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The Influence of the Synthesis Temperature on Phase Composition and Structure of Ternary Compounds Obtained from the Powder Mixture of the TiH₂-Al-C System

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This paper presents results of an investigation of the features of phase and structure formation of a ternary compound during thermal sintering use of compacted TiH₂-Al-C powder blends. The thermal sintering was carried out in vacuum furnace at temperature 1150, 1300 and 1400 °C. The x-ray diffraction pattern and structural analysis show that the main phase after synthesis at 1150 °C is titanium carbide. The ternary Ti₂AlC and intermetallic Ti₃Al compound were also identified in the phase composition of the alloy. Increasing the sintering temperature to 1300 °C leads to significant increases the content of Ti₂AlC ternary compounds and accordingly decrease the content of titanium carbide TiC. After synthesis at 1400 °C, the base phase of the alloy becomes the Ti₃AlC₂ ternary compound. Is propose a modified model thermal synthesis of ternary compounds of the Ti-Al-C system, which includes the melting of aluminum and its interaction with titanium at low-temperature stages of the process, formation of the Ti₃Al intermetallic compound, formation titanium carbide grains as a result of interaction of the Al₄C₃ intermediate metastable phase with titanium or Ti₃Al intermetallic compound and the synthesis of ternary Ti₂AlC and Ti₃AlC₂ compounds as a result of interaction of the Ti₃Al intermetallic compound with carbon and Ti₂AlC with titanium carbide TiC.

Key words: MAX-phase, titanium, aluminum, powder, thermal synthesis, structure, intermetallic compound, carbide, X-ray phase analysis.

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Introduction

In recent years, MAX phase – materials based on layered structures of ternary compounds, has attracted much interest. Its general formula Mn+1AX_n (n = 1÷3), where M is a transition metal, A is an A Group element, and X is either carbon or nitrogen [1-4]. These materials exhibit a unique combination of characteristics of both ceramics and metals. The MAX phases are natural nanolamines with high electrical and thermal conductivity (e.g. Ti₃SiC₂ displayed these characteristics better than pure titanium) and low coefficient of friction compared with known solid materials, high hardness in combination with low density and high resistance to mechanical injuries. Moreover, these properties of the MAX-phase can be maintained at high temperatures, in which they also exhibit high oxidation resistance and thermal shock. An important feature of materials based on MAX-phases is also the relative ease of their machining [1].

Materials based on laminated ternary MAX phases

can potentially be used in many fields of technology, e.g., as elements of gas turbine engines, parts with high abrasion resistance, chemical equipment elements, heat exchangers, electrical contacts working at high loads, etc. The most promising for practical use are materials based on the most fully studied Ti₃AlC₂, Ti₂AlC and Ti₃SiC₂ MAX phases [1,2].

Obtaining materials based on MAX phases is a complex task due to the low thermodynamic stimulus of the formation of mixed compounds from adjacent double phases, low diffusion rates of components in them, as well as the complexity and low accuracy of determining the actual phase content in synthesized materials. As a rule a mixture of titanium (titanium carbide), aluminum and carbon powders are used as a starting material for the production of MAX phases [1, 4-6].

At the same time, an effective approach to obtain sintered titanium based materials is use of titanium hydride TiH₂ powder instead of conventional metal titanium powder. Such substitution provides considerable activation of diffusion upon sintering and gives the opportunity to purify the material owing to action of

