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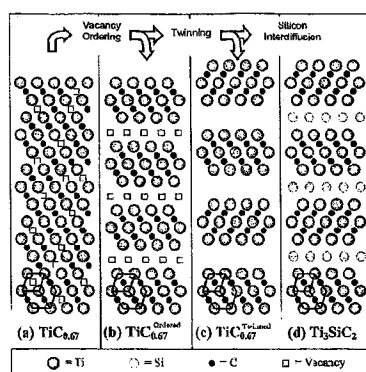
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(54) Title: CRYSTALLINE TERNARY CERAMIC PRECURSORS



(57) Abstract: A method of forming $M_{n+1}AX_n$, where M is an early transition metal (such as Ti) or mixtures thereof, A is a group III or IV element (such as Si) or mixtures thereof and X is C, N or mixtures thereof, the method comprising the steps of providing a precursor of formula $M_{n+1}AX_n$ and reacting the $M_{n+1}X_n$ with A to provide $M_{n+1}AX_n$. The $M_{n+1}X_n$ may be ordered and/or twinned (eg by mechanical alloying, thermal treatment etc. prior to reacting with A, ordered and/or twinned during its formation from M and X. A may be present during the formation of $M_{n+1}X_n$ from M and X or during the ordering and/or twinning of disordered $M_{n+1}X_n$. The $M_{n+1}AX_n$ produced is substantially free from MX and or other residual phases.

TITLE: CRYSTALLINE TERNARY CERAMIC PRECURSORS**5 FIELD OF THE INVENTION**

The invention relates to metal ceramic hybrid compounds of general formula $M_{n+1}AX_n$, such as Ti_3SiC_2 , and to the methods of efficient synthesis of such compounds with controlled stoichiometry and purity.

10 BACKGROUND ART

Compounds which exhibit both ceramic and metallic characteristics are of great interest as advanced materials. Metals are readily machined but can lose their machined form (especially cutting edges, for instance) at high temperatures. They are also subject to corrosion in chemical environments and oxidation at high temperatures. Ceramics on the
15 other hand retain their shape at extremely high temperatures, but are brittle and difficult to machine at low temperatures. Considerable effort has been put into engineering advanced materials that possess the desired properties of both metals and ceramics.

One group of compounds that exhibit the desired hybrid metal ceramic properties are the
20 "MAX" compounds. These are compounds of the general formula $M_{n+1}AX_n$ where M is an early transition metal, A is a group III or IV element, X is C or N and n is usually 1, 2 or 3. These materials are also commonly referred to as nano-laminates, or ternary Hägg and Nowotny phases. Although there are in excess of 100 such compounds, the most widely known $M_{n+1}AX_n$ compound is Ti_3SiC_2 , titanium silicocarbide or titanium silicon
25 carbide. The present invention will be generally described with reference to Ti_3SiC_2 as

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an example, although it will be appreciated that the scope of the invention is not limited to such an example but encompasses all compounds of the general $M_{n+1}AX_n$ formula.

$M_{n+1}AX_n$ compounds, including Ti_3SiC_2 , exhibit high fracture toughness at elevated
5 temperatures, and can be machined using conventional hard steel tooling. They have high temperature stability, high temperature strength (Compressive: 500 MPa at 1573K, Bend: 120 MPa at 1573K, Tensile: 60 MPa at 1473K) and chemical stability ($E(O_2) \cong 370$ kJ/mol) similar to ceramics. The Young's modulus is (320 GPa) and, unlike other ceramics, they possess extreme thermal shock resistance ($\Delta T > 1673K$) and high thermal
10 conductivity (34 W/m.K). These attributes make them useful in mechanical applications whereas their high electrical conductivity ($4.5 \times 10^6 \Omega^{-1}m^{-1}$) is suited to electrical applications. Together these represent an exciting combination of material properties.

It is believed that the layered structure of $M_{n+1}AX_n$ compounds, including Ti_3SiC_2 , is the
15 key to these compounds achieving this desirable combination of properties. There is solid evidence throughout the literature that the properties of other $M_{n+1}AX_n$ compounds are very similar to those of Ti_3SiC_2 , in particular other 3:1:2 compounds, but equally 2:1:1 and 4:1:3 compounds.

20 The scientific literature teaches that pure Ti_3SiC_2 is suitable for a diverse range of applications, including structural ceramics, corrosion/oxidation resistant films, or as an interlayer phase in bonding ceramics and metals. Composite materials where a MAX compound forms the majority phase that bonds together another phase with different properties are also of considerable utility in abrasive environments. An example would
25 be Ti_3SiC_2 with a controlled quantity and dispersion of TiC. However, reproducibly

achieving controlled stoichiometry and homogeneity of sub-phases in MAX materials has proved difficult

However, there are drawbacks with currently available $M_{n+1}AX_n$ compounds, including

5 Ti_3SiC_2 , namely that:

i) *known methods of synthesis do not allow for them to be obtained in ultra pure form*
(i.e. as a single compound).

