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MAX phase Ti_2AlN synthesis by reactive sintering in vacuum

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Abstract: The synthesis of MAX phase Ti_2AlN from several mixtures of Ti, Al, TiN, and AlN powders by vacuum sintering of green samples in the form of dense compacts, bulk powder in silica tubes, and plain layer in a closed rectangular molybdenum boat was studied upon variation in charge composition and sintering temperature Ts. The sintering of 2 : 1 Ti—AlN mixture was carried out at 1100, 1200, 1300, 1400, and 1500 °C with exposure time of 60 min. The largest MAX phase content (94 wt.%) was reached at T_s = 1400 °C. The sintering of 1 : 1 TiAl : TiN composition at the same temperature gave 93 wt.% Ti_2AlN. The best result (single-phase Ti_2AlN in a 100-% yield) was achieved upon the sintering of 1 : 1 : 1 Ti—Al—TiN composition at T_s = 1400 °C. The scalability of our process was checked by the fabrication of a large (0.5 kg) and uniform cake of single-phase Ti_2AlN. In experiments we used green samples with shielded lateral surface (bulk powder in silica tubes, plain layer in a closed molybdenum boat) and without shield (dense compacts). It has been shown that shielding of Ti—Al—TiN samples restricts the escape of Al vapor from a sintered mixture, thus providing more favorable conditions for the synthesis of single-phase Ti_2AlN. Our process can be readily recommended for practical implementation.

Keywords: MAX phase, sintering, phase transitions, *X*-ray diffraction.

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Синтез MAX-фазы Ti_2AlN реакционным спеканием в вакууме

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Аннотация: Проведены исследования процесса синтеза MAX-фазы Ti_2AlN спеканием в вакууме различных смесей порошков в зависимости от фазового состава исходных реагентов и режимов их термической обработки в вакуумной электропечи. На примере смеси порошков титана и нитрида алюминия в мольном соотношении Ti : AlN = 2 : 1 (состав *1*) прослежена последовательность изменения фазового состава смеси при увеличении температуры изотермической выдержки длительностью 60 мин при t = 1100÷1500 °C с шагом 100 °C и определено значение температуры 1400 °C, при которой в

продуктах спекания достигается максимальное значение содержания MAX-фазы Ti_2AlN — 94 мас.%. При этой температуре изотермической выдержки для исходной смеси TiAl : TiN = 1 : 1 (состав *2*) содержание MAX-фазы составило 93 мас.%. Наилучший результат по синтезу MAX-фазы (100 мас.% Ti_2AlN) был получен для смеси Ti : Al : TiN = 1 : 1 : 1 (состав *3*). На примере смеси данного состава массой 500 г при определенном режиме термовакуумной обработки экспериментально показана принципиальная возможность масштабирования процесса получения однофазного продукта состава Ti_2AlN спеканием в вакууме. Эксперименты проводились с двумя типами образцов: с закрытой и открытой боковой поверхностью. К образцам с закрытой боковой поверхностью относились образцы в кварцевых трубках, заполненных исходной смесью порошков с насыпной плотностью, и образец массой 500 г, помещенный в молибденовый тигель с крышкой. Образцы с открытой боковой поверхностью — это цилиндрические таблетки, спрессованные из исходной порошковой смеси. Было показано, что закрытие боковой поверхности образца из смеси Ti : Al : TiN (состав *3*) блокирует выход паров алюминия из порового пространства образца при нагреве, благодаря чему образуется только Ti_2AlN.

Ключевые слова: MAX-фаза, спекание, фазовые превращения, рентгенофазовый анализ.

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Introduction

The Ti_2AlN compound belongs to the family of MAX phases described by the general formula $M_{n+1}AX_n$, where M is a transition metal, A is an element of IIIA and IVA groups , X is carbon or nitrogen, $n = 1 \div 3$ [1]. Recently, many researchers have investigated MAX-phase based materials, as these materials simultaneously have a unique combination of metals and ceramic properties and a layered structure. Ti_2AlN-based materials also show an exceptional combination of properties: high elastic modulus, high thermal and electrical conductivity, low density, easy machinability and excellent thermal shock resistance [2—4]. This predetermines the use of Ti_2AlN-based materials as reinforcing agent in alloys, transition layers in semiconductors, etc. [5—7].

