FORMATION OF THE MAX PHASE Ti_2AlN BY HIGH-TEMPERATURE HEATING IN VACUUM

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The MAX phase (Ti_2AlN) was synthesized by reaction sintering of Ti, TiN, Al precursors in vacuum in quartz ampoules. The effect of temperature on the formation of the Ti_2AlN phase was estimated. The MAX phase with a minimum amount of impurities was obtained at 1300°C. The elemental and phase composition and structure of the synthesized samples were studied. According to the X-ray diffraction analysis, the obtained samples, along with the main phase Ti_2AlN, contain impurity phases TiN, TiAl, Ti_3Al. The results of electron microscopy show heterogeneity of the elemental composition of precursor particles, which differ in size and morphology. In well-formed crystallites of the MAX phase with a layered structure, the Ti/Al/N element ratio is close to the stoichiometric composition of Ti_2AlN. The quality of the layered structure of Ti_2AlN and the simplicity of the synthesis technique make the material promising for some applications, in particular, for obtaining 2D MXene (Ti_2N) particles.

KEY WORDS: *MAX phase Ti_2AlN, reactionary sintering, vacuum annealing, titanium nitride*

1. INTRODUCTION

Compounds of ternary carbides and nitrides, called MAX phase, and described by the general formula $M_{n+1}AX_n$, where M is a transition metal, A is an element from IIIA and IVA groups (Al, Si), X is carbon or nitrogen, n = 1, 2, 3, have unique properties due to the combination of metallic and ceramic properties (Toth, 1971; Barsoum, 2013). Numerous MAX phases can be classified depending on the value of n in their formula: 211, 312, 413. Other types of phases (n > 3) are less known. For titanium aluminum nitride, the following phases are known: (211) Ti_2AlN and (413) Ti_4AlN_3. MAX phases are promising for various applications and have been intensively studied in recent years (Barsoum, 2000; Barsoum et al., 2000a,b; Magnuson et al., 2007; Mauchamp et al., 2010; Wang et al., 2017; Gonzalez-Julian, 2021; Ovodok et al., 2023).

Interest in MAX phases is also due to the fact that they can be transformed into thin two-dimensional (2D) MXene particles by simple procedures (Naguib et al., 2014; Anasori et al., 2017). 2D MXene particles with chemical and structural diversity are of even greater interest to researchers due to their unique photonic, mechanical, electrical, magnetic, and catalytic proper-

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ties, which distinguish them from other 2D materials (Naguib et al., 2014). MXene Ti_2N have been synthesized from Ti_2AlN and their properties and potential applications, including anticancer activity, have been studied (Eklund et al., 2017; Soundiraraju et al., 2017; Sokol et al., 2019; Szuplewska et al., 2019; Shao et al., 2020; Akhtar et al., 2022). However, to date, MXene based on titanium carbide (Ti_3C_2) have been widely studied, MXene Ti_2N have been less studied, since there are some difficulties in their synthesis (Sokol et al., 2019).

Synthesis of high-purity homogeneous Ti_2AlN samples for research purposes is a very difficult task. High controlled temperature, high purity gas atmosphere, or high vacuum are required for synthesis. Therefore, since the first synthesis of Ti_2AlN by hot isostatic pressing (Barsoum, 2000a), many studies have been conducted to develop different synthesis methods, to optimize parameters to obtain a single-phase product without impurities, and to study the reaction mechanism under various conditions.

