Synthesis, sintering, and effect of surface roughness on oxidation of submicron Ti$_2$AlC ceramics

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Abstract
Submicron Ti$_2$AlC MAX phase powder was synthesized by molten salt shielded synthesis (MS$^3$) using a Ti:Al:C molar ratio of 2:1:0.9 at a process temperature of 1000°C for 5 hours. The synthesized powder presented a mean particle size of ~0.9 µm and a purity of 91 wt. % Ti$_2$AlC, containing 6 wt. % Ti$_3$AlC$_2$. The Ti$_2$AlC powder was sintered by pressureless sintering, achieving a maximal relative density of 90%, hence field-assisted sintering technology/spark plasma sintering was used to enhance densification. The fine-grained microstructure was preserved, and phase purity of Ti$_2$AlC was unaltered in the latter case, with a relative density of 98.5%. Oxidation was performed at 1200°C for 50 hours in static air of dense monolithic Ti$_2$AlC with different surface finish, (polished, ground and sandblasted) which resulted in the formation of an approx. 8 µm thin aluminum oxide (Al$_2$O$_3$) layer decorated with titanium dioxide (rutile, TiO$_2$) colonies. Surface quality had no influence on Al$_2$O$_3$ scale thickness, but the amount and size of TiO$_2$ crystals increased with surface roughness. A phenomenon of rumpling of the thermally grown oxide (TGO) was observed and a model to estimate the extent of deformation is proposed.

KEYWORDS
FAST/SPS, MAX phases, molten salt shielded synthesis, oxidation behavior, Ti$_2$AlC

1 | INTRODUCTION

The ternary carbides and nitrides of general formula M$_{n+1}$AX$_n$, where M corresponds to an early transition metal, A to an A-group element (mainly IIIA and IVA) of the periodic table and X being either carbon or nitrogen, have received considerable attention in the past two decades. These nanolaminated structures possess an unusual combination of both ceramic and metallic features. In addition to good thermal and electrical conductivities, this unique nature endows them with good elastic stiffness, machinability, high fracture toughness, thermal shock resistance, and damage tolerance. In addition, Al-containing MAX phases exhibit excellent oxidation resistance and a self-healing ability. Being encompassed in the category of alumina-forming materials, their outstanding oxidation resistance emanates from the formation of a protective slow growing Al$_2$O$_3$ scale. Especially, Ti$_2$AlC (8.2 × 10$^{-6}$/K between 25°C and 1300°C) arouse interest because of the good match of coefficient of thermal expansion (CTE) to that of Al$_2$O$_3$ (8.0 × 10$^{-6}$/K and 9.0 × 10$^{-6}$/K in the 25°C-1000°C and 25°C-1500°C ranges, respectively), hence reducing thermal stresses at high temperature.
However, synthesis of Ti$_2$AlC—and in general of all the MAX phase compositions—remains challenging when it comes to finding a compromise between high purity, large quantities (>1 kg) and affordable costs. Ti$_2$AlC can be synthesized by solid-state reaction methods at high temperature, but the bulk samples must be ground and milled to produce fine powders. First, the milling step consumes time and energy, with the risk of potential contamination and alteration of properties. Second, inert atmospheres are always employed to avoid oxidation of raw materials during synthesis, increasing the costs and complexity of the process. Additionally, the eventuality of upscaling the synthesis process should be considered. Furthermore, the synthesis of MAX phases in the Ti-Al-C system is

**TABLE 1** Various reported synthesis routes and corresponding phase composition

| Year | Reference | Synthesis route | Raw materials and synthesis parameters | Quantitative phase analysis | Observed phases (mass fraction) |
|------|-----------|----------------|----------------------------------------|----------------------------|--------------------------------|
| 2000 | 5         | Reactive hot isostatic pressing | Ti, Al$_2$C$_3$, graphite powders, argon, 30 h at 1300°C, 40 MPa | SEM + image analysis | Ti$_2$AlC (96%), Ti$_3$P + Al$_2$O$_3$ (4%) |
| 2007 | 8         | Solid-liquid reaction synthesis | Ti, Al, graphite powders | XRD + Rietveld refinement | Ti$_2$AlC (>99%) |
| 2016 | 11        | Pressureless sintering | Ti, Al, TiC powders with (Ti:Al:TiC = 1.00:1.05:0.95), argon, 1400°C | XRD + SEM + EBSD + image analysis | Ti$_2$AlC (95.14%), Al$_2$O$_3$ (3.3%), TiAl (1.4%), TiC (0.1%) |
| 2010 | 12        | Pressureless sintering | Maxthal 211, argon, 1 h at 1500°C | XRD | Ti$_2$AlC (92%), TiC (5%), Al$_2$O$_3$ (3%) |
| 2010 | 13        | Spark plasma sintering | CVD in-situ grown CNTs on TiAl particles using Co(NO$_3$)$_2$.6H$_2$O as catalyst, vacuum, 1200°C, 50 kN | XRD | Ti$_2$AlC (92%), TiC (5%), Ti$_2$Al$_3$ (3%) |
| 2015 | 14        | (A) Arc melting + (B) annealing + (C) quenching | (A) Ti, Al, graphite powders, argon, 5 min + (B) 6 h at 1350°C + 12 h at 1250°C + 750 h at 650°C + (C) 200°C/s in water | XRD + Rietveld refinement | Ti$_2$AlC (47%), Ti$_3$AlC$_2$ (30%), TiAl$_3$ (23%) |
| 2009 | 15        | Self-propagating high-temperature synthesis (SHS) | Ti, Al, carbon black powders + additions of TiC or Al$_2$C$_3$ with (Ti:Al:C = 2:1:1), argon | XRD + Peak intensity integration formula | Ti$_2$AlC (80%–90%), TiC (20%–10%) |
| 2010 | 16        | Mechanically activated SHS | Ti, Al, graphite powders, ~2000 K, argon | XRD + Pattern deconvolution | Ti$_2$AlC (95%), Ti$_3$AlC$_2$ (99.7%) when increasing Al content |
| 2019 | 17        | SHS | Ti, Al, graphite powders, argon | XRD + Rietveld refinement | Ti$_2$AlC (95.4%), TiAl$_2$ (4.6%) |
| 2011 | 20        | Proprietary method developed by 3-ONE-2 | N/A | XRD + Rietveld refinement | Ti$_2$AlC (67%), TiC (19%), Ti$_3$AlC$_2$ (14%) |
| 2011 | 21        | Proprietary method developed by Kanthal AB (Sandvik) | Maxthal 211 | XRD + Rietveld refinement | Ti$_2$AlC (84.3%), Ti$_3$AlC$_2$ (6.5%), TiC (5.1%), TiAl (4.1%) |
| 2017 | 22        | Proprietary method developed by Kanthal AB (Sandvik), combustion synthesis | Maxthal 211 | XRD + Rietveld refinement | Ti$_2$AlC (68.33%), Ti$_3$AlC$_2$ (14.02%), TiC (7.86%), Ti$_1.2$Al$_{0.8}$ (9.79%) |
| 2018 | 19        | Molten salt synthesis | Ti, Al, graphite powders, in 50:50 NaCl:KCl mixture, argon, 2 h at 1000°C | XRD + Rietveld refinement | Ti$_2$AlC (88%), Ti$_{0.9}$Al$_{1.1}$ (12%) |

*Volume fraction.

*Molar fraction.
usually known for competitive reaction pathways between Ti$_2$AlC and Ti$_3$AlC$_2$ phases, thus restricting purity criteria. Different synthesis routes with diverse outcomes were pursued and some of them (with purity values) are listed in Table 1. Solid-state-based synthesis routes such as reactive hot pressing, robotic hot isostatic pressing, solid-liquid reaction synthesis, reactive sintering, pressureless sintering, spark plasma sintering, arc melting, and self-propagating high-temperature synthesis (SHS) can be distinguished from ionic-liquid medium-assisted routes such as molten salt synthesis.

Barsoum et al. aimed the production of bulk polycrystalline Ti$_2$AlC via reactive hot pressing (HP) of a Ti:Al:C mixture at 1600°C and 40 MPa. The same authors managed to synthesize Ti$_2$AlC by reactive hot isostatic pressing of a similar powder blend at 1300°C and 40 MPa, almost removing all traces of secondary phases after annealing for 30 hours. Another solid-state reaction synthesis method with Ti, Al, and graphite was employed by Kisi et al., yielding a >99 wt. % pure product. An identical starting composition to that of Barsoum et al. was used by Gauthier-Brunet et al. They proceeded by reactive sintering between 570°C and 1400°C for 1 hour of a high pressure cold-compacted mixture, eventually having TiC impurities in the as-synthesized product. By means of pressureless sintering, Benitez et al. obtained high purity Ti$_2$AlC along with TiAl, TiC, and Al$_2$O$_3$ ancillary phases, using Ti, Al, and TiC as reactants. The same approach was used by Zhou et al. with fine commercial Maxthal® Ti$_2$AlC powder. Elemental powders of Ti, Al, and C have been used in various other routes, such as arc melting or SHS. Ti-aluminides and TiC were always found in the final product. A maximum yield of 99.7% of Ti$_2$AlC and Ti$_3$AlC$_2$ was obtained by Hendaoui et al. after a mechanical activation of elemental powders and additions of excess Al. As mentioned earlier, these techniques lead to bulk dense samples, necessitating additional high-energy pulverization means to end up with a powdered product. Ti$_2$AlC produced by proprietary methods developed by 3-ONE-2 and Kanthal AB also contained non-negligible amounts of impurities, knowing TiC, TiAl, and Ti$_{1.2}$Al$_{0.8}$.

Recently, Ti$_2$AlC was synthesized by Galvin et al. using a molten salt method. They separately used NaCl, KCl, and a NaCl/KCl mixture as synthesis medium. They reached a maximal purity of 88 wt. % Ti$_2$AlC, when performing the experiment at 1000°C in argon for 5 hours and using the NaCl/KCl mixture. The as-synthesized Ti$_2$AlC was recovered by grinding with mortar and pestle and washing out the salt with water.