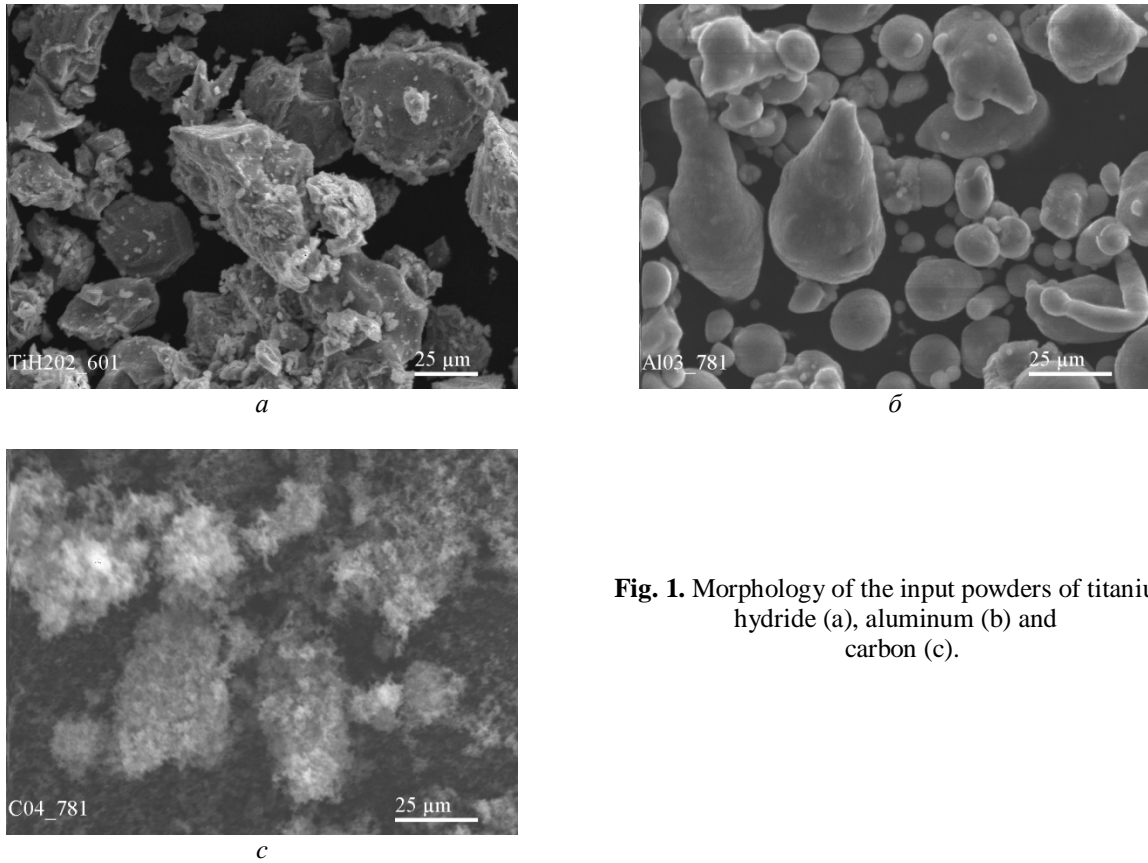


Fig. 1. Morphology of the input powders of titanium hydride (a), aluminum (b) and carbon (c).



Fig. 2. Appearance of the samples obtained by thermal synthesis from the mixture powders of titanium hydride, aluminum and carbon

atomic hydrogen evolved from crystal lattice of titanium hydride on vacuum heating [11, 12]. Due to hydrogen effect on the material, the unique structural conditions of sintered titanium alloys possessing high physics and mechanical properties are formed [7, 8]. Also, the use of TiH_2 as raw material leads to cost-efficiency, because of titanium hydride is cheaper than conventional titanium powders.

Given all the above, the purpose of this work was to establish the basic patterns of phase and structure formation of MAX-phase compounds during thermal sintering use of compacted TiH_2 -Al-C powder blends.

I. Materials and Methodology of Experiment

Titanium hydride, aluminum, semiconductor silicon

and technical carbon powders were used as starting materials. The initial powder morphology showed in Figure 1. The initial powders were mixed in a molar ratio of 3: 2: 1 = Ti-Al-C components in a “drum tumbler” within 2 hours. The powder mixtures were subjected to two-way cold pressing (400 MPa), which subsequently were sintered in vacuum furnace at temperature 1150, 1300 and 1400 °C with isothermal holding of 60 minutes.

The micrographs of initial powders and sintered sample surfaces were investigated by XJL-17AT optical microscope and JEOL Superprobe 733 scanning electron microscope. The phase composition of the master alloy was X-ray analyzed using a DRON-3 diffractometer with a $\text{Co-K}\alpha$ -radiation source in the range of $20 \div 130^\circ$ angles with step-by-step scanning. The specimen rotated around its axis during the diffraction. The correspondence of the diffraction lines in the Ti-Al-C systems was carried out using the PDF-2 database.