Due to the narrow stability range of Ti_2AlN at high temperature, as well as the stage-by-stage nature of the Ti_2AlN phase formation process, various impurity phases, such as TiAl and TiN, are usually formed during synthesis. Therefore, the efforts of researchers are aimed at studying the reactions occurring in different temperature ranges in reagent mixtures of different compositions in order to optimize the parameters for the synthesis of a single-phase Ti_2AlN product. The review by Haemers et al. (2020) analyzes all known methods for the synthesis of carbides and nitrides. The methods for the synthesis of carbides of different compositions are more widely implemented, significantly fewer studies are devoted to the synthesis of nitrides: Ti_2AlN and Ti_4AlN_3. The synthesis of Ti_2AlN is implemented using the following methods: combustion synthesis (Yeh et al., 2010; Tian et al., 2013; Aydinyan, 2023), thermal explosion (Liu et al. 2015, 2017), hot-pressing (Lin et al., 2007; Ming et al., 2008; Chlubny et al., 2017), microwave sintering (Liu et al., 2015; Chen et al., 2020), reaction sintering (Luginina et al., 2016; Kovalev et al., 2017; Kondakov et al., 2019; Ivanovskaya et al., 2020; Linde et al., 2022), spark plasma sintering (Yan et al., 2008; Liu et al., 2011; Christopher et al., 2021). The review by Haemers et al. (2020) contains an analysis of individual works, specifies the synthesis parameters for each method and the results obtained, and notes the synthesis parameters that ensure obtaining a product with a minimum amount of impurities. The sintering temperature range for Ti:AlN or Ti:Al:TiN mixtures is 1200–1450°C. In addition to the review by Haemers et al. (2020), one can note reviews and articles devoted to individual methods of Ti_2AlN synthesis. An analysis of combustion synthesis of MAX Phases is presented in the review by Aydinyan (2023). In the reviews by Gonzalez (2021) and Ovodok et al. (2023), along with carbides, the synthesis methods and properties of Ti_2AlN are also considered. Achievements in the field of microwave sintering Ti_2AlN synthesis are analyzed by Chen et al. (2020).

The latest publications also contain information on other methods of Ti_2AlN synthesis or modifications of known methods: of Ti_2AlN prepared by FAST/SPS field-assisted sintering technology (Li et al., 2020), formation of Ti_2AlN_x MAX phase by "hydride cycle" and SHS methods (Aleksanyan et al., 2022), molten salt shielded synthesis of oxidation prone materials in air synthesis using molten salts (Dash et al., 2019; Roy et al., 2020). Impact activation of the Ti_2AlN synthesis reaction was also used earlier (Jordan and Thadhani, 2002).

There are examples of successful synthesis of polycrystalline thin Ti_2AlN films with a predominant orientation (000l) on a polycrystalline Al_2O_3 substrate by applying several double layers of Ti-AlN by the physical vapor deposition (PVD) method and subsequent annealing (Gröner et al., 2018). In this case, during the deposition process using traditional PVD technologies, TiAlN phases are usually formed (Grigoriev and Metel, 2004; Grigoriev et al., 2022a,b, 2023a,b, 2004; Vereschaka et al., 2018, 2023). The impossibility of forming the Ti_2AlN phase is associated with an insufficiently high deposition temperature.

Most of the studies have focused on obtaining high-purity Ti_2AlN materials to study their properties and formation mechanism. It is noted that only some of the implemented methods have the potential for scaling and commercial production of Ti_2AlN (Chen et al., 2022).

Mixtures of reagents in different combinations and ratios are used as initial reagents for obtaining Ti_2AlN: Ti:Al:TiN are used more often, Ti:AlN; TiAl:TiN; TiH2:Al:TiN; TiH2:AlN are used less often. High-temperature synthesis of 1200–1400°C is usually carried out in an argon atmosphere. It has been shown that replacing argon with nitrogen reduces the product yield during synthesis by the spark plasma sintering method (Christopher et al., 2021) (influence of sintering atmosphere and mechanical activation on the synthesis of bulk Ti_2AlN MAX phase obtained by spark plasma sintering). There are several works that compare the results of Ti:AlN synthesis by sintering in argon and vacuum (Kovalev et al., 2017; Linde et al., 2022). It is noted that during reaction sintering of Ti:AlN, the impurity content in the product is lower when heated in argon than in vacuum. The effect of the chemical composition of the initial mixture on the yield of Ti_2AlN during reaction sintering in a vacuum was studied by Linde et al. (2022). It was shown that a single-phase product Ti_2AlN is formed from a mixture of Ti, Al, TiN at 1400°C, 60 min and a pressure of 7.73×10^{-4} Pa. When using initial mixtures of other compositions – Ti:AlN and TiAl:TiN – a single-phase product is not formed, the content of the main phase Ti_2AlN is 94 and 93 wt. %, respectively.