The molten salt shielded synthesis (MS3) method described elsewhere can be considered as an efficacious alternative to synthesis techniques mentioned earlier. A gas-tight salt encapsulation enables experiments to be conducted in air and at lower temperatures than conventional synthesis routes—commonly employing protective atmospheres such as argon—hence reducing processing costs. In addition, pure (>96 wt. %) and homogeneous MAX phase powders can be obtained and the technique yielded promising results for the synthesis of Ti$_3$SiC$_2$. The inter-diffusion of elements in the menstruum of molten salt is enhanced and the recovery of the final product is done through a simple water-based leaching step, without additional milling steps. The finely granulated powder can be further processed into desired components via conventional ceramic processing.

For reasons mentioned above, Ti$_2$AlC has high potential for uses in oxidizing environments. It naturally forms a protective Al$_2$O$_3$ scale, limiting the diffusion rate of oxygen and therefore slowing down further material consumption. Differences in oxidation kinetics are found in literature due to the discrepancies in microstructural features. Large grains (>10 μm) indeed promote parabolic to linear oxidation behavior, while cubic or power law fitted kinetics are usually observed for fine-grained (between 1 and 10 μm) microstructures. However, the influence of surface quality on oxidation is not documented so far. To the best of the authors’ knowledge, only one study mentioned about breakaway oxidation of damaged surfaces and fast buildup of large inter-twined rutile crystals. Nevertheless, further studies about the relation between surface quality and oxidation response are required to understand the behavior of the material in harsh environments.

In this work, Ti$_2$AlC powder synthesized by MS3 was densified by following two approaches, pressureless sintering (PS) and field-assisted sintering technology/spark plasma sintering (FAST/SPS). The samples with the highest density were used for oxidation experiments. Prior to oxidation, their surfaces were prepared using three degrees of finishing, viz., polishing to 50 nm silica suspension, grinding with grit size P80 SiC abrasive paper and sandblasting with F36 Al$_2$O$_3$ particles. Oxide growth was essentially correlated with the initial surface roughness.

2 | EXPERIMENTAL PROCEDURE

2.1 | Material synthesis

Ti$_2$AlC powder was synthesized by the MS3 method, following a similar procedure as elsewhere. Briefly, elemental powders of Ti (−325 mesh, 99.5%, Alfa Aesar), Al (−325 mesh, 99.5%, Alfa Aesar) and graphite (APS 7-11 μm, 99%, Alfa Aesar) were mixed in different molar proportions as shown in Table 2. KBr (99%, Alfa Aesar) powder was mixed with the starting precursors in a 1:1 weight ratio. The
raw materials were mixed in ethanol using zirconia balls (Ø 5 mm) and a 3D shaker mixer (Turbula, Willy A. Bachofen AG, Switzerland) for 24 hours. Afterward, the mixture was dried in a rotary evaporator (Rotavapor R-215, BÜCHI Labortechnik AG, Switzerland) at 70°C, followed by sieving through a 300 µm sieve.

The dried mixture was compacted into 20-mm diameter pellets at 200 MPa with a uniaxial hand press (PW 10, P/O/Weber GmbH, Germany).

The samples were placed in a cylindrical alumina crucible, which was subsequently filled with KBr. The alumina crucibles were heated in a high-temperature furnace (HT 32/17, Nabertherm GmbH, Germany) in air at a rate of 5°C/min with different holding times at peak temperatures from 950°C to 1050°C, as indicated in Table 2. Beyond cooling, the crucible was washed with hot water to remove the salt. Vacuum filtration of Ti2AlC powder was carried out with boiling deionized water and ethanol to further reduce the salt content. Finally, the powder was dried at 70°C and passed through a 25 µm sieve.

The influence of three process temperatures (950°C, 1000°C and 1050°C), four holding times (1, 5, 10, and 15 hours) and different Ti:Al:C stoichiometries (2:1:1, 2:1:0.8, 2:1:0.9, and 2:1:0.95) on phase composition were investigated (Table 2).

### Table 2

| Sample Nomenclature | Temperature (°C) | Holding time (h) | Stoichiometry Ti:Al:C | Detected phases (mass fraction) |
|---------------------|-----------------|------------------|-----------------------|---------------------------------|
| TAC-1               | 950             | 5                | 2:1:1                 | Ti₂AlC (83%), Ti₃AlC₂ (13%), TiC (3%), Ti²⁺ |
| TAC-2               | 1000            | 5                | 2:1:1                 | Ti₂AlC (83%), Ti₃AlC₂ (73%), TiC (27%) |
| TAC-3               | 1050            | 5                | 2:1:1                 | Ti₂AlC (41%), TiAl (24%), TiC (23%), Ti₅Al (8%), O (4%) |
| TAC-4               | 1000            | 1                | 2:1:1                 | Ti₂AlC (83%), Ti₃AlC₂ (17%) |
| TAC-5               | 1000            | 10               | 2:1:1                 | Ti₂AlC (75%), Ti₃AlC₂ (25%) |
| TAC-6               | 1000            | 15               | 2:1:1                 | Ti₂AlC (75%), Ti₃AlC₂ (25%) |
| TAC-7               | 1000            | 5                | 2:1:0.8               | Ti₂AlC (90%), Ti₃Al (3%), TiAl (3%), TiC (2%), Ti (2%) |
| TAC-8               | 1000            | 5                | 2:1:0.9               | Ti₂AlC (91%), Ti₃AlC₂ (6%), Ti (2%), TiC²⁺ |
| TAC-9               | 1000            | 5                | 2:1:0.95              | Ti₂AlC (82%), Ti₃AlC₂ (13%), Ti (3%), TiC (2%) |
| TAC-2               | 1000            | 5                | 2:1:1                 | Ti₂AlC (83%), Ti₃AlC₂ (17%) |
| TAC-10              | 1000            | 5                | 2:1:0.05              | Ti₂AlC (82%), Ti₃AlC₂ (16%), TiAl (2%) |
| TAC-11              | 1000            | 5                | 2:1:1:1               | Ti₂AlC (67%), Ti₃AlC₂ (23%), TiAl (5%), Ti₂Al₅ (4%), Ti²⁺ |

*Indicates the presence of non-negligible traces. Minute amounts (<1%) of KBr, Al₂O₃, and free carbon were detected in all samples. TAC-2 is the reference batch.

2.2 | Material processing

Sintering studies and densification were performed using the optimized composition (2:1:0.9, 1000°C, 5 h, particle size <25 µm). Ti₂AlC was consolidated using two different techniques: pressureless sintering (PS) and field-assisted sintering technology/spark plasma sintering (FAST/SPS). For PS, green compacts (Ø 13 mm) were pressed at
200 MPa in a steel die using a uniaxial press (PW 10, P/O/Weber GmbH, Germany). Densification was carried out in a vacuum chamber furnace (HTK 25 Mo/16-1G Ar, Gero Hochtemperaturöfen GmbH, Germany), under argon atmosphere. The samples were heated up to maximal temperatures of 1300°C and 1400°C at a rate of 5°C/min with an isothermal holding time of 3 hours. For FAST/SPS, as-synthesized Ti₂AlC powder was pre-compactated at 50 MPa in a graphite die (inner diameter of 20 mm). Graphite foil was used between powder and graphite die/punches to enable mechanical, electrical and thermal contact during sintering as well as to prevent reactions between the die and Ti₂AlC. The die was additionally lined with a carbon felt for better thermal insulation. The Ti₂AlC powder was densified in a FAST/SPS furnace (FCT-HPD5, FCT Systeme GmbH, Germany) at a heating rate of 100°C/min up to 1200°C and 50 MPa uniaxial pressure in vacuum (~4 mbar). The pressure was applied at the beginning of the sintering cycle, before heating. The samples were hold at the maximal temperature and pressure for 10, 30, and 60 minutes. Temperature was monitored using an axial pyrometer, which was focused on the surface of the upper drilled punch, close to the specimen. Samples were ground after densification to remove the remainder of graphite foil.

For microstructural analysis, samples were cut, mounted, ground, and polished to a 50 nm colloidal silica suspension (OP-S, Struers ApS, Denmark).

A pellet sintered by FAST/SPS was cut into three portions using a diamond-studded wire saw. The first portion was ground with P80 silicon carbide (SiC) abrasive paper, meanwhile the second sample was sandblasted (MHG Strahlanlagen GmbH, Germany) at a pressure of 4 bar with coarse F36 (420-595 µm) Al₂O₃ particles. The third part was ground with P4000 SiC paper, followed by diamond polishing (3 and 1 µm) and eventually polished with OP-S. All three parts were oxidized in static air in a high-temperature furnace (HTC 03/15, Nabhertherm GmbH, Germany) at a rate of 10°C/min until 1200°C, and kept at this temperature for 50 hours.

2.3 | Material characterization

Particle size distribution (PSD) of the Ti₂AlC powders was measured by laser diffraction (Horiba LA950-V2, Retsch GmbH, Germany). Phase composition of the synthesized powders and consolidated samples were determined by X-ray diffraction (XRD) using a Bragg-Brentano diffractometer in 0-20 geometry (D4 Endevor, Bruker AXS GmbH, Germany). The scans were conducted with a step size of 0.02° 20 and a step time of 0.75 seconds in the 20 = 5°-80° range. Diffractograms were plotted in the 20 = 7°-80° range. Qualitative phase analysis was performed with the HighScore Plus 3.0.5 software (PANalytical BV, Netherlands). Rietveld refinement was done with TOPAS V4 (Bruker AXS GmbH, Germany). Titanium, aluminum, and potassium contents were determined using inductively coupled plasma optical emission spectrometry (ICP-OES, iCAP 7600, Thermo Fisher Scientific, USA), meanwhile carbon and oxygen contents were analyzed using carbon/sulfur and nitrogen/oxygen/hydrogen-determinators (CS600 and TCH600, Leco Instrumente GmbH, Germany), respectively.

Morphology of as-synthesized powder particles, microstructure of bulk samples, cross-sections and fracture surfaces were observed using scanning electron microscopy (SEM, Zeiss Ultra55 and Zeiss Crossbeam 540, Carl Zeiss AG, Germany). In addition, elemental composition was characterized by energy-dispersive X-ray spectroscopy (EDS), which is attached to the SEM. Grain size and morphology were characterized using electron backscatter diffraction (EBSD-Camera, Nordlys II, EBSD-Software, Aztec, Oxford Instruments, United Kingdom) coupled to SEM (Zeiss Merlin, Carl Zeiss AG, Germany). Crystal structures were retrieved from the Inorganic Crystal Structure Database (ICSD).

