THE EFFECT OF CONDITIONS OF THERMAL TREATMENT OF TI+AL+C MIXTURE ON THE FORMATION OF MAX PHASES

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https://doi.org/10.37904/nanocon.2025.4999

Abstract

MAX phase materials are nano-layered, hexagonal, metal carbides, and nitrides, where M is a transition metal, A is an element of the A-group (mostly groups 13 and 14), and X is C and/or N. These phases exhibit a unique combination of properties of both metallic and ceramic materials. Physical and technological troubles usually affect the high-temperature synthesis of MAX phases, resulting in decreased yields of the MAX phase and promoting the formation of undesirable phases. For example, in the case of Ti-Al-C based MAX phases, the titanium carbide TiC and the Al_3Ti, TiAl and Ti_3Al intermetallic can also be formed under the synthesis process of Ti_3AlC_2 and Ti_2AlC phases. Additionally, Al can be oxidized, and Al_2O_3 often occurs in resulting products. The successful preparation of MAX phases depends on various conditions such as: heating temperature, holding time, heating rate, or gas flow. In this study, the Ti-Al-C MAX phases were prepared, by high-temperature treatment of mixture of Ti, Al, and C powders. The synthesis was conveniently conducted in the furnace of thermal analyzer, which enables precisely control the heating conditions. The effect of various parameters used during the synthesis on the MAX phases formation was tested, and the resulting products were analyzed using powder X-ray diffraction.

Keywords: MAX phase, Ti_3AlC_2, Ti_2AlC, TG/DTA analysis, phase analysis

1. INTRODUCTION

MAX phases are ternary, hexagonal compounds with formula $M_{n+1}AX_n$ where M is the transition metal, A is the element from A – Groups of the periodic table, and X stands for carbon or nitrogen. These crystalline compounds have a layered structure, in which carbide or nitride blocks are separated by monolayers of atoms of Group A [1]. MAX phases combine the advantages of both metal and ceramic materials. Like metals, they are thermally and electrically conductive, readily machinable at room temperature, resistant to thermal shock, have crack propagation resistance, and deform plastically at elevated temperatures. Similarly to ceramics, they have low density, high elastic modulus, low thermal expansion coefficient, excellent heat resistance, and high temperature strength [2].

Ternary compounds in the Ti-Al-C system, mainly Ti_2AlC and Ti_3AlC_2, are the phases of the largest area of interest in the series of MAX phases [1]. In these compounds, TiC layers are alternately interspersed with Al layers, and weak metallic bonds are formed between Ti and Al atoms, while stronger covalent-ionic bonds are formed between Ti and C. The properties of Ti_3AlC_2 make it a great candidate in applications such as electrical contact coating [3,4], high temperature refractory materials [5], as a material for electrodes of batteries and supercapacitors [6], and in combination with magnesium also for hydrogen storage applications [7]. In 2011, Gogotsi, et. al described the exfolation of Ti_3AlC_2 by etching Al out in hydrofluoric acid [8] and discovered a new class of 2D materials called MXenes.

As reported by Desay et al. [9], the MAX phase Ti_2AlC was firstly synthesized by Jeitschko et al. [10] in 1963 through process of Chemical Vapour Deposition. Similarly, Desay et al. [9] mentioned that successful synthesis of Ti_3AlC_2 was firstly reported in 1994 by Peitzka and Schuster [11] who had used a cold compaction of Ti, C and Al_4C_3 powder followed by its sintering in hydrogen atmosphere at 1300 °C for 2 h. Currently, there are a variety of methods by which these compounds may be synthesized, for example hot isostatic pressure (HIP) [12], self-propagating high temperature synthesis (SHS) [13], or spark plasma sintering (SPS) [14]. These synthesis methods are based on high temperature treatment of the mixture of powdered titanium, carbon, and aluminum. The selected process of Ti+Al+C mechanical mixture heating influence the quality of the final product. For example, Zhou et al. [15] observed that the heating conditions used during the synthesis determine the amount of residual phases, especially TiC and high rates of temperature increase is recommended to suppress TiC formation. Ovodok et al. [16] studied the effect of the temperature on Ti_3AlC_2 formation during the heating of Ti+Al+C mechanical mixture under vacuum and observed the formation of the Ti_3AlC_2 already at the temperature 1100 °C. The authors also indicated the lowest amount of TiC and Ti_2AlC impurities for the sample prepared at 1300 °C.

As evident, the heating conditions during the preparation of Ti-Al-C MAX phases play an important role in the formation and purity of the final product. In our research, we focused on the indication of how the heating rate, temperature, and holding time at this temperature influence the phase composition of the product obtained by heating of the Ti+Al+C mechanical mixture.