The conventional synthesis of higher order (ternary, quaternary, etc) ceramic compounds such as $M_{n+1}AX_n$ compounds, including Ti_3SiC_2 , requires that the reaction pathway
10 proceeds via one or more intermediate phases. Residual intermediate phases are the major source of product imperfection, to the detriment of final material properties.

When even minor impurity phases are present, the strength, oxidation resistance and ductility of the final $M_{n+1}AX_n$ compound are reduced. Reduced ductility leads to an increase in unpredictable fast fracture.

15

Because the reactions occur primarily in the solid phase, they are controlled by diffusion and the possibility exists of isolated, unreacted island of intermediate compounds remaining within the final product. It is generally the case that unwanted phases have high thermodynamic stability and are difficult (uneconomical) to remove from the solid
20 matrix once formed.

ii) *methods of synthesis require very high temperatures with associated economic and environmental cost.*

The need to break down stable intermediate compounds such as Ti_5Si_3 to form the desired MAX compound requires considerable time at very high temperature, typically

5 in the range (1400-1600°C).

Consequently, in order to obtain improvements in product purity, reduced synthesis temperatures and reduced synthesis times, significant modification of synthesis techniques is required.

10

It is an object of the present invention to overcome or ameliorate at least one of the disadvantages of the prior art, or to provide a useful alternative.

Any discussion of the prior art throughout the specification should in no way be
15 considered as an admission that such prior art is widely known or forms part of common general knowledge in the field.

SUMMARY OF THE INVENTION

20

In a broad aspect, the invention provides a method of forming $M_{n+1}AX_n$, where M is an early transition metal or mixtures thereof, A is a group III or IV element or mixtures thereof and X is C, N or mixtures thereof, the method comprising the steps of:

providing a precursor of formula $M_{n+1}X_n$ and

25 reacting the $M_{n+1}X_n$ with A to provide $M_{n+1}AX_n$.

- 5 -

$M_{n+1}X_n$ may be ordered and/or twinned prior to reacting with A. It may for instance be ordered and/or twinned during its formation from M and X, or alternatively $M_{n+1}X_n$ is ordered and/or twinned by treatment of disordered $M_{n+1}X_n$.

- 5 Optionally, A is present during the formation of $M_{n+1}X_n$ from M and X, or alternatively, A is present during the ordering and/or twinning of disordered $M_{n+1}X_n$.

Alternatively, A may be introduced immediately prior to, or during the reaction with $M_{n+1}X_n$.

10

According to a first aspect, the invention provides a method of forming $M_{n+1}AX_n$, where M is an early transition metal or mixtures thereof, A is a group III or IV element or mixtures thereof and X is C, N or mixtures thereof, comprising:

providing a precursor of formula $M_{n+1}X_n$;

- 15 adding element A to the precursor of formula $M_{n+1}X_n$; and
treating the mixture of A and $M_{n+1}X_n$ to provide $M_{n+1}AX_n$.

The invention also provides a method of forming $M_{n+1}AX_n$, where M is an early transition metal or mixtures thereof, A is a group III or IV element or mixtures thereof

- 20 and X is C, N or mixtures thereof, comprising:

providing a precursor of formula $M_{n+1}X_n$;

treating $M_{n+1}X_n$ if required to provide an ordered and/or twinned $M_{n+1}X_n$

phase;

adding element A to the ordered $M_{n+1}X_n$ phase; and

- 25 treating the mixture of A and $M_{n+1}X_n$ to provide $M_{n+1}AX_n$.

A may be for example Al, Si, P, S, Ga, Ge, As, Cd, In, Sn, Tl or Pb, but is preferably Si, Ge or Al. M is preferably Sc Ti V Cr, Zr, Nb, Mo, Hf, Ta or W. Most preferably, M is Ti.

5

A is preferably Si. X is preferably C. n may be any number, but is preferably an integer, preferably 1, 2, or 3, more preferably 2. The most preferred compound is Ti_3SiC_2 , however the invention extends to the production of compounds within other ternary systems such as Ti-Ge-C systems, Ti-Al-C systems (including $\text{Ti}_{n+1}\text{AlC}_n$ systems like Ti_2AlC , Ti_3AlC_2 and Ti_4AlC_3 which are also highly preferred compounds), Ti-Al-N systems, Ti-Si-N systems etc.

10

The precursor of formula M_{n+1}X_n may be of any structure, for example, it may be disordered, ordered, twinned, alloyed. If desired, M_{n+1}X_n may be treated to provide an ordered and/or twinned M_{n+1}X_n phase.

15

Adding element A to the ordered M_{n+1}X_n phase may be, for instance, by mixing the two in powdered form. Alternatively, this may occur by gaseous phase or liquid phase mixing.

20

The process is extendable to solid solutions between MAX compounds where any or all of the M, A and X crystallographic sites are occupied by multiple elements for example, M can be any combination of early transition metals, such as a combination of Ti and V, A can be a combination of Si and Al, while X can be a combination of C and N.