Bulk and absolute densities of green compacts and sintered samples were determined using mass-volume measurements and volume displacement by Archimedes’ principle respectively. Based on these results, on Rietveld refinement and on values of theoretical density, relative density of multiphase specimen was estimated using the rule of mixture. Porosity of pressureless-sintered samples was determined by image analysis using the Fiji package of the ImageJ software. The degree of preferred orientation (η) of raw powders and sintered samples was calculated after determining the March-Dollase parameter (r) with the TOPAS software. The following formula (Equation 1) was used:

\[
\eta = 100\% \left( \frac{1 - r^3}{1 - \eta^3} \right)^{1/2}. \tag{1}
\]

Surface roughness of parts intended for oxidation experiments was characterized using a noncontact profilometer (cyberSCAN CT 350T, cyberTECHNOLOGIES GmbH, Germany) equipped with a chromatic sensor head (CHRocodile E1000, Precitec Optronic GmbH, Germany). Surfaces (~4 mm × 4.5 mm) were analyzed with a scan step size of 50 µm in x-direction and increments of 1 µm in y-direction. Arithmetical mean roughness (R_a), root mean squared roughness (R_q), mean roughness depth (R_z), and maximum roughness depth (R_max) were determined using the SCAN CT 8.10 surface metrology software.

Thermogravimetric analysis (TGA) was performed in a high-temperature silicon carbide furnace (STA 449 F1, Netzsch GmbH, Germany) in the same conditions as the oxidation experiments and the data analyzed with the
Proteus® software. Parabolic and cubic fitting was performed using the equations relating the mass gain per unit area, the corresponding rate constants and the oxidation time, and the R² values were determined to estimate goodness-of-fit.

3 | RESULTS AND DISCUSSION

3.1 | Synthesis

Three synthesis parameters were varied independently, temperature, composition, and holding time (Table 2). At first, the maximal temperature was optimized with values between 950°C and 1050°C, keeping the stoichiometry and holding time constant. The sample predominantly contained Ti₂AlC for all the temperatures (Figure 1A), although the diffractograms revealed the presence of secondary phases such as Ti₃AlC₂, TiC, unreacted Ti and residual graphite. KBr is also detected in low amounts in all samples (most visible at 2θ = 27° and 2θ = 47.7°), being entrapped within uncrushed hard agglomerates. The main peak of graphite (002) overlaps with KBr (200). The remainder of Ti reacted at higher temperature (T ≥ 1000°C), and its reflection (101) at 2θ = 40.1° disappeared on the corresponding diffractograms. The fraction of Ti₃AlC₂ gradually increased with temperature due to the reactions between Ti₂AlC and TiC. As stated by Wang et al., three nonoverlapping peaks (2θ = 9.5° for Ti₃AlC₂ (002), 2θ = 13° for Ti₂AlC (002) and 2θ = 35.9° for TiC (111)) can be considered in order to have a first estimation of phase composition. Rietveld refinement corroborated the presence of 83 wt. % Ti₂AlC, 13 wt. % Ti₃AlC₂, 3 wt. % TiC, and traces of Ti at 950°C (Table 2). The expected formation mechanisms of Ti₂AlC resemble reactions proposed in literature, but do not unequivocally constitute an evidence of each product formation via the molten salt synthesis route. Type-I aluminides, TiAl and Ti₃Al, nucleated on Ti particles (Equations 4 and 5). Gauthier-Brunet et al. reported the formation of Ti₃Al layers around Ti particles in the case of reactive sintering. Školáková et al. demonstrated that Ti particles were surrounded with Ti₃Al, TiAl, as well as aluminum rich TiAl₂ and TiAl₃ phases in the case of reactive sintering of a mixture of Ti and Al at 700°C for 20 minutes. In our case at this range of temperature, KBr is still in a solid state.

\[
\begin{align*}
\text{Ti}_2\text{AlC}_2 \quad \text{+ xC} & \rightarrow \text{TiC}_x
\end{align*}
\]

\[
\begin{align*}
\text{Al} & \rightarrow \text{Al}\,(l)
\end{align*}
\]

\[
\begin{align*}
\text{Ti}_2\text{AlC}_2 \quad \text{+ Al}\,(l) & \rightarrow \text{TiAl}
\end{align*}
\]

\[
\begin{align*}
3\text{Ti}\,(s) & + \text{Al}\,(l) \rightarrow \text{Ti}_3\text{Al}\,(s) \quad (−22.6\text{kJ.mol}^{-1} < ΔG_0^f < −21.2\text{kJ.mol}^{-1})
\end{align*}
\]

At 735°C, KBr reached its melting point, enveloping the remainder of molten Al, graphite, unreacted Ti, TiC-, and Ti₃Al-templated Ti particles. As expected in a molten salt process, atomic diffusion is enhanced by the presence of a liquid media. Quenching performed with a Ti-Si-C system and molten salt diffusion experiments with pure Ti showed that large diffusion spheres were present around elements from...
the starting materials and that elements diffused deeply into the molten salt. It suggests a high solubility of Ti in molten KBr. The dissolution of graphite in titanium aluminides was reported in the 800-900°C range for reactive sintering. In a molten salt medium though, it is unlikely that graphite dissolves and the process is believed to be based on a “template growth” scheme as reported by Liu et al. for TiC coatings on graphite flakes. The formation of the intermediate Ti$_2$AlC phase (Equation 6) can be expected in the present work, but through a different mechanism. However, its presence was not evidenced.

$$\text{Ti}_3\text{Al} + \text{C} \rightarrow \text{Ti}_2\text{AlC} + \text{TiC} \quad (–83.8 \text{kJ mol}^{-1} < \Delta G^\circ < −67.4 \text{kJ mol}^{-1})$$

(6)

This phase was found to be stable up to 1200°C during reactive sintering. However, in the present work, Ti$_3$AlC may have reacted in its entirety with C and Ti-Al intermetallic compounds before 950°C (Equations 7), since no peaks attributed to this phase were observed on the corresponding diffractogram (Figure 1A). The reduction of reaction temperatures is enabled by the presence of the KBr melt and the improved solid-liquid diffusion in this medium, hence reaction kinetics are different from solid-state synthesis. In fact, the formation of Ti$_2$AlC at 900°C was already reported by Galvin et al. for a molten salt synthesis process in argon.

$$\text{Ti}_3\text{AlC} + \text{C} \rightarrow \text{Ti}_2\text{AlC} + \text{TiC} \quad (–183 \text{kJ mol}^{-1} < \Delta G^\circ < −175 \text{kJ mol}^{-1})$$

(7A)

$$\text{Ti}_3\text{AlC} + \text{C} \rightarrow \text{Ti}_3\text{AlC}_2 + \text{TiC} \quad (−12 \text{kJ mol}^{-1} < \Delta G^\circ < −10 \text{kJ mol}^{-1})$$

(7B)

At 1000°C, the composition was essentially biphasic (83 wt. % Ti$_2$AlC, 17 wt. % Ti$_3$AlC$_2$). Ti$_2$AlC may have further reacted with TiC to form Ti$_3$AlC$_2$ according to Equation 8. This reaction occurred at lower temperature than reported. The possibility of a peritectic reaction between TiC$_4$ and liquid Ti-aluminides as reported by Khoptiar et al. for SHS is dismissed. The reaction temperature reached in the present work is far below the melting point of these intermetallics. At 1050°C, the content of Ti$_3$AlC$_2$ increased at the expense of Ti$_2$AlC. In fact, an increase of 50°C in the process temperature caused a decrease of 10% in the Ti$_2$AlC content.

$$\text{Ti}_2\text{AlC} + \text{TiC} \rightarrow \text{Ti}_3\text{AlC}_2 \quad (\Delta G^0 = +165 \text{kJ mol}^{-1})$$

(8)

Standard free energies of reaction were calculated in the 1000-1273 K range for Equations (5), (6), (7A), (7B) and (8) according to data found in literature and yielded negative values for (5), (6), (7A), and (7B) but positive for (8). It appears that Equation 8 may not be thermodynamically favorable, and that the formation of Ti$_3$AlC$_2$ may originate from Equation 7B instead.

Thus, below 1000°C, reactions were not completed and residual TiC, Ti, and C were detected. At 1000°C, the composition was essentially biphasic and samples predominantly contained Ti$_2$AlC and Ti$_3$AlC$_2$. Above 1000°C, phase transformation started to occur, hence a reduction in Ti$_2$AlC purity was noticed. Therefore, the intermediate temperature of 1000°C was considered as a good compromise to maintain a high Ti$_2$AlC phase purity, without having detrimental impurities for oxidation experiments.

Furthermore, the holding time was optimized, fixing the other parameters at 1000°C for the maximal temperature and 2:1:1 for the molar ratio. Figure 1B displays XRD patterns of samples held for 1, 5, 10, and 15 hours. For the shortest holding time, intermetallics (TiAl, Ti$_3$Al) and TiC were present in considerable amounts due to incomplete reactions between raw materials, representing over half the weight fraction of the sample (Table 2). Presence of TiC and aluminides were also reported for short dwell times (2 hours), and an increase to 5 hours promoted formation of more Ti$_3$AlC. The absence of Ti$_3$AlC suggests that formation kinetics of Ti$_3$AlC and Ti$_2$AlC are probably much different. Gauthier-Brunet et al. assumed a slow and fast formation of both Ti$_3$AlC and Ti$_2$AlC, respectively. Additionally, no peak for Ti$_3$AlC$_2$ was evidenced for an 1 hour dwell time, pointing out slow formation kinetics for this phase too (Equation 7B). Increasing the holding time to 5 hours promoted the reaction of Ti-aluminides, TiC and Ti$_3$AlC$_2$ phases. The characteristic strong reflections of both phases appeared and overlapped over the 2θ=38-40° range. Longer holding times generated an increasing percentage of Ti$_3$AlC$_2$, visible through a slight dissociation of Ti$_3$AlC$_2$ (008) and Ti$_3$AlC$_2$ (006) in the above mentioned 20 range and a decrease in the Ti$_2$AlC (002) to Ti$_3$AlC$_2$ (002) peak intensity ratio.

