Профілі густини електронних станів DOS фаз TiC та VN, що містять велику кількість структурних вакансій, істотне розмити (як валентної зони, так і зони провідності) та містять додаткові піки поблизу рівня Фермі, що в сукупності свідчить про високий ступінь структурної нестабільності, яка створює передмови для подальшого формування твердих розчинів. Профілі густини електронних станів DOS сформованих твердих розчинів (Ti, V)C та (V, Ti)N із деякими нюансами подібні до DOS вихідних сполук, що їх породжують. Спираючись на результати проведених теоретичних розрахунків параметрів електронної структури та на дані інших авторів, показано, що легування ванадієм карбіду TiC в цілому покращує його механічні характеристики, а ступінь впливу механохімічної обробки на нітрид ванадію VN в складі суміші TiC-VN дещо вища за вплив на карбід титану.

Ключові слова: Механохімічний синтез, Карбід, Нітрид, Кристалічна структура, Електронна структура.