CHARACTERIZATION OF Ti_3AlC_2 SYNTHESIZED BY USING A COST-EFFECTIVE APPROACH

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Abstract

Ternary carbide materials have been proposed for novel technological applications due to the combination of their specific properties as metals and ceramic materials. Among this vast family of compounds, Ti_3AlC_2 earned particular attention because it can be transformed through an etching process into the famous MXene Ti_3C_2, a laminar material with attractive properties for different fields of research and application. In our previous work, we showed the optimization of the synthesis of Ti_3AlC_2 (temperature gradient, soaking time, temperature, and gas flow) in a highly controlled furnace in an Ar atmosphere. In this work, we present the phase and morphological characterization of the Ti_3AlC_2 MAX phase produced by an innovative industry-oriented approach. For this purpose, the previously activated Ti/Al/C precursor mixture was subjected to a thermal regime at several soaking temperatures (1150°C, 1200°C, 1250°C, 1300°C, 1350°C, 1400°C), in a molten salt environment. The procedure allowed us to achieve products with ~ 60 wt% of Ti_3AlC_2 in all the cases, according to the phase composition analysis based on the X-ray diffraction patterns. The scanning electron microscopy, along with the EDS analysis, confirms the presence of Ti, Al, and C as the majority elements and its analysis allowed us to identify possible secondary products. In addition, the skeletal density of the samples was evaluated by He pycnometry, resulting in all cases in close values to the theoretical one, indicating a successful synthesis process. The slight deviation was attributed to the presence of non-desired phases.

Keywords: Max phases, cost-effective method, characterization

1. INTRODUCTION

Ternary carbides and nitrides are materials characterized by their distinct combination of ceramic and metal properties [1]. Since their discovery by Nowotny and his coworkers in the 1960s [2,3], this expanding family of compounds has been investigated due to their wide range of potential applications. Among the most appealing features is the possibility to serve as MXenes precursors [4].

From the structure point of view, the $M_{n+1}AX_n$ or MAX phases are layered hexagonal materials, where “M” as an early transition metal (e.g.,Ti, V, Cr, Hf); “A” as an element of the group 13 or 14 (usually Al, Si, P, S or Ga) and “X” as C or N atoms. The subscript *n* accepts the values 1, 2, 3, or even higher numbers according to the most recent discoveries [5]. Within their unit cells, M-X strong covalent interactions constitute layers of edge-sharing $M_{n+1}X_n$ octahedra, interspersed with weakly bonded (M-A) “A” type of atom layers.

Properties such as low density, fracture toughness, mechanical response at high temperatures, damage tolerance, corrosion and erosion resistance, and machinability are just some of the characteristics of these

attractive MAX phases [6]. However, the limitless number of potential applications is tightly related to the synthesis method used to obtain the desired product [7]. The thermal methods prioritize the prevention of the oxidation of the precursors by protecting the atmosphere with some commonly expensive gas, such as Ar [8], or are conducted in vacuum, allowing a careful control of final particle characteristics [9,10]. These methodologies do not thoroughly consider the environmental and cost-effective aspects of the synthesis. In this sense, the molten salt method represents a versatile technique for sintering complex materials that could avoid the use of gas protection [11,12]. Besides, it is a relatively easy-to-scale methodology that allows the reduction of the reaction temperature and the increment of the reaction rate [13]. During this procedure, a salt is melted to form a chemically inert liquid medium that aids the diffusion of the atoms, increasing the probability of their mutual reactive collisions to form the desired phase [11]. To perform this process, the mixture of selected precursors is either manually or mechanically mixed with chosen salts (usually in higher proportion) [14]. The milling pre-treatment grants the precursors energy to enlarge their active surface areas, bringing them into an activated state, favoring the further sintering process [15]. The subsequent mixture is then covered by an excess of salt and subjected to thermal treatment in air environment. This thermal alternative could permit the reduction of the energy consumption by reducing the temperature of synthesis and allow the re-use of the salts, recuperating them by recrystallization during the isolation stage.

The principal aim of this work was to present the characterization of Ti_3AlC_2 MAX phase prepared by a cost-reduced thermal method in the presence of molten salts from a Ti/Al/C system.