All the described methods of Ti_2AlN synthesis include two stages: first the preparation of the reagent mixture for the sintering process and then the synthesis process itself. The preparation stage usually includes mechanical activation (MA) and the pressing stage. Less often, synthesis is carried out from powders. There are conflicting data on the effect of MA on the synthesis parameters and product yield for different synthesis methods. MA can both favor the synthesis of Ti_2AlN and reduce its yield. However, only two studies noted the negative effect of mechanical activation on the formation of a single-phase product (Kovalev et al., 2017; Linde et al., 2022). In most publications, mechanical activation is a necessary stage of sample preparation in order to obtain Ti_2AlN without impurity phases (Christopher et al., 2021). It is worth noting the work of Akhtar et al. (2022), in which a combination of two MA stages with different loads (270 rpm and 400 rpm) and two heating stages with different speeds and durations (up to 600°C, 1 h and 1100°C, 3 h) made it possible to significantly reduce the synthesis temperature. The resulting bulk Ti_2AlN product with a small admixture of TiN was transformed by chemical etching into 2D Ti_2N layers with subsequent fabrication of quantum dots.

Analysis of the available data shows that many methods are promising for the synthesis of Ti_2AlN. For scaling, as the authors themselves note, the most promising are the methods of reaction sintering (Linde et al., 2022) and microwave sintering (Chen et al., 2020). In Linde et al. (2022), 0.5 kg of Ti_2AlN was synthesized to confirm the possibility of scaling. It should be noted that synthesis by reaction sintering in a vacuum is the least studied.

The purpose of the work is to synthesize the MAX phase of Ti_2AlN by reaction sintering a mixture of Ti, Al, TiN powders in a vacuum and to study its structure and composition.

2. EXPERIMENTAL

2.1 Synthesis of Materials

MAX-phase Ti_2AlN samples were prepared by calcination of precursors (Ti, Al, and TiN powders) under vacuum, in high-temperature muffle furnace LHT4/18 (Nobertherm, Germany). Powders of Ti (99.9% w/w, 44 µm average size of particles), Al (99.5% w/w, 150 µm average size of particles), and TiN (99.5% w/w, 2 µm average size of particles) were mixed in molar ratio of 1.0:1.1:1.0, grinded thoroughly in an agate mortar and tableted by pressing. Then, these tablets were heated in quartz reactors under vacuum ($P \approx 2$ Pa), with the rate of 20°C/min, to their final temperatures (1200, 1300°C), kept during 30 minutes, and then cooled to room temperature, with no forced cooling. Sintered ceramic tablets were grinded, their structure was analyzed.

2.2 Structural Characterization

The samples were characterized by X-ray diffraction (XRD) analysis, scanning (SEM) electron microscopy, energy dispersive X-ray analysis (EDX). The XRD analysis was performed using a Philips X-ray PANalytical Empyrean diffractometer with CuKα radiation (λ = 0.154184 μm). A LEO-1455 VP scanning microscope were used to analyze the morphological features of the samples. The elemental composition of the samples was determined by EDX spectroscopy using a LEO-1455 VP electron microscope.

3. RESULTS AND DISCUSSION

3.1 Structure Description

Precursors (Ti, Al, and TiN powders) preliminarily ground and pressed into tablets were heated in vacuum at high temperatures (1200–1300°C). After heating, the tablets were crushed and the structure and phase composition of the obtained powder samples were studied. Figure 1 shows the X-ray diffraction patterns of the samples obtained by heating the precursors at temperatures of 1200°C, 1300°C, and the X-ray diffraction patterns of Ti, Al, and TiN powders. Table 1 shows

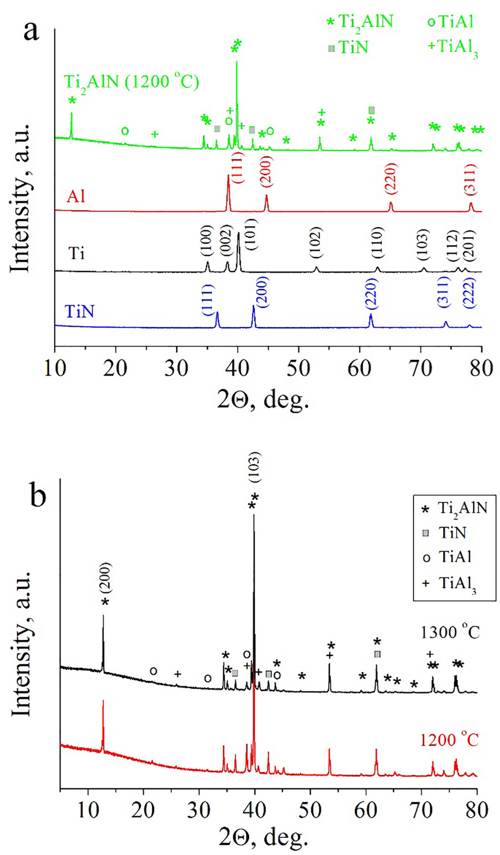

FIG. 1: X-ray diffraction patterns of the initial reagents (Ti, TiN, Al) (a) and samples of the MAX phase Ti_2AlN obtained by reaction sintering in a vacuum at 1200°C (a, b) and 1300°C (b)