2. MATERIALS AND METHODS

As a raw materials, the titanium powder from AP&C company containing spherical particles of size 15-45 μm, the aluminium powder (99,5% purity, particle size > 120 mesh) from International Enzymes Ltd. Company (United Kingdom) and graphite in its powder form (99,8% purity, <0.1 mm granulometry) from Fluka Chemie AG (Germany) were used. All reagents were used as received without any further pre-treatment. Individual components (Ti, Al and C) were mixed in molar ratio 3 : 1.1 : 2 and homogenized 30 min in in planetary ball mill.

Thermogravimetry analysis/differential scanning calorimetry (TGA/DSC) was carried out on a simultaneous thermal analyzer SDT 650 TA Instruments, USA which has a DSC/TGA system with horizontal dual-beam design for heat flow and weight measurements. Each sample (~ 20 mg) was inserted into α-Al_2O_3 crucible and heated up according to the conditions specified in **Table 1**, argon atmosphere (6.0) of flow rate 200 $cm^3\ min^{-1}$ was used for all the experiments. The crucibles were covered with α-Al_2O_3 lid during the experiments. All the tested parameters during the thermal treatment of Ti+Al+C mechanical mixtures are listed in **Table 1**.

Table 1 Conditions during the high temperature treatment of Ti+Al+C mechanical mixtures

Sample	heating rate (°C min^{-1})	holding time (min)	gas flow ($cm^3\ min^{-1}$)	temperature (°C)
P1_A	10	60	200	1300
P1_B	50	60	200	1300
P1_C	50	0	200	1300
P1_D	10	60	200	1400
P1_E	10	60	200	1500

The phase composition of the resulting products was characterized by X-ray powder diffraction method using diffractometer MiniFlex600 (Rigaku, Japan). Registered diffraction patterns were evaluated using SmartLab Studio II software (Rigaku, Japan), the database PDF 2 release 2019 (International Centre for Diffraction Data, USA) was used for the identification of the crystalline phases.

3. RESULTS AND DISCUSSION

As already mentioned in section Introduction, Zhou et al. [15] reported that higher heating rates are preferable for the elimination of the impurities, mainly TiC during the high temperature synthesis of Ti-Al-C MAX phases. Based on this recommendation, we tested heating rates 10 and 50 °C·min^{-1} respectively and obtained samples P1_A and P1_B (all the parameters are listed in **Table 1**). Registered diffraction patterns of these samples are compared in **Figure 1**.

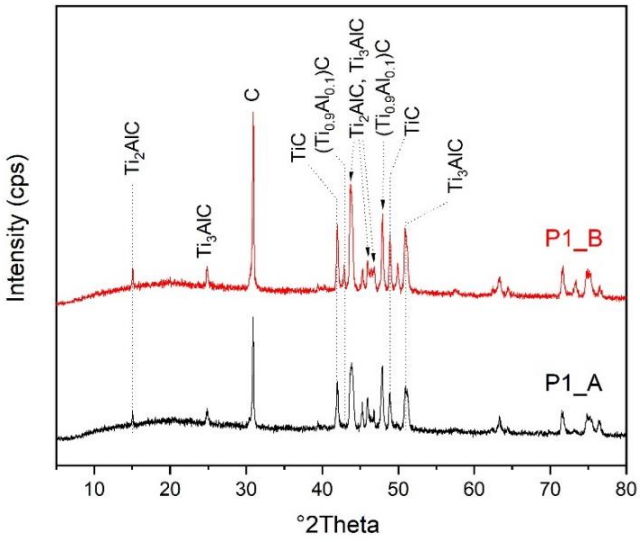

Figure 1 X-ray diffraction patterns documenting the effect of heating rate on the phase composition of final product (P1_A (10°C min^{-1}) and P1_B (50°C min^{-1}))

The phase composition documented by X-ray diffraction patterns of samples prepared at different heating rates (**Figure 1**) did not reveal significant difference in phase composition of the samples. With respect to this observation, the heating rate 50°C min^{-1} was selected for next experiment with holding time.

The effect of the time at which the sample is kept at given temperature (holding time 0 and 60 min) on the phase composition of the resulting products is documented with diffraction patterns pictured in **Figure 2**.