Thus, short holding times were not suitable for completion of reactions. After 1 hour, the amount of impurities was substantial. After 5 hours, the composition was mainly biphasic and samples predominantly contained Ti$_2$AlC and Ti$_3$AlC$_2$. After 10 hours, the amount of Ti$_2$AlC decreased by 8%, as a result of gradual phase transformation, even though Ti$_2$AlC and Ti$_3$AlC$_2$ were still the only two detected phases. Thereby, an optimal holding time of 5 hours was retained.

Finally, the third parameter was optimized, where both Al and C contents were varied alternately (Figure 1C and Table 2), keeping the temperature and holding time constant according to former optimization. The stoichiometric sample served as reference. Sub-stoichiometric carbon contents as well as minor excesses of Al were investigated. Al hyper-stoichiometries were reported by various authors as a way to promote reactions between TiC and intermetallics and to counterbalance losses of high vapor pressure A-element during the synthesis of Al MAX phases. A carbon-deficient stoichiometry of 2:1:0.8 suppressed the formation of Ti$_3$AlC$_2$. Reflections of Ti-aluminides, TiC as well as unreacted Ti were observed. Carbon deficiency limited the overall reaction, though unreacted graphite was still
observed after magnifying XRD diffractograms in the specific 2θ range. High content of Ti₂AlC (90 wt. %, Table 2) suggested fast completion of Equation 7A. However, remaining Ti showed that Equation 2 was limited by the lack of graphite. At a molar ratio of 2:1:0.9 the intermetallic phases reacted. The content of TiC was strongly reduced and detected as traces, meanwhile presence of unreacted Ti was still evidenced. The maximum Ti₂AlC and MAX phase (Ti₂AlC + Ti₃AlC₂) yields were achieved (91 wt. % and 97 wt. % respectively). At a molar ratio of 2:1:0.95, contents of Ti₃AlC₂ and TiC increased to the expense of the Ti₂AlC MAX phase. An increase in the Al content (not shown on diffractograms) did not lead to higher Ti₂AlC phase purity (Table 2). The excess of Al is confined in the salt bed during MS³, hence losses of A-element are not expected, unlike during conventional synthesis routes. Al-rich intermetallic compounds, such as titanium trialuminide (TiAl₃) and Ti₂Al₅ were evidenced. Ti-rich compounds (TiAl and Ti₃Al) were not detected. Their free energies of formation are higher than that of TiAl₃ for the considered temperature range. The formation of TiAl₃ can be given by Equation 9. Ti₂Al₅ is known to require TiAl₃ as intermediate product and forms through a series of reactions. Its formation can be explained via Equations 10, 11, and 12.

\[ Ti₂Al₅(s) + Al(l) \rightarrow 2TiAl₃(s) \]  
\[ TiAl₃(s) + TiAl₂(s) \rightarrow Ti₂Al₅(s) \]  
\[ 2Ti(s) + 5Al(l) \rightarrow Ti₂Al₅(s) \]

TABLE 3  Element analysis of raw materials and as-synthesized Ti₂AlC MAX phase powders (B₁, B₂, and B₃ indicate batch numbers)

| Powders    | Element content (wt. %) | O     | K     | Ti    | Al    | C     |
|------------|-------------------------|-------|-------|-------|-------|-------|
| Ti         | Balance                 | 0.855±0.010 | -     | Balance | -     | -     |
| Al         | 0.420±0.040              | -     | -     | Balance | -     | -     |
| C          | 0.242±0.003              | -     | -     | -     | Balance | -     |
| TAC-8-B₁   | 2.399±0.003, 0.308±0.005 | 71.800±0.800 | 21.800±0.800 | 7.957±0.012 |
| TAC-8-B₂   | 1.91±0.090, 0.324±0.004  | 69.700±0.600 | 22.900±0.300 | 7.926±0.007 |
| TAC-8-B₃   | 1.760±0.060, 0.509±0.003 | 69.700±0.500 | 22.700±0.300 | 8.010±0.050 |

FIGURE 2  Features of Ti₂AlC powder produced by MS³. (A) presence of uncrushed hard agglomerates, (B) surface morphology, and (C) nanolaminated structure [Color figure can be viewed at wileyonlinelibrary.com]
Table 3. It was the reason for the presence of alumina after MS. Potassium cations were also detected in minute amounts by ICP-OES, which may be due to the residual amount of KBr present in uncrushed agglomerates.

Secondary electron (SE) SEM images (Figure 2) show features of as-synthesized Ti$_2$AlC. Figure 2A shows one of these large hard agglomerates contained in the as-synthesized Ti$_2$AlC powder. The morphology of Ti$_2$AlC synthesized by MS$^3$ was rather globular, not acicular like Ti$_3$AlC$_2$. Galvin et al.$^{19}$ reported broad peaks in their XRD patterns and pointed out the presence of nanocrystals. In this work, submicron sized primary particles were also observed (Figure 2B). These primary particles formed larger clusters with smooth surfaces, unlike Ti$_3$SiC$_2$ for which the sharp nanolaminated structure has been distinctly seen.$^{24}$ Higher magnifications were required to identify individual layers (Figure 2C).

The powder showed a bimodal PSD, with $D_{10}$, $D_{50}$, and $D_{90}$ values of 8.4, 18.8, and 54.8 $\mu$m, respectively (Figure 3A). A narrow monomodal PSD was achieved using a 500-mesh sieve, attaining $D_{10}$, $D_{50}$, and $D_{90}$ values of 7.5, 13.6, and 22.9 $\mu$m respectively.

EBSD analyses of cold-compacted as-synthesized Ti$_2$AlC powders (Figure 4) gave an insight into primary particle size, particle shape, and phases. The phase map (Figure 4B) shows that Ti$_2$AlC particles are agglomerates of Ti$_2$AlC nanocrystals with a mean size of $\sim$0.9 $\mu$m (Table 4). In addition, isolated grains of Al$_2$O$_3$ and Ti$_3$AlC$_2$ in small proportions were detected. EBSD images demonstrated that Ti$_2$AlC particles were composed of a multitude of primary particles and highlighted the fine-grained microstructure of Ti$_2$AlC synthesized by MS$^3$. It is potentially due to multiple nucleation of product phases on particles of elemental reactants assisted by the molten salt during synthesis. Grain size was submicrometric for both Ti$_2$AlC and Ti$_3$AlC$_2$, and average grain aspect ratio was between 1 and 2, indicating a quasi-equiaxed grain morphology (Table 4).

This powder was used for subsequent steps in the present work.

### 3.2 Sintering

#### 3.2.1 Pressureless sintering

Pressureless sintering (PS) of Ti$_2$AlC in argon was investigated. Bulk green density of cold-compacted bodies was 54% of the theoretical. At 1300°C (Figure 5A), samples (PS-1300) exhibited a relative density of $\sim$70%–75% with a continuous network of large interconnected pores ($\sim$20 $\mu$m). At 1400°C (Figure 5B), samples (PS-1400) achieved higher relative density ($\sim$88%–90% of the theoretical), similar to values mentioned in literature$^{43,44}$. The microstructure of these samples showed a multitude of submicrometer-sized pores scattered between a few larger ones ($\sim$5-10 $\mu$m). Higher

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**Table 4** Grain size and grain aspect ratio outcomes of EBSD analyses for as-synthesized Ti$_2$AlC powder

|          | Average grain size ($\mu$m) | Average grain aspect ratio |
|----------|-----------------------------|---------------------------|
| Ti$_2$AlC | 0.93 ± 0.42                 | 1.75 ± 0.52               |
| Ti$_3$AlC$_2$ | 0.66 ± 0.12               | 1.73 ± 0.63               |

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**Figure 3** Sieving of Ti$_2$AlC powder produced by MS$^3$: (A) volume particle size distributions of as-synthesized and sieved powders, (B) presence of agglomerates homogeneous in size after sieving [Color figure can be viewed at wileyonlinelibrary.com]

**Figure 4** EBSD analysis of compacted as-synthesized Ti$_2$AlC powder: (A) SE image and (B) phase map corresponding to the dashed area [Color figure can be viewed at wileyonlinelibrary.com]
magnification (Figure 5C) showed the presence of needle-shaped grains/clusters of grains of Ti$_3$AlC$_2$ confirmed by EDS. The submicrometer-sized pores were predominantly located within clusters of Ti$_3$AlC$_2$ grains. Dark-grey Al$_2$O$_3$ grains were observed with backscattered electrons (BSE). The sintering atmosphere certainly contained few ppm of oxygen, responsible for local oxidation of Al, though, it is believed that Al$_2$O$_3$ was essentially present before PS, as evidenced by the oxygen content in as-synthesized Ti$_2$AlC powders (Table 3). The observed relief was due to disparate etching of Ti$_2$AlC and Ti$_3$AlC$_2$ MAX phases during the final polishing step. The Al content being higher in Ti$_2$AlC, it is more predisposed to etching by OP-S than Ti$_3$AlC$_2$. The differences in topography between Ti$_2$AlC and Ti$_3$AlC$_2$ were not caused by differences in hardness. Specimen sintered at both temperatures showed a substantial increase in the Ti$_3$AlC$_2$ phase content (Figure 6 and Table 5). Rietveld refinement evidenced 81 wt. %, 17 wt. %, and 2 wt. % of Ti$_2$AlC, Ti$_3$AlC$_2$, and Al$_2$O$_3$, respectively. Unreacted graphite was gradually consumed (disappearance of the C (002) reflection at $2\theta = 27^\circ$) and contributed to the formation of Ti$_3$AlC$_2$ via mechanisms described above. Additionally, a phenomenon of phase interconversion is believed to occur, as described by Kisi et al.$^8$ Al planes are thought to slowly diffuse out of Ti$_2$AlC into TiC. Ti$_6$C octahedra come close to each other forcing Ti to diffuse out. The Ti$_3$AlC$_2$ structure eventually collapses into Ti$_3$AlC$_2$.

