

Direct evidence of the formation mechanisms of TiC nanoparticles and Al₃Ti intermetallics during synthesis of an Al/TiC metal matrix nanocomposite

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Abstract

Microstructure control of *in situ* metal matrix nanocomposites (MMNCs) poses a barrier to their large-scale production. Here, we interrogate in unprecedented detail the formation mechanisms, morphologies, and microstructures of an *in situ* Al/TiC MMNC processed *via* salt flux reaction. Through synchrotron-based X-ray nanotomography (TXM) and scanning and transmission electron microscopy, we visualize in over five orders-of-magnitude of length-scale the TiC nanoparticles, Al₃Ti intermetallics, and their co-locations. 3D reconstructions from TXM revealed a surprising variety of Al₃Ti morphologies, including an orthogonal plate structure. By combining our experimental results with phase-field simulations, we demonstrate that this growth form originates from the intermetallic nucleating epitaxially on a TiC particle which is larger than a critical size at a given undercooling. Yet TiC particles that are too small to nucleate Al₃Ti can also impact the growth of the intermetallic, by splitting the intermetallic plates during solidification. These insights on the divalent roles of the nanoparticles offer general guidelines for the synthesis and processing of MMNCs.

Keywords: Metal matrix nanocomposites; heterogeneous nucleation; intermetallics; nanoparticles; advanced characterization; synchrotron radiation; X-ray nanotomography.

1. Introduction

Current demands for fuel-efficiency and increased electric vehicle range in the automotive and aerospace industries continue to push the necessity for strong and lightweight materials. Al alloys have been used extensively due to their high strength-to-weight ratio, but the reduction of mechanical properties at elevated temperatures limits their application. In comparison to base alloys, Al-based metal matrix nanocomposites

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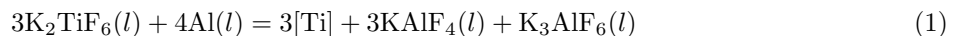
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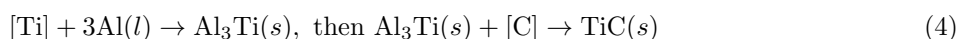
(MMNCs) have improved mechanical properties at both ambient and elevated temperatures, which depend on the reinforcement characteristics (*e.g.*, size, volume fraction, and morphology of nanoparticles) [1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13]. TiC is particularly attractive as a reinforcement phase because of its high hardness and elastic modulus, low density, and low chemical reactivity [14]. Such Al/TiC MMNCs are often produced through *ex situ* methods, where the reinforcement particles are premade and mixed into the matrix [3, 5, 6, 8, 12], thereby allowing for control over particle size, type, and volume fraction. However, these *ex situ* processing methods can lead to reinforcement contamination [4, 15], undesirable particle-matrix interfacial reactions [15, 16], and poor particle-matrix wetting [4, 17], thus hindering production of large-scale MMNCs.

Alternatively, *in situ* methods generate reinforcing particles directly in the melt *via* reactive processes, thereby avoiding some of the difficulties mentioned above [2, 14, 12, 18, 19, 20, 21]. The reactions to form particles *in situ* are typically complex and can involve intermediate reaction steps, parallel reaction pathways that result in different reinforcement morphologies, and the generation of undesirable secondary phases, including intermetallics, all of which influence the final microstructure and mechanical properties [19, 20, 22, 23, 24, 25, 26, 27, 28]. Therefore, a fundamental understanding of the particle formation kinetics and reaction pathways is warranted for microstructural control of *in situ* MMNCs.

A promising *in situ* approach for creating Al/TiC MMNCs involves reacting a mixture of C powder and a Ti-bearing salt-based flux (dipotassium titanium hexafluoride, K_2TiF_6) in an Al melt [2, 19, 25, 26, 27, 28, 29, 30, 31]. When the flux is reduced by the Al melt, it releases solutal Ti following **Eq. 1** [25, 26, 32, 33, 34]:



This method is promising for its improved wetting and infiltration, reduced oxidation, and for its potential to be integrated into a foundry workflow since surface fluxes are already an industry practice. In fact, Lee *et al.* have found that different compositions of the Ti-bearing flux all produced TiC [31]. Once Ti is liberated in the melt *via* **Eq. 1**, it can react with either solid C or solutal C to produce TiC; see **Eqs. 2-3**. Yet this is not the only hypothesized pathway: it is also possible for the solutal Ti to react with Al to form Al_3Ti , which then reacts with solutal C to form TiC; see **Eq. 4**. It has also been speculated that TiC can form using Al_4C_3 as an intermediate phase, but that intermetallic has not been observed in salt flux reactions [20, 35, 36].



It remains to be determined which mechanism(s) of nanoparticle formation dominate in salt flux reaction synthesis, including what role the Al_3Ti plays in the production of TiC (if any; see **Eq. 4** above). This question is challenging to answer due to the sub-micrometer length-scale of the TiC particles, which limits

the characterization techniques that can be used to study the reaction. A second, confounding issue is how the TiC nanoparticles interact with secondary phases (*e.g.*, Al₃Ti), post reaction. For example, the nanoparticles may impact the nucleation and growth processes of the secondary phases, thereby influencing their morphologies and distributions in the as-solidified microstructure.

In the past decade, synchrotron-based X-ray microscopy has opened the doors to a number of investigations on MMNCs, including the effects of reinforcing particles on grain growth [37, 38, 39], additive manufacturing [40, 41], ultrasonic processing [42], and void formation [43]. Furthermore, it can be utilized to investigate the intricate morphologies of intermetallic [44, 45, 46, 47] and semiconducting phases [48, 49]. The ability to probe microstructure in 3D gives us an unparalleled opportunity to test the predictions of models and theories. Since such a characterization is nondestructive, it is possible to combine it with other techniques to bring together perspectives from multiple length-scales and imaging modalities [50, 51].

Most of the prior studies listed above harnessed X-ray microtomography, whereas here, we used synchrotron nanotomography based on the transmission X-ray microscope (TXM) to visualize in 3D the complex and multi-phase microstructure of *in situ* Al/TiC MMNCs and to gain a deeper understanding of salt flux reaction synthesis. Our previous experiments [19] indicated that the TiC particles produced *via* salt-flux reaction are generally tens of nm in diameter, as alluded to above. In comparison, X-ray microtomography can achieve a pixel size of only $\sim 1 \mu\text{m}^2$, making it impossible to distinguish individual TiC particles. Instead, with the aid of TXM, we visualize the as-synthesized nanoparticles and their microstructural neighborhoods in a sufficiently large volume ($50^3 \mu\text{m}^3$) and at sufficiently high spatial resolution (50^3nm^3). The experiments can be done in under one minute [52], thereby facilitating rapid acquisition of 3D data.

Understanding the details of phase formation during nucleation *via* real-time experiments poses several challenges. First, achieving rapid cooling rates necessary for undercooled solidification at synchrotron facilities using *in situ* furnaces is nontrivial, limiting the range of attainable rates. Variable cooling rates can result in diverse morphologies of Al₃Ti, as will be shown later. Furthermore, rapid cooling necessitates a higher time-resolution, which would compromise the spatial resolution owing to a reduced signal-to-noise [53]. Second, due to the complexity of the 3D growth forms, we require 4D experiments; unfortunately, however, the time required for collecting 3D datasets at high spatial resolution (on the order of one minute [52], as noted above) inhibits capturing in real-time nucleation and growth at modest undercoolings. Third, TXM demands small samples, altering solidification conditions and impacting phase formation due to the imposed boundary conditions. Fourth, experimental procedures for *in situ* studies would involve prohibitively high temperatures (to melt the particles and the intermetallics). Finally, the density of Al₃Ti is higher than that of Al, and hence the Al₃Ti crystals will sediment to the bottom of the crucible *via* gravitational settling; maintaining their position in a stationary state is not feasible. These challenges motivated us to conduct phase-field simulations to provide mechanistic insight on the nucleation and growth of the intermetallic crystals. These simulations enable us to fill in spatiotemporal gaps in the experiments and propose a mechanism for microstructure evolution. Our nanoscopic characterization, together with electron microscopy and the

corresponding phase field simulations, allows us to draw important conclusions regarding the *in situ* salt flux reaction pathway as well as the interaction between nanoparticles and secondary phases.

2. Experimental details

2.1. Salt-flux reaction synthesis

The *in situ* MMNC samples were prepared using Al shot (99.99%, 2-5 mesh, Belmont Metals) as the metal matrix. K_2TiF_6 flux ($>100\ \mu\text{m}$, Millipore Sigma) and super activated C ($<100\ \text{nm}$, SkySpring Nanomaterials, Inc.) powders were chosen as reactants. They were weighed in a 1:1 molar ratio to target stoichiometric TiC production. The powders were mixed with mortar and pestle until homogeneous, then some was added to the Al for a targeted yield of 3 vol.% TiC. Molten Al at $850\ ^\circ\text{C}$ has a solubility of 1 wt.% Ti, which would constitute 20 wt.% of the Ti from the flux. While some loss of Ti to the melt is expected, the salt-flux reaction is thought to take place at the liquid flux-melt interface, so it was assumed that a majority of the Ti would react to form TiC rather than dissolve into the melt [26].

In the experiment, approx. 500 g of Al was melted in a 49 mm ID graphite crucible (3 kg capacity) without a protective gas cover in a Lindberg/MPH crucible furnace. Once the melt had reached $850\ ^\circ\text{C}$, as measured by an immersion temperature probe (K-type thermocouple), the powder mixture was added on top of the melt and allowed to remain stagnant until the flux liquified fully. The melt was mixed with a BN-coated steel impeller (four 2.5 in. dia. blades) placed at the liquid Al/liquid flux interface rotating at 300 RPM for 10 min. Surface entrainment of air, surface oxide, or flux into the Al matrix during stirring is unavoidable as is known in any industrial setting and can only be minimized. That said, the flux is of sufficiently low density to float to the top of the melt for skimming post-reaction. Subsequently, the melt was poured in a straight line (8-11 mm thick and 25-40 mm wide) onto a chilled Cu plate ($1\ ^\circ\text{C}$) to prevent particles from settling and thus to ensure their presence in the TXM samples [20].

A surrogate experiment was performed to measure the cooling rate during solidification. For this study, a 99.99% purity Al was heated to $850\ ^\circ\text{C}$ and poured onto a chilled Cu plate while multiple thermocouples were placed along the path of the pour. Data from the thermocouples was recorded using a DataDI 1100 (DataQ Instruments, Akron, OH). A maximum cooling rate of $24\ ^\circ\text{C/s}$ was measured immediately after the Al was poured onto the Cu, while a minimum cooling rate was recorded as $2\ ^\circ\text{C/s}$.

2.2. Multi-modal characterization

As a first step, metallographic specimens for scanning electron microscopy (SEM) were sectioned from the as cast material and then prepared using standard polishing procedures with a $1\ \mu\text{m}$ diamond suspension finishing step. Microstructural characterization (in 2D) was performed using a Tescan MIRA3 field emission gun (FEG) SEM operating in backscatter electron (BSE) mode at 15 kV and a beam intensity of 8-12. An integrated EDAX energy dispersive spectroscopy (EDS) system was utilized for chemical identification. X-ray diffraction (XRD) analysis was performed using a Rigaku SmartLab XRD operating at 40 kV and 44 mA with Bragg-Brentano para-focusing optics and a D/tex Ultra 250 detector.

