A NEW SOLID STATE SYNTHESIS METHODOLOGY FOR TERNARY AND HIGHER ORDER COMPOUNDS

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ABSTRACT

A persistent problem in the synthesis of complex materials from three or more constituents is the retention of very stable intermediate phases with properties grossly different from the target phase. In our recently developed two-stage synthesis methodology, a binary precursor is prepared and then directly converted into the product phase, thereby avoiding intermediate phase formation. Crystallographic similarities between the precursor and product phases are manipulated such that the major structural elements remain chemically intact. Ordered structural vacancies are used to facilitate rapid and highly selective diffusion of the third element into the precursor. Since no crystallographic reconstruction is required, no extraneous phases can form. The method has been tested on the solid state synthesis of Ti3SiC2 and Ti3AlC2, producing synthesis temperature reductions of 400 – 600°C. It is postulated that similar crystal structural relationships in layered oxides, nitrides and intermetallic compounds will allow an extension to many other systems.

KEYWORDS: MAX Phases, In-situ neutron diffraction, Ti3AlC2, Ti3SiC2

1. INTRODUCTION

Synthesis of higher order ternary or quaternary compounds must proceed via the reaction of two or more reactant or intermediate phases. During reactive sintering, (a diffusion-limited process) the initial reactivity and final phase homogenisation relate to the relative inter-diffusion of constituent elements through reactant, intermediate and final product phases. The resulting phase purity may be improved if the motion of constituent elements is uninhibited, which can only occur if sufficient diffusion “pathways” exist. In many systems (e.g. highly disordered grain boundaries), these pathways can best be described as “diffusion short-circuits” due to the relatively higher diffusivities resulting from lower atomic co-ordination. Similar affects can be found in substoichiometric systems, e.g. Me-C1-x and Me-O2-y, where interstitial vacancies can contribute to localized relaxation and hence higher atomic flux through these regions. However, in both these examples low impurity concentrations can lead to disruption of these diffusion pathways and hence initiate the nucleation of unwanted intermediate phases—an affect exacerbated by the formation of diffusion boundaries at the juncture of reactant particles. More specifically, it has recently been shown 1,2 that site occupancy can influence diffusivity of an element (Si) through a binary intermediate phase (TiC1-x) during higher order synthesis of Ti3SiC2. The rate of diffusion of carbon through substoichiometric titanium carbide (TiC1-x) was then shown to influence both the nucleation and continued precipitation of the final product phase, Ti3SiC2. If however, the carbon concentration became fully stoichiometric then the pathways available for silicon diffusion would be closed and hence the reaction cease before completion of the reaction.

Fundamental knowledge of the crystallographic “building blocks” from which materials are made holds the key to optimizing advanced materials synthesis without necessitating direct atomistic manipulation. By capitalizing on the structural relationships between lower and higher order materials an innovative technique employing solid state self-assembly has been developed for the synthesis of a unique class of ternary carbides, Mn+1AXn (or MAX Phases). This technique has significant advantages over traditional methods by simplifying synthesis routes, lowering processing costs and improving product phase purity. Although ubiquitous in chemistry and biology for revolutionizing molecular synthesis 3, applications of solid state self-assembly remain rare. In brief, the Authors have used a customised precursor to synthesize the Mn+1AXn Phases, Ti3SiC2 and Ti3AlC2 4.
Figure 1. The crystal structure of the model MAX Phase, titanium silicon carbide (Ti₃SiC₂). Note that substitution of the A-site element of Si for Al results in the isostructural compound, titanium aluminium carbide, (Ti₃AlC₂).

1.1 Review of MAX Phases

Mₙ₊₁AXₙ Phases, where M is an early transition metal, A is a Group III or IV element, and X is either C or N, form a large class of materials (>100) with a strategic combination of metallic and ceramic properties. Of these materials, Ti₃SiC₂ has been the most widely studied example with in excess of 250 research papers published in the last 10 years concerning its structure, synthesis, and properties. Although the remaining materials have been less intensely studied, there is solid evidence that their properties are very similar to those of Ti₃SiC₂. With a brittle-to-ductile transition mechanism, Ti₃SiC₂ is readily machinable with conventional tools, reminiscent of a metal. Paradoxically, the material exhibits high temperature strength (Compressive: 500 MPa at 1573K, Bend: 120 MPa at 1573K, Tensile: 60 MPa at 1473K) and chemical stability (E(O₂) ≅ 370 kJ/mol) similar to ceramics. Along with a high Young’s modulus (320 GPa), thermal shock resistance (ΔT>1673K) and hardness (4 GPa), this unique material also demonstrates high thermal (34 W/m.K) and electrical conductivity (4.5×10⁶ Ω⁻¹m⁻¹). It has been widely reported these properties arise from the ordered layering of the Mₙ₊₁AXₙ crystal structure. Figure 1 illustrates the relative co-ordination of the 312 MAX Phase, Ti₃SiC₂, clearly indicating the lamella crystal structure that is characteristic of these materials. These materials are presently being investigated for such diverse applications as high temperature semiconductors, ultra-low friction coatings, and diffusion bonding layers. The major obstacle in realizing these applications lies with controlling the synthesis process, with a particular emphasis on reducing residual impurity phases; when minor impurity phases are present, the strength, oxidation resistance and ductility are reduced.