As a result, full densification of Ti$_2$AlC without any alteration cannot be attained by pressureless sintering. Consequently, an electric field/pressure assisted sintering technique was employed in order to rapidly reach near full densification with minimal purity degradation.

### 3.2.2 | FAST/SPS

Ti$_2$AlC powders were sintered by FAST/SPS at lower temperatures (1200°C) than PS under a pressure of 50 MPa in vacuum. For reasons mentioned in the section above, aim was to achieve near full densification by concomitantly limiting phase transformation. A higher heating rate (100°C/min) as compared to PS was used. The onset of densification was around 800-850°C, and the specimen (Figure 7A) exhibited higher relative density (98.5% of the theoretical) after a 10 minutes dwell time at
1200°C, with pore size below 5 µm. Topographical differences were also observed due to different chemical etching of Ti2AlC and Ti3AlC2 phases during the final polishing step. On account of denser microstructures, clusters of Ti3AlC2 grains were more discernable on SEM images of SPS-1200 samples (Figure 7B). They were ~10-20 µm in size. Less phase transformation (Figure 8 and Table 6) was observed as compared to PS samples due to the shorter sintering times, slightly reducing the extent to which Ti2AlC2 is formed. Quantitative phase analysis evidenced 84 wt. %, 14 wt. %, and 2 wt. % of Ti2AlC, Ti3AlC2, and Al2O3, respectively. Traces of unreacted Ti present in as-synthesized Ti2AlC were entirely consumed (disappearance of the Ti (101) reflection at 2θ = 40.1°), contributing to the formation of Ti2AlC and Ti3AlC2. The TiC (111) reflection at 2θ = 35.9°, hardly discernable for Ti2AlC powder (unsintered sample), was not evidenced after SPS. It was consumed during sintering, proving that the remainder of unreacted Ti did not promote the formation of additional TiC. However, minute amounts of free carbon were still detectable. A non-negligible amount of Al2O3 was detected in SPS-1200, as for PS. The degree of preferred orientation was 7.37 for SPS-1200, indicating a slight texturing.

EBSD analyses (Figure 9) gave an insight into grain size, grain shape and phases of SPS samples. The previously observed relief, also appearing on Figure 9A, are either single grains of Al2O3 or clusters of Ti3AlC2, as displayed on the phase map (Figure 9B). Ti2AlC produced by MS3 and sintered by FAST/SPS showed a submicron fine-grained microstructure. Grain sizes of the three phases are below 1 µm (Table 7), indicating that sintering by FAST/SPS did not promote grain growth. Increasing holding times had no influence on grain growth and the microstructure remained the same after one hour of sintering. To the authors’ best knowledge, it is the smallest grain size reported so far for Ti2AlC. For instance, direct synthesis of Ti2AlC by FAST/SPS of elemental

| Sample                  | Detected phases (mass fraction)                                      | Density (% of TD) | March-Dollase parameter | Degree of preferred orientation (η) |
|-------------------------|---------------------------------------------------------------------|-------------------|-------------------------|-----------------------------------|
| Unsintered (raw powder) | Ti2AlC (91%), Ti3AlC2 (6%), Ti (2%), TiC, Ca                        | 54                | 1b                      | → 0°                               |
|                         |                                                                     |                   | 1c                      | → 0°                               |
| SPS-1200                | Ti2AlC (84%), Ti3AlC2 (14%), Al2O3 (2%), Ca                         | 98.5              | 0.88b                   | 7.37b                              |
|                         |                                                                     |                   | 1c                      | → 0°                               |
| PS-1300                 | Ti2AlC (81%), Ti3AlC2 (17%), Al2O3 (2%)                             | 70-75             | N/A                     | N/A                                |
| PS-1400                 | Ti2AlC (78%), Ti3AlC2 (20%), Al2O3 (2%)                             | 88-90             | N/A                     | N/A                                |

*Indicates the presence of traces.

bmeasured for Ti2AlC (002).
cmeasured for Ti3AlC2 (002). Density is given as compared to the theoretical density (TD). Values for PS samples are indicated for comparison.
reactants at 1100°C and 30 MPa in vacuum, using a heating rate of 80°C/min and a dwell time of one hour, yielded large elongated grains of 20 µm by 5 µm\textsuperscript{41}. Another work\textsuperscript{13} based on FAST/SPS of TiAl-carbon nanotube powder at 1200°C and 160 MPa in vacuum produced coarse grains as well (>10 µm according to SEM images). The average aspect ratio of Ti\textsubscript{2}AlC grains was close to 1.6 (Table 7), indicating a more symmetrical nature than for Ti\textsubscript{3}AlC\textsubscript{2} grains. Longer holding times had no influence on grain aspect ratio either. Al\textsubscript{2}O\textsubscript{3} grains were in the same size range. The average aspect ratio was closer to that of Ti\textsubscript{2}AlC. Al\textsubscript{2}O\textsubscript{3} grains, when not spherical, had a more equiaxed morphology as compared to both Ti\textsubscript{2}AlC and Ti\textsubscript{3}AlC\textsubscript{2} grains.

Fractured surfaces (Figure 10A) confirmed the fine-grained microstructure evidenced with EBSD analysis. Higher magnifications (Figure 10B) were required to visualize single MAX phase layers and mesopores.

Thereby, FAST/SPS turned out to be a rapid sintering method to enable near full densification of Ti\textsubscript{2}AlC powders with 10 minutes of dwell time at 1200°C. At the same time, phase transformation/conversion was limited and original grain size was retained, which are important features for good oxidation resistance.\textsuperscript{28}

### 3.3 Oxidation

Ti\textsubscript{2}AlC samples were oxidized at 1200°C in static air for 50 hours, at a rate of 10°C/minute. The temperature was selected according to other works.\textsuperscript{3,30,45,46} Most oxidation studies of Al-MAX phases have been based on polished surfaces. The effect of surface quality was therefore studied, by means of polished, ground, and sandblasted Ti\textsubscript{2}AlC before oxidation. Values for polished and ground samples are indicated with a cut-off wavelength $\lambda_c = 250$ µm and for sandblasted samples with a cut-off wavelength $\lambda_c = 800$ µm. $R_a = \text{arithmetical mean roughness}$, $R_q = \text{root mean squared roughness}$, $R_z = \text{mean roughness depth}$, $R_{max} = \text{maximum roughness depth}$

| Samples | $R_a$ (µm) | $R_q$ (µm) | $R_z$ (µm) | $R_{max}$ (µm) |
|---------|------------|------------|------------|----------------|
| Polished (OPS) | 0.09 ± 0.01 | 0.12 ± 0.01 | 0.77 ± 0.08 | 0.96 ± 0.15 |
| Ground (P80) | 1.18 ± 0.14 | 1.46 ± 0.18 | 6.23 ± 0.74 | 8.33 ± 1.96 |
| Sand blasted (F36) | 3.26 ± 0.40 | 4.05 ± 0.50 | 19.42 ± 4.37 | 24.77 ± 19.34 |

### Table 7

| | Average grain size (µm) | Average grain aspect ratio |
|-----------------|----------------------|--------------------------|
| | Ti\textsubscript{2}AlC | Ti\textsubscript{3}AlC\textsubscript{2} | Al\textsubscript{2}O\textsubscript{3} |
| Ti\textsubscript{2}AlC | Ti\textsubscript{3}AlC\textsubscript{2} | Al\textsubscript{2}O\textsubscript{3} |
| TAC-SPS-10 | 0.75 ± 0.34 | 0.62 ± 0.30 | 0.70 ± 0.37 | 1.62 ± 0.46 | 1.85 ± 0.65 | 1.58 ± 0.43 |
| TAC-SPS-30 | 0.78 ± 0.36 | 0.60 ± 0.31 | 0.62 ± 0.28 | 1.64 ± 0.48 | 1.96 ± 0.69 | 1.50 ± 0.33 |
| TAC-SPS-60 | 0.79 ± 0.36 | 0.64 ± 0.30 | 0.74 ± 0.36 | 1.62 ± 0.49 | 1.85 ± 0.65 | 1.47 ± 0.34 |

### Table 8

EBSD analysis of “SPSed” Ti\textsubscript{2}AlC: (A) SE image and (B) corresponding phase map [Color figure can be viewed at wileyonlinelibrary.com]
of three degrees of finishing, to wit, polished (OPS), ground (P80), and sandblasted (SB) samples.

In this work, the extent to which oxides grew on the specimen's surface was correlated with roughness. The different values are listed in Table 8. It is obvious that surfaces of TAC-SB samples were the roughest (highest $R_a$ value) due to the harsh abrading conditions. Other parameters such as the mean and maximum roughness depth ($R_z$ and $R_{\text{max}}$, respectively) provided additional information. Table 8 shows that SB samples exhibited deep troughs (up to $R_{\text{max}} = 24.77 \pm 19.34 \mu m$ and almost $R_z = 20 \mu m$ in average). These are due to strong impacts of F36 $\alpha$-$\text{Al}_2\text{O}_3$ particles, projected at 4 bar on the surface of Ti$_2$AlC. TAC-P80 had different R-values, almost three times lower than TAC-SB. Depressions of less than $R_{\text{max}} = 1 \mu m$ were achieved by polishing Ti$_2$AlC, the $R_a$ value being close to 100 nm.