TABLE 1: Phase composition of samples obtained by heating precursors (Ti, TiN, Al) at temperatures of 1200°C, 1300°C in a vacuum

Heating temperature, °C	Phase content, %			
	Ti_2AlN	TilN (Osbornite)	TiAl	Ti_3Al
1200	71	10	15	4
1300	82	7	5	6

the results of quantitative phase analysis of the samples obtained at temperatures of 1200°C, 1300°C.

X-ray diffraction patterns in Fig. 1a show that, at a temperature of 1200°C, the MAX phase of Ti_2AlN (P63/mmc) is formed from the initial precursors (Ti, TiN, Al). The figure shows the peaks characteristic of this phase. The most intense reflexes of the MAX phase of Ti_2AlN (002) at 2Θ = 13.0° and (103) at 2Θ = 40.1°. The crystal lattice parameters of this phase: a = 0.2987 nm; b = 0.2987 nm; c = 1.3264 nm. The sample also contains impurity phases AlTi, TiN, Ti_3Al, as can be seen from Fig. 1b. It should be noted that at a temperature of 1200°C there are no peaks of the Ti and Al precursor phases, which indicates their complete interaction during the calcination process. The percentage content of the MAX phase Ti_2AlN in the sample heated at 1200°C is 71% (see Table 1).

To increase the content of the MAX phase Ti_2AlN in the sample, the precursors were heated at 1300°C in a vacuum. At this temperature, the content of the MAX phase increases to 82%, while the same impurity phases are recorded: AlTi, TiN, Ti_3Al. As can be seen from Table 1, with increasing temperature, the proportion of the MAX phase increases, and the proportion of the TiN and TiAl phases decreases. At the same time, there is a slight increase in the amount of the Ti_3Al phase.

3.2 Particle Morphology

One of the important parameters for potential applications of MAX phases is the size of the obtained particles. SEM images of particles of the synthesized MAX phase Ti_2AlN at 1300°C and the TiN precursor powder are shown in Fig. 2. The MAX phase particles have a size from units to tens of microns. The size of these particles is comparable to the size of the TiN precursor particles, which are the basis for the formation of the MAX phase during high-temperature synthesis (see Fig. 2). However, unlike TiN, the MAX phase crystallites have a pronounced faceting, sharp angles, which is due to the formation of a layered structure of the MAX phase Ti_2AlN, in which layers of Ti/N/Ti/Al/Ti/N/Ti/Al/… atoms alternate (Barsoum, 2013).

3.3 Elemental Composition

To better understand the processes occurring during high-temperature synthesis of the MAX phase of Ti_2AlN, a study was conducted on the elemental composition of the TiN precursor powder and the sample obtained at 1300°C.

3.3.1 TiN Powder

The state of the precursor is important for obtaining high-quality carbide and nitride MAX phases (Ivanovskaya et al., 2020). Figure 3 shows an SEM image of TiN powder with highlighted areas where elemental analysis (EDX) was performed. Table 2 compares