To date, the synthesis of bulk Ti₃SiC₂ has been attempted by a wide variety of methods. These have met with various degrees of success, with even the best technique (Reactive Hot Isostatic Pressing) resulting in up to 5% of unwanted TiCx. Alternatively, the perceived economies of combustion synthesis have previously been offset by higher impurity levels (>5%). Although the reaction kinetics of individual techniques are most certainly unique, there is evidence to suggest that when using common synthesis temperatures (e.g. >1400°C) and reactants (e.g. 3Ti+SiC+C) the processes may be related. Throughout the literature, there has been a considerable reliance on post-reaction microstructure analyses, often leading to incorrect or ambiguous interpretations of reaction pathways. Using in-situ neutron diffraction, the authors have identified features within the various reaction pathways that are not apparent using traditional means of investigation. From these observations it was found that depending on the synthesis method Ti₃SiC₂ evolves from unique binary and/or ternary phases. This provided the key to a more controlled synthesis technique. It was observed that during reactive sintering, two intermediate phases, TiCₓ and Ti₅Si₃Cₓ initially form with very low concentrations of carbon (x ≅ 0.4). They simultaneously increase in quantity and become more stoichiometric (i.e. x→1.0) until they dominate the microstructure. Ti₃SiC₂ grows via a solid-state reaction between the two intermediates. However, once the TiCx attains a value of x ≅ 1.0, conversion to the product phase virtually ceases. The diffusion-controlled reaction is limited by the rate at which silicon can diffuse through TiCx, with the rate slowing as x increases. This is compelling evidence that the TiCx intermediate phase must be sub-stoichiometric to allow for the nucleation of Ti₃SiC₂. Once fully stoichiometric, TiC is difficult to remove from the product material. Alternatively, during Self-Propagating High-Temperature Synthesis (SHS) experiments, a single pseudo-binary intermediate phase, essentially a solid solution of silicon in TiCₓ, was rapidly formed. Ti₃SiC₂ precipitated directly from the solid solution upon cooling. This confirmed a hypothesis in
the literature that, under the correct conditions, large amounts of silicon can be incorporated within the TiC$_{x}$ structure\textsuperscript{16}. Independent identification of similar solid-solutions have been reported from the reaction of SiC particles with titanium alloys\textsuperscript{17}. The results obtained from in-situ neutron diffraction of these two synthesis techniques provided significant insight into the reaction mechanisms of the Ti-Si-C system and led to the use of a solid state precursor to synthesize titanium silicon carbide, Ti$_3$SiC$_2$. 

1.2 Reaction Kinetics and the Precursor Design

The problems associated with the synthesis of ternary MAX phases have been reviewed in detail by Kisi and Riley [ibid.]. The problem of intermediate phase retention is far more widespread than just the MAX phases. In general, the kinetic path followed during the conventional solid state synthesis of a hypothetical ternary phase ABC from powders of its constituent elements A, B and C serves to illustrate the key points. We assume that the powders have been cold pressed in a die and placed into a furnace for solid-state reactive sintering. Up to five stages are recognisable:

1) Diffusion begins at powder contact points; A into B, B into A into C, A into C, C into A etc.

2) Unless completely soluble, the contacting elements will form intermediate phases. In ceramics these are generally compounds (e.g. A$_2$B and BC$_2$) which are thermodynamically very stable. Their low diffusivities for their constituents usually make them diffusion barriers around the un-reacted cores of the constituent particles.

3) The reacting particles consolidate somewhat due to surface diffusion (like the sintering of a single phase).

4) It has been observed that these processes often continue until all the constituents have been converted into intermediate phases\textsuperscript{2,3}.

5) Eventually, the intermediate phases react with each other to form the ternary phase (e.g. A$_2$B + BC$_2$ → 2ABC). This stage is necessarily slow as the activation energy for the dissolution of the intermediate phases is high.