SE images showed different oxide morphologies for the three samples after oxidation (Figure 11). The oxide morphology on TAC-OPS samples (Figure 11A) was globular with interconnected fine-grained blisters. They were ~10-20 µm in size. In between, larger faceted grains were evidenced. TAC-P80 (Figure 11B) exhibited unidirectional grooves, in which preferred growth of the large faceted grains was observed. Their size was similar to those observed for TAC-OPS and barely exceeded 10 µm in length for the larger ones. SB specimen (Figure 11C) exhibited similar blister-like structures as for polished samples. They were additionally covered with a substantial fraction of large crystals (~10-20 µm) organized in islands. BSE images (Figure 12), XRD (not shown here) and EDS analyses (not shown here) evidenced $\alpha$-$\text{Al}_2\text{O}_3$ as main oxide, meanwhile larger grains were found to be rutile TiO$_2$. Analyses (XRD and SEM not shown here) of the SB surface before oxidation showed that the $\text{Al}_2\text{O}_3$ content was

**FIGURE 11** SE images of oxidized Ti$_2$AlC samples with different surface finish: (A) polished to 50 nm colloidal silica, (B) ground with P80 abrasive SiC paper, (C) sandblasted with F36 alumina particles. Oxidation conditions were 1200°C, 50 h in static air [Color figure can be viewed at wileyonlinelibrary.com]

**FIGURE 12** BSE images of oxidized Ti$_2$AlC samples with different surface finish: (A) polished to 50 nm colloidal silica, (B) ground with P80 abrasive SiC paper, (C) sandblasted with F36 alumina particles. Oxidation conditions were 1200°C, 50 h in static air. Corresponding pie charts show results from Rietveld refinement (in wt. %) [Color figure can be viewed at wileyonlinelibrary.com]
non-negligible and evidenced embedding of Al₂O₃ particles in the surface of Ti₂AlC during surface preparation. Rutile’s typical elongated prismatic crystal habit with striation along the c-axis was noticed on TAC-SB (Figure 11C) because grains were large enough. TAC-OPS showed small rutile grains (~3-5 μm), scattered across the fine-grained blistered surface of Al₂O₃, and TiO₂ islands of less than 20 μm (Figure 12A). The higher content in MAX phases as compared to TAC-P80 and TAC-SB is on account of less TiO₂ in the analyzed volume. TAC-P80 (Figure 12B) exhibited a significant increase in TiO₂ content and larger light grey patches were observed on BSE images. TiO₂ grain size ranged from submicron to ~15 μm in length, while fine grains of Al₂O₃ composed the remainder of the oxide layer. These results are in agreement with reported features. TAC-SB showed a strong increase in TiO₂ content (Figure 12C). In fact, large colonies of TiO₂ crystals, reaching several hundreds of micrometers in size, were observed with BSE images, almost covering the whole surface of the sample. A model was proposed in which rutile TiO₂ grains preferentially grow over depressions initially existing in the base material. The higher roughness is supposed to be the reason of excessive TiO₂ expansion and ensuing grain coarsening.

Cross-sectional analyses (Figure 13) revealed the thickness of Al₂O₃ scale and size of TiO₂ islands. For the three samples, the Al₂O₃ scale was ~8 μm thick, highlighting similar Al-oxidation rates. These results are consistent with reported oxidation outcomes of fine-grained Ti₂AlC. Improved short-term oxidation resistance is indeed expected in such cases due to the fast build-up of the Al₂O₃ scale. In fact, fine-grained microstructures provide multiple pathways through grain boundaries for Al out diffusion, leading to the rapid formation of a thin protective Al₂O₃ layer. In this work, TGA outcomes (not shown here) indicated a rather parabolic oxidation behavior of Ti₂AlC. The coefficient of determination (R²) for both parabolic and cubic fitting was almost identical, yielding values of 0.999 and 0.990, respectively, but the residual sum of squares indicated a better fit for the parabolic (0.26) than for the cubic behavior (12.08). Despite the fact that fine-grained Ti₂AlC was reported to demonstrate cubic oxidation kinetics, in our case, the presence of ~15 wt% Ti₃AlC₂ may have modified the overall oxidation kinetics towards a more parabolic-like behavior, without having a detrimental effect on the oxidation response of the material. Thinner TiO₂ islands/nodules were found atop the Al₂O₃ scale of TAC-OPS (Figure 13A and D) and TAC-P80 (Figure 13B and E) samples. The smooth surface of polished samples (see Table 8) allowed for a smooth Al₂O₃ scale growth (Figure 13D), with few localized spots where delamination occurred. This Al₂O₃ scale appearance is what is most observed in literature, for mirror polished samples. A more porous and irregular thin Al₂O₃/TiO₂ layer was observed above the dense protective Al₂O₃ scale. The former layer might be the one observed in Figure 11A, there appearing as small protuberances. The Ti₂AlC/Al₂O₃ interface of TAC-P80 showed a more pronounced formation of pores and cracks (Figure 13E). TAC-SB showed a strong undulated profile already before oxidation due to surface preparation (Table 8). Strong rippling/rumpling/ratcheting of the oxide scale was observed (Figure 13C and F). On top of the Al₂O₃ scale, the sections between ripples were filled with large rutile grains as already evidenced on

**FIGURE 13** Cross-sectional BSE images of oxidized Ti₂AlC samples with different surface finish: (A and D) polished to 50 nm colloidal silica, (B and E) ground with P80 abrasive SiC paper, (C and F) sandblasted with F36 alumina particles. Oxidation conditions were 1200°C, 50 h in static air [Color figure can be viewed at wileyonlinelibrary.com]
previous SEM images (Figures 11C and 12C). Rumpling was observed for MAX phases already, in the case of thermal cycling of SB Cr$_2$AlC substrates coated with an yttria stabilized zirconia thermal barrier coating. Despite uncertainties as for the cause(s) of rumpling, it was alluded to fast thermal shock conditions, leading to substantial strain during oxide scale growth and thickening. However, in the present case, Ti$_2$AlC was isothermally oxidized within shorter times (50 hours) as compared to thermal cycling experiments (several hundreds even thousands of hours) and not under cyclic conditions. A common feature though, is the surface roughening procedure employed before oxidation, which in both cases led to initial undulations on the surface of the MAX phase base material and, in all likelihood, to the build-up of internal stresses in the near surface area. The amplitude of these undulations prior to oxidation has a determining role in promoting ratcheting and its critical value, above which rumpling is triggered, tends to decrease with the substrate yield strength. The higher the amplitude, the higher the stresses which initiate rumpling. Additionally, the build-up of in-plane stresses in the Al$_2$O$_3$ scale due to lateral growth strain were found by He et al. to arise in the first oxidation cycle and did not substantially change with further cycling. In this work, this would contribute to explain why rumpling was observed in the case of isothermal oxidation (one-cycle) of Ti$_2$AlC. In addition, undulation in the oxide scale potentially gave rise to a normal stress component at the Al$_2$O$_3$/Ti$_2$AlC interface, consequently deforming the first layers of the Ti$_2$AlC base material, which is known to plastically deform at 1200°C. In fact, the equivalent stresses induced in the substrate by the in-plane stresses in the oxide scale were determined to be the largest right underneath recessions in the Al$_2$O$_3$ scale. Upon cooling, when the compressive stresses exceed the yield strength of the substrate, the latter plastically deforms allowing the oxide scale to move downwards.

The Al$_2$O$_3$ scale is believed to accommodate increasing in-plane compressive stresses by stretching, a phenomenon of release of elastic energy. Thus, the increase in the overall length of the Al$_2$O$_3$ scale caused localized buckling and folds, which irremediably led to decohesion between Al$_2$O$_3$ and Ti$_2$AlC as a result of substantial tensile stresses (Figure 13C and F).

Unlike platinum-modified nickel aluminide (PtNiAl) bond coats, for which thermal expansion mismatch between Thermally Grown Oxide (TGO) and alloy is well known, the mismatch in CTE between Ti$_2$AlC (8.2 x 10$^{-6}$/K between 25°C and 1300°C), Al$_2$O$_3$ (8.0 x 10$^{-6}$/K and 9.0 x 10$^{-6}$/K in the 25°C-1000°C and 25°C-1500°C ranges respectively) and TiO$_2$ (8-9 x 10$^{-6}$/K in the 25°C-1000°C range) is reduced, hence a decrease of the mismatch stresses in the Al$_2$O$_3$ scale. In addition, for rumpling in EB-PVD TBC systems, typically, the mismatch between substrate and bond coat also plays a significant role. As no bond coat is used here, the given explanations can only be partly applicable. Even though several studies performed on PtNiAl bond coats exist, straightforward conclusions about the origin of rumpling and a generalization to other materials (e.g. MAX phases) are still missing.

In this work, we propose a simplified model to simulate the phenomenon of rumpling observed in the case of isothermal oxidation of Ti$_2$AlC and to highlight a potential correlation with surface roughness prior to oxidation. Growth stresses emerging in the TGO will induce radial stresses at a wavy interface between Ti$_2$AlC and TGO. TGO growth stresses are assumed to be at a constant level of 1000 MPa in the present model, according to values found in literature, while stress relaxation in the TGO is neglected. The presented model aims to estimate deformation and rumpling of the TGO as a consequence of these stresses. Therefore, the creep deformation of the Ti$_2$AlC first upper layers as a function of the initial substrate’s surface roughness prior to oxidation is calculated. The stress approximation model is based on the stresses in a homogeneous hollow sphere, made of an elastic material, subjected to an internal pressure $P$. The internal and external radii are denoted $a$ and $b$ respectively (Figure 14A). In the system of spherical coordinates ($r, \theta, \varphi$), the solution in terms of stress (Figure 14B) for a pure elastic response are as follows:

$$
\sigma_r = \frac{E}{1 - 2v} \cdot \left( C_1 - \frac{2Ev}{1 + v} \cdot C_2 \cdot r^{-3} \right) = -\frac{a^3}{b^3 - a^3} \cdot \left( \frac{b^3}{r^3} - 1 \right) \cdot P \quad (A1)
$$

**FIGURE 14** Stress approximation model based on stresses in a hollow sphere: (A) cross-section of a homogeneous hollow sphere subjected to internal pressure $P$, (B) solution in terms of radial stress versus radius of the sphere, (C) section of the sphere considered for the present model [Color figure can be viewed at wileyonlinelibrary.com]
\[ \sigma_\theta = \sigma_\varphi = \frac{E}{1-2\nu} \cdot C_1 + \frac{E}{1+\nu} \cdot C_2 \cdot r^{-3} = \frac{a^3}{b^3-a^3} \cdot \left( \frac{b^3}{2b^2} + 1 \right) \cdot p \]  
\text{(A2)}

\[ \sigma_{\varphi(a)} = \frac{a^3}{b^3-a^3} \cdot \left( \frac{b^3}{2b^2} + 1 \right) \cdot p = \frac{b^3}{2p^3} + \frac{a^3}{b^3-a^3} \cdot p = \frac{b^3 + a^3}{2(p^3-a^3)} \cdot p \]  
\text{(A3)}

\[ \sigma_\varphi(b) = \frac{a^3}{b^3-a^3} \cdot \left( \frac{1}{2} + 1 \right) \cdot p = \frac{3}{2} \frac{a^3}{b^3-a^3} \cdot p \]  
\text{(A4)}

\[ A_{tr} = a, \sigma_{tr} = p = \frac{b^3-a^3}{b^3+a^3} \sigma_\varphi \]  
\text{(A5)}

with \( E, \nu, r, C_1, \) and \( C_2, \) respectively, the Young’s modulus, the Poisson’s ratio, the mean radius of the sphere and constants determined from boundary conditions.