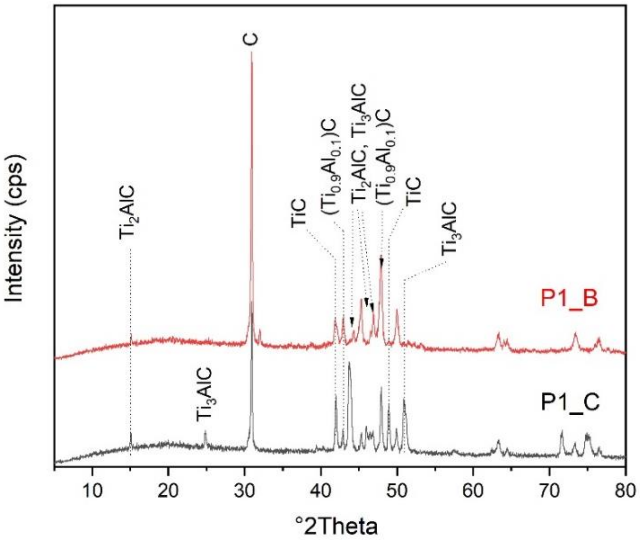

Figure 2 X-ray diffraction patterns documenting the effect of holding time on the phase composition of the final products (P1_C (0 min) and P1_B (60 min))

Comparing the phase composition of the samples, it is noticed, that with prolonged time of heating, the product contains lower amount of TiC, and does not contain Ti_3AlC phase, on the other hand the content of $(Ti_{0.9}Al_{0.1})C$ phase was increasing. The MAX phase Ti_2AlC originated for both tested holding times (0 and 60 min). Higher intensities of diffraction peaks belonging to Ti_2AlC was observed for holding time 60 min, and this value was used for next experiments. The positive effect of prolonged holding time led also to decision to conduct the experiments with lower value of heating rate 10 °C·min^{-1}, which in fact also affect the total time at which the sample stays in higher temperature range.

The effect of the final temperature (1300, 1400 and 1500 °C) on the phase composition of the resulting products is documented with diffraction patterns pictured in **Figure 3**. Only at the temperature 1500 °C the phase Ti_3AlC_2 was formed as evident from diffraction pattern of sample P1_E showed in **Figure 3**. The diffraction pattern of this sample proved also the presence of Ti_2AlC, low intensive diffraction peak centred at approximately 41 °2Theta (CoKα) demonstrate also the presence of Al_2O_3 phase.

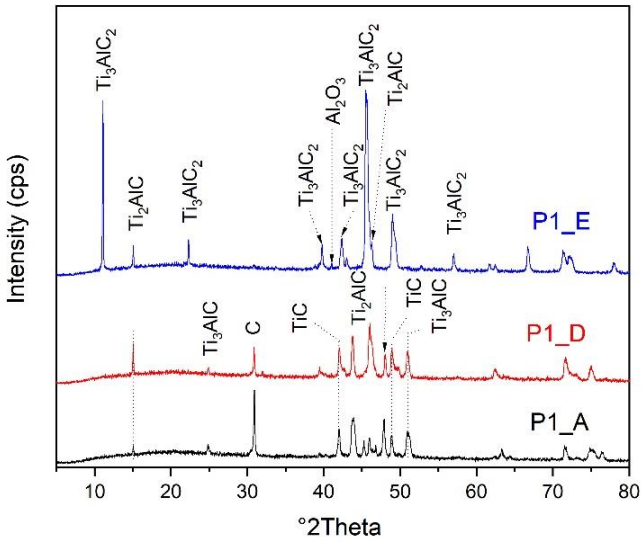

Figure 3 X-ray diffraction patterns documenting the effect of the final temperature on the phase composition of final products (P1_C (1300 °C), P1_D (1400 °C) and P1_E (1500 °C))

4. CONCLUSIONS

The aim of this study was to investigate the effect of different parameters of heating on synthesis of MAX phases based on the system Ti-Al-C in the furnace of thermal analyzer. The X-ray diffraction patterns showed that the heating rate had no significant effect on the composition. In the case of duration of the sample retention at final temperature, it was observed, that longer holding time resulted in the lower amounts of TiC and higher amount of one of the desired MAX phase. Lastly the effect of temperature on MAX phases was investigated. The diffraction patterns showed that the sample prepared at temperature of 1500 °C contained both, Ti_3AlC_2 and Ti_2AlC, while the treatment of the sample at lower temperatures caused the formation of only Ti_2AlC as the target MAX phase. Performed study provided us with the conditions at which the MAX phase Ti_3AlC_2 and Ti_2AlC can originate and will be used for the treatment of the Ti+Al+C mixtures on a larger scale in a tube furnace.

DATA AVAILABILITY

10.5281/zenodo.13918242

ACKNOWLEDGEMENTS

This research was supported by project No. CZ.02.01.01/00/22_008/0004631 Materials and technologies for sustainable development within the Jan Amos Komensky Operational Program financed by the European Union and from the state budget of the Czech Republic. Authors also thank the VSB-Technical University of Ostrava project SP2024/025) for the financial support.

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