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Specific examples of such compounds include $\text{Ti}_3\text{Si}_m\text{Al}_{1-m}\text{C}_2$, $\text{Ti}_y\text{V}_{3-y}\text{AlC}_2$ or $\text{Ti}_3\text{SiC}_x\text{N}_{2-x}$.

The process is also extendable to composite materials based upon MAX phases. An
 5 example is a matrix of Ti_3SiC_2 with embedded TiC particles.

The process is further extendable to oxide ceramics which have a layered structure such as the superconductor $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ or the dielectric $\text{Ca}_3\text{Ti}_2\text{O}_7$.

10 Preferably, the treating of M_{n+1}X_n to provide an ordered and/or twinned M_{n+1}X_n phase is a mechanical treatment. Preferably the mechanical treatment is a milling treatment.

Alternatively, the treating of M_{n+1}X_n to provide an ordered and/or twinned M_{n+1}X_n
 15 phase is a thermal treatment. Preferably the thermal treatment is carried out in the range 600-1000°C.

Preferably, treating the mixture of A and M_{n+1}X_n to provide a $\text{M}_{n+1}\text{AX}_n$ is a thermal treatment sometimes referred to as reactive sintering or liquid phase sintering. The
 20 treatment may be carried out at any suitable temperature, and for any length of time.

Preferably the thermal treatment is carried out about 1100°C or below. In one embodiment, the thermal treatment is at temperatures between 400-1000°C for between 30 –60 minutes. In alternative preferred embodiments, the temperature is less than 500°C , with the process carried out for 100 minutes or more.

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Unless the context clearly requires otherwise, throughout the description and the claims, the words "comprise", "comprising", and the like are to be construed in an inclusive sense as opposed to an exclusive or exhaustive sense; that is to say, in the sense of "including, but not limited to".

5

According to a second aspect, the invention provides a method of forming $M_{n+1}AX_n$ where M is an early transition metal or mixtures thereof, A is Si, Ge, Al or mixtures thereof and X is C, N or mixtures thereof, comprising:

treating a mixture of $n+1M$ and nX to provide an ordered and/or twinned $M_{n+1}X_n$ phase

10 adding element A to the ordered $M_{n+1}X_n$ phase

treating the mixture of A and $M_{n+1}X_n$ to provide a $M_{n+1}AX_n$.

Preferably, the treating a mixture of $n+1M$ and nX to provide an ordered and/or twinned $M_{n+1}X_n$ phase is a mechanical treatment, and more preferably the mechanical treatment

15 involves mechanical alloying. Preferably the mechanical alloying is milling.

Mechanical alloying is preferably milling of graphite and any suitable source of M. For example, if Ti_3SiC_2 is desired, mechanical alloying is between graphite or any suitable source of pure carbon and a Ti source such as, but not limited to TiH_2 , TiO_2 , Ti powder.

20 According to a third aspect, the invention provides a method of forming a $M_{n+1}AX_n$

compound, where M is an early transition metal or mixtures thereof, A is Si, Ge, Al or mixtures thereof and X is C, N or mixtures thereof, comprising:

treating a mixture of $n+1M$ and nX in the presence of A to provide an ordered and/or twinned $M_{n+1}X_n$ phase

25 and

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treating the mixture of A and $M_{n+1}X_n$ to provide a $M_{n+1}AX_n$.

The ordered and/or twinned phase may be formed in conjunction with element A, which may facilitate ordering and/or twinning

5

The present invention relates to the use of $M_{n+1}X_n$ as a precursor for $M_{n+1}AX_n$.

In particular, the invention relates to the use of Ti_3C_2 phases in the preparation of Ti_3SiC_2 . Those skilled in the art will be aware that Ti_3C_2 is sometimes referred to as

10 $TiC_{0.67}$ and the two forms are used herein interchangeably.

According to a fourth aspect, the invention provides a method of forming $M_{n+1}AX_n$ comprising combining twinned $M_{n+1}X_n$ with A. Preferably, the method includes thermal treatment to insert Si into twinned Ti_3C_2 .

15

According to a fifth aspect, the invention provides ultra pure $M_{n+1}AX_n$. By ultra pure is meant that the $M_{n+1}AX_n$ is substantially free from MX or other residual phases, ie it is substantially free from starting materials or other impurities. MX is <5% of the total $M_{n+1}AX_n$, preferably less than 1% and more preferably less than 0.5%. Percentages,

20 where not specified, relate to mole%.

In one particular embodiment, the invention provides ultra pure Ti_3SiC_2 having no or substantially no TiC , Ti_5Si_3 or other impurity phases. In other particular embodiments, the invention provides Ti_3SiC_2 having no or substantially no unwanted impurities, but

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containing a predetermined amount of another phase, for example Ti_3SiC_2 with a predetermined amount of TiC .

According to a sixth aspect the invention provides an ordered M_{n+1}X_n phase

5 According to a seventh aspect the invention provides a twinned M_{n+1}X_n phase

An advantage of these ordered and or twinned precursors is that they readily facilitate the introduction of the A species such as silicon. Not only does this lead to increased purity, it also decreases the cost of production. This occurs because the need to

10 decompose highly stable intermediate phases such as TiC and Ti_5Si_3 is circumvented.