A section of the base material (Ti2AlC) is considered by taking part of the sphere (Figure 14C), so that one ends up with a cone of slant length \( a \) attached to a spherical cap of height \( H \) and base radius \( L/2 \). In the 2D plane, following relations are verified:

\[ a^2 = \frac{L^2}{4} + (a-H)^2 \]  
\text{(A6)}

\[ \rightarrow 0 = \frac{L^2}{4} - 2aH + H^2; a = \frac{H}{2} + \frac{L^2}{8H} \]  
\text{(A7)}

From expression A6,

\[ \rightarrow a - H = \pm \sqrt{a^2 - \frac{L^2}{4}} \]  
\text{(A8)}

\[ \rightarrow H = a \pm \sqrt{a^2 - \frac{L^2}{4}} \]  
\text{(A9)}

In this case, only the minus sign gives a meaningful condition. The surface roughness of the material can be approximated by a series of these 3D geometric shapes, the amplitude of surface peaks being directly linked to the condition. The surface roughness of the material can be approximated by a series of these 3D geometric shapes, the amplitude of surface peaks being directly linked to the condition.

The evolution of \( H \) is then calculated using Equation A9 and with the values of \( \frac{da}{dt} \) using Equation A17.

As rumpling appeared to be triggered by increasing surface roughness, the case of sandblasted samples is considered using the model above. \( H \) is retrieved from roughness
measurements (see Table 8) and \( L \) can be estimated by considering SEM cross-sections of Ti2AlC right after surface preparation and before oxidation: \( H = 3.26 \) µm and \( L = 100 \) µm. According to Equation A7, \( a \) is then 13 µm. The TGO thickness is approximately 8 µm after 50 hours at 1200°C (Figure 13F).

The extent to which rumpling occurs is then given by the following relation:

\[
X = \left( \frac{H(t_{50}) - H(t_0)}{H(t_0)} \right) \cdot 100\% \tag{A19}
\]

with \( t_0 \) and \( t_{50} \) being the start and the end of the isothermal (\( T = 1200\)°C) plateau, respectively.

By plotting the degree of rumpling vs Ti2AlC surface roughness prior to oxidation (Figure 15A), a steep increase is observed. Smooth surfaces (\( R_a < 1 \) µm) experience almost no rumpling (max. 0.49%) while rumpling can exceed 600% for surfaces presenting a roughness higher than 6.45 µm. As sandblasted surfaces exhibit higher \( R \) values than polished (Figure 15B) and ground surfaces (Table 8), rumpling is essentially observed in these conditions (Figure 15C). The limit to which the system accommodates the deformation is dictated by the interfacial adhesion between TGO and Ti2AlC and localized decohesion occurs at spots where stress concentration reaches a maximum.

This model shows that rough surfaces (typically achieved with sandblasting) present higher propensity to rumpling. As mentioned earlier, the phenomenon of rumpling is believed to be caused synergistically by different mechanisms and needs further investigation for Ti2AlC and in general, for MAX phases used in oxidizing environments. The present model thus paves the way for more exhaustive considerations in order to potentially prevent rumpling in systems subjected to similar conditions.

Studies on Ti3AlC2 mentioned about the preferential formation of TiO2 in porous areas because of the nature of Al2O3 crystal growth. In fact, it was found that low packing of Al2O3 crystals in larger cavities facilitate the outward grain boundary diffusion of Ti ions leading to the formation of TiO2 atop Al2O3. Here, similar features may account for the excessive formation of TiO2 on TAC-SB. More TiO2 was found above the Al2O3 layer as it appears that more from the Ti2AlC base material was oxidized. At the base material/oxide scale interface, no Ti-rich layer was observed, contrary to what is reported in literature. Instead, the presence of Ti3AlC2 clusters was noticed, the same way these clusters were present in the bulk. However, they were always present in the vicinity of TiO2 colonies.

The oxidation outcomes in the present work can complement the model proposed by Yang et al., which only considered localized cavities in case of a mirror polished surface. Their theory can be corroborated by taking into account several recesses in the base material and, herewith, a schematic is proposed (Figure 16). With cavities less than 2 µm in size, they found that the thickness of rutile was almost zero. No large TiO2 colonies were indeed observed in the present work for polished surfaces with a roughness below 1 µm. Some rutile grains were disseminated over the Al2O3 scale, without forming a consistent layer. Valleys are filled with Al2O3 first since Al atom self-diffusion along (0001) basal planes in Ti2AlC requires low activation energy. Al is not entirely depleted in the surface’s vicinity. Al2O3 within cavities are found to be present in small equiaxed grains on account of curved surfaces and subsequent multiple nucleation on existing grains. When larger depressions are present, additional Al diffuses out, gradually leading to exhaustion of the A-element content in near-surface areas. For cavity sizes ranging from 2 to 6 µm, Yang et al. observed ~3-5 µm thick rutile crystals. In the present work, an increase in rutile content was also observed for ground surfaces with similar roughness (see \( R_z \) in Table 8), with preferential growth within recesses (grooves in the non-oxidized state). The depletion in Al is even more pronounced with increasing surface roughness because its diffusion from peaks towards valleys is multidirectional. The same occurred with Ti, hence more TiO2 was found filling valleys above Al2O3 in TAC-SB. Diffusion pathways for Ti across the equiaxed microstructure are numerous and eased due to loose packing of Al2O3 crystals. For cavities larger than 6 µm, the thickness of TiO2 almost doubled.

**FIGURE 15** TGO rumpling during isothermal oxidation of Ti2AlC: (A) Evolution of TGO rumpling with increasing Ti2AlC surface roughness prior to oxidation, (B) quasi-plane surfaces (typically polished or gently ground) do not experience rumpling while (C) rough surfaces (typically sandblasted) show significant rumpling [Color figure can be viewed at wileyonlinelibrary.com]
Additionally, the growth rate of TiO$_2$ is much higher than that of Al$_2$O$_3$. Therefore, a great amount of large rutile grains was observed in SB samples in the present work. Some of them formed up to ~10 µm thick layers within valleys of ripples above the Al$_2$O$_3$ scale.

A trend was observed in which increasing roughness leads to the formation of larger amounts of TiO$_2$ above the protective Al$_2$O$_3$ scale. The thickness of the latter is invariant with increasing roughness, though, due to large undulations on the substrate’s surface before oxidation, the total length of Al$_2$O$_3$ after oxidation of sandblasted samples was the largest, hence more Al was depleted in that case. Above a critical amplitude of undulations present before oxidation, the oxide scale started to rumple, followed by localized failure of the Ti$_2$AlC/Al$_2$O$_3$ interface. The microstructure and impurity concentration being identical in all instances, one can say that the observed differences in oxide morphology are exclusively correlated to a surface roughness dependent mechanism.

4 | CONCLUSIONS

Ti$_2$AlC powder was synthesized by the means of the newly invented molten salt shielded synthesis (MS$^3$) route. The molten potassium bromide salt improved atomic inter-diffusion of elemental constituents. The optimal synthesis parameters were as follows: a temperature of 1000°C, lower than for conventional routes, a Ti:Al:C = 2:1:0.9 molar ratio, and a holding time of 5 hours. Ti$_2$AlC powders with an optimal purity of 91 wt. % were rapidly produced and the MAX phase yield was 97 wt. % (Ti$_2$AlC and Ti$_3$AlC$_2$). The powder agglomerates exhibited a globular morphology and were composed of a multitude of submicron sized primary particles.

Pressureless sintering at 1300°C in argon resulted in incomplete densification and increasing the sintering temperature to 1400°C promoted the phase conversion of Ti$_2$AlC to Ti$_3$AlC$_2$ and a reduction in Ti$_2$AlC purity. Therefore, FAST/SPS was required to almost fully densify Ti$_2$AlC, achieving a relative density of 98.5% at 1200°C and 50 MPa. Dense Ti$_2$AlC samples did not show texture and their microstructure was fine-grained with an average grain size below 1 µm, indicating that this sintering method had no influence on grain growth.

The fine-grained microstructure was an advantage during oxidation experiments. Multiple pathways for Al out-diffusion allowed for fast buildup of protective Al$_2$O$_3$ scales atop Ti$_2$AlC specimen. Surface roughness strongly influenced the morphology of the oxide scale. Smooth surfaces were mainly composed of small Al$_2$O$_3$ grains with preferential growth of rutile observed above recesses initially present in the base material. Rough surfaces showed more disproportionate formation of rutile crystals. It is assumed that protrusions were areas where rapid Al depletion occurred, followed by outward diffusion of Ti through Al$_2$O$_3$ grain boundaries. Large rutile islands were found above Al$_2$O$_3$ scales in sandblasted samples. A phenomenon of scale rumpling (or ratcheting) was noticed for latter samples, most probably due to a synergy between various mechanisms. It is believed that strong roughening of the Ti$_2$AlC surface by sandblasting coupled with growth stresses in the thermally grown Al$_2$O$_3$ scale promoted its rumpling, causing interfacial decohesion.

These outcomes complement data about oxidation of Ti$_2$AlC gathered in the last decades and are worth being considered in the case of high-temperature applications in oxidative media.
ACKNOWLEDGMENTS
This work has been funded by the Germany’s Federal Ministry of Education and Research (“Bundesministerium für Bildung und Forschung”) under the MAXCOM project (03SF0534). The authors thank Dr Doris Sebold (IEK-1), Beatrix Göths (IEK-4) for SEM/EDS and Dr Egbert Wessel (IEK-2) for EBSD measurements. Open access funding enabled and organized by Projekt DEAL.