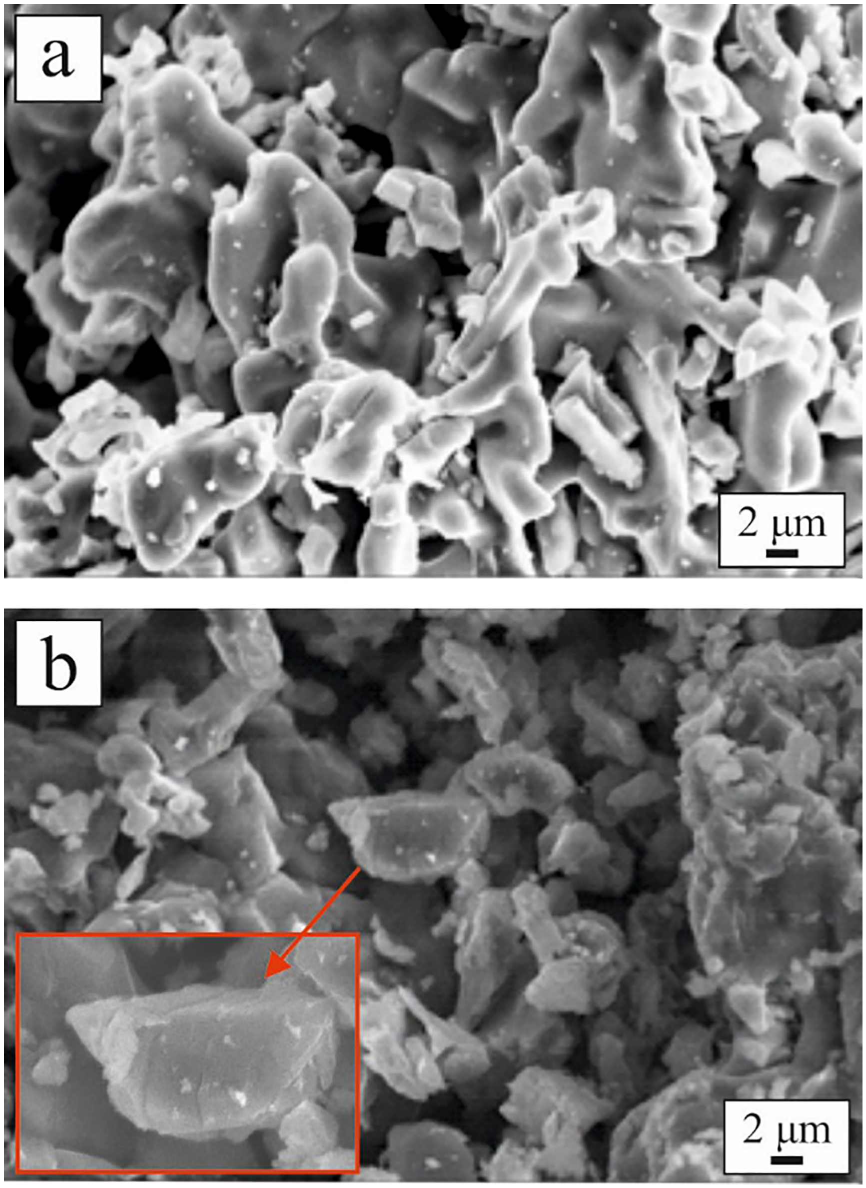

FIG. 2: SEM images of TiN (a) and Ti_2AlN (1300°C) (b) powders

the results of elemental composition analysis of titanium nitride in different areas of the sample.

It can be noted that the initial titanium nitride is non-uniform in terms of particle dispersion and morphology. Therefore, before synthesis, the TiN powder must be thoroughly ground. The difference in the ratio of Ti and N atoms in different areas is due to the fact that titanium nitride can be considered as a phase of nitrogen insertion into titanium and therefore a deviation from the stoichiometric ratio is possible.