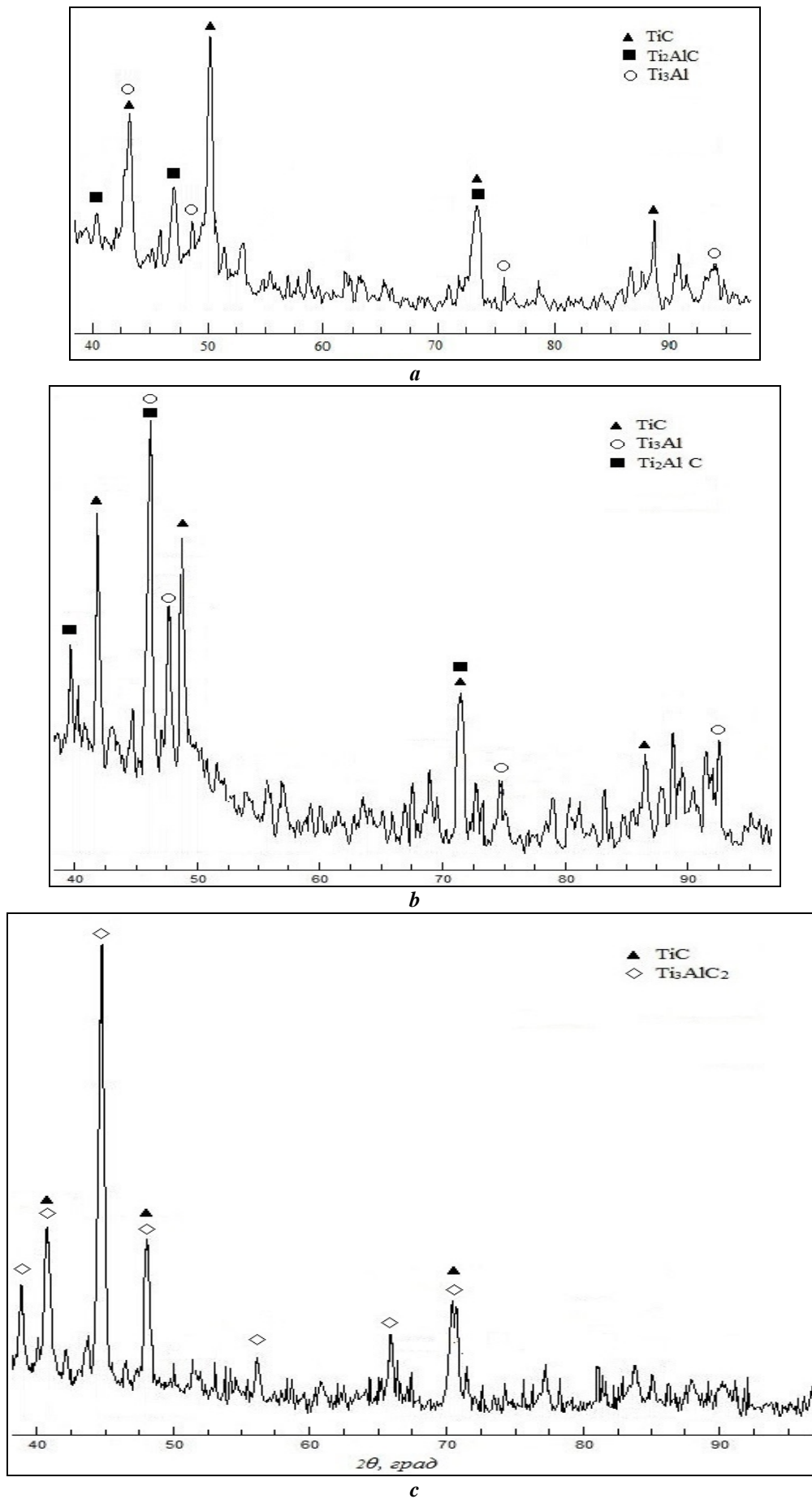


Fig. 3. Fragments of X-ray diffraction patterns of alloys of Ti-Al-C system after thermal synthesis at 1150 (a), 1300 (b) and 1400 °C (c).