High temperature furnaces are costly to purchase, operate and maintain and reducing the synthesis temperature from 1400-1600°C to below 1100°C significantly reduces the energy requirement and the degree of sophistication of the furnace required to carry out the process.

15

The present approach also enables the possibility of selected alloying or doping by partial replacement of any or all of the M, A or X species. For example, a twinned or ordered M_{n+1}X_n phase can be mixed with a stoichiometric amount of A if required to produce pure $\text{M}_{n+1}\text{AX}_n$. However, if deemed desirable, a predetermined

20 substoichiometric quantity. Other elements, or mixtures of elements, can be doped in at this stage in a controlled manner.

Ti_3SiC_2 belongs to a large group of ternary carbides that exhibit a unique combination of high temperature ceramic properties with the electrical and thermal conductivity of

25 metals. As mentioned above, while these compounds are potentially very useful, their

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full potential to date is limited by the presence of residual intermediate compounds and starting materials that result in a degradation of these properties. The present invention seeks to reduce or eliminate the presence of unreacted intermediates by employing ordered and/or twinned precursors which provide a direct path to the product MAX phase. In the case of Ti_3SiC_2 , the present invention employs a custom engineered crystalline phase precursor, Ti_3C_2 , which can circumvent intermediate compound formation.

Without wishing to be bound by theory, it is believed that by using structural units common to the product phase, the crystalline precursors improve purity by effecting product formation at an atomic level in a controlled manner.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 shows one possible mechanism behind the engineering of Ti_3SiC_2 from a $\text{TiC}_{0.67}$ precursor.

Figure 2 shows one possible mechanism behind silicon diffusion through random vs ordered TiC_x phases.

Figure 3a shows the efficacy of mechanical milling in making the raw materials more reactive; in this case a reduction in the SHS combustion temperature of Ti_3SiC_2 as a function of milling time.

Figure 3b shows the temperature profile of the exterior of the milling vial during the mechanical alloying reaction.

Figure 4 shows real-time changes in the neutron diffraction data obtained during one embodiment of the invention.

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Figure 5 shows a series of BSE (back scattered electron) images from samples containing 3Ti + SiC + C milled for 15, 30, 45, 60, 75 and 90 minutes.

DESCRIPTION

As mentioned above, the present invention will be generally described with reference to Ti_3SiC_2 as an example, although it will be appreciated that the scope of the invention is not limited to this particular example but encompasses all compounds of the general $\text{M}_{n+1}\text{AX}_n$ formula, their solid solutions and composites based upon them.

To date, the synthesis of bulk Ti_3SiC_2 has been attempted by a wide variety of methods, such as M.W. Barsoum, T. El-Raghy, *J. Am. Ceram. Soc.*, Vol. 79, 1953-56 (1996); *J. Mat. Synth. and Proc.*, Vol. 5, [3], pp.197-216, 1997; *J. Am. Ceram. Soc.*, Vol. 82, 2849-54 (1999); *J. Am. Ceram. Soc.*, Vol. 82, 2855-60 (1999); E.H. Kisi, J.A.A. Crossley, S. Myhra, M.W. Barsoum, *J. Phys. Chem. Solids*, Vol. 59, 1437-1443 (1998); S. Myhra, J.W.B. Summers, E.H. Kisi, *Materials. Letters.*, Vol. 39, 6-11 (1999); T.Goto, T. Hirai, *Mat. Res. Bull.*, Vol. 22, 1195-1201 (1987); R. Pampuch, J. Lis, J. Piekarczyk, L. Stobierski, *J. Mat. Synth. & Proc.*, Vol. 1, 2, 93-100 (1993); F. Goesmann, R. Schmid-Fetzer, *Mat. Sci. & Engng.*, Vol. B46, 357-362 (1997); F. Goesmann, R. Wenzel, R. Schmid-Fetzer, *J. Am. Ceram. Soc.*, 81, 11, 3025-3028 (1998); A. Feng, T. Orling, Z.A. Munir, *J. Mater. Res.*, Vol. 14, 3, 925-939 (1998).

These synthetic methods have met with various degrees of success, however, even the best technique (reactive hot pressing) can result in up to 5% of unwanted TiC present in the final product. Generally, the more economical the method, the higher the impurity levels. Combustion synthesis, perceived as the most economical method, has TiC impurity levels above 5%.

Although a variety of different reactive pathways are employed in the abovementioned documents, there are commonalities of processing temperatures ($>1400^{\circ}\text{C}$) and reactants used (either $3\text{Ti} + \text{Si} + 2\text{C}$ or $3\text{Ti} + \text{SiC} + \text{C}$). The latter combination was found in some cases to improve the purity of the product material obtained.

5

Throughout the literature, there has been a considerable reliance on *post*-reaction microstructure analyses, often leading to incorrect assumptions of how the reaction proceeds. Without wishing to be bound by theory, the present inventors established by *in-situ* neutron diffraction that, depending on the synthesis method, Ti_3SiC_2 evolves
10 from binary and ternary phases that can provide the key to a more controlled synthesis.