To obtain a holistic view of microstructure in 3D, we utilized synchrotron-based TXM. For this purpose, 1 mm rods were cut out of the quenched MMNC samples *via* wire EDM (Cut Rite EDM, Inc.), after which the rods were thinned to a diameter of 80-100 μm by electropolishing, as described in our previous work [20]. Subsequently, micropillar specimens approximately 50 μm in diameter and 100 μm in height were fabricated for TXM from the electropolished rods *via* Xe^+ plasma focused ion beam (P-FIB) milling with a FEI HeliosTM G4 P FIB operating at 30 kV and 2.5 μA for general milling. Polishing cuts were made using 30 kV and 60 nA. A representative micropillar is shown in **Fig. S1** in the Supplementary Information (SI).

Following sample preparation, we conducted nanotomography measurements with the TXM at the Full-field X-ray Imaging beamline 18-ID at Brookhaven National Laboratory’s National Synchrotron Light Source II (Upton, NY, USA). A monochromatic X-ray beam operating at 7 keV illuminated the sample, then a zone plate used as an objective lens with 323 $\times$ magnification focused the forward transmitted beam onto an Andor Neo 5.5 detector that is coupled with a 10 $\times$ optical objective lens. The pixel size on the detector measured 20² nm², with a FOV of 51.2 $\times$ 43.2 μm^2 . A more detailed description of the experimental setup can be found elsewhere [54]. During data acquisition, the sample was rotated at 2 $^\circ/\text{s}$ from 0 to 180 $^\circ$, with an exposure of 0.1 s, thus giving 900 projection images. We used these projections to reconstruct the sample volume in 3D using TomoPy, a Python-based open source framework for tomographic data processing [55]. We first subtracted a dark background image from each projection image, normalized them with a reference illumination beam image, then removed “ring” artifacts [56], and finally reconstructed the data used the Gridrec algorithm, a direct Fourier-based method with a Parzen window filter [57]. Further data processing was done in the MATLAB R2020b computing environment (Natick, MA, USA).

Sufficient absorption contrast at 7 keV enabled identification of the phases present in the microstructure, namely, the Al matrix (dark gray), Al_3Ti intermetallic (intermediate gray), and TiC (light gray); see **Fig. S2** in the SI. A histogram of the grayscale intensities of the phases within the reconstructed TXM data is shown in **Fig. S3** in the SI, and theoretical attenuation lengths, attenuation coefficients, crystal structures, and other pertinent information for these and other potential phases that may form during the salt-flux reaction are shown in **Table S1** in the SI. Values for density ρ and attenuation length L_{atten} are taken from Refs. [58] and [59], respectively. Accordingly, the linear and mass attenuation coefficients μ_L and μ_M can be calculated as $\mu_L = 1/L_{\text{atten}}$ and $\mu_M = 1/(L_{\text{atten}}\rho)$, respectively. In the SI, we also quantify the resolution of TXM technique using a Fourier-based criterion [60, 61] and demonstrate an effective spatial resolution of ~ 50 nm (see **Fig. S4**). The high fidelity of the TXM reconstruction thus enables a quantitative 3D analysis.

To gain a comprehensive understanding of the localized features observed in the TXM data, we used high-resolution scanning transmission electron microscopy (HR-STEM). For this purpose, TEM lamella samples were prepared from the bulk specimen utilizing the Focused Ion Beam (FIB) lift-out technique, employing a FEI HeliosTM scanning electron microscope (SEM) with parameters analogous to those used in preparing micropillars for TXM. Subsequent scanning/transmission electron microscopy (S/TEM) imaging was performed using the Thermo Fisher Scientific Talos F200X G2 S/TEM, operating at an accelerated

voltage of 200 kV.

Additionally, the same sample prepared for S/TEM was investigated *via* Transmission Kikuchi Diffraction (TKD) to determine the crystallographic orientation of one of the Al_3Ti morphologies (the so-called “orthogonal plates”, described below). Another region of this sample, featuring nearly perpendicular plates of Al_3Ti , was specifically chosen for Electron Backscatter Diffraction (EBSD) to ensure a comprehensive, cross-sectional perspective. These samples were ion-milled using the Focused Ion Beam (FIB) technology within the FEI HeliosTM SEM, allowing seamless acquisition of TKD and EBSD patterns within the same instrument setup. To ensure high-quality Kikuchi patterns, the samples were cleaned at a voltage of 5 keV to eliminate any surface damage before data acquisition.

3. Results

3.1. Taxonomy of intermetallic morphologies

The SEM image in **Fig. 1(a)** shows Al_3Ti intermetallics of various sizes and shapes (green arrows). Generally, we observe overlapping plates of various orientations, although there is also one large individual plate (orange arrow at top-left). TiC particles (red arrows) can be seen as agglomerates in the grain boundaries, likely pushed there during solidification [62]. KAlF_4 particles (black arrows), produced from the reaction between the flux and Al, can be seen within the TiC agglomerates as small black circles. For typical use of K_2TiF_6 flux, the KAlF_4 and other byproducts are removed from the melt *via* degassing and can be found in the dross [2, 26, 28, 63], but we did not perform this step prior to quenching. XRD peaks for TiC, Al_3Ti , and KAlF_4 can be seen in **Fig. 1(b)**, verifying that both TiC particles and Al_3Ti intermetallics were created during the *in situ* process. There is no sign of excess C in either the SEM or XRD, likely because it stays afloat in the liquid flux layer and is skimmed off before pouring.

A 3D visualization can help us determine if the overlapping plates of Al_3Ti are single, contiguous structures or agglomerated, independent entities. **Fig. 2(a)** shows a representative TXM reconstruction, wherein the TiC is illuminated in red and the Al_3Ti in green, and the edges of the sample in translucent blue. From this data, we calculated the volume fraction of the TiC and Al_3Ti to be 3.3 and 0.8 vol.%, respectively, which is close to the expected 3.0 vol.% TiC (*vide supra*). **Fig. 2(b)** displays only the Al_3Ti phase, for clarity. Multiple contiguous structures of Al_3Ti were discovered therein, including “orthogonal plates” (**Fig. 2(c)**), “individual plates” (**Fig. 2(d)**), cuboids (**Fig. 2(e)**), and large blocks (**Fig. 3**). The renderings on the left in **Figs. 2(c-e)** show the smallest intermetallic of the given morphological type found in the data, while those on the right depict a more developed version of that morphology (presumably at a later stage in the growth process, after a growth instability sets in and accentuates the corners of the three structures [64, 65, 66]). In all, 41 orthogonal plates, 18 individual plates, 11 cuboids, and 3 groups of large blocks were found in the TXM data. That the Al_3Ti phase is faceted in all cases is expected given that the Jackson α -factor exceeds the threshold value of two (above which layer growth is predicted [67]). Nevertheless, the great diversity of Al_3Ti nanostructures is surprising and calls for further analysis, especially since their morphology can directly impact mechanical properties [68].

The morphology of Al_3Ti has been shown to be highly dependent on the cooling rate [27, 28, 68, 69, 70, 71, 72, 73, 74]. To measure the cooling rates during solidification, a surrogate experiment was conducted as detailed in Sec. 2.1. The obtained cooling rates fall within the range of 2-24 °C/s. According to existing literature, this range of cooling rates typically results in the formation of plate-like Al_3Ti structures, often termed “flaky” or “needle-like”, resembling those depicted in Fig. 2(d). At the lower cooling rates in this range, coarser and blocky formations of Al_3Ti are expected to emerge, akin to those shown in Fig. S5 in the SI and Refs. [27, 28, 68, 69, 70, 71, 72, 73, 74]. Those studies align with ours, offering an explanation for some of the diverse intermetallic morphologies visualized herein.

The origins of the cuboids and orthogonal plates remain far less clear. It has been suggested by El Mahallaway *et al.* that Al_3Ti rich in Ti (closer to Al_2Ti), tends towards a cuboid shape, or that the cuboid is a more developed version of a globular Al_3Ti precipitate [29]. On the other hand, Majumdar and Mudde found similar cuboid structures and identified them as Al_3Ti in a metastable β' phase of composition Al-20wt.% Ti (space group: $\text{Pm}\bar{3}\text{m}$, Strukturbericht designation: L1_2) [74]. An inhomogeneous distribution of Ti in the melt may have led to similar trends as seen in these two studies since some regions of the TXM data showed a local volume fraction of the TiC exceeding the expected overall volume fraction of 3 %. This would imply a chemical segregation of Ti in the melt. Small globular Al_3Ti (with equivalent radii $< 1 \mu\text{m}$) was also found in the TXM data, but their small size made it difficult to discern if they were precursors to cuboid shapes or would grow into other morphologies. Of note is that other Al-containing intermetallics have cuboidal shapes, such as Al_3Zr , Al_3Hf , and Al_3Sc [73, 75, 76], and all have also shown a pronounced morphological sensitivity to cooling rate [73, 75, 76]. Therefore, it is plausible that the Al_3Ti cuboids are either due to macrosegregation of solutal Ti, leading to Ti-rich (or poor) Al_3Ti intermetallics, or otherwise from impurities in the matrix.

Previously, researchers have attributed the orthogonal plates of Al_3Ti to multiple twinning [77] or else did not study them in depth [9, 25]. There are multiple examples of thin flakes of Al_3Ti forming perpendicular structures, although they tend to be much larger ($\gtrsim 5 \mu\text{m}$), more dendritic, and obtained under far lower cooling rates ($\lesssim 1 \text{ }^\circ\text{C/s}$) [27, 28, 68, 69, 70, 71, 72, 73, 74]. Importantly, in our work, the TXM data reveals particles (later proved to be TiC) at or near the intersection of the orthogonal Al_3Ti plates; see Fig. 3(a). In comparison, there are no such instances of TiC particles embedded within any of the other Al_3Ti structures nor any other consistent relationships between the two phases. That said, there are a few examples of TiC on/near the surface of the intermetallics, likely pushed by Al_3Ti during its growth.

Based on these observations, we propose that the orthogonal plate morphology arises during nucleation, *i.e.*, the Al_3Ti phase nucleates heterogeneously on the TiC particle (crystal structure: cubic, $\text{Fm}\bar{3}\text{m}$) and grows epitaxially on its solid-liquid interfaces. Importantly, due to non-reciprocal nucleation theory [78, 79, 80], if TiC is nucleating Al_3Ti , then the converse cannot be true, thus ruling out the indirect route of TiC formation *via* the breakdown of Al_3Ti by Eq. 4 (in general, non-reciprocal nucleation postulates that there exists a significant disparity in the undercoolings required for the heterogeneous nucleation of phase α on

substrate β compared to phase β on substrate α). It also follows that the TiC forms by salt-flux reaction prior to the Al_3Ti intermetallic. It has been shown that Al_3Ti can nucleate heterogeneously on TiB_2 [29, 81] and on Al_2O_3 [82] but neither of these processes results in an orthogonal plate structure. Below, we offer evidence to support our hypothesis on the emergence of this unexpected morphology.