II. Results and Discussion

There is a noticeable volume growth of initial compact during of thermal synthesis obtained from a mixture of titanium, aluminum and carbon hydride powders. Samples are sufficiently strong spongy conglomerates after thermal synthesis, reminiscent of the ones obtained by the SHS methods (Fig. 2).

The results of analysis of X-ray diffraction patterns of materials synthesized at different temperatures (Fig. 3) showed that the main phase of the sintered mixture at 1150 °C is titanium carbide with a cubic crystalline lattice.

The reflexes of the ternary Ti_2AlC titanium aluminum carbide and intermetallic Ti_3Al with the hexagonal lattice are also identified on the X-ray diffraction pattern along with the titanium carbide (Fig. 3a).

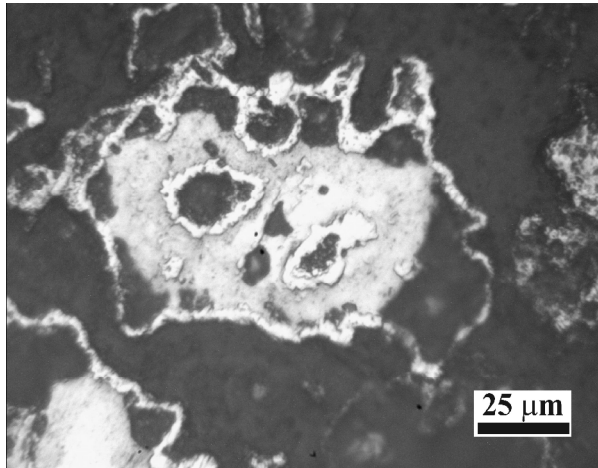
Increasing the sintering temperature to 1300 °C leads to significant increases the content of Ti_2AlC ternary compounds which becomes the main phase and accordingly decreases the content of titanium carbide TiC (Fig. 3b).

Further increase of the sintering temperature to 1400 °C along with monocarbide of titanium TiC leads to the appearance in the composition a new ternary Ti_3AlC_2 compound which becomes the preferred phase of the

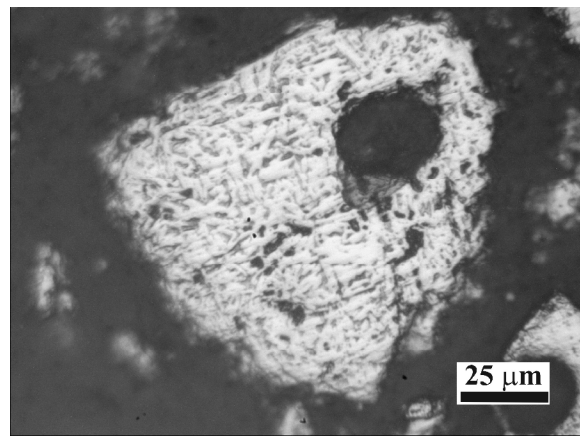
sintered at 1400 °C alloy. It should be noted that independent TiC lines and intermetallic lines were not detected on the X-ray diffraction of the alloy (Fig. 3c).

Changes in the phase composition of the material with an temperature synthesis increase were also caused, as well as the corresponding changes in the composition and morphology of the structural components in the alloy (Fig. 4). As you can see from figure 4a, the structure of samples synthesized at 1150 °C is characterized by the presence of at least three structural components. Dark inclusions are free carbon particles that have not reacted during the synthesis process. According to the results of the EDS analysis, graphite inclusions are surrounded by a bright light ring is identified as titanium aluminum carbide Ti_2AlC which is evidently formed as a result of the interaction of intermetallic Ti_3Al compound with carbon. The light gray field of the main background of the microsection consists of intermetallic Ti_3Al and dispersed particles of monocarbide titanium TiC .