It was observed that during reactive sintering from $3\text{Ti} + \text{SiC} + 2\text{C}$ starting materials, two intermediate phases, TiC_x and $\text{Ti}_5\text{Si}_3\text{C}_x$ form, initially with very low concentrations of carbon ($x \approx 0.4$). They simultaneously increase in quantity and become more
15 stoichiometric (i.e. $x \rightarrow 1.0$) until they dominate the microstructure. Ti_3SiC_2 grows via a solid-state reaction between the two intermediates. Once the TiC_x attains a value of $x \approx 1.0$, conversion to the product phase virtually ceases. The diffusion-controlled reaction is limited by the rate at which silicon can diffuse through TiC_x , with the rate slowing as x increases. This is compelling evidence that the TiC_x intermediate phase
20 must be *sub-stoichiometric* to allow for the precipitation of Ti_3SiC_2 . Once fully stoichiometric, TiC cannot be fully removed from the product material in a reasonable time scale.

During *in-situ* neutron diffraction studies of combustion synthesis, a single pseudo-
25 binary intermediate phase, essentially a solid solution of silicon in TiC_x , was rapidly

formed. Ti_3SiC_2 precipitated *directly* from this solid solution upon cooling, confirming that, under the correct conditions, large amounts of silicon can be incorporated within the TiC_x structure.

- 5 Hägg and Nowotny or MAX phases, including Ti_3SiC_2 , contain structural units that are common to one or more lower order phases. Of particular relevance are the Ti_6C octahedra of which TiC is constructed and which can also be found repeated as ordered layers in Ti_3SiC_2 , as shown in Figures 1(a) and 1(d), respectively.
- 10 In Ti_3SiC_2 a single layer of Si atoms separates twinned layers of TiC , with an elongated Ti-Si bond joining the structure together. In Ti_3SiC_2 the double carbide layer (which is Ti_3C_2) must be fully occupied with carbon. In contrast, TiC may be sub-stoichiometric (TiC_x) over a wide range of composition ($\text{TiC}_{0.33}$ to $\text{TiC}_{1.0}$). Without wishing to be bound by theory, it is believed that the structural similarities between the designed
- 15 precursor Ti_3C_2 described here and Ti_3SiC_2 form the basis for the high level of purity achieved in the synthesis of Ti_3SiC_2 using the method described herein.

A critical aspect of the present invention comes from understanding the crystallographic relationship between the $\text{TiC}_{0.67}$ (Fm3m) and Ti_3SiC_2 (P6₃/mmc) structures. Figure 1(a)

20 illustrates a two-dimensional projection of the $\text{TiC}_{0.67}$ (110) plane. In general, sub-stoichiometric TiC_x contains only randomly distributed carbon vacancies, as indicated for $\text{TiC}_{0.67}$.

Various treatments can cause the vacancies on the octahedral site to form into ordered

25 arrangements for example into layers. Ordering in TiC_x is possible over a wide range of

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compositions – at least $\text{TiC}_{0.5}$ – $\text{TiC}_{0.87}$. In $\text{TiC}_{0.67}$ this ordered structure, illustrated in Figure 1(b), is expressed one-dimensionally by the stacking sequence -Ti-C-Ti-C-Ti-□- (or equally Ti_3C_2 -□-), where □ = vacancy, a vacant carbon position within the structure. The vacancy ordering in this instance occurs in layers, accompanied by an enlargement
5 of the vacant site as titanium atoms relax towards the carbon atoms. This and related forms of ordering are critical to the method developed here.

Previous examples of vacancy ordering in TiC_x have been very slow processes, requiring annealing times of up to a month. It is known that the microstructure of
10 mechanically milled materials is highly disordered, the diffusion rates over short distances are significantly higher than normal lattice diffusion and that this allows microstructural processes to occur much faster and at lower temperature. An example from the work of the inventors is the effect of mechanical milling on the temperature required to initiate a self-propagating high-temperature synthesis (SHS) reaction in $3\text{Ti} +$
15 $\text{SiC} + \text{C}$ mixtures as shown in Fig 3. Milling was found to lower the SHS ignition temperature by as much as 850°C . This reduction is equivalent to an increase in diffusivity of many orders of magnitude, and dramatically illustrates that pre-processing by MA is effective in altering the kinetic state of reactants, significantly reducing processing times and temperatures. The invention relies upon this higher mobility to
20 allow vacancy ordering to occur on industrially realistic timeframes.

Short range ordering and twin faulting is known to exist in TiC_x where silicon was present. Through either segregation of Si to pre-existing faults or by causing further enlargement of the vacant site, sub-stoichiometric TiC_x was shown to have a higher than
25 expected twin fault density when silicon was introduced into the system.