The Ti_2AlN compound was discovered in 1963 by Jeitschko [8]. Since then, researchers have made many attempts to obtain this compound by various methods.

In 2000 Barsoum et al. [4, 5] obtained Ti_2AlN by Ti and AlN mixture hot isostatic pressing (process parameters were the following: pressure 40 MPa, temperature 1400 °C and soaking for 48 h). However, they failed to achieve the purity of the final product, the content of other phases was 10—15 vol.%.

The authors [9, 10] synthesized Ti_2AlN from the Ti and AlN mixture of powders (in the molar ratio of 2 : 1) under isothermal annealing in argon atmosphere for 2 h at 1300 ° C and pressure of 0.3 MPa. At the same time the TiN impurity fraction was not more than 1 wt.%. It was also found during the researches that the preparatory mechanical activation of the powder causes an increase in the content of the TiN secondary phase and that the synthesis in vacuum does not lead to the formation of a single-phase product.

The authors [11] obtained a Ti_2AlN single-phase material by hot pressing a mixture consisting of Ti, TiN and Al powders in an argon atmosphere at 25 MPa and 1400 °C. The resulting material characteristics were as close as possible to the theoretical evidence — this led to the conclusion that hot pressing is a promising way to obtain pure Ti_2AlN due to the short duration of the process, the low applied load and the final product high purity.

In the research [12] Ti_2AlN was obtained by titanium powders (2 mol.) and aluminum nitride (1 mol.) spark plasma sintering with soaking for 5 min. Provided that at 1400 °C Ti_2AlN MAX-phase with an admixture of titanium nitride was obtained in the final product, and

Ti_2AlN was obtained practically pure after increasing the sintering temperature to 1450 °C — there were only traces of titanium nitride. The same method, but already at 1200 °C [13] let obtain the material consisting of one MAX-phase.

The authors [14] describe the Ti_2AlN production by 30 min microwave sintering a mixture of titanium, aluminum and titanium nitride powders (in an approximate molar ratio of 1 : 1.03 : 1) in an argon atmosphere at 1200 °C. A further increase in the sintering temperature to 1350 °C resulted in the MAX-phase destruction and the appearance of TiN (4 wt.%). This method is promising due to the lowest temperature for obtaining the pure MAX phase and the short process time.

In the research [15] the Ti_2AlN phase was obtained by thermal explosion of Ti, Al and TiN mixture of powders at 700 °C and $\tau = 2$ min. However, the content of the secondary TiN phase was 4 wt.%. The Ti_2AlN powder in the research [16] was synthesized by microwave sintering from a TiH_2, Al and TiN mixture of powders with a molar ratio of 1 : 1.15 : 1 at 1250 °C. The sample with the highest MAX phase content consisted of 96.68 wt.% Ti_2AlN and 3.32 wt.% Ti_4AlN_3.

Electrospark sintering in vacuum at 1200 °C [17] produced compressed pellets 15 mm in diameter with a Ti_2AlN content of about 98 wt.% from a initial Ti and AlN powders mixture. Ti_2AlN with TiAl admixture was obtained by two-stage annealing in an argon atmosphere [18] with holding temperatures of 600 °C ($\tau = 1$ h) and 1100 °C ($\tau = 3$ h) from mechanically activated Ti, Al and AlN powders mixed in a molar ratio of 2 : 0.8 : 1 and pressed into tablets of 13 mm in diameter. In research [19] Ti_2AlN (pellets 20 mm in diameter) was obtained by electrospark sintering from a Ti, Al and TiN powders mixture with a molar ratio of 1 : 1.02 : 1.

The analysis of literature data shows that virtually all of the above mentioned methods require expensive equipment, while allowing to obtain only a small amount of containing pure MAX-phase material and with impurity phases often present in the final products.

In this work the Ti_2AlN MAX-phase synthesis process by vacuum sintering of different powders mixtures depending on the initial chemical agents phase composition and their thermal treatment modes in a vacuum electric furnace was studied. However, the ultimate goal was to determine the optimum conditions for obtaining a Ti_2AlN single-phase product by such a relatively simple method, as well as the possibility of obtaining product significant batches weighing up to 0.5 kg.