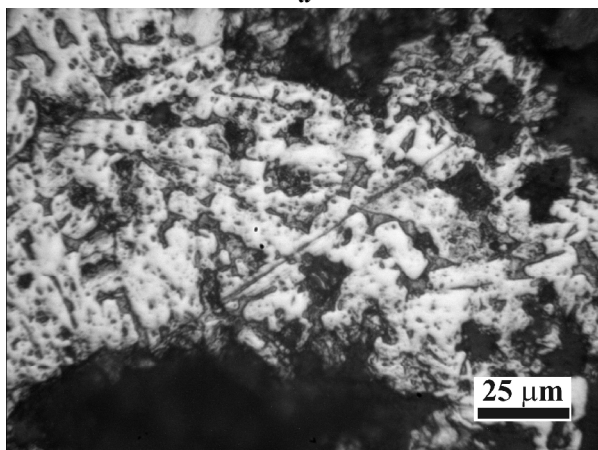
Increasing the sintering temperature to 1300 and 1400 °C leads to significant change in the morphology of the alloy components. The content of titanium monocarbide TiC , free carbon and intermetallic Ti_3Al decreases significantly, while the predominant phase of the alloy is the needlelike grains of titanium aluminum carbide Ti_2AlC for 1300 °C (Fig. 4b), and laminate-like Ti_3AlC_2 grains for 1400 °C (Fig. 4c). The content of titanium monocarbide TiC , free carbon and intermetallic Ti_3Al is significantly reduced, while the predominant



a



b

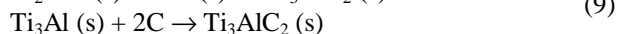
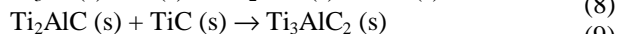
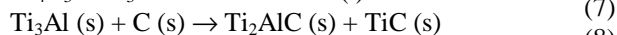
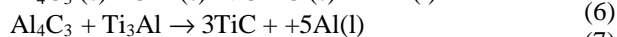
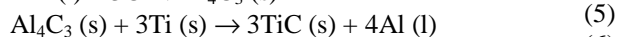
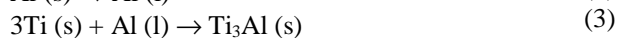


c

Fig. 4. Microstructure of alloys of Ti-Al-C system synthesized at 1150 (a), 1300 (b), and 1400 °C (c) temperature.

phase of the alloy at 1300 °C become titanium aluminum carbide Ti_2AlC with the needlelike grains (Fig. 4b), and Ti_3AlC_2 laminate-like grains at 1400 °C (Fig. 4c). Attracts attention more coarse character of the grain structure of the carbide phase of the alloy obtained at 1400 °C in comparison with the alloy synthesized at 1300 °C. While the diameter of the cross-section of the needle-shaped grains Ti_2AlC usually does not exceed $2 \div 4$ microns (Fig. 4b), then, after synthesis at 1400 °C, the transverse size of the Ti_3AlC_2 grains is already $5 \div 10$ μm (Fig. 4c).

The models of the synthesis of ternary compounds in the Ti-Al-C system are proposed in the [9-11] works. Taking into account the above results and the data of the DTA [10] of this system, known models can be modified to a variant of the model described by the following reactions (1) ÷ (8):



where index (s) corresponds to the solid state of matter, and index (l) corresponds to the corresponding melt.

According to the proposed model, starting from 480 °C the atomic hydrogen is released from the crystalline lattice of titanium hydride (reaction (1)) at the initial stage of heating of the initial charge. Aluminum melts at about a temperature of 660 °C and interacts with titanium, resulting in formation of phases of intermetallide Ti_3Al (reaction (3)).

According to the results of X-ray spectral analysis (Fig. 3, a), Ti_2AlC and TiC phase appear in the material with increase in temperature to 1300 °C. However, the thermodynamic evaluation of the direct reaction of TiC synthesis from titanium and carbon indicates that the passage of such a reaction is possible at substantially higher temperatures (not lower than 1600 °C) [11].

This fact leads to the conclusion that for the formation of carbide phases of titanium at relatively low temperatures it is necessary to have more fusible intermediate phases, from which titanium carbide crystals can be formed and grow. Thus, the authors [11] assumed that, at temperatures $\sim 660 \div 800$ °C, the intermediate metastable phase of Al_4C_3 synthesized by reaction (4), and the presence of which is possible to form titanium carbides at relatively low temperatures (reactions (5) and (6)).