3.2. Origin of orthogonal plate structures

First, we investigate the directionality of the Al_3Ti structures that contain particles within. The normal vectors along the Al_3Ti -Al interfaces can be projected stereographically to yield a so-called interfacial normal distribution (IND); see Ref. [83]. The zone axis for the calculation is represented by the pink arrow in **Fig. 3(a)**, and the corresponding IND is shown in **Fig. 3(b)**. The peaks along the edge of the primitive circle represent a preponderance of normal vectors with a given orientation in the specimen frame — in this case, they come from the broad faces that are $\sim 90^\circ$ away from the zone axis (in pink), and also $\sim 90^\circ$ away from one another. This confirms that the plates are indeed orthogonal to one another, and this is no coincidence. There is some noise in the IND due to the fact that TiC particles sometimes border the surfaces of Al_3Ti ; these particles were removed for the IND analysis in order to focus exclusively on the directionality of the intermetallics. The orthogonality of the Al_3Ti plates is consistent with an underlying cubic symmetry, which is naturally absent in the Al_3Ti crystal structure (body-centered tetragonal, refer to **Sec. 4.2**). Therefore, we hypothesize that this orthogonality originates from the symmetry of the nucleant particle.^[1]

While the basic structure of three intersecting orthogonal plates was common, many intermetallic structures had “extra” plates growing in parallel to basic ones (see **Figs. 3(c,e)**), or had extraneous plates unrelated to these ones. The additional planes are likely caused by crystallographic twinning of Al_3Ti [85, 86], and/or by stress that develops in the evolving structure during solidification.

Some other orthogonal plates had one or multiple plates underdeveloped. **Fig. 3(c)** shows two such Al_3Ti orthogonal plate structures that grew next to each other (but were misaligned from one another). The plates located between the two structures are stunted in comparison to the rest of the plates. This underdevelopment is reasonable given that the two intermetallics share the same Ti solute field (a “soft” collision in solidification [64], leading to competitive growth). We plotted the INDs of both structures; see **Fig. 3(d)**. The zone axis is given as the pink vector associated with the structure at right. In this case, the IND represents the superposition of two independent crystals: those hotspots with the white arrows come from the left-hand, or “misaligned” intermetallic (in this frame-of-reference). The misorientation between the two structures is about $15\text{--}30^\circ$ off-axis, depending on the axis.

Fig. 3(e) shows a single Al_3Ti structure with two large TiC embedded within, and two parallel plates in each orthogonal direction. The distance between the centroids of the two TiC particles was found to be 202 nm, while that between the two parallel plates was 197 ± 21 nm (obtained from 12 measurements). The

¹The external morphology of the nucleant reflects its point group isogonal with its space group [84].

agreement between the particle and plate distances suggests that this structure was formed by two individual Al_3Ti orthogonal plate structures nucleating on separate TiC particles; during growth, the two impinged on one another (a “hard” collision in solidification) and likely rotated over time to reduce the grain boundary energy [87, 88]. This rotation could be accomplished *via* rigid sliding of one intermetallic with respect to the other along their shared boundary [88]. The IND of this coalesced structure is shown in **Fig. 3(f)**. It depicts an almost-perfect alignment of the plates in each direction, *cf.* **Fig. 3(b)**.

The TXM experiment provides not only morphological information but also detailed chemical information. This is because the grey-scale value of each voxel in the reconstruction is linearly related to the attenuation coefficient of the sample at the position of the voxel. With this in mind, we used the greyscale intensity values to identify the phases more conclusively, with attention to the bright particle(s) within the orthogonal Al_3Ti plates. Using the methodology outlined by Ebner *et al.* [89], we normalize the intensity values of the Al/TiC MMNC sample, using two internal standards for the normalization (see **Table S2**). One is the air that is outside the sample, and the other is the Al matrix. The Ti solubility in Al at room temperature is low enough that it is reasonable to assume the matrix is essentially pure Al . From these two values, we determine the linear normalization function, $\mu_L = aW + b$, where W is the grayscale intensity value and a and b are constants ($7.96\text{E}-5$ $1/\text{cm}$ and -70.27 $1/\text{cm}$, respectively). Accordingly, we predict the greyscale intensity values W for all phases which could have formed during the salt-flux reaction synthesis, using their theoretical linear attenuation coefficients μ_L as input (see **Table S1** for possible phases and **Table S3** for calculated intensity values). Conversely, we predict the linear attenuation coefficients μ_L for the phases in the TXM data using their intensity values W (see **Table S2**). This enabled a direct assessment of the chemistry of the phases in the TXM data, which we later confirm *via* TEM (*vide infra*).

In **Table S4**, we compare between theoretical and calculated values for μ_L and W . The top portion considers the Al , air, and Al_3Ti , while the lower portion compares the values for the core particles with all possible cubic, tetragonal, trigonal, and orthorhombic phases, as all those structures have internal angles of 90° (between like or unlike planes) and could explain the symmetry of the orthogonal plate structures. As expected, the percent error for air and Al is nil as they were used for the normalization function, but for the intermetallics (plate and orthogonal plate structure), there is consistently a $\sim 10\%$ error. This may suggest some systematic error in the normalization procedure (more than two standards would increase the accuracy of this method). Alternatively, the intermetallic may well be off-stoichiometry, such that there is 5-10% more Ti than would be anticipated [90].

The results in the bottom portion of **Table S4** rule out several possible phases for the core particle as their intensities and linear attenuation coefficient values do not fall within the systematic error range noted above. The only phases with μ_L and W that are remotely close to the experimental values include a high temperature Ti cubic phase and TiC ; however, the former is not likely since its transition to cubic Ti occurs at 882°C (assuming thermodynamic equilibrium), which is well above our operating temperature. Furthermore, we did not find evidence for pure Ti in SEM, XRD, or TEM. It follows that the core particle

is most likely TiC, although the match is not perfect. If not for a systematic error, the core TiC particles may be off-stoichiometry, much like the intermetallics. It has been shown previously that TiC often forms in sub-stoichiometric Ti/C ratios in salt-flux reaction, ascribed to C vacancies in the TiC lattice [91]. In this case, we can expect that there are far more C-vacancies in the core TiC particle than in $\text{TiC}_{0.95}$, which should result in an increase in its greyscale value W .

Fig. 4 shows the distribution of the TiC particle sizes (measured as equivalent radii R). The size range in the histogram is limited to those TiC particles that are discernable, *i.e.*, particles of size $R < 50$ nm were ignored as they are approaching the spatial resolution of TXM, and likewise particles of size $R > 500$ nm were assumed to be large agglomerates and therefore not considered here. The brown bins of the histogram represent the subset of TiC particles that were found to be at or near their center of the Al_3Ti orthogonal plates, *i.e.*, the heterogeneous nucleating sites (see also the inset of **Fig. 4**). It was found that the average size over all particles is 160 ± 99 nm, while that for the TiC nucleants is 290 ± 59 nm.

The above analysis suggests that there is a minimum size of TiC required for heterogeneous nucleation of Al_3Ti . To rationalize this result, we invoke the free-growth model by Greer and coworkers [92, 93, 94]: *particles* (here, TiC), with faces of size R' are ideally wet by a *crystal* (here, Al_3Ti); they remain dormant until the radius of the homogeneous crystal nucleus becomes smaller than R' and free growth sets in. This will occur at a particular undercooling $\Delta T_{fg} = \frac{2\gamma}{\Delta S_V R'}$ where γ is the interfacial free energy between the crystal and liquid, and ΔS_V is the entropy of fusion per unit volume of the crystal. In a polydisperse system (*i.e.*, one with a range of particle sizes, such as ours), it follows that all particles of size R' and greater will be activated at an undercooling of ΔT_{fg} . Using $\Delta S_V \cong 1.3 \frac{J}{\text{cm}^3 K}$, $\gamma = 0.074 \frac{mJ}{\text{cm}^2}$ [95] and, at minimum, $R' = 4 \times 10^{-5}$ cm (see **Fig. 4**), we find $\Delta T_{fg} \cong 6$ °C. Given the reaction occurs at 850 °C, this would imply a liquidus temperature of 856 °C for Al_3Ti , which corresponds to an alloy of composition Al-1wt.% Ti (the solubility limit of Ti in Al). Hence, about one quarter of the Ti by weight from the K_2TiF_6 did not react to yield TiC. This conclusion reasonably fits the volume fractions of TiC and Al_3Ti that we measured *via* TXM, reaffirming the amount of Ti which did not form TiC. The self consistency also provides support for the free growth model for heterogeneous nucleation [2].

3.3. Intermetallic morphologies without TiC

To assess the influence of TiC on Al_3Ti morphology, we conducted an additional experiment under identical processing conditions. However, in this case, we omitted the carbon necessary for TiC formation. That is, this control experiment led to the formation of Al_3Ti in the absence of TiC, providing a basis for comparison with the samples containing TiC. The results are depicted in **Fig. 5**, showcasing the morphological differences observed with and without TiC. Importantly, we find that the presence of TiC resulted in orthogonal plate morphologies, distinct from those blocky structures observed in the absence of TiC. The latter case would

²The suitability of the free-growth model in this study would suggest that the anisotropy of the solid-liquid interfacial free energy of the TiC nucleant is relatively weak [96].

suggest a difficulty in achieving cube-symmetric orthogonal plate structures solely through the tetragonal symmetry of Al_3Ti . It follows that TiC must catalyze the formation of the orthogonal plates. Finally, we note that despite the consistent supply of titanium through the flux in both scenarios, the absence of TiC resulted in a relatively higher volume fraction of Al_3Ti , owing to the fact that more Ti remains in the liquid (*i.e.*, it is not tied up in the salt flux reactions; see **Eqs. 2-4**).

3.4. Epitaxy between particle and intermetallic

We employed scanning transmission electron microscopy (STEM) to investigate the interface between the two solid phases, aiming to gain deeper insights into the efficacy of Al_3Ti nucleation on TiC . **Fig. 6(a)** shows a low-magnification bright-field STEM image of an Al_3Ti plate. We magnified a region of interest denoted by the white dotted circle in **Fig. 6(a)**; see the high resolution STEM micrograph in **Fig. 6(b)**. This image unequivocally establishes the presence of coherency between Al_3Ti and TiC phases.

To further elucidate the crystallographic relationship between the phases, we conducted simulations of electron diffraction along the $[010]$ beam direction *via* fast Fourier transform. **Figs. 6(c-d)** give the diffraction patterns corresponding to Al_3Ti and TiC , respectively. The observed diffraction patterns convey an orientation relationship (OR) between the (002) planes of Al_3Ti and TiC phases. For this same OR, it is possible to coincide the $\{110\}$ family of planes for both crystals, as shown stereographically in **Fig. S6** in the SI.

While this specific TiC particle does not serve as the central “core” particle, situated at the centre of the orthogonal plates and initiating the nucleation of the intermetallic, it serves as a suitable surrogate to validate the potential epitaxial relationship between Al_3Ti and TiC . Note there is only a 5% chance³ that a randomly-oriented plane will intersect the larger TiC particles that are capable of nucleating Al_3Ti at the aforementioned undercooling ΔT_{fg} . A second confounding issue is that the milling depth achieved by a single FIB pass is on the same order of magnitude as the particle diameter, preventing its successful capture. Instead, the smaller particle shown in **Fig. 6** likely encountered the surface of an already-nucleated Al_3Ti intermetallic and underwent rotational repositioning to minimize the interphase boundary energy, a common occurrence in semi-solid sintering [87].