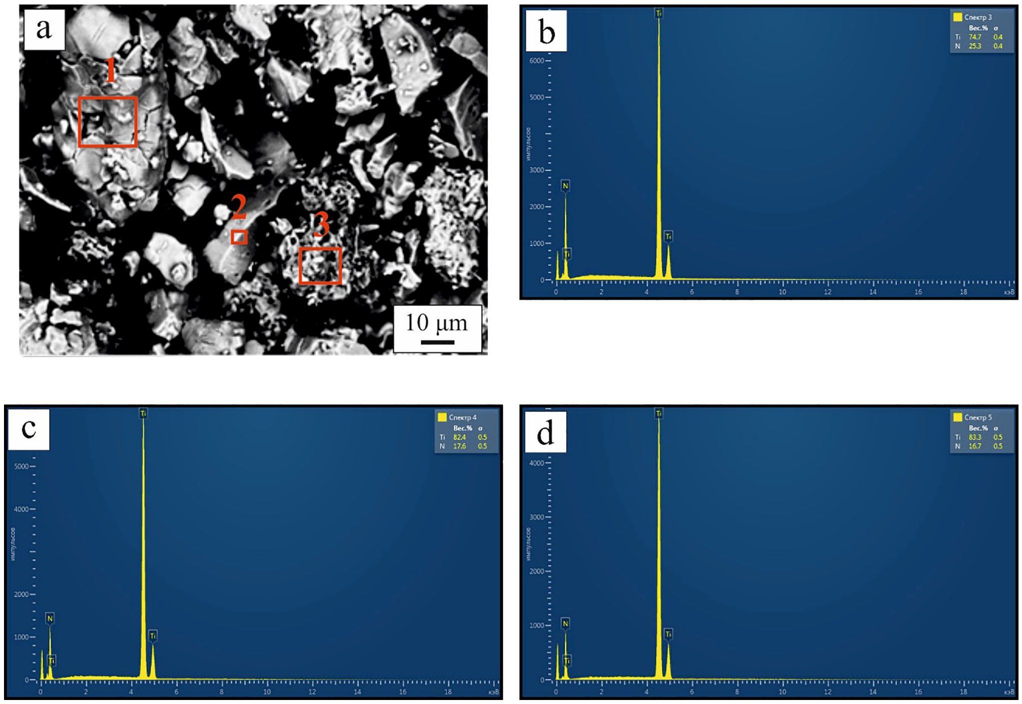

FIG. 3: SEM image of TiN powder with highlighted areas where elemental analysis (EDX) was performed (a). EDX spectra of highlighted areas 1(b), 2(c), 3(d)

TABLE 2: Analysis of the elemental composition of titanium nitride according to EDX data (Fig. 3)

Region	Nature of the structure fragment	Ti, at.%	N, at.%
1	A cluster of grains of different sizes and shapes	46.3	53.7
2	Single crystallite, edge	57.7	42.3
3	Fine grain fragment	59.4	40.6

3.3.2 Ti_2AlN Powder

Figure 4 shows an SEM image of the powder obtained by heating the precursors (Ti, TiN, Al) at 1300°C in a vacuum, with a highlighted area in which the EDX was performed. Table 3 shows the results of the elemental composition analysis in the highlighted area of the sample.

The results of the analysis of the flat crystallite surface in the sample obtained at 1300°C confirm the formation of the MAX phase of Ti_2AlN. The ratio of elements in the sample differs from the stoichiometric value for the composition Ti_2AlN (Ti/Al/N = 2/1/1) (Table 3). On the flat face of a well-crystallized grain (in which a layered structure is visible), the titanium content exceeds the stoichiometric value relative to aluminum, and the nitrogen content is below the stoichiometric value. Such a ratio of titanium and nitrogen relative to aluminum may indicate the presence of a certain amount of impurity phases Ti_3Al, TiAl, TiN, formed at