2. MATERIALS AND METHODS

2.1 Materials

Titanium powder Grade 1, Size 15-45 µm purchased from AP&C company (Canada), aluminum powder obtained from Albo SCHLENK, s.r.o. (Czech Republic) and carbon black pearls 2000 from CABOT, spol. s r.o. (Czech Republic) were used as received for the MAX phases thermal synthesis. Commercial Ti_3AlC_2 was purchased from Merck spol. s.r.o. (Czech Republic), NaCl (p.a.) and KCl (p.a.) salts were purchased from Penta Chemical Unlimited (Czech Republic) and all the compounds were used as received without any pre-treatment.

2.2 Samples preparation

Ti, Al, and carbon powders in a molar ratio 3:1.1:2 were homogenized and pre-activated in a planetary ball mill PM100 (Retsch, Germany) for 30 minutes at 450 rpm using a 250 mL stainless steel vessel. The powder-to-ball weight ratio used was 1:20. After this, the resulting mechanically activated mixture of Ti/Al/C was combined with a eutectic mixture of KCl/NaCl in a molar ratio 1:1 and milled for 10 extra minutes. Then, 10 g of the milled product was placed into an alumina crucible, followed by the addition of 25 g of the eutectic KCl/NaCl mixture in order to cover the surface of the precursors and avoid their exposure to the air during the thermal treatment. This step is crucial because it would allow us to achieve the desired product without atmosphere protection. The alumina crucible with the reaction mixture was introduced into the laboratory furnace (LAC, VP 10/17) (LAC, s.r.o., Czech Republic) and the soaking temperature varied depending on the sample (1150°C, 1200°C, 1250°C, 1300°C, 1350°C, 1400°C). The heating rate and soaking time were optimized in a previous work and set at 10°C/min and 90 minutes, respectively [16]. Upon completion of that time, the furnace was cooled down naturally to room temperature (~5.5 °C /min) and the sample was taken out of the furnace and subjected to the washing step. For this, the cooled crucible with the sample attached at the bottom was inverted upside down into a beaker containing 500 mL of distilled water and a magnetic stirring bar. The content was warmed up to 50°C and stirred to favor the dissolution of the salts. Once the solid was suspended, the suspension was vacuum filtered (Pragopor 5, 60 µm pore size), and the solid product was dried in an oven at 115°C while the salts were recrystallized from the liquid phase to be reused. The dried powder was crushed in an agate mortar and subjected again to the washing procedure. Finally, the isolated, grounded, dry solids were labeled as

MAX-T (where T stands for 1150°C, 1200°C, 1250°C, 1300°C, 1350°C, 1400°C) and stored in a desiccator for further characterization.

2.3 Characterization methods

The crystalline phase identification of the prepared samples was realized by evaluation of X-ray diffraction patterns registered by the MiniFlex600 X-ray diffractometer (Rigaku, Japan) equipped with Co radiation (600 W, λ=0.179 nm) and a D/teX Ultra detector. The diffraction (XRD) patterns were recorded in the range of 5 – 80° 2θ with a step of 0.02° and 5 °/min scan speed. Quantitative phase composition analysis was performed by using the program Powder cell 2.3 (BAM, Germany). Preferred orientation was considered for Ti_3AlC_2 (0, 1,-4) and TiC (1,0,0) phases and fitted according to the March-Dollase model.

The morphology of the samples was studied by using a tabletop scanning electron microscope (Hitachi T4000). In addition, a chemical semi-quantification was performed with an XploreCompact 30 energy dispersive detector (Oxford Instruments, UK). Samples were coated with Pt (5 nm thickness) and fixed on metal pins of 10 mm diameter using conductive carbon tape.

The skeletal density of samples was determined by the helium expansion technique. For this purpose, a conventional gas pycnometer (Pycnomatic-ATC, POROTEC) operating at 20 °C was utilized. The measurements were performed in 3 cycles over the previously dried samples.