Research preliminary results were previously published in concise form [20] — the phase composition of the products for quartz tubes samples filled with the initial powders mixture with bulk density was presented.

The present article describes more detailed experimental procedure giving the exact parameters of the samples and comparing the samples phase composition in quartz tubes and samples with open side surface in the cylindrical tablets form pressed from the initial powder mixture. The reason for the compared samples phase composition difference has been revealed and it has been established why under the same composition and the same heating conditions in one case (samples with closed side surface) the Ti_2AlN MAX-phase concentration is 100 %, and in the other case (pressed samples with open side surface) the MAX-phase content does not reach 100 %. A detailed analysis of the phase formation sequence during samples with open and buried lateral surface heating, which has not been investigated before, was out.

Experimental procedures

Initial chemical agents mixtures were prepared from AlN [21] and TiN [22] powders obtained by the SHS method at ISMAN, as well as Al (ASD-1 grade), Ti (PTS-1), and TiAl (PT65U35) powders.

The dispersibility of the initial components is presented in the table.

Three mixtures were prepared to obtain the Ti_2AlN single-phase product Ti : AlN = 2 : 1 (composition *1*); TiAl : TiN = 1 : 1 (composition *2*) and Ti : Al : TiN = = 1 : 1 (composition *3*). Initial powders were mixed in a planetary mill with a charge-to-ball mass ratio of 2 : 1 for 30 min. Tablets of 15 mm in diameter were pressed from compositions *1*, *2* and *3* (mass of 15 g) with the

Dispersity of initial powders

Дисперсность исходных порошков

Chemical agent	Grade	Dispersity d_{50}, μm
Ti	PTS-1	60.5
Al	ASD-1	16.3
AlN	SHS ISMAN	2.05
TiN	SHS ISMAN	29.7
TiAl	PT65U35	23.3

same pressing force of 354 MPa, when the final height of tablets was 32.5; 29.2 and 28.7 mm (with porosity of 36, 34 and 32 %, respectively).

In order to exclude the tablet pressing stage, experiments with quartz tubes samples were carried out. To compare with the pressed tablets results, mixtures *2* and *3* with the same mass of 15 g were poured into quartz tubes with the same inner diameter of 15 mm as of the pressed tablets, consequently the samples bulk porosity was 59—61 %. According to the quartz tubes samples experiments results and in order to check the process scaling possibility, composition *3* samples of 500 g in weight and bulk porosity of 57 % were sintered in a rectangular molybdenum closed container 88 × 88 × 70 mm in size with a fill height of 35 mm.

Sintering was carried out in a vacuum electric resistance furnace SNVE-16/16 (OOO «NPPMosZETO», Moscow) at the following holding temperatures, °C: 1100, 1200, 1300, 1400 и 1500. In all experiments the samples soak time was 60 min at a minimum pressure of $7.73 \cdot 10^{-4}$ Pa. Since the sintering pressed tablets results at different holding temperatures determined the optimum temperature of 1400 °C, at which the Ti_2AlN MAX-phase maximum content in the final product was observed (see below), successive experiments with quartz tubes samples in a molybdenum container were carried out at this holding temperature.

The sintering products phase composition was studied by *X*-ray diffraction analysis on diffractometer DRON-3M (NPP «Burevestnik», St. Petersburg). Phase identification on the diffractograms was carried out using the following standards: Ti (CAS number 5-672), Al (CAS number 4-787), TiN (CAS number 38-1420), AlN (CAS number 25-1133), TiAl (CAS number 5-678), Ti_3Al (CAS number 14-451), Ti_3AlN (PDF number 01-071-4029), Ti_2AlN (PDF number 00-055-0434). The quantitative phase content was determined by the corundum number method. The sintered samples fracture microstructure and the local elemental composition were studied on an ultra-high field emission scanning electron microscope «Zeiss Ultra Plus» based on «Ultra 55» (Carl Zeiss, Germany) with the *X*-ray microanalysis attachment «INCA Energy 350 XT» (Oxford Instruments, UK).