In **Fig. 7**, we examine these smaller particles more closely. **Fig. 7(a)** shows a STEM image wherein Al_3Ti is dark gray, TiC is black and dotted, and the Al matrix is light gray. The Al_3Ti intermetallic shows a splitting of its plates (see green arrows) with TiC particles wedged between them. **Fig. 7(b)** is a HAADF image of the boxed region in **Fig. 7(a)** depicting clusters of TiC (marked with red arrows) trapped between intermetallic plates. **Figs. 7(c-e)** are HAADF images which verify that these particles have high concentration of Ti and C, as expected. Some examples of entrapped Al were also found in the TXM data, although, for simplicity, this phase was left out of the 3D visualizations (**Figs. 2-3**).

³According to **Fig. 4**, the so-called larger particles are $0.25\ \mu\text{m}$ in size. About 10 of them are in a TXM scan (see **Fig. 2(b)**), where the sample dia. is $50\ \mu\text{m}$. Thus, $0.25 \times 10/50 = 0.05$, or a probability of 5%, assuming uniformly distributed particles

The STEM images reveal that the TiC particles have dual effects on the morphology of Al_3Ti : those TiC particles above a critical radius of curvature act as nucleants for the Al_3Ti , leading to the formation of the orthogonal plate structures; meanwhile, the smaller TiC particles perturb the growth process of the intermetallic, similar to how grain-refining particles split dendrite arms during free growth [21, 37, 38, 39]. The presence of the small carbides in the liquid may either disrupt the local solute field [97, 98], leading to variations of the driving force for solidification, or else collide with the Al_3Ti growth front directly. The exact mechanism remains a topic for future study. Due to the strong crystalline anisotropy of Al_3Ti [68], the two branches of Al_3Ti maintain their facets, grow in parallel, and never coalesce. This phenomenon can be seen in 2D with SEM (**Fig. 1(a)**) and in 3D with TXM (**Fig. 3(c)**). A corollary of this finding is that the TiC particles were not uniformly dispersed in the melt: single plates of Al_3Ti found in the TXM data (refer again to **Fig. 2(d)**) did not show this splitting behavior, which would imply that these plates nucleated in regions devoid of the TiC particles.

3.5. Crystallographic orientations of orthogonal plates

To discern the crystallographic orientations of the orthogonal plate structures, TKD was performed on the same sample examined above in TEM. The results are presented in **Fig. 8**, wherein the inverse pole figures convey the orientations of the distinct grains of Al_3Ti . These pole figures reveal that the broadest surfaces of the plates are bounded by $\{001\}$ planes, while the narrow surfaces are oriented $\{100\}$, as schematized in **Fig. 8(d)**. Given the orthogonality of the structure, the two plates imaged are misoriented by 90° .

To corroborate these findings, EBSD was conducted on a different orthogonal plate structure; see **Fig. 9**, where again the plates exhibit an approximate perpendicular alignment. The resultant pole figures (**Figs. 9(a-b)**) correspond to the orthogonal plates boxed in blue and red, respectively, consistently illustrating that the largest surfaces of Al_3Ti are constituted by $\{001\}$ planes, while the complementary set of interfaces are formed by $\{100\}$ planes. These findings are distilled in the schematic given in **Fig. 9(e)**. Taken altogether, this picture suggests that the orthogonal plates are not the product of a growth-front instability of a *single* grain, but instead the simultaneous formation of *multiple* grains. That said, individual plates of the orthogonal structure may later split into two branches due to disruptions in the local solute field, as noted above in **Sec. 3.4**.

3.6. Phase-field simulations

To lend credence to the above ideas, a phase-field model was constructed to examine the formation of orthogonal Al_3Ti plates on TiC particles. Each Al_3Ti plate was described by a solidification model developed by Folch *et al.* [99] with an anisotropic interfacial energy to match the experimentally observed Al_3Ti shape. To simulate multiple Al_3Ti plates on the same nucleant particle, we adopted the multi-order-parameter approach developed by Fan *et al.* [100]. We closely followed the implementation by Ofori-Opoku *et al.* [101], in which this approach was applied to a solidification model. Additionally, we incorporated the Extended Smooth Boundary Method [102] to introduce an inert TiC particle serving as the nucleant substrate. The

governing equations were solved using the PRISMS-PF framework [103, 104], an open-source phase-field equation solver. Additional details regarding the model and parameters can be found in the SI. The use of these well-established phase-field models for our simulations, as well as the parameterization that is calibrated to qualitatively match the experimental observations, ensures an accurate representation of essential physical processes occurring in the experimental system, including heterogeneous nucleation and solidification with anisotropic interfacial energy.

In an effort to unravel the formation mechanism for the orthogonal morphology of Al_3Ti , we considered various initial placements of the nuclei on planes of cubic symmetry. Specifically, we simulated using a different number of grains on different TiC planes, as shown in **Table S6**. We focused particularly on TiC $\{100\}$ and $\{110\}$ planes, given that nucleation on $\{111\}$ planes cannot lead to orthogonal symmetry. For the $\{100\}$ planes, we tested nucleation on three and six sites. While the arrangements of three and six grains allowed for orthogonal growth, they did not lead to the targeted morphology. For $\{110\}$ planes, fewer than 12 grains resulted in missing plates in the orthogonal structure. Ultimately, the simulations indicate that 12 nucleated grains of Al_3Ti are required to form the orthogonal structures seen experimentally.

4. Discussion

4.1. Formation of TiC nanoparticles

According to our interpretation, the formation of TiC precedes that of Al_3Ti . Consequently, the coexistence of TiC with liquid Al saturated in solutal Ti triggers the nucleation and growth of Al_3Ti (discussed in detail below). This line of reasoning finds support in both the existing literature on the ternary Al-Ti-C phase diagrams [105, 106, 107] as well as our experimental observations: notably, we observe TiC embedded *within* the Al_3Ti structures. Alternatively, if Al_3Ti were to form as an intermediate, later reacting with C to produce TiC according to **Eq. 4**, we would expect to see TiC at the interface between Al_3Ti and the C-enriched liquid. Such an occurrence is not evident in the TXM data. In addition, we do not see small particles (< 50 nm dia.) within the intermetallic crystals *via* higher resolution imaging in TEM (note such small particles are below the spatial resolution of TXM).

4.2. Formation of Al_3Ti single and orthogonal plates

Al_3Ti is a body-centered tetragonal (BCT) crystal, characterized by Laue symmetry 4/mmm, with lattice parameters $a = 0.386$ and $c = 0.868$ nm (space group: I4/mmm, Strukturbericht designation: DO_{22}). The growth morphology of Al_3Ti depends on its crystallographic anisotropy and cooling rate, as noted previously. For instance, the slower growth of $\{001\}$ planes is anticipated due to factors such as bonding and packing fraction [108]. Consequently, these slow-growing planes can manifest as the larger surfaces of the single Al_3Ti plates, as evidenced by **Figs. 8-9**. The EBSD results in particular suggest that a growth tip along $\langle 110 \rangle$ is formed with (100) and (010) facet planes, as depicted in **Fig. 9**. Moreover, growth along $\langle 110 \rangle$ is expedited owing to looser atomic packing in that direction and/or micro-facets of $\{100\}$. With minimal growth in the direction normal to the (001) plane, the process is confined to two-dimensions. The growth

orientation and morphology of individual plates shares semblance to other faceted crystals growing in a diffusion field [44, 45, 49, 46, 47].

The formation of the orthogonal plates shares similar growth characteristics to the single plate, but the key distinction lies in the fact that there are three set of plates growing perpendicular to each other, originating from a common site. Relying on kinetic arguments alone is not sufficient to explain the spontaneous emergence of three mutually perpendicular grains (nor is the orthogonal plate structure seen in the control Al-Ti sample). Therefore, we investigated the potential role of TiC in shaping the Al₃Ti structure. TEM analysis (**Fig. 6**) reveals the alignment between the (001) of TiC and (001) of Al₃Ti, as well as that between [100] of TiC and [100] of Al₃Ti. This alignment is based on the orientation of the TEM lamella with respect to the crystallographic coordinates. Based on the same OR between both phases, it follows that (110) of TiC must align with (110) of Al₃Ti (the growth tip of the plates, from above). The interface between (110) TiC and (110) Al₃Ti is hence key for the formation of the orthogonal plate structures, refer again to the stereographic diagram shown in **Fig. S6** in the SI. TiC has 12 symmetrically equivalent planes within the {110} family, including (110), ($\bar{1}\bar{1}0$), ($1\bar{1}0$), ($\bar{1}10$), ($\bar{1}01$), ($10\bar{1}$), (101), ($\bar{1}0\bar{1}$), (011), ($0\bar{1}\bar{1}$), ($01\bar{1}$), ($0\bar{1}1$), and each of them is parallel to the growth tip of Al₃Ti. Hence, this bicrystallography is consistent with the growth morphology of three intersecting plates (and a total of 12 growth tips) of Al₃Ti. In contrast, other interfaces of TiC like {100} or {111} only have four and eight symmetrically equivalent planes and cannot support the formation of orthogonal plate structures, as confirmed *via* phase field simulations.

To understand why nucleation may preferentially occur on the {110} planes, we investigate the discrepancies between Al₃Ti and TiC for various combinations of surface planes, assuming coherent interfaces. Bramfitt [109] gives a method to quantify the planar disregistry level between a potential pair of a nucleus surface (denoted by a subscript n) and a substrate surface (denoted by a subscript s). The Bramfitt disregistry is found as [109]

$$\delta_{(hkl)_n}^{(hkl)_s} = \sum_{i=1}^3 \frac{|d_{[uvw]_s}^i \cos \theta - d_{[uvw]_n}^i|}{3d_{[uvw]_n}^i} \times 100 \quad (5)$$

Here, (hkl) represents a low-index plane, $[uvw]$ is a low-index direction in (hkl) , $d_{[uvw]}$ is the interatomic spacing along $[uvw]$, and θ is the angle between $[uvw]_n$ and $[uvw]_s$. The expression takes into account the three lowest-index directions (indicated by subscript i) within the first quadrant of the interface plane. According to Bramfitt [109], a surface is active as heterogeneous nucleation site when $\delta_{(hkl)_n}^{(hkl)_s}$ is less than 12%. Notably, if $\delta_{(hkl)_n}^{(hkl)_s}$ is under 5%, the interface is expected to remain coherent [110]. In **Table 1**, the Bramfitt planar disregistries between Al₃Ti and TiC for potential low-index ORs are presented. As the table indicates, there is significant potential for nucleation on TiC {110} planes. See **Fig. 11** for a schematic illustration. The disregistry level between Al₃Ti {110} and TiC {110} is lower than the coherence threshold from above.