The preferential segregation of silicon to these enlarged stacking faults has been observed to be accompanied by the nucleation of $\text{Ti}_5\text{Si}_3\text{C}_x$ and Ti_3SiC_2 itself. One possible, non limiting mechanism for the progressive ingress of silicon into the TiC_x structure is illustrated by comparing Figures 1(c) and 1(d), a [1210] projection, demonstrating that the ordered vacancies in $\text{TiC}_{0.67}$ closely approximate the silicon positions in Ti_3SiC_2 . The enlarged vacancies allow Si to preferentially diffuse into these sites without disrupting the ordering of the pre-existing Ti and C atoms. Again, without wishing to be bound by theory, Figure 2, provides one particular model illustrating the significance of vacancy ordering in providing diffusion paths into the crystal structure.

Figure 1 summarises the relationships between (a) $\text{TiC}_{0.67}$, (b) ordered $\text{TiC}_{0.67}$, (c) twinned $\text{TiC}_{0.67}$, and (d) Ti_3SiC_2 and serves to highlight their structural similarities, pointing the way to a new and highly versatile synthesis methodology using precursor phases. Used as a reactant material, the precursor Ti_3C_2 is structurally similar to (c) twinned $\text{TiC}_{0.67}$, with a deliberate, controlled ordering of carbon vacancies. Upon the addition of silicon, Ti_3SiC_2 is directly synthesized from this precursor phase *without* proceeding via any intermediate phases. The precursor is thus able to produce an alternate, continuous pathway to the product phase, eliminating residual impurity phases by preventing their initial formation. The key to designing and manufacturing such a specific precursor lies with understanding the structure and synthesis of Ti_3SiC_2 and controlling the ordering of TiC_x . In these compounds, the value of x can usually range from 0.44 to 1. Particularly preferred are $\text{TiC}_{0.5}$, a precursor to 2:1:1 MAX phases, $\text{TiC}_{0.67}$, a precursor to 3:1:2 MAX phases, and $\text{TiC}_{0.75}$, a precursor to 4:1:3 MAX phases.

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The mechanistic pathway to Ti_3SiC_2 via a $\text{TiC}_{0.67}$ (Ti_3C_2) precursor is shown primarily with reference to Figure 1. The mechanism may be described by three key stages:

- *Vacancy ordering of sub-stoichiometric $\text{TiC}_{0.67}$* Figure 1 (a)→(b)
- 5 ▪ *Twinning to re-align the structural units* Figure 1 (c)→(d)
- *Preferential diffusion of Si into the ordered vacancies, forming Ti_3SiC_2* Figure 1 (b)→(c)

The three physical steps in the synthesis of Ti_3SiC_2 from a $\text{TiC}_{0.67}$ precursor, which is one embodiment of the present invention is given below by way of a non-limiting example:

▪ ***Milling Pre-Processing***

Mechanical alloying (MA) of Ti (source TiH_2 , TiO_2 , Ti-powder etc) and C (graphite, glassy carbon, amorphous carbon etc) reactants forms a highly reactive, homogeneous powder. The degree of activation is proportional to the milling time, starting material particle size, milling energy and temperature. Microstructural analysis using Neutron/X-ray diffraction (ND/XRD) and Scanning Electron Microscopy (SEM) can be used to establish average particle size and morphology, respectively.

20

Once MA activated, the reactant powders were pressed and then annealed to allow solid state reaction to form $\text{TiC}_{0.67}$. The annealing time and temperature are dependent upon the degree of milling achieved in the previous step. Increased homogeneity and activation (i.e. increased milling) reduce both annealing time and temperature.

25

When the milling was continued for longer, the $\text{TiC}_{0.67}$ precursor material was produced directly by a mechanically activated self-propagating high-temperature synthesis (MASHS) reaction within the mill. Unlike previously referenced techniques, no secondary heating stage was required giving a substantial saving in time and cost. The [C]/[Ti] concentration ratio can be quantified using ND and crystal structure refinements eg Rietveld analysis.

▪ ***Order-Disorder Transition in $\text{TiC}_{0.67}$ (Figure 1(b))***

10

In-situ neutron diffraction (ND) were used to identify ordering in the $\text{TiC}_{0.67}$ precursor by looking at the $(\frac{h}{2}, \frac{k}{2}, \frac{l}{2})$ super-lattice reflections. Crystal structure refinements eg Rietveld analysis allow the degree of ordering to be determined. In addition, the C concentration can be simultaneously determined.

15

For example, using the D20 neutron diffractometer of the Institut Laue-Langevin (ILL, France), operating at a wavelength of $\lambda = 1.3 \text{ \AA}$, the presence of superlattice reflections, eg at 15.5° and $29.6^\circ (2\theta)$ was confirmed in powders of the sub-stoichiometric precursor.

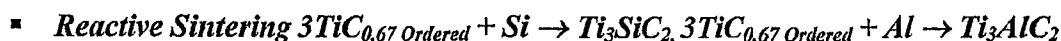
This superlattice reflection is consistent with a degree of vacancy ordering. Additional

analysis performed using time-resolved *in-situ* neutron diffraction (1 minute acquisitions, $10^\circ - 140^\circ 2\theta$) identified no further ordering of the precursor material when independently heated from RT to 1000°C at 5°C/min .