Results of experiments

Fig. 1 shows mixture *1* (Ti : AlN) pressed samples diffractograms, which show that at temperatures from 1100 to 1200 °C the product is multiphase and con-

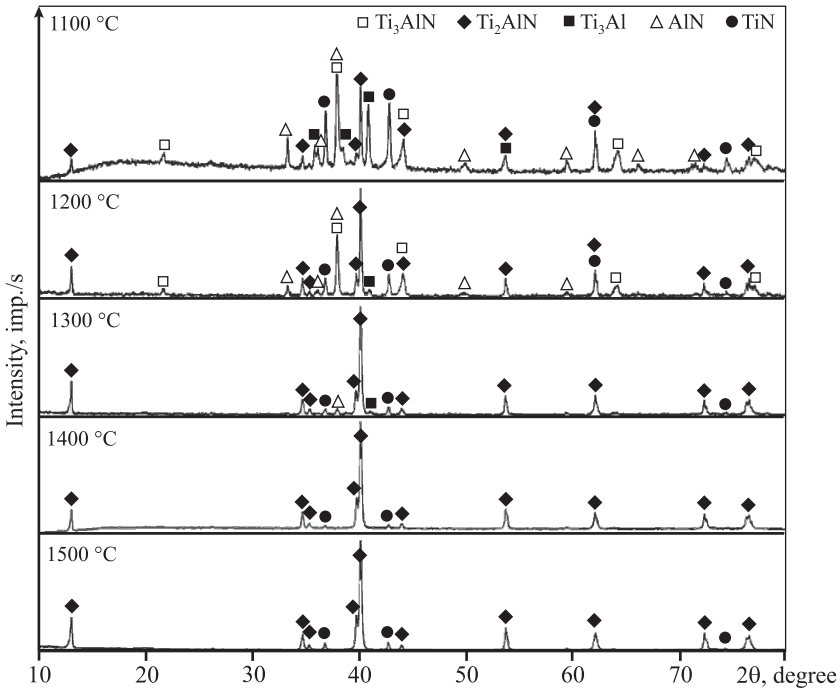

Fig. 1. Mixture *1* pressed samples diffractograms after sintering at different temperatures

Рис. 1. Дифрактограммы пресованных образцов смеси *1* после спекания при различных температурах

tains the following phases: Ti_2AlN, TiN, AlN, Ti_3AlN, Ti_3AlN.

With increasing temperature up to 1200 °C the amount of Ti_2AlN MAX phase increases from 20 to 52 wt.% (see Fig. 2). At 1300 °C the product contains the following phases, wt.%: Ti_2AlN — 83, TiN — 12, AlN — 5. Further temperature rise to 1400 °C leads to the two-phase product formation consisting of Ti_2AlN (94 wt.%) and TiN (6 wt.%). After reaching 1500 °C the product also remains biphase, but there is a slight decrease of the Ti_2AlN MAX-phase to 91 wt.% and an increase of the titanium nitride proportion to 9 wt.%. Reducing the Ti_2AlN amount corresponds with the research data [23], which shows that in a dynamic vacuum at 1550 °C the aluminum evaporation from the MAX-phase with the titanium non-stoichiometric nitride formation is observed: $Ti_2AlN_{(s)} \rightarrow 2TiN_{0.5} + Al_{(g)}$. High-temperature aluminum evaporation in MAX-phase obtaining by sintering was also noted in the research [24].

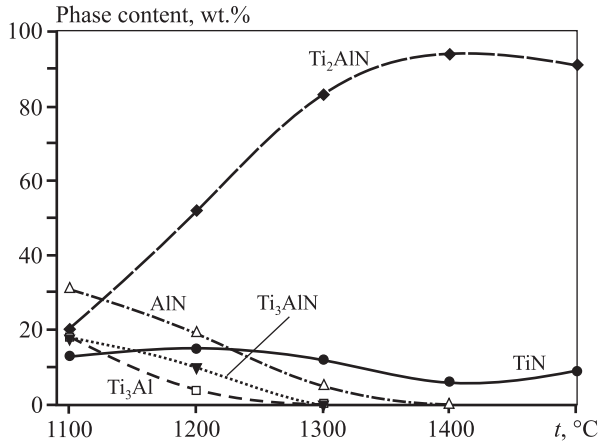

Fig. 2. Phases contents at composition *1* (2Ti + AlN) pressed samples various sintering temperatures

Рис. 2. Содержание фаз при различных температурах спекания прессованных образцов состава *1* (2Ti + AlN)

By this means, the composition *1* (2Ti + AlN) maximum Ti_2AlN MAX-phase content of 94 wt.% was obtained at 1400 °C, which corresponds with Ti_2AlN obtaining results by spark plasma sintering [12], for that reason sintering of samples from mixtures *2* and *3* was performed at this very temperature.