The calculated misfit between (110) planes of Al₃Ti and TiC is also lower (4.77%) than that of other sets of planes such as (100) or (111) (**Table 1**). This point lends support to the idea that (110) planes

Potential ORs	$\delta_{(hkl)_n}^{(hkl)_s} / \%$
$(110)_{Al_3Ti}, (110)_{TiC}$	4.77
$(112)_{Al_3Ti}, (111)_{TiC}$	7.96
$(100)_{Al_3Ti}, (100)_{TiC}$	21.8
$(400)_{Al_3Ti}, (100)_{TiC}$	21.85

Table 1: Bramfitt planar disregistry $\delta_{(hkl)_n}^{(hkl)_s}$ between Al_3Ti and TiC for some close-packed planes.

of TiC nucleate (110) planes of Al_3Ti . As noted previously, Al_3Ti is tetragonal while TiC is cubic, thus necessitating three sets of Al_3Ti grains to complete the orthogonal plate structure aligned with $\{110\}$ of TiC (*cf.* TKD/EBSD data in **Figs. 8-9**). It follows that a single nucleant with the requisite cubic symmetry, such as a TiC particle, is more likely than multiple clustered TiC particles. That is, a single TiC particle nucleates a total of 12 grains of Al_3Ti , four of which exhibit the same orientation (see **Sec. 3.6**), *i.e.*, there are three misoriented grains of Al_3Ti . The growth mechanism is summarized in **Fig. 12(a-c)**. **Fig. 12(d)** presents a high-magnification image from a deeply etched specimen, revealing the orthogonal structure and noticeable gaps between individual plates. Finally, if the three grains form at different times, the orthogonal plate structures will not be perfectly symmetric — some plates will be longer than others, as shown in **Fig. 3**.

5. Conclusions

We have undertaken a multi-scale, multi-modal experimental and computational investigation to study Al/TiC MMNCs produced *via* salt-flux reaction, with a focus on the formation of TiC nanoparticles and their impact on the final microstructure. Several conclusions can be drawn from this study:

1. There exists not a singular but a diversity of Al_3Ti growth forms that are obtained in this *in situ* process, including single plates, orthogonal plates, and cuboidal structures. They are caused by different cooling rates, Ti concentrations, and nucleation modes.
2. Those intermetallics with the orthogonal plate structure are a direct result of Al_3Ti nucleating on TiC . Consistent with the prediction of free-growth theory, we find a critical radius of TiC above which heterogeneous nucleation can occur at a given undercooling.
3. The crystallographic orientations of the orthogonal plates, together with phase field simulations, indicate that 12 grains of Al_3Ti nucleate on the $\{110\}$ interfaces of TiC . If the grains form at different times and/or grow at different rates (depending on the local supersaturation), the orthogonal plates are not symmetric with respect to the core TiC particle.
4. TiC particles smaller than the critical size threshold for heterogeneous nucleation (200 nm dia.) may contribute to a branching of the already nucleated Al_3Ti plates during free growth. This demonstrates a secondary, and often overlooked, effect of the carbide on the intermetallic morphology.
5. Due to non-reciprocity of heterogeneous nucleation, TiC cannot nucleate on Al_3Ti . Furthermore, the 3D reconstructions from TXM suggest that TiC forms before Al_3Ti . Accordingly, we can rule out

indirect formation mechanisms of TiC which require Al_3Ti as an intermediary step. It follows that the TiC forms directly from the salt-flux reaction.

Based on the above findings, we hypothesize that orthogonal Al_3Ti structures would arise in heterogeneous nucleation when the following three conditions are met: (1) the nucleating agent is thermodynamically stable, (2) it has cubic symmetry, and (3) it exhibits epitaxy with Al_3Ti . More broadly, the detailed characterization presented herein can lead to an informed production of MMNCs *via* salt flux reaction. Understanding the formation pathway of TiC nanoparticles and their interaction with secondary phases in solidification brings us one step closer to optimizing the heterogeneous microstructure of MMNCs.

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7. Declaration of competing interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Figures

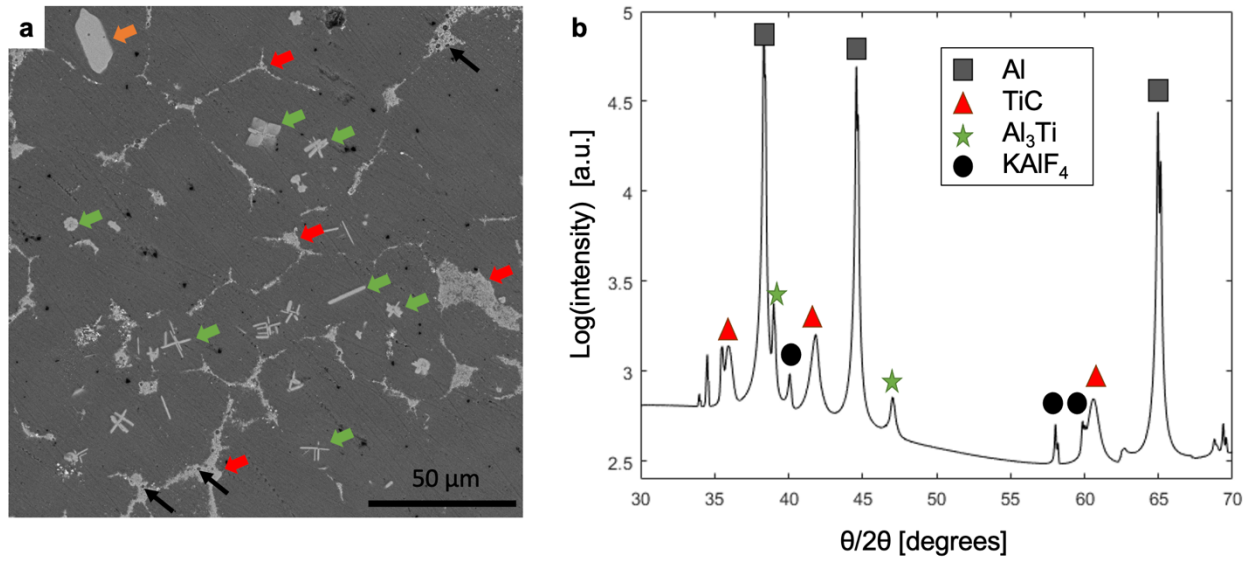


Fig. 1: Microstructure of quenched Al-TiC MMNC. (a) Representative SEM micrograph. TiC (red arrows) and Al₃Ti (green and orange arrows) are both present. Black arrows point to residual flux. (b) XRD pattern of the as-made material. Peaks for Al, TiC, Al₃Ti and KAlF₄ are indicated.

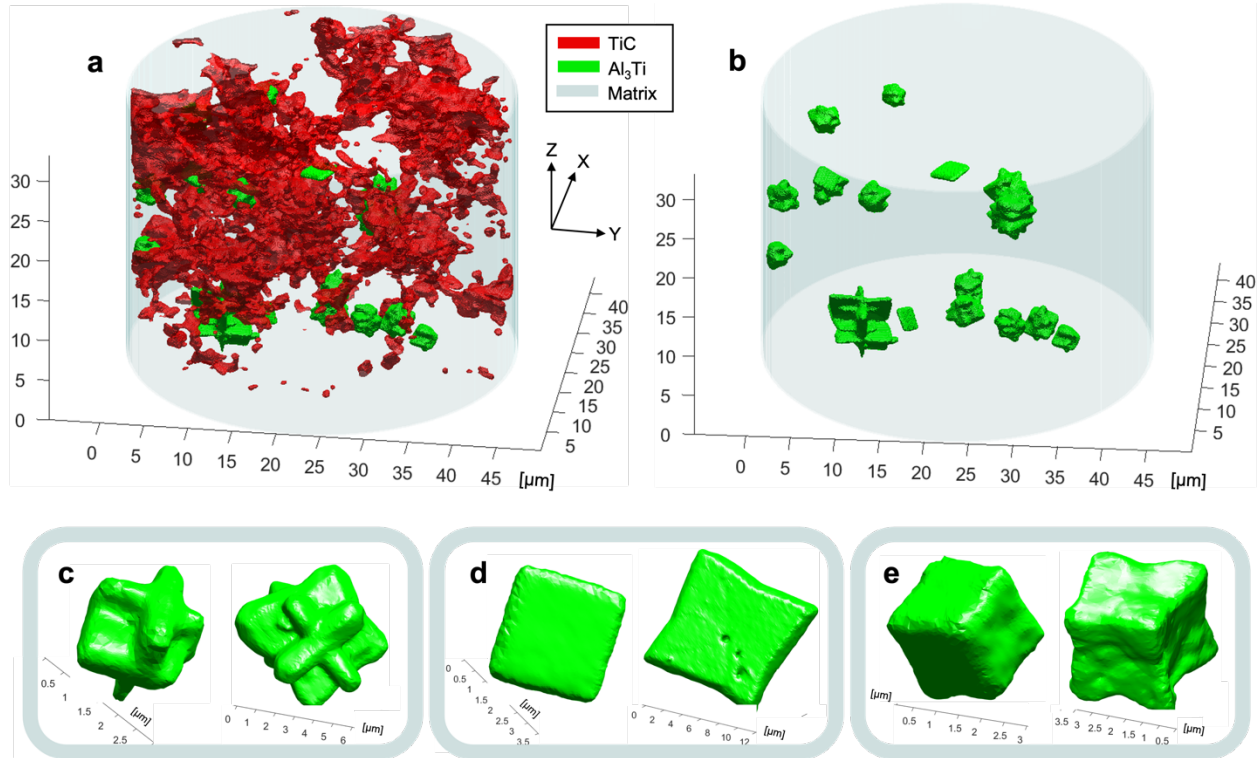


Fig. 2: Nanoscopic visualization via synchrotron TXM, showing (a) a cylindrical section of a micropillar sample (translucent blue) that contains Al₃Ti particles (green) and TiC agglomerates (red). (b) Same volume rendering as in (a), but now displaying only Al₃Ti for clarity. (c-e) Magnified views of three types of Al₃Ti intermetallics: (c) "orthogonal plates," (d) "individual plates," and (e) cuboidal structures. Two examples are given of each, where the only difference between the left and right structure is the length-scale. The larger Al₃Ti intermetallics at right in (c-e) have sides that have been bowed out likely due to a corner instability in solidification.