However, when the precursor was mixed with elemental Al in molar concentrations of

3:1 and subsequently heated from RT to 1000°C at 5°C/min , spontaneous self-ordering

of the precursor structure resulted and (see below) lead to the direct synthesis of Ti_3AlC_2 . A similar effect was seen using Si in place of Al.



5 (Figure 1(c) \rightarrow 1(d))

The reactive sintering of the ordered MX precursor with A, such as the reaction of $(TiC_{0.67\text{ Ordered}})$ and silicon to form Ti_3SiC_2 or aluminium to form Ti_3AlC_2 can be studied using *in-situ* ND. Phase identification can be used to show the progress of Si or Al migration into the precursor, thus aiding control of the synthesis. Crystal structure
10 analysis can be used to study the extent of Si diffusion onto the vacant carbon site, (x), in $Ti_3Si_xC_2$. The kinetics of this conversion can be studied using Quantitative Phase Analysis (QPA).

In-situ diffraction techniques allow detailed observation of reaction kinetics during
15 processing. Due to their low absorption by most materials, neutrons will be the primary source of analysis for diffraction based experiments. This allows large quantities of material to be analysed during each experiment, thus reducing the influence of chemical and thermal gradients within the sample.

20 The complete reaction sequence was determined for the Ti_3SiC_2 and Ti_3AlC_2 examples using *in-situ* neutron diffraction and is illustrated in Figure 4 for the aluminium case. Figure 4 is a contour plot of scattered neutron intensity as a function of scattering angle (2θ) and time (y-axis). The horizontal lines mark the melting of Al at 660°C (I), the centre of the zone where the precursor has absorbed the Al and has formed an ordered
25 phase (II) and the mid-point of the precipitation of the Ti_3AlC_2 product phase (III). The

precursor may be tracked using its strongest Bragg reflection indicated at C. The strongest Bragg reflection from the ordered precursor + Al is indicated by B and one of the Bragg reflections showing partial ordering in the as-milled $\text{TiC}_{0.67}$ by the letter A. The letter D indicates diffuse scattering due to the molten Al. With particular reference

5 to the reaction mechanism, the reaction was shown to be initiated by the melting of elemental Al at 660°C ; clearly identified at *Point A* by the disappearance of characteristic Al Bragg reflections. Simultaneous increases in the diffracted background after *Point A* are consistent with diffuse scattering from an amorphous phase (i.e. molten Al). As the remaining Bragg reflections index only to the initial precursor structure, this

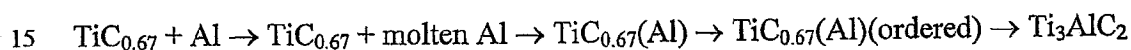
10 suggests a two-phase mixture of $\text{TiC}_{0.67}$ + molten Al. Following steady heating towards 1000°C at $5^\circ/\text{min}$ the precursor structure began to spontaneously self-order, identified by the appearance of additional superlattice reflections approximately 45 mins after the initial Al liquification (*Point B* of Figure 4). This stage can be sped up by faster heating (eg occurs in just 5 minutes when heated at $25^\circ/\text{min}$). Critically, the appearance of these

15 accompanying superlattice reflections at around 700°C was preceded by a reduction in the diffuse background, providing direct evidence of molten Al entering the $\text{TiC}_{0.67}$ structure. Further evidence for Al ingress into the $\text{TiC}_{0.67}$ is the simultaneous increase in the intensities of the $\text{TiC}_{0.67}$ Bragg reflections. Once Al ingress and ordering is complete, the stacking sequence of the ordered precursor approximates the alternating

20 sequence of M_{n+1}X_n ($= \text{Ti}_3\text{C}_2$) and Al layers characteristic of Ti_3AlC_2 . Importantly, self-ordering of the precursor state on these very short timeframes has not been observed without the presence of an A species (Al, Si etc), indicating that A element ingress speeds up long range ordering by a factor that can exceed 8,000 (five minutes instead of up to one month). This point is a crucial demonstration that the self-assembly

mechanism is triggered by the stabilising affects of Al entering and then ordering the defective precursor structure.

A final decrease in the superlattice intensities was shown to coincide with the precipitation of the Ti_3AlC_2 phase, confirming nucleation from the precursor material. Significantly, these results demonstrate that successful synthesis of Ti_3AlC_2 using an intercalating precursor can be achieved at temperatures as low as 1000°C , which is up to 600°C below conventional synthesis techniques. Furthermore, the higher atomic mobility associated with this intercalation mechanism allow for an appreciable reduction in Ti_3AlC_2 synthesis time, down to <60 minutes and as little as 5 minutes. Similar results (without melting of the A element) have been observed in the system $\text{TiC}_{0.67} + \text{Si}$ and are believed to be a general feature of such systems. The final reaction sequence is consistent with the schematic of Figure 1, providing:



Appendix I – Illustration of the effect of mechanical milling

1. Experimental Procedure

Unless otherwise stated, all samples were prepared using high-purity powder mixtures of titanium (Sigma-Aldrich, -100 mesh, 99.98%), silicon carbide (Performance Ceramics,

- 5 Japan, <100 μ m, 99.9%) and graphite (Aldrich, <100 μ m, 99.9%). Stoichiometric mixtures (3Ti + SiC + C) were weighed within a recirculated argon glove-box (<2ppm O₂, <2ppm H₂O). Mechanical alloying was performed using a SPEX8000 mill in a hardened steel milling vial loaded with six 5mm and three 10mm steel bearings. A 6.261g charge of starting powder produced a ball to powder mass charge ratio of 10:1.
- 10 Samples were milled for between 15 minutes and 120 minutes in 15-minute increments. A K-type thermocouple was attached to the exterior of the milling vial and sampled at 1Hz.