3. RESULTS AND DISCUSSION

3.1 X-Ray diffraction

X-ray diffraction patterns for all samples show the presence of crystalline peaks corresponding to the desired phase Ti_3AlC_2, along with Al_2O_3 and TiC as principal impurities (**Figure 1a)**). In addition, MAX-1150 and MAX-1200 presented signals associated with the Ti_2AlC phase. **Figure 1b)** depicts the phase quantification results for the samples synthesized at different temperatures. Commercial TI_3AlC_2 was also measured and analyzed and its quantification was included for comparison. As a result of this evidence, the quantitative phase analysis carried out indicated that the optimal soaking temperature to favor the production of Ti_3AlC_2 phase with less impurity presence is 1250°C. The data suggest that all samples contain more than 60 wt% of the desired phase and TiC results in the most present impurity, with a mass fraction up to 27% for MAX-1300.

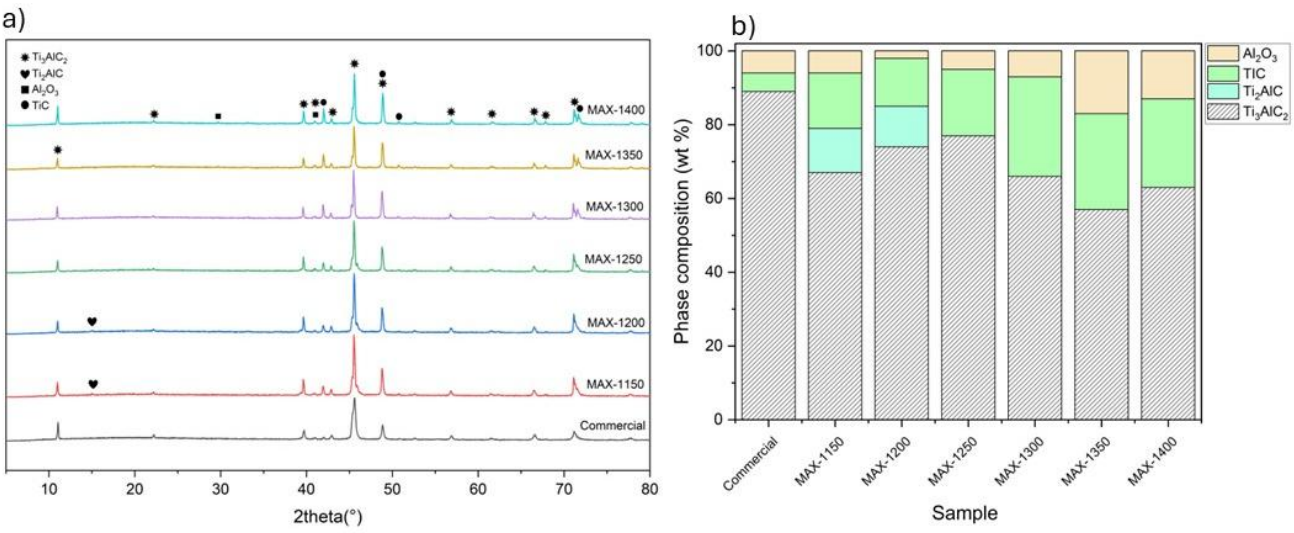

Figure 1 a) XRD patterns and b) phase quantification results for the indicated samples

3.2 SEM and EDS analysis

Scanning Electron Microscopy images shown in **Figure 2** suggest that there is a morphology evolution during the thermal process related to the increase in the sintering temperature. An initial orbicular shape is evident in the particles synthesized at low temperatures. This shape could derive from the spherical precursors, which can serve as a template, and it is less frequently observed at higher temperatures. This precursor shape-oriented product was previously identified by Liu et. al [17] who directed the synthesis of hollow Ti_3AlC_2 microrods by using carbon fibers as a precursor. The increase in soaking temperature could allow for the rapid melting of all components and activate a different sintering route, leading to the transformation of the spherical particles. All the samples exhibited grains of random size and a laminar (or needle-like) morphology corresponding to Ti_3AlC_2 [11]. The presence of impurities, forming well-defined and robust hexagonal particles, was also observed and further analyzed by EDS.