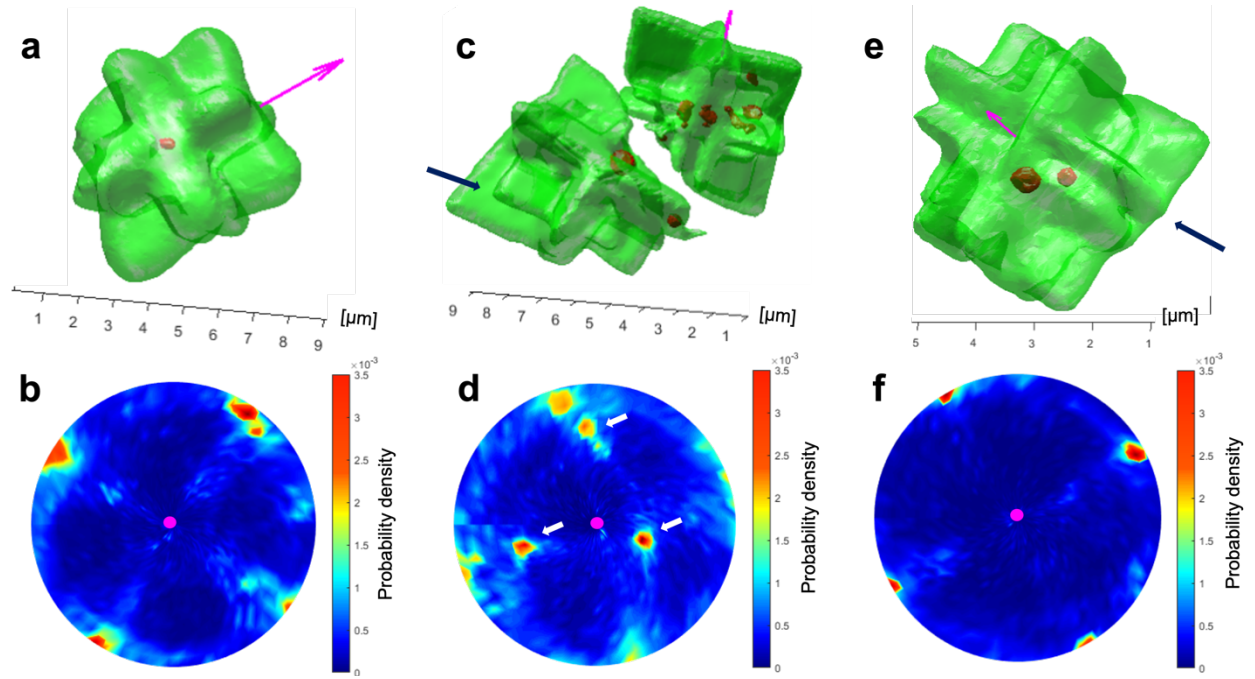


Fig. 3: Directionality of orthogonal plates. (top row) 3D snapshots of (a) Al_3Ti intermetallic (translucent green) with TiC particle (red) in its center, (c) two misaligned Al_3Ti intermetallics each containing a TiC particle, and (e) Al_3Ti intermetallic with two TiC particles and two sets of orthogonal plates. The latter was likely born from two separate intermetallics that later coalesced in solidification. (bottom row: b, d, f) Interfacial normal distributions corresponding to the same structures in (a, c, e), respectively, where the zone axis is taken as the pink arrow in each. White arrows in (d) point to facets of the misaligned intermetallic (at left in c). Extra plates in (c,e) indicated by blue arrows. See text for details.

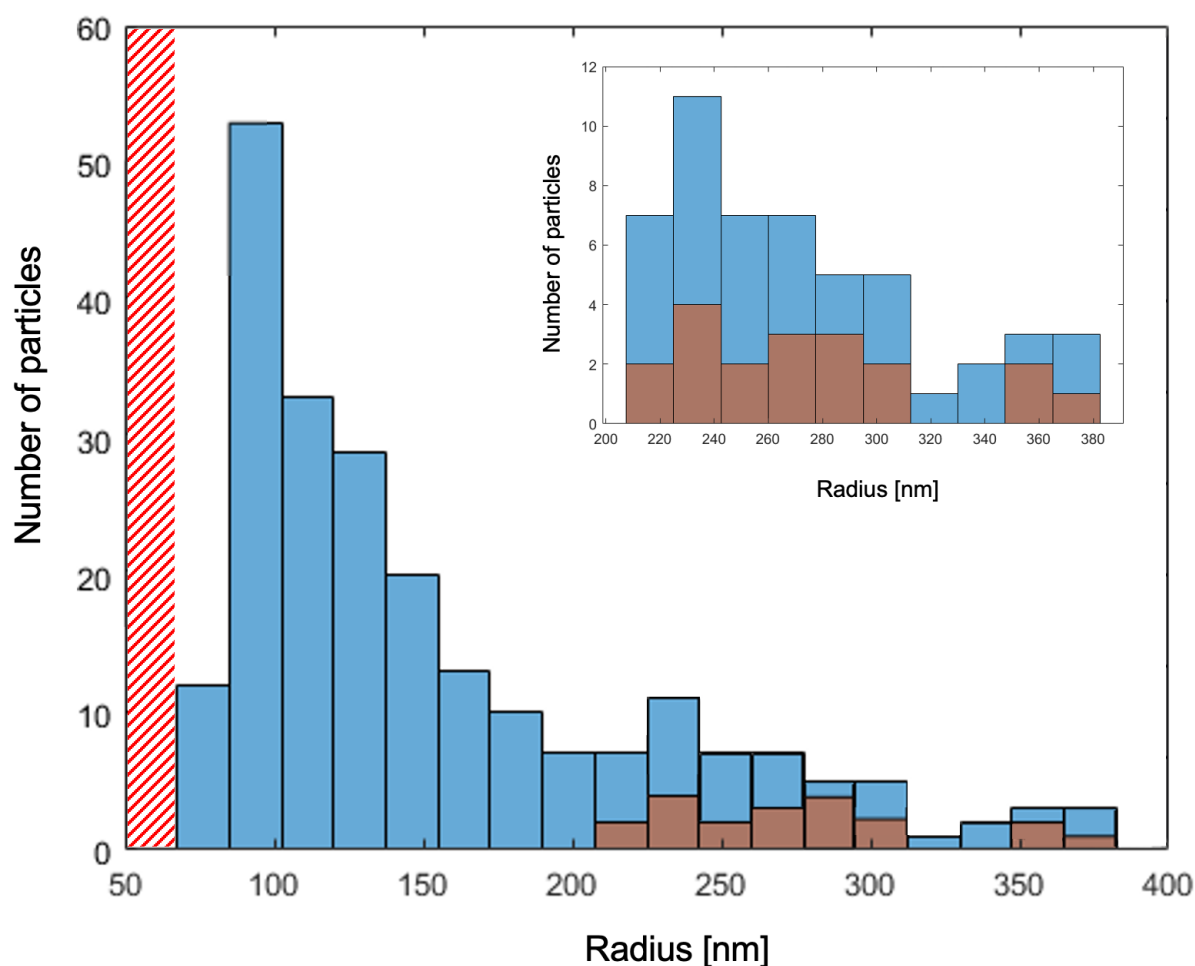


Fig. 4. Size distribution of 236 TiC particles by equivalent radii, defined as the radius of a sphere having the same volume as the particle (in 3D). Orange bins are associated with those TiC particles that are embedded within the orthogonal plates of Al₃Ti (see Fig. 3(a)). The minimum radius reported here (60 nm, corresponding to the left-most edge of the histogram) is greater than the measured spatial resolution of TXM (50 nm, see the Supplementary Information) while the maximum was chosen to avoid counting agglomerates of TiC. That is, particles within the red-hatched area may not be observable using TXM due to resolution limitations. Inset is a magnified view, focusing on the radius-range covered by the embedded TiC. Meanwhile, TiC particles to the right of the hatched area are not generally embedded within the orthogonal plates of Al₃Ti (unless they are of the size indicated by the orange bins).

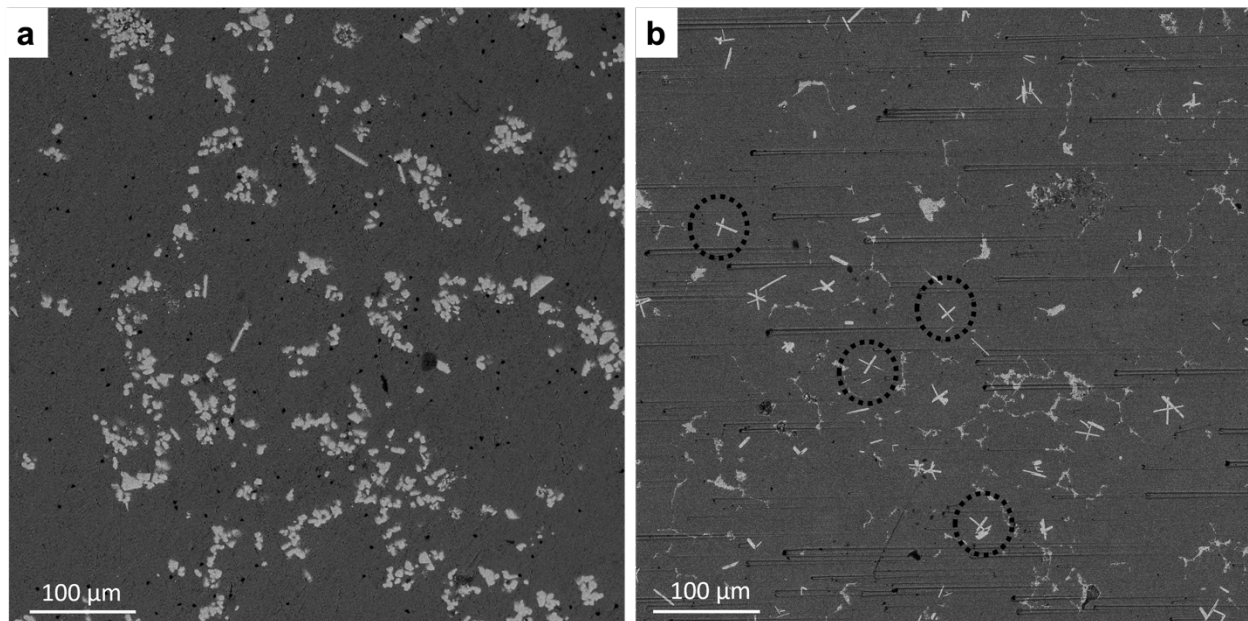


Fig. 5: Morphologies of Al_3Ti with and without inoculation: (a) an alloy prepared utilizing flux to form Al_3Ti , quenched using a copper plate, and without the addition of carbon to form TiC ; (b) identical material processed under the same conditions but including TiC . We observe the formation of orthogonal plates in the presence of TiC (see black-circled regions in (b)).

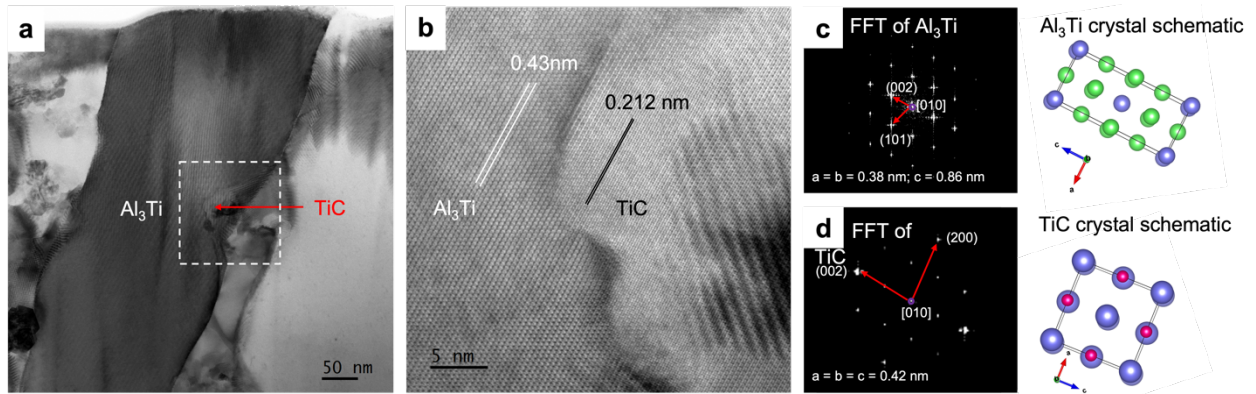


Fig. 6: Interface between nanoparticle and intermetallic. (a) Low magnification HAADF STEM image. (b) High resolution STEM micrograph (boxed region in a), showing the epitaxial relationship between Al_3Ti and TiC . (c-d) FFT patterns from (b), with schematics of the Al_3Ti crystal along $[010]$ beam direction and TiC crystal along $[010]$.