Ternary Ti_2AlC , the presence of which in the alloy sintered at 1150 and 1300 °C, is confirmed by the data of

of X-ray spectral analysis shown in Fig. 3, b, c. It can be obtained as a result of the interaction of an intermetallic Ti_3Al with carbon (reaction (7)).

In the case of an increase in the synthesis temperature up to 1400 °C, the interaction of the Ti_2AlC ternary compound with TiC carbide and Ti_3Al intermetallic compound with carbon (reactions (8) and (9)) is possible. As a result of such reactions, the main phase of the alloy becomes a ternary Ti_3AlC_2 compound, the presence of which in the alloy synthesized at 1400 °C is confirmed by the data of spectroscopy (Fig. 3, c).

Conclusions

1) It was shown a significant dependence of the structure and phase composition of the alloy system Ti-Al-C by thermal fusion temperature. It is established that the main phase after synthesis at 1150 °C is titanium carbide. The ternary Ti_2AlC and intermetallic Ti_3Al compound were also identified in the phase composition of the alloy. Increasing the sintering temperature to 1300 °C leads to significant increases the content of Ti_2AlC ternary compounds and accordingly decrease the content of titanium carbide TiC . After synthesis at 1400 °C, the base phase of the alloy becomes the Ti_3AlC_2 ternary compound.

2) Increasing the sintering temperature from 1150 to 1300 and 1400 °C also leads to significant change in the morphology of the alloy components. Whereas in the alloy synthesized at 1150 °C, the carbide phase is represented by equilibrium grains of titanium carbide, in the materials synthesized at elevated temperatures predominant area of the microscale occupy needle-like (laminate) grains of Ti_2AlC and Ti_3AlC_2 ternary compounds.

3) Is propose a modified model thermal synthesis of ternary compounds of the Ti-Al-C system, which includes the melting of aluminum and its interaction with titanium at low-temperature stages of the process, formation of the Ti_3Al intermetallic compound, formation titanium carbide grains as a result of interaction of the Al_4C_3 intermediate metastable phase with titanium or Ti_3Al intermetallic compound and the synthesis of ternary Ti_2AlC and Ti_3AlC_2 compounds as a result of interaction of the Ti_3Al intermetallic compound with carbon and Ti_2AlC with titanium carbide TiC .

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Вплив температури синтезу на фазовий склад та структуру потрійних сполук, отриманих із порошкових сумішей системи TiH_2-Al-C

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В роботі наведені результати досліджень особливостей фазо- та структуроутворення при термічному синтезі потрійних сполук із порошкової шихти системи TiH_2-Al-C . Термічний синтез проводили у вакуумі при температурах 1150, 1300 та 1400 °С. За результатами рентгенофазового та структурного аналізу встановлено, що після синтезу при 1150 °С основною фазою сплаву є карбід титану. У фазовому складі сплаву ідентифікуються також потрійна сполука Ti_2AlC та інтерметалід Ti_3Al . Підвищення температури синтезу до 1300 °С призводить до суттєвого збільшення вмісту потрійної сполуки Ti_2AlC та відповідного зменшення вмісту карбіду титану TiC , а після синтезу при 1400 °С базовою фазою сплаву стає потрійна сполука Ti_3AlC_2 . Запропонована модифікована модель термічного синтезу потрійних сполук в системі $Ti-Al-C$, що включає плавлення алюмінію та його взаємодію з титаном на низькотемпературних стадіях процесу, формування фази інтерметаліду Ti_3Al , утворення зерен карбіду титану в результаті взаємодії проміжної метастабільної фази Al_4C_3 з титаном або інтерметалідом Ti_3Al , та синтез потрійних сполук Ti_2AlC та Ti_3AlC_2 в результаті взаємодії інтерметаліду Ti_3Al з вуглецем та Ti_2AlC з карбідом титану TiC .

Ключові слова: МАХ-фаза, титан, алюміній, порошок, термічний синтез, структура, інтерметалід, карбід, рентгенофазовий аналіз.