After pressed sample from composition *2* mixture (TiAl : TiN = 1 : 1) sintering at 1400 °C a multiphase product (Fig. 3, *a*) with the following phase content (wt.%) was obtained: Ti_2AlN — 93; TiN — 4; Ti_3AlN — 2; Ti_3Al — 1.

After pressed sample from composition *3* mixture (Ti : Al : TiN = 1 : 1 : 1) sintering the product phase composition was as follows, wt.%: Ti_2AlN — 89, TiN — 9, %; Ti_3Al — 2 (Fig. 4, *a*).

To prevent the reactive volume aluminum vapor escape through the pressed samples surface during heating process and vacuum blowing experiments with quartz tubes samples were carried out. After composi-

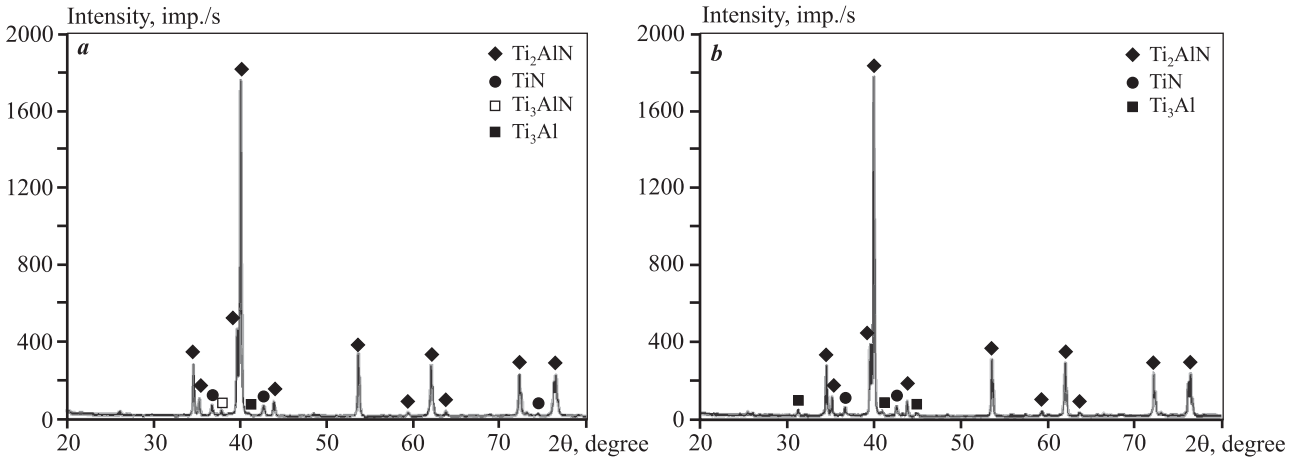

Fig. 3. Product diffractogram after composition *2* (TiAl + TiN) pressed sample (***a***) and the quartz tube sample (***b***) reactive sintering at 1400 ° C in a vacuum

Рис. 3. Дифрактограмма продукта после реакционного спекания прессованного образца (***a***) и образца в кварцевой трубке (***b***) состава *2* (TiAl + TiN) при t = 1400 °C в вакууме