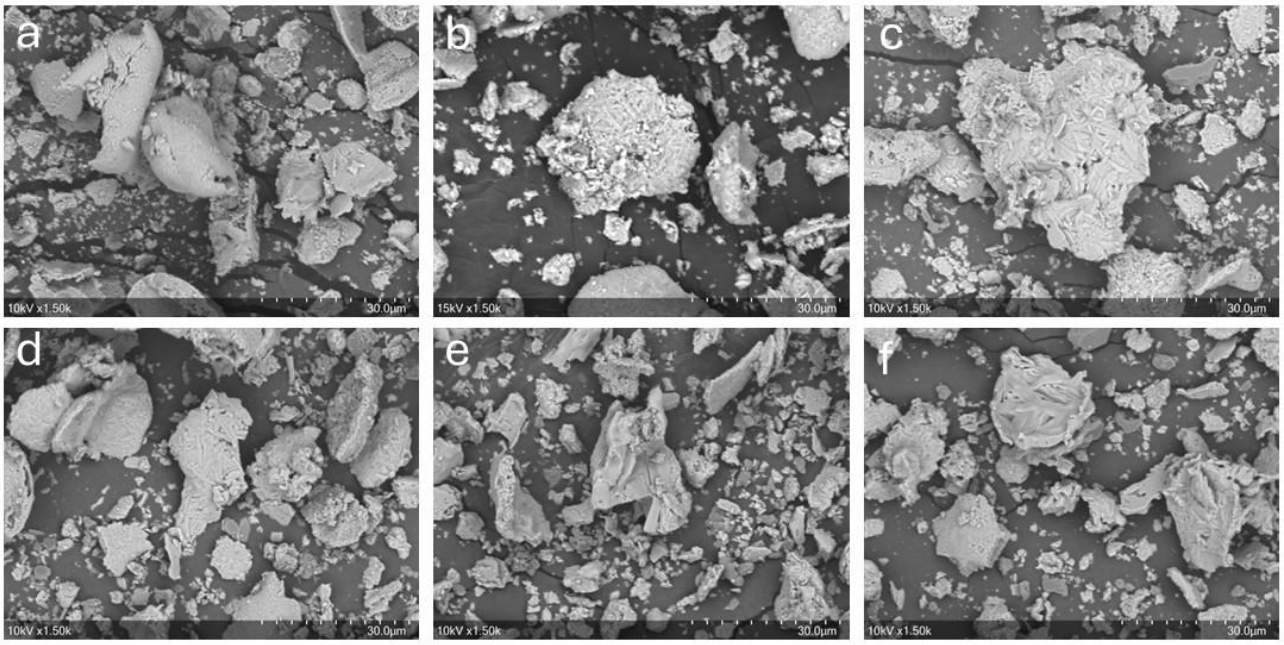

Figure 2 SEM images of a) MAX-1150, b) MAX-1200, c) MAX-1250, d) MAX-1300, e) MAX-1350, f) MAX-1400. All the images were magnified 1500 times

Therefore, EDS analysis was performed in both the suspicious and the Ti_3AlC_2 particles for comparison. **Figure 3** presents the EDS spectra carried out in two different zones on sample MAX-1400, although the presence of non-desired phases was confirmed in samples prepared at lower temperatures too (images not shown). The electron image shows the presence of hexagonal particles (#2 in SEM image, **Figure 3**) together with Ti_3AlC_2 grains (#1 in SEM image, **Figure 3**). The comparative spectral result suggests that there is relatively high aluminum and oxygen concentration on the suspicious particle, indicated by an increment of their X-ray signal, denoting the presence of α-Al_2O_3 as an impurity, as found by Li et al. [18]. Additionally, the composition percentages are presented in **Table 1**, which shows a significantly higher aluminum and oxygen weight % in zone 2 compared to zone 1. Particularly, the α-Al_2O_3 is a common intermetallic impurity formed during this process, and it was previously evidenced by XRD (PDF card No: 00-046-1212). In addition, some traces of potassium and chlorine were identified over the MAX phase originating from the eutectic mixture used as a molten salt.