The retention of intermediate phases can therefore be seen to be the result of several attributes of this process and is often accompanied by undesirable side effects. The need to overcome the “diffusion barrier” effect of the intermediate phases (stage 2) and to later decompose the intermediate phases (stage 5) dictates very high temperatures. This has side effects ranging from severe economic penalties to evaporative loss of constituents making the attainment of a pure ternary phase impossible. Additionally, towards the end of stage 5, crystals of the intermediate phases are isolated by the growing product phase which acts as a diffusion barrier for the necessary exchange of atoms to grow the product phase. Hence, in the conventional synthesis, some intermediate phases are always retained in the final product.

There have been many strategies to overcome these difficulties – all aimed at pre-processing the powders in ways that allow rapid short-range diffusion. These have included solution chemistry in the form of co-precipitation and sol-gel methods; gas-phase syntheses and melt-flux-growth methods\textsuperscript{18} etc. They all have notable successes on the laboratory scale and there has been some large-scale implementation, especially for oxide systems. However there are numerous problems with their widespread and large scale use. These include (i) cost, (ii) they are difficult to adapt to carbides, nitrides, borides etc, (iii) they are difficult to adapt to ternary and higher order systems and (iv) there is undesirable environmental impact of wastes or additional cost to avoid it.

We have pioneered a new solid state method for the synthesis of layered phases which, in the systems tested thus far, circumvents the formation of intermediate phases\textsuperscript{4}. This not only leads to the pure ternary phase, but in the systems tested, allows synthesis to proceed rapidly at temperatures well below the conventional solid state route due to the removal of stages 1, 2 and 4 above. The method is specifically aimed at layered ternary or higher order phases which invariably have crystal structures based upon simpler binary phases. Our example here is the M$_{n+1}$AX$_{n}$ (or MAX) Phase, Ti$_3$SiC$_2$. The Ti-Si-C phase diagram has several possible intermediate phases of which Ti$_5$Si$_3$ and TiC$_{1-x}$ have been shown to be pivotal during in-situ neutron diffraction studies of the conventional synthesis\textsuperscript{1,2,15}. Note from Figure 1 that M$_{n+1}$AX$_{n}$ phases contain sheets of binary M$_{n+1}$X$_{n}$ phase n layers thick, where n is most commonly 1, sometimes 2 and only a single example is known where n = 3. Between the sheets of M$_{n+1}$X$_{n}$ are single layers of the A element (Si in our example). Successive M$_{n+1}$X$_{n}$ sheets in the ternary structure are related by a shear. The carbon vacancies in TiC$_{1-x}$ and indeed in all MX$_{1-x}$ phases are known to form ordered structures under certain conditions\textsuperscript{19}. It was also found that the presence of A-group elements in MX phases (e.g. TiC) lowers the stacking fault energy, perhaps allowing the ready formation of the twin-faulted structure\textsuperscript{20}. We have used this knowledge to propose a synthesis method for MAX phases in which a precursor is synthesised from sub-stoichiometric M$_{n+1}$X$_{n}$ phase (e.g. TiC$_{0.67}$) which contains structural vacancies. A vacancy ordered state is then induced and the resulting powder mixed with the A-group element and sintered. The process is somewhat analogous to the intercalation of atoms into the graphite structure. Ideally, the A-group
atoms diffuse in to vacant carbon sites and catalyse regular twin-faulting to give the target phase. The ordered vacancies form a direct kinetic path for the A elements to access the sites they will occupy in the MAX phase. Far higher diffusional flux can develop in such a process because the vacancy population is 4-6 orders of magnitude higher than the thermally induced vacancy population. As designed, the process should deliver intermediate phase free synthesis at greatly reduced temperatures.

2. PROCEDURE

The method used here has previously been discussed in relation to the synthesis of Ti₃AlC₂ has been discussed elsewhere ⁴, but will now be extended to include the synthesis of Ti₃SiC₂. Briefly, the precursor material was produced by mechanically milling Ti powder (Sigma-Aldrich, -100 mesh, 99.7%) and graphite powder (Aldrich, <100μm, 99.9%) in a SPEX 8000 mixer mill using a hardened steel vial and balls. A spontaneous SHS reaction produced TiC₀.₆₇, usually after about 109 minutes. The mechanisms of this mechanically activated SHS (MASHS) reaction have been previously been shown to vary with the degree of milling energy as related to the mass-to-charge ratio (MCR) ²⁰. The TiC₀.₆₇ powders so formed were hand mixed with the desired A-group element, which for these experiments included Al (Sigma-Aldrich, -100 mesh, 99.8%) and Si (Sigma-Aldrich, -100 mesh, 99.98%) powders in molar concentrations of 3:1 and the resulting mixture pressed into pellets (Ø10mm, 15mm high) at a pressure of 180MPa. Control samples of pressed TiC₀.₆₇ precursor were also prepared in the same way. All powder handling was conducted in an argon atmosphere containing <2 ppm O₂ and <2 ppm H₂O. The synthesised precursor powders were examined using laboratory XRD (Ni-filtered Cu Kα radiation, Panalytical X’Pert diffractometer, X’Celerator detector) and SEM (Philips XL30). No signs of unreacted Ti or C was found.