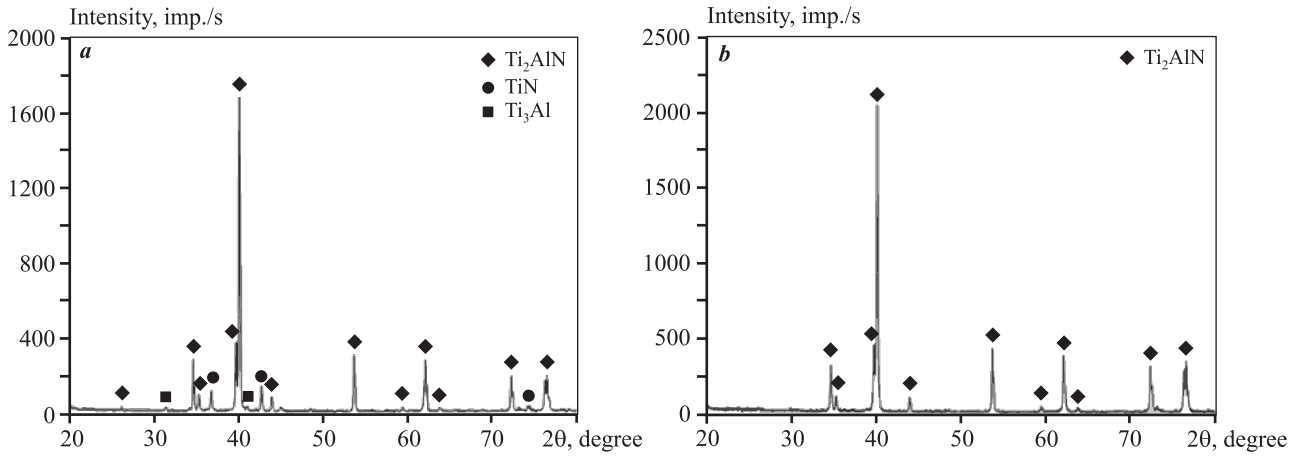

Fig. 4. Product diffractogram after composition *3* (Ti + Al + TiN) pressed sample (***a***) and a quartz tube sample (***b***) reactive sintering at 1400 °C in vacuum

Рис. 4. Дифрактограмма продукта после реакционного спекания прессованного образца (***a***) и образца в кварцевой трубке (***b***) состава *3* (Ti + Al + TiN) при *t* = 1400 °C в вакууме

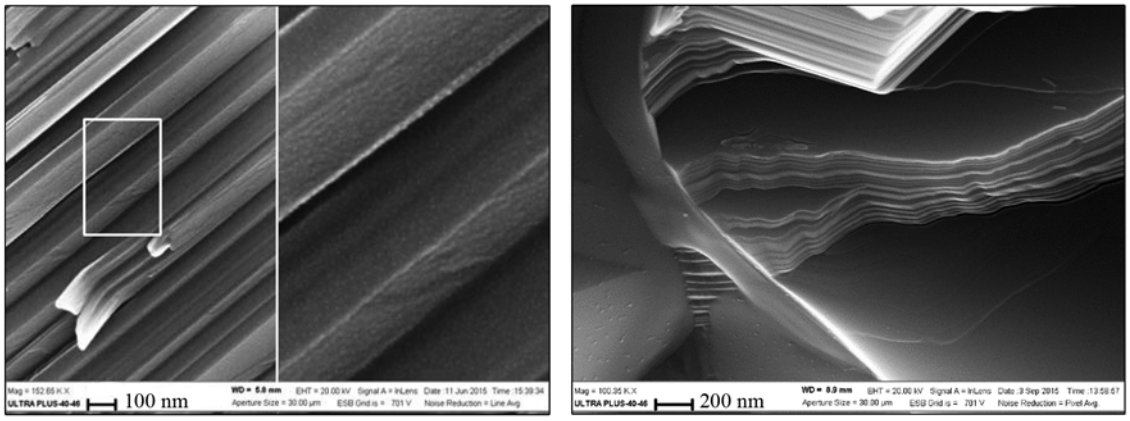

Fig. 5. Composition *3* sample photomicrograms at different scales

Рис. 5. Микрофотографии образца состава *3* с различным масштабом

tion *2* (TiAl : TiN = 1 : 1) sample sintering at 1400 °C a multiphase product (Fig. 3, *b*) with the following phase content (wt.%) was obtained: Ti_2AlN — 94, TiN — 4, Ti_3Al — 2. After the composition *3* (Ti : Al : TiN = = 1 : 1 : 1) sample sintering the monophase product Ti_2AlN — 100 % was obtained as evidenced by the diffractogram in Fig. 4, *b*. The photomicrograms presented in Fig. 5 show that the composition *3* sample consists of so-called nanolaminates with the layers thickness of a few tens of nm.