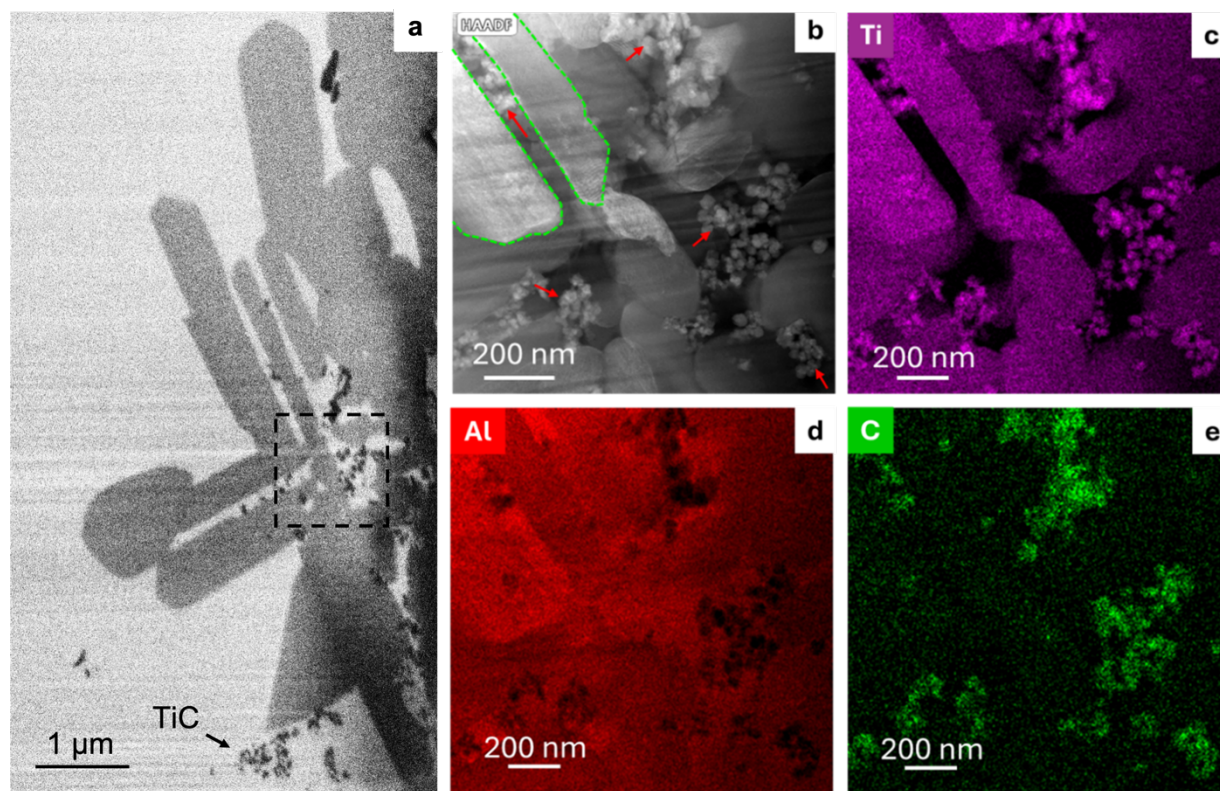


Fig. 7: Locating the smaller TiC particles. (a) Secondary electron micrograph, where light gray is the Al matrix, dark gray is Al₃Ti, and black specks are TiC. (b) HAADF imaging of the boxed region in (a). The green outline in (b) highlights some of the parallel plates of Al₃Ti. Red arrows point to TiC particles that lie outside of the Al₃Ti intermetallic structure (see, *e.g.*, the top left red arrow). (c-e) Ti, Al, and C spectra for the region-of-interest shown in (b), respectively, showing a strong Ti signal in both Al₃Ti and TiC phases.

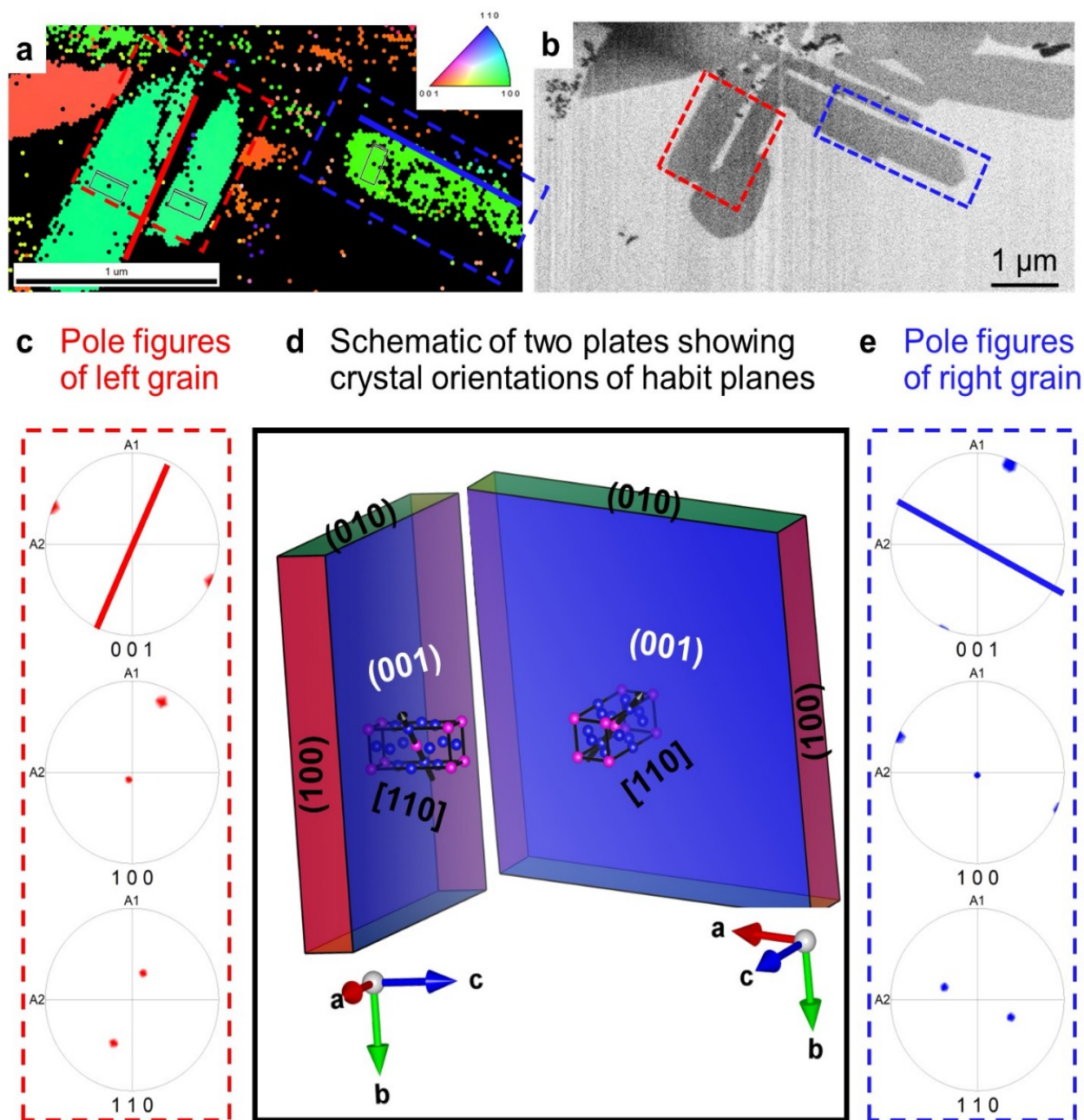


Fig. 8: (a) Inverse pole figure map corresponding to the morphology depicted in (b), obtained using TKD. Pole figures for the left grain are displayed in (c) (highlighted by a red box), while those for the right grains are shown in (e) (highlighted by a blue box). Data from both grains determines the orientations of the 3D plates as depicted schematically in (d).

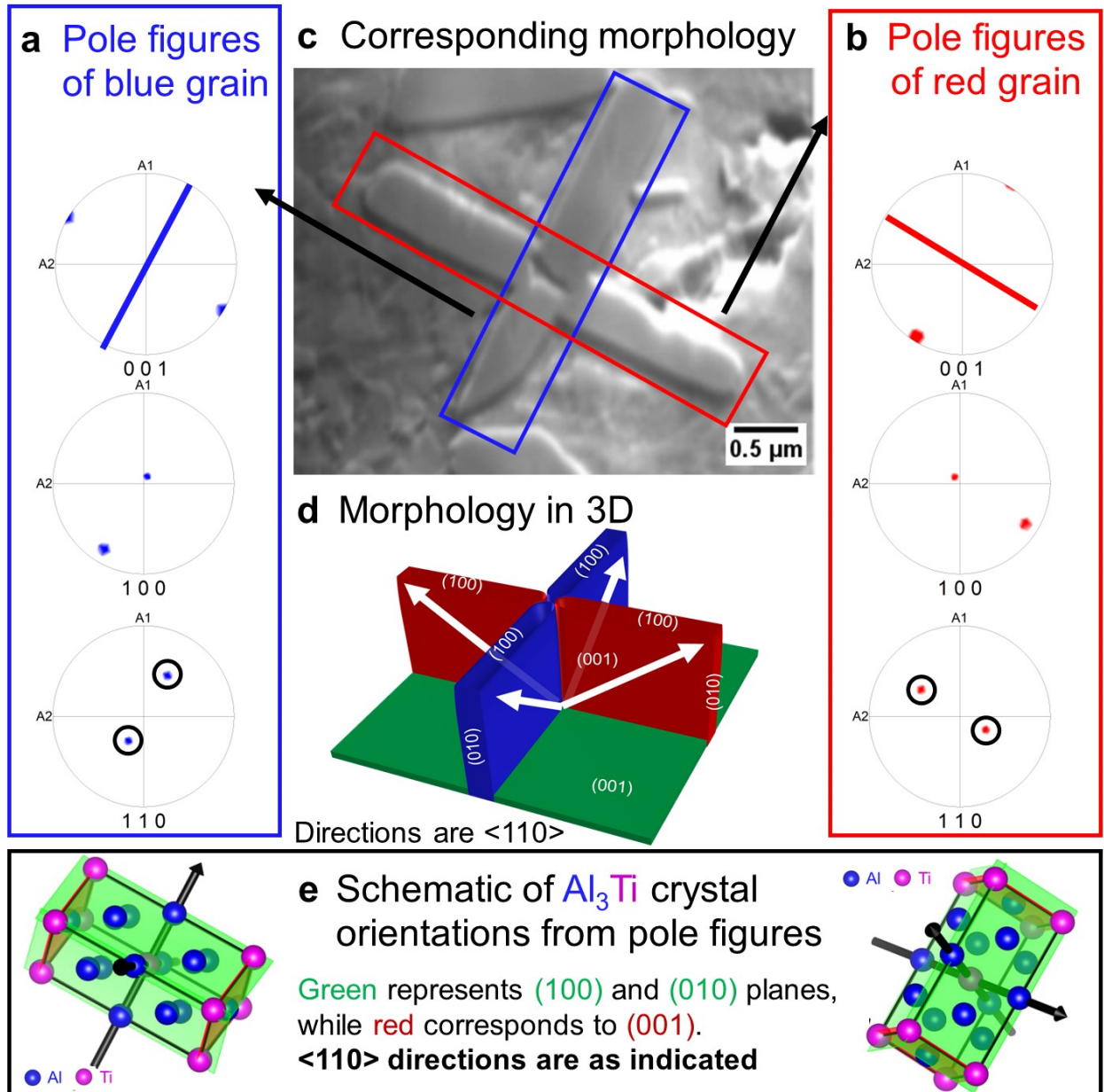


Fig. 9: (a-b) pole figures corresponding to the blue and red highlighted regions, respectively, of the orthogonal plate structure in (c). The observed orientations have been conveyed on an illustration of the 3D structure in (d). Crystal schematics corresponding to (a-b) are shown in (e).