2.1 In-situ Neutron Diffraction

To test this new method, an experimental technique capable of real-time monitoring of both the crystal structure and presence of secondary phases in bulk samples was required. During analysis of the reaction mechanisms involved in MAX Phases synthesis via self-propagating high-temperature synthesis (SHS), the Authors developed a methodology for using time-resolved, in-situ neutron diffraction ¹⁵. Crucial to this was the used of the D20 instrument situated at the Institut Laue-Langevin (ILL, Grenoble, France), which presently constitutes the world’s fastest neutron diffractometer. D20 has a position sensitive detector (PSD) capable of downloading data from 5-160° (2θ) in less then 0.4s. As the rate of any SHS reaction is limited only by the spontaneous self-combustion of reactants it was previously essential to use the most rapid settings of the D20 PSD, resulting in a time-resolution of 300ms, though this was typically operated for 500ms acquisition time. However, as the interdiffusion mechanisms of the present investigation were considered to be diffusion limited, the data acquisition rate was set considerable lower (i.e. minutes). In slowing the acquisition time we were able to significantly reduce the volume of material required for each experiment and hence focus more of precusor and reactant purity. All heating experiments were conducted in-situ on D20. The diffractometer, it’s vacuum furnace and the experimental arrangement used are as-described previously for the SHS synthesis of Ti₃SiC₂ ¹⁵. In-situ neutron diffraction patterns were recorded with 1 minute time-resolution in the angle range 10° – 140° 2θ. The thermal cycles used comprised heating from room temperature to 1000°C at rates between 5°C/min and 25°C/min, holding for 2hrs and cooling to room temperature at 5°C/min. The sequence of neutron diffraction patterns was examined using the Large Array Manipulation Program (LAMP) and selected patterns subjected to intense analysis using standard crystallographic methods and Rietveld refinements. The programs used and typical parameters varied during the analyses have been described in earlier work ¹⁵. The synthesised samples were examined using SEM.

3. RESULTS & DISCUSSION

The reaction mechanism of silicon diffusing into the TiC₀.₆₇ precursor was clearly revealed using time resolved in-situ neutron diffraction. Figure 2 illustrates the data obtained during the reaction, with time shown on the vertical axis and diffraction angle on the horizontal axis (LAMP plot).
Figure 2. Time-resolved neutron diffraction data of the precursor, TiC_{0.67}, reacting with silicon powder to form a solid solution of (3Ti,Si)C_{0.67} from which Ti_{3}SiC_{2} then precipitated. Diffracted intensity is shown by the increasing colour intensity, while time and diffraction angle (2θ) are as indicated on the vertical and horizontal axis, respectively.

Diffraction intensity can be observed as increasing colour intensity in the plot such that a section at any instance in time provides data akin to traditional 2-D diffraction plots, an example of which is shown in Figure 3. The LAMP plots provide a visual method for rapidly interpreting the coarser features of the reactions sequence, including phase transitions; e.g. the dissolution of Si is clearly evident as a discontinuity in the Bragg reflections at ~16°, ~26°, ~40° and ~47° after approximately 130 mins of heating. Another example of these features is the precipitation of the product MAX Phase, Ti_{3}SiC_{2} after an incubation time of ~10 mins, again clearly evidenced by the appearance of the respective Bragg reflections. More specific information may be obtained via Rietveld analysis of the individual diffraction patterns, such as that provided in Figure 3. More detailed interrogation of data may be obtained by plotting the LAMP contour plot of the same data previously shown in Figure 2. This contour plot is provided in Figure 4 and clearly shows the contributions of the intercalating silicon to the background.