Since the Ti_2AlN monophase product was obtained from mixture *3*, it was interesting to make a point of the scale factor influence on this composition. The composition *3* initial charge 500 g in weight was poured into a molybdenum container 88 × 88 × 70 mm in size in an even layer 35 mm in height. The container was covered with a lid and placed in a vacuum furnace. A view of the after-sintering mixture is shown in Fig. 6. The after-sintering composition was homogeneous over the entire cross section. The resulting product diffractogram was completely identical to the diffractogram in Fig. 4, *b* — 100 % Ti_2AlN MAX-phase without any other phases.

Fig. 7, *a* shows an after-sintering composition *3* fracture microphotograph, which shows the MAX-phases typical layered structure. Local elemental analysis data from approximately of the 5 mm^2 after-sintering product fracture area (marked by lines

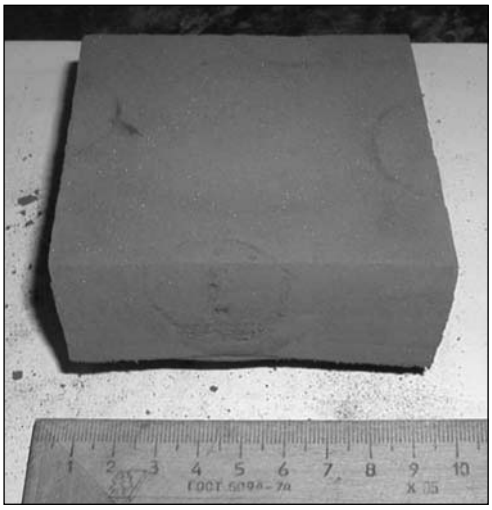

Fig. 6. 500 g in weight after-sintering composition *3* photograph

Рис. 6. Фотография полученного спека состава *3* массой 500 г

in Fig. 7, *b*) showed the following element content (at.%): N — 23.56, Al — 25.68, Ti — 50.76, which corresponds well with the Ti_2AlN MAX-phase elemental composition.

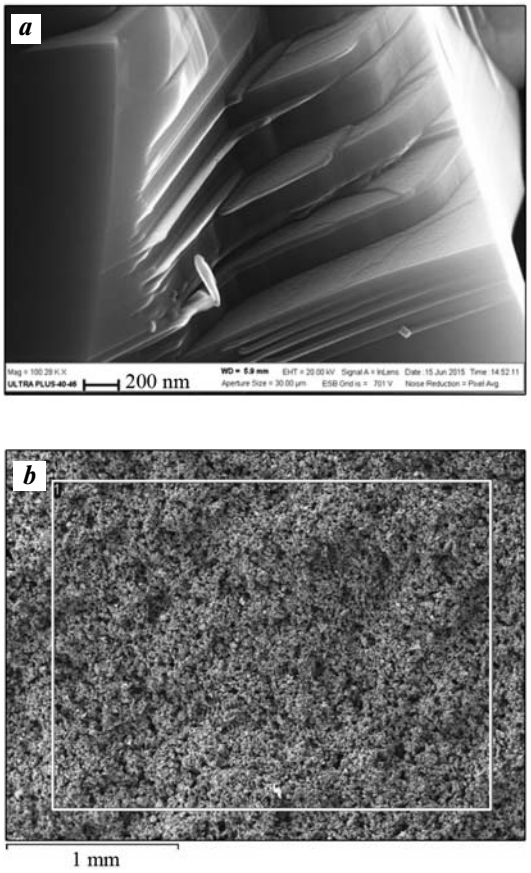

Fig. 7. After-sintering composition *3* sample fracture local microanalysis and microphotographs at different scales

Spectrum, at.%: N — 23.56; Al — 25.68; Ti — 50.76

Рис. 7. Микрофотографии излома образца полученного спека состава *3* с различным масштабом