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REFERENCES
1. Barsoum MW. The M_{n+1}AX_n phases: a new class of solids. Prog Solid State Chem. 2000;28:201–81.
2. Barsoum MW, El-Raghy T. Synthesis and characterization of a remarkable ceramic: Ti_3SiC_2. J Am Ceram Soc. 1996;79:1953–6.
3. Yang HJ, Pei YT, Ruo JC, De Hosson JTM, Li SB, Song GM. High temperature healing of Ti_2AlC: on the origin of inhomogeneous oxide scale. Scr Mater. 2011;65:135–8.
4. Li S, Song G, Kwakernaak K, van der Zwaag S, Sloof WG. Multiple crack healing of a Ti_2AlC ceramic. J Eur Ceram Soc. 2012;32:1813–20.
5. Barsoum MW, El-Raghy T, Ali M. Processing and characterization of Ti_2AlC, Ti_3AlN, and Ti_2AlC_{0.5}N_{0.5}. Metall Mater Trans A. 2000;31:1857–65.
6. Morrell R. Handbook of properties of technical & engineering ceramics Pt.1, an introduction for the engineer and designer. Richmond: H.M. Stationery Office. 1985:348 p.
7. Barsoum MW, Brodkin D, El-Raghy T. Layered machinable ceramics for high temperature applications. Scr Mater. 1997;36:535–41.
8. Kist EH, Wu E, Zobec JS, Forrester JS, Riley DP. Inter-conversion of M_{n+1}AX_n phases in the Ti-Al-C system. J Am Ceram Soc. 2007:90:1912–6.
9. Wang X, Zhou Y. Solid-liquid reaction synthesis and simultaneous densification of polycrystalline Ti_2AlC. Zeitschrift für Met. 2002;93:66–71.
10. Gauthier-Brunet V, Cabioch T, Chartier P, Jaouen M, Dubois S. Reaction synthesis of layered ternary Ti_2AlC ceramic. J Eur Ceram Soc. 2009;29:187–94.
11. Benitez R, Kan WH, Gao H, O’Neal M, Proust G, Radovic M. Room temperature stress-strain hysteresis in Ti_2AlC revisited. Acta Mater. 2016;105:294–305.
12. Zhou AG, Barsoum MW. Kinking nonlinear elastic deformation of Ti_2AlC_{2}, Ti_2AlC, Ti_3Al(C_{0.5}, N_{0.5})_{2} and Ti_2Al(C_{0.5}, N_{0.5}). J Alloys Compd. 2010;498:62–70.
13. Kulkarni SR, Wu AVDK-H. Synthesis of Ti_2AlC by spark plasma sintering of TiAl-carbon nanotube powder mixture. J Alloys Compd. 2010;490:155–9.

14. Sleptsov SV, Bondar AA, Witusiewicz VT, Hecht U, Hallstedt B, Petyukh VM, et al. Cocrytallization of MAX-Phases in the Ti–Al–C system. Powder Metall Met Ceram. 2015;54:471–81.
15. Yeh CL, Shen YG. Effects of TiC and Al_{4}C_{3} addition on combustion synthesis of Ti_2AlC. J Alloys Compd. 2009;470:242–8.
16. Hendaoui A, Vrel D, Amara A, Langlois P, Andasmas M, Guerionne M. Synthesis of high-purity polycrystalline MAX phases in Ti–Al–C system through mechanically activated self-propagating high-temperature synthesis. J Eur Ceram Soc. 2010;30:1049–57.
17. Rutkowski P, Huebner J, Kata D, Chublny L, Lis J, Witulsk P. Thermal properties and laser processing of hot-pressed materials from Ti–Al–C system. J Therm Anal Calorim. 2019;137:1891–902.
18. Khoptiar Y, Gotman I. Ti_2AlC ternary carbide synthesized by thermal explosion. Mater Lett. 2002;57:72–6.
19. Galvin T, Hyatt NC, Rainforth WM, Reaney IM, Shepherd D. Molten salt synthesis of MAX phases in the Ti-Al-C system. J Eur Ceram Soc. 2018;38:4585–9.
20. Spencer CB, Córdoba JM, Obando N, Sakulich A, Radovic M, Odén M, et al. Phase evaluation in Al_{4}O_{3} fiber-reinforced Ti_2AlC during sintering in the 1300°C–1500°C temperature range. Zhou Y, editor. J Am Ceram Soc. 2011:94:3327–34.
21. Pang WK, Low IM, O’Connor BH, Peterson VK, Studer AJ, Palmquist JP. In situ diffraction study of thermal decomposition in Maxthal Ti_2AlC. J Alloys Compd. 2011;509:172–6.
22. Zhang Z, Lim SH, Dai DMY, Tan SY, Koh XQ, Chai J, et al. Probing the oxidation behavior of Ti_2AlC MAX phase powders between 200 and 1000°C. J Eur Ceram Soc. 2017;37:43–51.
23. Dash A, Vaßen R, Guillon O, Gonzalez-Julian J. Molten salt shielded synthesis of oxidation prone materials in air. Nat Mater. 2019;18:465–70.
24. Dash A, Sohn YJ, Vaßen R, Guillon O, Gonzalez-Julian J. Synthesis of Ti_3SiC_2 MAX phase powder by a molten salt shielded synthesis (MS3) method in air. J Eur Ceram Soc. 2019;39:3651–9.
25. Tallman DJ, Anasori B, Barsoum MW. A critical review of the oxidation of Ti_2AlC, Ti_3AlC_2 and Cr_2AlC in air. Mater Res Lett. 2013;1:115–25.
26. Barsoum MW. Oxidation of Ti_{n+1}AlX_n (n=1–3 and X=C, N): I. Model. J Electrochem Soc. 2001;148:C544.
27. Barsoum MW, Tzenov N, Procopio A, El-Raghy T, Ali M. Oxidation of Ti_{n+1}AlX_n (n=1–3 and X=C, N): II. Experimental results. J Electrochem Soc. 2001;148:C551.
28. Yu W, Vallet M, Levraut B, Gauthier-Brunet V, Dubois S. Oxidation mechanisms in bulk Ti_2AlC: influence of the grain size. J Eur Ceram Soc. 2020;40:1820–8.
29. Basu S, Obando N, Gowdy A, Karaman I, Radovic M. Long-term oxidation of Ti_2AlC in air and water vapor at 1000–1300°C temperature range. J Electrochem Soc. 2011;159:C90–C96.
30. Smialek JL. Unusual oxidative limitations for Al-MAX phases. NASA/TM—2017-219444. 2017;1:29 p.
31. Zolotoyabko E. Determination of the degree of preferred orientation within the March-Dollase approach. J Appl Crystallogr. 2009;42:513–8.
32. Wang C-A, Zhou A, Qi L, Huang Y. Quantitative phase analysis in the Ti–Al–C ternary system by X-ray diffraction. Powder Diffr. 2005;20:218–23.
33. Bai Y, He X, Li Y, Zhu C, Zhang S. Rapid synthesis of bulk TiAlC by self-propagating high-temperature combustion
synthesis with a pseudo–hot isostatic pressing process. J Mater Res. 2009;24:2528–35.

34. Fan Q, Chai H, Jin Z. Microstructural evolution in the combustion synthesis of titanium carbide. J Mater Sci. 1996;31:2573–7.

35. Sujata M, Bhargava S, Sangal S. On the formation of TiAl3 during reaction between solid Ti and liquid Al. J Mater Sci Lett. 1997;16:1175–8.

36. Školáková A, Letínner J, Salvetr P, Novák P, Deduysche D, Kopeček J, et al. Kinetic and thermodynamic description of intermediary phases formation in Ti-Al system during reactive sintering. Mater Chem Phys. 2019;230:122–30.

37. Liu X, Zhang S. Low-temperature preparation of titanium carbide coatings on graphite flakes from molten salts. J Am Ceram Soc. 2008;91:667–70.

38. Shatynski SR. The thermochemistry of transition metal carbides. Oxid Met. 1979;13:105–18.

39. Chen CC. Phase equilibria at Ti–Al interface under low oxygen pressure. Atlas J Mater Sci. 2014;1:1–11.

40. Zhou WB, Mei BC, Zhu JQ, Hong XL. Rapid synthesis of Ti2AlC by spark plasma sintering technique. Mater Lett. 2005;59:131–4.

41. Cui B, Jayaseelan DD, Lee WE. Microstructural evolution during high-temperature oxidation of Ti3AlC2 ceramics. Acta Mater. 2011;59:4116–25.

42. Gonzalez-Julian J, Go T, Mack DE, Vaßen R. Thermal cycling testing of TBCs on Cr2AlC MAX phase substrates. Surf Coatings Technol. 2018;340:17–24.

43. He MY, Evans AG, Hutchinson JW. The ratcheting of compressed thermally grown thin films on ductile substrates. Acta Mater. 2000;48:2593–601.

44. Balint D, Hutchinson J. An analytical model of rumpling in thermal barrier coatings. J Mech Phys Solids. 2005;53:949–73.

45. Tolpygo VK, Clarke DR. On the rumpling mechanism in nickel-aluminide coatings. Acta Mater. 2004;52:5115–27.

46. Tallman DJ, Naguib M, Anasori B, Barsoum MW. Tensile creep of Ti3AlC2 in air in the temperature range 1000–1150°C. Scr Mater. 2012;66:805–8.

47. Song GM, Pei YT, Sloof WG, Li SB, De Hosson JTM, van der Zwaag S. Oxidation-induced crack healing in Ti3AlC2 ceramics. Scr Mater. 2008;58:13–6.

48. Wang J, Zhou Y, Liao T, Zhang J, Lin Z. A first-principles investigation of the phase stability of Ti2AlC with Al vacancies. Scr Mater. 2008;58:227–30.

How to cite this article: Badie S, Dash A, Jung Sohn Y, Vaßen R, Guillon O, Gonzalez-Julian J. Synthesis, sintering, and effect of surface roughness on oxidation of submicron Ti2AlC ceramics. J Am Ceram Soc. 2021;104:1669–1688. https://doi.org/10.1111/jace.17582