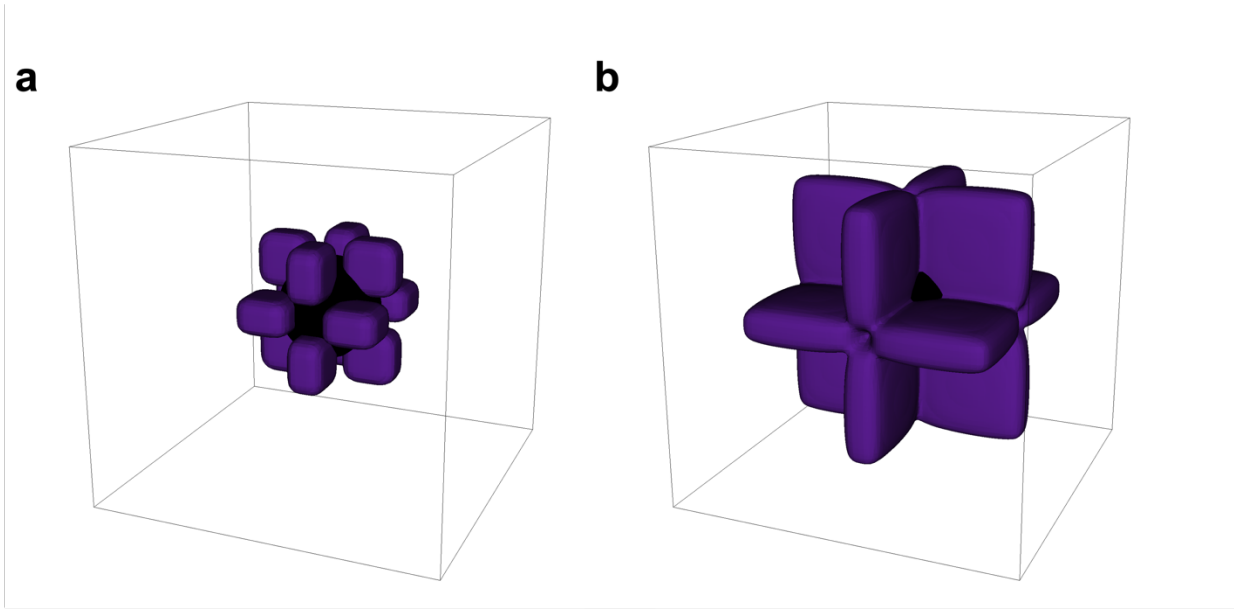
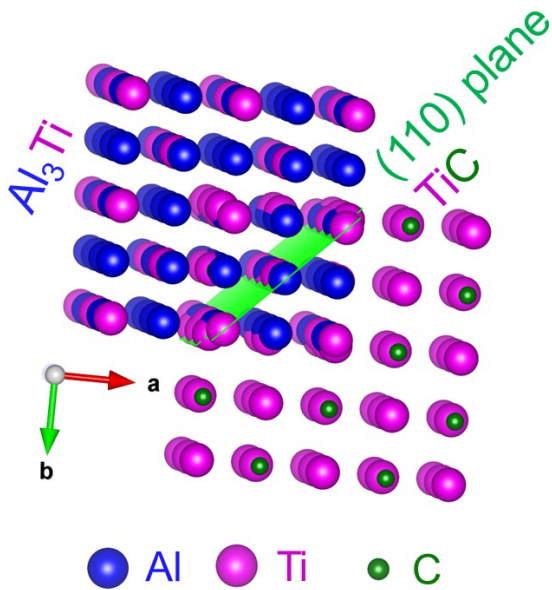


Fig. 10: Morphologies of Al₃Ti grains in an orthogonal configuration: (a) the initial condition and (b) at simulation time of 0.2185 s. The box shown in the figure is $2.5\ \mu\text{m} \times 2.5\ \mu\text{m} \times 2.5\ \mu\text{m}$ in size.

a Epitaxy between bulk
TiC and Al₃Ti crystals



b Overlap of (110) planes in
TiC and Al₃Ti crystals

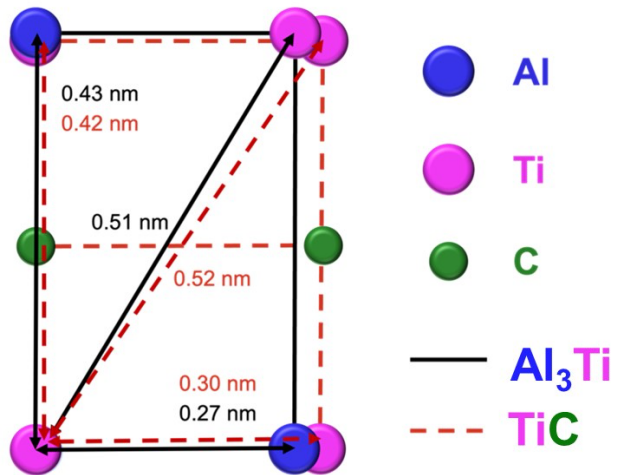
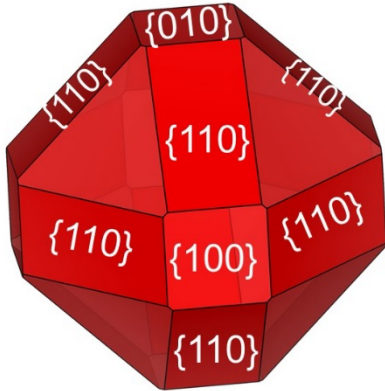
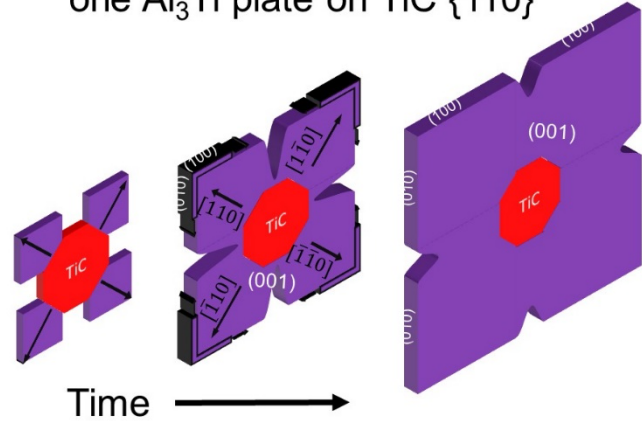


Fig. 11: (a) Illustration of epitaxy between TiC and Al₃Ti, where the light green surface indicates the common plane (110). (b) Overlay of (110) crystallographic planes of Al₃Ti and TiC, in which the Al₃Ti plane is represented by black solid lines with blue and magenta circles denoting Al atoms and Ti atoms, respectively, and the TiC plane is noted with dashed red lines with magenta circles for Ti atoms and green circles for C atoms. Fig. (b) provides the three sets of interatomic spacing values used in the calculation of the disregistry level. See text for details.

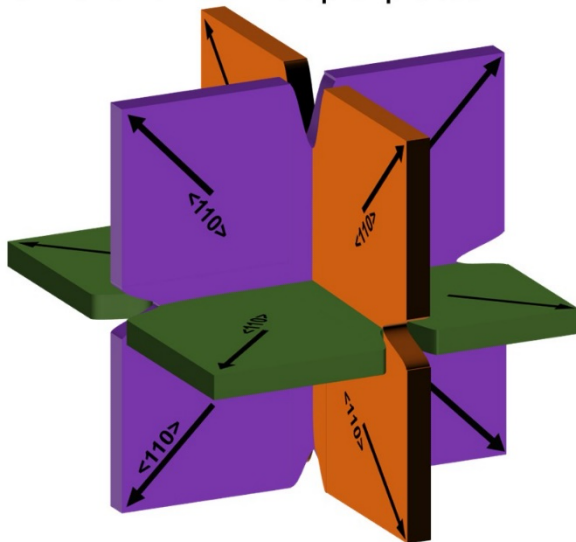
- a $\{100\}$, $\{110\}$, $\{111\}$ planes of TiC nucleant particle



- b Nucleation and growth of one Al_3Ti plate on TiC $\{110\}$



- c Growth of multiple plates



Arrows indicate $\langle 110 \rangle \text{Al}_3\text{Ti}$
Three colors show three grains

- d SEM image of etched specimen

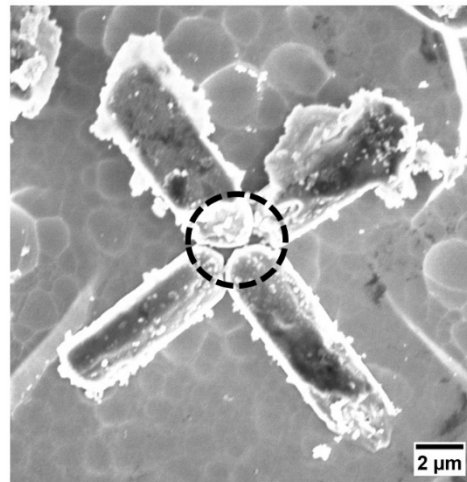


Fig. 12: (a) Depiction of $\{100\}$, $\{110\}$, and $\{111\}$ planes within the TiC crystal. (b) Visualization of the nucleation and growth of four Al_3Ti crystals on four out of 12 $\{110\}$ TiC planes, corresponding to one of the three orthogonal grains. (c) Growth of all three grains, where the three colors correspond to their three unique orientations (see also Figs. 8-9). (d) SEM image displaying orthogonal structure in an etched specimen, showing gaps between the individual plates (see circled region), *cf.* Figs. (b-c).