Спектр выделенной области, ат.%: N — 23,56; Al — 25,68; Ti — 50,76

Results discussion

Basing on Ti—N and Al—N experimental data and phase diagrams the following sequence of composition *1* phase formation while heating in a dynamic vacuum can be suggested:

1. Extrapolating the aluminum nitride dissociation data [25] to the low pressure area, we obtain that at a pressure of $7.73 \cdot 10^{-4}$ Pa the dissociation temperature will be 913 °C. Therefore, it comes logical to assume that at the process initial stage dissociation occurs on the aluminum nitride particles surface:

$$AlN \rightarrow Al_{(g)} + N_{2(g)}.$$

2. The AlN dissociation products stream diffuses in the sample pore space to the titanium particles surface. Since both aluminum and nitrogen have considerable titanium dissolution and are α-stabilizers, solid solution $Ti(Al_x,N_y)$ is formed. At 1100÷1200 °C it will be α-$Ti(Al_x,N_y)$ solution, and when the temperature rises to 1300—1500 °C — a β-$Ti(Al_x,N_y)$ solution.

3. From the α-$Ti(Al_x,N_y)$ solid solution, so far as it saturates with aluminum and nitrogen, and at < 1200 °C the TiN_x, Ti_3Al phases, the Ti_3AlN triple nitride and the Ti_2AlN MAX-phase crystallize.

4. From the β-$Ti(Al_x,N_y)$ solid solution at > 1300 °C the TiN_x phases and the Ti_2AlN MAX-phase crystallize.

5. At 1400 °C the Ti_2AlN formation process completes and the MAX-phase sample content reaches its maximum value.

6. At further temperature increase up to 1500 °C and under dynamic vacuum conditions a MAX-phase partial decomposition occurs assisted by the titanium nitride phase and aluminum vapor formation which leave the sample pore space into the furnace volume.

Ti_2AlN MAX-phase content in the compositions *1* and *2* pressed samples sintering products practically do not differ (94 and 93 wt.% respectively), and in the composition *3* is noticeably lower (89 wt.%). It

can be assumed that this difference was noted due to the fact that in the mixtures *1* and *2* initial compositions aluminum is in a bound state in the form of compounds (AlN and TiAl respectively), and in mixture *3* — in the free state. Given the aluminum low melting temperature (660 °C), it goes under that logic that for mixture *3* aluminum vapor appears earlier than for mixtures *1* and *2* as the temperature rises in the furnace and they leave the samples pore space under open-side vacuuming through the side surface during a longer period of time. The lower Ti_2AlN MAX-phase content in the composition *3* pressed samples sintering products is explained by the formed aluminum deficit.

Closing the composition *2* samples side surface with the quartz tube walls had a relatively weak effect in terms of obtaining the Ti_2AlN MAX-phase, because its content in both samples (93 % in the pressed one and 94 % in a quartz tube) is almost the same. The products total phase composition changed insignificantly either. Apparently, when the reaction takes place at a holding temperature close to the TiAl melting temperature (~1450 °C), the aluminum mass transfer in mixture *2* takes place predominantly through the liquid phase. In the absence of aluminum vapor, closing the sample side surface does not lead to a significant change in the phase composition compared to the open side surface sample.

Closing the composition *3* sample side surface had a significant effect on the Ti_2AlN formation. Free aluminum present in the initial mixture, evaporating when heated, does not leave the reaction zone due to the closed side surface and reacts completely with the Ti_2AlN formation.

Conclusion

Summing up what has been stated, as a result of the sintering process research in a vacuum furnace the Ti_2AlN MAX-phase content dependence has been determined in the final product on the holding temperature and the composition of the initial charge. According to *X*-ray diffraction and energy-dispersive analyses a single-phase product with 100 % Ti_2AlN MAX-phase content was obtained for the composition Ti : Al : TiN = 1 : 1 : 1 at 1400 °C. It was shown that closing the Ti : Al : TiN mixture side surface blocked the aluminum vapor escape from the sample pore space resulting in the formation of Ti_2AlN only. The example of a 500 g filling sintering and obtaining a Ti_2AlN single-phase product the fundamental possibility of sintering process scaling in a dynamic vacuum and the prospects of this method of production for industrial development have been demonstrated.

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