3.1 Reaction Sequence

The key to designing and implementing the use of a crystalline precursor was in understanding the role of interstitial vacancies in enabling long-range diffusion of the intercalating A-group element (e.g. Si). The complete reaction sequence for the intercalation of Si into the crystalline precursor, TiC_{0.67}, has been interpreted to have occurred in four main stages. These stages are illustrated in Figure 5 and may be summarised as, (a) The initial randomised vacancy state of the TiC_{0.67} precursor, (b) Spontaneous ordering of the vacancies in the presence of silicon, (c) Spontaneous twinning of the precursor sub-lattice and (d) the inter-diffusion of the silicon A-site element resulting in the precipitation of Ti_{3}SiC_{2}. Unlike the reaction of aluminium with TiC_{0.67} during which the intercalating element (Al) melted prior to reaction, it has been confirmed that silicon remains in the solid state during the reaction. This is confirmed using in-situ neutron diffraction with a gradual decrease in the silicon diffracted intensity, matched by a growth in the TiC_{1-x} diffracted intensity, as silicon substitutions into the crystalline state of the precursor.
Figure 3. 2-D diffraction data, illustrating the reaction of silicon with the customised precursor, TiC$_{0.67}$, immediately before the precipitation of the titanium silicon carbide.

Figure 4. Contour plot of the neutron diffraction data, clearly identifying the contributions of the aluminium liquid phase to the overall background, which decreases as the Al is intercalated into the crystalline structure of the TiC$_{0.67}$ precursor. It is from this crystalline state that the MAX Phase, Ti$_3$SiC$_2$ precipitates.
Significantly, a reduction in the background diffuse scattering evident in Figure 4 between 15 – 25° (2θ) indicates that the initial inter-diffusion of silicon into the sub-lattice of TiC$_{1-x}$ increases order within this partially disordered material. Consistent with this observation is the rate of increase in TiC$_{1-x}$ intensity as this diffuse scattering is reduced over the following 60 min time interval. The absence of an “incubation time” that was evident in the reaction sequence of 3TiC$_{0.67}$ + Al also suggests that Ti$_3$SiC$_2$ precipitates directly from the ordering of silicon on the TiC$_{0.67}$ sub-lattice. Furthermore, the precipitation of Ti$_3$SiC$_2$ occurred at ~920°C and after only 120 mins of processing, approximately 600°C below traditional reactive synthesis techniques requiring more then twice the processing time (~4 hrs total).

The reaction sequence for 3TiC$_{0.67}$ + Si → Ti$_3$SiC$_2$ has been shown to differ from the previously investigated use of a solid state precursor. Specifically, previous observations that the ordering of interstitial vacancies within the customised precursor, TiC$_{0.67}$, was facilitated by the ingress of molten aluminium to form Ti$_3$AlC$_2$ have been verified during the purely solid state reaction of crystalline silicon within an identical precursor compound. This suggests that independent of the physical state of the intercalating element (e.g. liquid or solid) the formation and stabilisation of vacancies within the TiC$_{1-x}$ sub-lattice is facilitated by the A-group MAX Phase layer. More broadly, the expected lowering of this activation energy can only occur in the presence of the A-group element, with identical thermal treatment of pure precursor material producing no further comparable ordering of vacancies. Significantly, reductions in processing times and temperatures suggest this novel approach to MAX Phase synthesis will find immediate application in reducing the associative costs of synthesizing these unique materials.

4. CONCLUSIONS

MAX Phase materials exhibit a unique combination of ceramic and metallic properties, potentially suitable for a wide range of applications. Conventional synthesis techniques have largely relied on the reaction of macroscopically distinct powders, resulting in the
retention of intermediate phases formed at particle boundaries. Due to their high activation energies these intermediate phases remain in the final product where they detrimentally reduce the physical properties of the MAX Phase. We have demonstrated a novel synthesis technique for the synthesis of titanium silicon carbide (Ti₃SiC₂) that relies on structural similarities between the final product’s structure and a binary precursor, TiC₀.₆₇. When mixed and reacted with an A-group element (e.g. silicon) the MAX Phase forms via the reaction,

\[3\text{TiC}_{0.67} + \text{Si} \rightarrow 3\text{TiC}_{0.67}(\text{Si})(\text{disordered}) \rightarrow 3\text{TiC}_{0.67}(\text{Si})(\text{ordered}) \rightarrow \text{Ti}_3\text{SiC}_2\]

When compared with conventional synthesis techniques, this use of a solid state precursor reduces the processing time and temperatures by 50% and 44%, respectively. This technique has now been demonstrated to work for both Ti₃SiC₂ and Ti₃AlC₂ using the same solid state precursor, despite the reaction mechanisms remaining different (solid state versus liquid phase). This synthesis technique has been verified using in-situ neutron diffraction.

Acknowledgements

This work has been funded by the Australian Research Council (ARC) under grant DP0451429. The Authors would like to show their appreciation for the staff of Institut Laue-Langevin (ILL) who remain supportive of this research; namely Thomas Hansen, Alan Hewat and Paul Henry.

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