Table 1 Atomic content and deviation determined by EDS expressed as weight percentage

	Spectrum zone 1		Spectrum zone 2	
Element	**Weight (%)**	**Weight (%) σ**	**Weight (%)**	**Weight (%) σ**
C	33.5	1	47.5	0.5
O	3.9	0.7	28.9	0.4
Al	10.1	0.2	19.8	0.2
Ti	49.3	0.8	3.9	0.1
K	1.2	0.0	-	-
Cl	2.0	0.1	-	-
Total	100	-	100.1	-

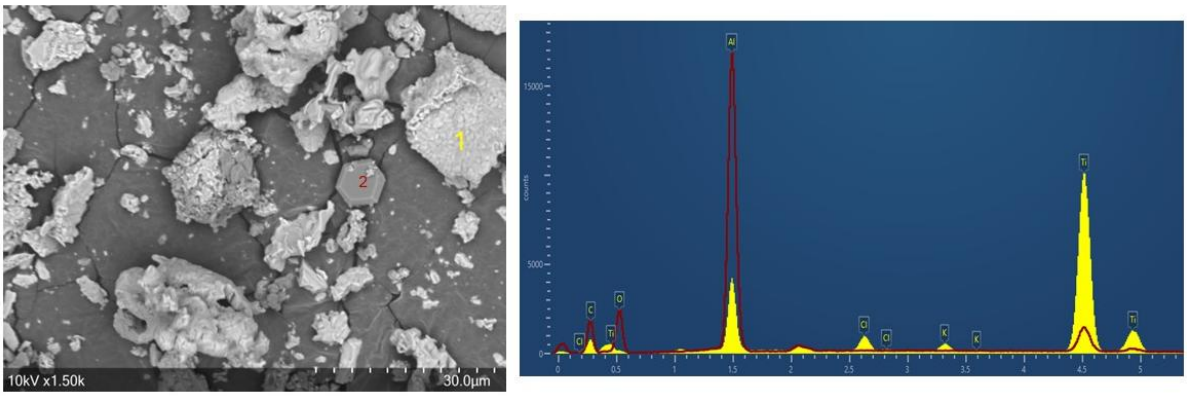

Figure 3 EDS analysis of MAX-1400. The numbers in the electron image indicate the data acquisition zones. The full yellow spectra and the red line ones correspond to zones 1 and 2, respectively

3.3 Skeletal density measurements

Skeletal volume analysis by He pycnometry is one of the most reliable methodologies to calculate the density of material since it includes only the physically inaccessible closed pores. **Table 2** shows the density values obtained for each sample. It can be seen that the measurements were close to each other, being comparable to the theoretical density of Ti_3AlC_2 4.5 g/cm^3 [19]. The slight discrepancy with the latter value is attributed either to the presence of impurities or the occurrence of pores smaller than the He kinetic diameter (0.26 nm).

Table 2 Skeletal density values and their deviation for the indicated samples

Sample	**Density (g/cm^3)**
MAX-1150	4.37 ± 0.02
MAX-1200	4.23 ± 0.01
MAX-1250	4.31 ± 0.01
MAX-1300	4.37 ± 0.01
MAX-1350	4.31 ± 0.01
MAX-1400	4.31 ± 0.01

4. CONCLUSIONS

The aim of this study was to demonstrate the feasibility of synthesis of a technologically interesting material through cost-effective conditions. The MAX phase Ti_3AlC_2 has been synthesized by the molten salt method at

temperature values ranging between 1150-1400 °C. The optimal synthesis temperature, based on the sample composition, results in 1250 °C, achieving 77 wt% % of Ti_3AlC_2. A morphology change with an initial abundance of spherical particles, likely templated on the precursor particles, and the presence of the impurities, were observed in the SEM images and identified by XRD. Although further refinements are required to optimize the yield and improve the intermetallic impurity removal, the present methodology demonstrates suitability for the synthesis of Ti_3AlC_2 from a Ti/Al/C system, enabling possible salt reuse and eliminating the need for an air-protected atmosphere.

DATA AVAILABILITY

The data presented in this study are available in ZENODO at https://doi.org/10.5281/zenodo.19128759.

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