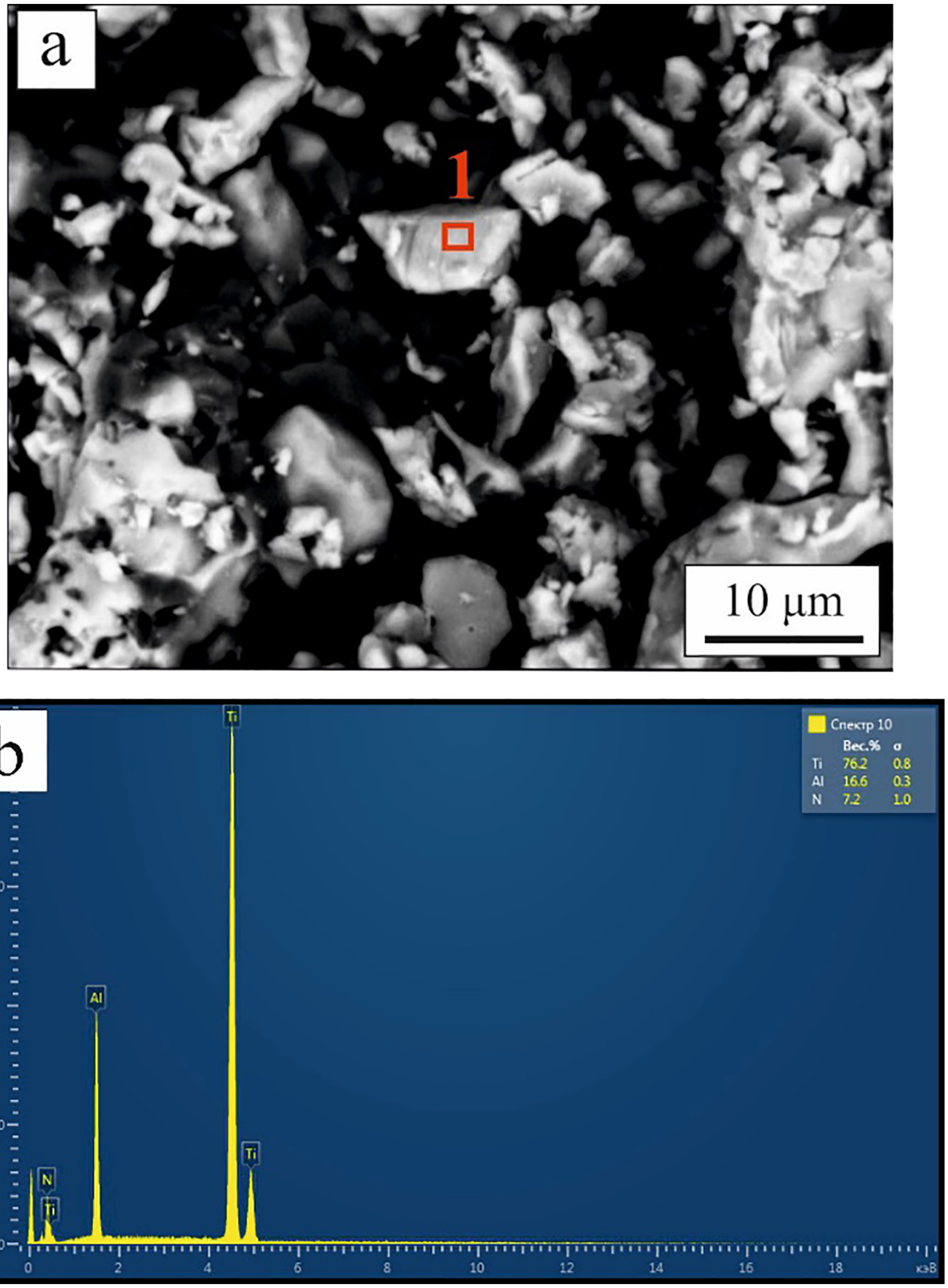

FIG. 4: SEM image of a sample obtained at 1300°C, with the area in which elemental analysis (EDX) was performed highlighted (a). EDX spectrum of the highlighted area 1(b).

the intermediate stages of synthesis. The presence of impurities is confirmed by the above-discussed X-ray diffraction results (see Fig. 1). However, the discrepancy between the EDX

TABLE 3: Analysis of the elemental composition of the sample obtained at 1300°C, according to EDX data (Fig. 4)

	Grain characteristics	Ti, at.%	Al, at.%	N, at.%	Ratio Ti/Al/N
Region 1	Flat grain edge	58.4	22.7	18.9	2.6/1.0/0.8

data and the expected composition is very typical for crystallites with anisotropic structure. These are the crystallites of the MAX phase of Ti_2AlN with a layered structure with alternating layers: Ti/N/Ti/Al/Ti/N/Ti/Al/… the results of the analysis will depend on the atoms of which element are on the surface of the crystallite face. In the completed crystallite faces, a layer of titanium atoms should be expected on the surface. The layered structure of the MAX phase of Ti_2AlN is schematically shown in Fig. 5. Additionally, the laminated microstructure contributed to transgranular and intergranular fractures, which are similar to textured. However, not all of the grains grew in a direction parallel to the basal plane of Ti_2AlN crystals (Liu et al., 2015).

The high-temperature process of Ti_2AlN phase formation from a mixture of Ti, Al, and TiN powders is multi-stage and includes various reactions with the formation of intermediate products (Chen et al., 2020; Haemers et al., 2020; Linde et al., 2022). In the literature, based on experimental data, reaction schemes are substantiated that occur at different temperatures during microwave synthesis (Liu et al., 2015; Chen et al., 2020) and reaction sintering in a vacuum (Linde et al., 2022), leading to the formation of the MAX phase of Ti_2AlN. The $TiAl_x$ and TiN phases are intermediate products in the process of Ti_2AlN synthesis.

The formation of Ti_2AlN occurs as a result of the following reactions. At temperatures above the melting point, aluminum Al (liquid) reacts with Ti and TiN to form $TiAl_2$, TiAl, and Ti_2Al.

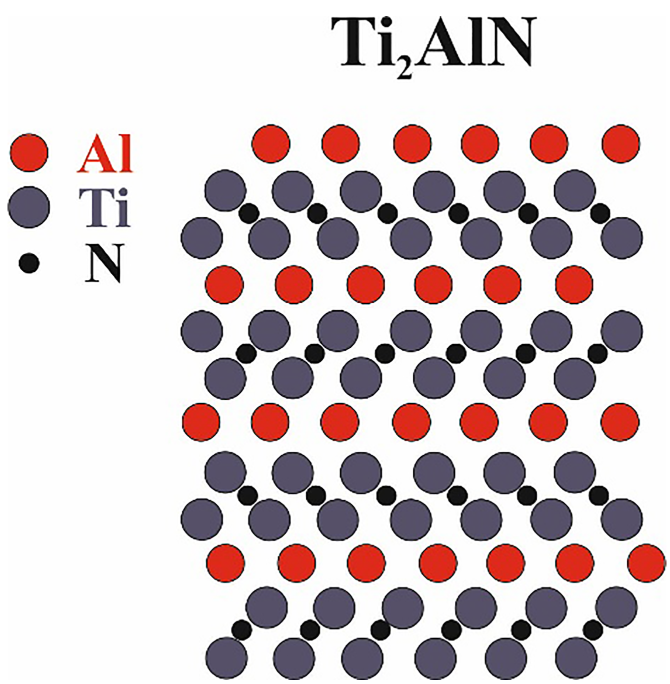

FIG. 5: Schematic representation of the layered structure of the MAX phase of Ti_2AlN

Other substances (e.g. Ti_3Al, Ti_3AlN) may also be among the impurities (Linde et al., 2022). Then $TiAl_2$ and Ti_2Al react with each other to form TiAl. At temperatures below 1200°C, the solid phase (sp) reaction between TiN and TiAl to form Ti_2AlN according to the scheme below is difficult:

$$\mathrm{TiN(sp) + TiAl(sp) \rightarrow Ti_2AlN} \quad (1)$$

With an increase in temperature to 1300°C, this reaction intensifies, the yield of Ti_2AlN can be up to 100%, only TiN remains as an impurity in the temperature range of 1300–1400°C (Linde et al., 2022). However, with some synthesis methods at 1300°C, the content of impurities can increase due to the evaporation of aluminum, which causes partial decomposition of Ti_2AlN and secondary formation of TiN. When synthesizing in a vacuum in closed ampoules, aluminum, evaporating, does not leave the reaction zone, and aluminum is not lost (Linde et al., 2022).

Taking into account the diversity of the reactions occurring, the temperature regime in each of the synthesis methods can be optimized in order to obtain a single-phase Ti_2AlN product. In the approach we use for synthesizing the MAX phase of Ti_2AlN, it is possible to increase the heating time at 1300°C to reduce the amount of impurities. Also, for this purpose, it is possible to carry out a repeated sintering cycle in a vacuum, including additional stages of grinding and pressing the product obtained at 1300°C, which will allow uniformly distributing the intermediate phases throughout the sample volume and thereby ensure more effective interaction between them. The obtained results confirm the opinion of some researchers that the method of reaction sintering in a vacuum can be promising for the synthesis of the MAX phase of Ti_2AlN, which is promising for various applications. The presence of TiN and TiAl impurities is a hindrance when it is necessary to study some fundamental physicochemical properties of Ti_2AlN, when the purest product is required. However, for some practical applications, the presence of impurities is not a hindrance. A promising direction of Ti_2AlN application may be its use for obtaining 2D layered materials MXene Ti_2N. If MXene based on carbides (Ti_3C_2) have been comprehensively studied and their prospects have been shown, then the studies of MXene based on nitrides (Ti_2N) are at an early stage. Therefore, the development of simple and accessible methods for synthesizing the MAX phase of Ti_2AlN is a very urgent task.

4. CONCLUSIONS

The MAX phase of Ti_2AlN was synthesized by the method of reaction sintering of Ti, TiN, Al in a quartz reactor in vacuum. It was found that:

- The MAX phase with a minimum amount of impurities is formed in vacuum at 1300°C. At this temperature, the content of the MAX phase of Ti_2AlN in the sample is 82%.
- TiAl, Ti_3Al, TiN are recorded as impurity phases, which are intermediate phases in the high-temperature synthesis of the MAX phase of Ti_2AlN from the precursors Ti, TiN, Al.
- The crystallite size of the synthesized MAX phase is from units to tens of microns.
- According to EDX data, the elemental composition of Ti_2AlN crystallites deviates from the stoichiometric one, which is due to the peculiarities of using this method in studying materials characterized by structural anisotropy.
- One of the promising areas of application of the synthesized MAX phase Ti_2AlN powder may be its use for obtaining 2D layered MXene Ti_2N materials.

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