- Un-reacted mixtures milled for 0, 30, 60 and 90 minutes were cold pressed at 180 MPa
- 15 into pellets of 16.2mm diameter and 6mm height. SHS ignition of each pellet was performed in a resistively-heated vanadium-element furnace, under a vacuum of 10⁻² Torr. An initial heating rate of 100°C/min was used, with a projected hold temperature of 1100°C. The ignition temperature was monitored via two K-type control thermocouples positioned within the heating element and close to the base of each
- 20 sample.

- Milled powders not used for SHS ignition experiments were divided for microstructural characterisation. Some of the mixture was vacuum infiltrated by epoxy resin, while the remainder was kept in powder form. Upon curing, the epoxy mounted samples were
- 25 prepared for microanalysis by polishing with a 1- μ m diamond suspension and sputter

coated with an ultra-thin carbon film (~20nm). Scanning electron microscopy and microanalysis was conducted using a Philips XL30 fitted with an Oxford ISIS EDS system with a Be window detector. X-ray powder diffraction (XRD) patterns (10° - 120° 2θ) were recorded from the loose powders using a Philips PW1810 and $\text{CuK}\alpha$ radiation.

- 5 Phase identification was performed with reference to the ICDD PDF Database and phase quantification performed using the Rietveld analysis scale factors and the LHPM-Rietica software. Parameters refined during Rietveld analysis were global parameters (zero offset and a fourth order polynomial background), scale factors, lattice parameters and the peak width parameters U and K initially for all phases, the latter only for Ti and SiC.

10

2. Results

2.1 Ignition Temperatures

- Consolidated 3Ti+SiC+C samples, with no pre-milling, were shown to have an SHS ignition temperature of $T_{ig} = 920^\circ\text{C} \pm 20^\circ\text{C}$ in earlier work. By pre-milling samples for
15 30, 60 and 90 minutes, the respective SHS ignition temperatures were reduced to $640^\circ\text{C} \pm 20^\circ\text{C}$, $400^\circ\text{C} \pm 20^\circ\text{C}$, and $260^\circ\text{C} \pm 20^\circ\text{C}$, as shown in Figure 3(a). By increasing the milling time to >105min a spontaneous mechanically activated SHS (MASHS) reaction was achieved within the milling vial. The temperature profile of this reaction, indicating an exothermic response at $67^\circ\text{C} \pm 3^\circ\text{C}$, is shown in Figure 3(b).

20

Three distinct zones are apparent. In *Zone I* (0 to 45 min) there is a rapid temperature rise due to the milling action. In *Zone II* (45 to 105 min) the vial temperature continues to rise though at a significantly reduced rate due to increased losses to the surrounds.

Zone III (105 to 120 min) begins with an abrupt temperature rise of $\sim 25^\circ\text{C}$ after 107

- 25 minutes of milling ($T_{vial} = 67^\circ\text{C}$) indicating an exothermic reaction within the milling

- 25 -

vial. It should, however, be noted that the overall vial temperature is not the instantaneous ignition temperature of the SHS reaction, but rather the average temperature at which the reaction is spontaneously self-sustaining. This temperature excursion decays over the ensuing 15 minutes or so. The reaction was considered to have extinguished and the milling halted when the temperature of the milling vial returned to thermal equilibrium with its surrounds. X-ray diffraction of the product indicated two majority phases, Ti_3SiC_2 and substoichiometric TiC_x as shown in the inset of Figure 1(b). A minor amount of the silicide, $\text{Ti}_5\text{Si}_3\text{C}_x$ is observed (e.g. by the peak at $38.2^\circ 2\theta$). These product phases and their quantities are consistent with SHS reactions in dispersed 3Ti+SiC+C powders where discontinuity of the reactants limits inter-particle mass transport.

2.2 Changes to the milled powders

The milling induced morphological trends are illustrated in Figure 5 with a series of BSE images from samples of 3Ti+ SiC + C milled for 15, 30, 45, 60, 75 and 90 minutes. Also given are key regions of the corresponding XRD patterns. After only 15 minutes of milling, the Ti is relatively intact and the microstructure is primarily a mixture of the original powders. A slight amount of plastic deformation is visible around the margins of the Ti particles and a small amount of SiC has become incorporated in them. The XRD peaks are considerably broadened but show no new phases. As milling continues, the most striking feature of the BSE images in Figure 5 is the effect of milling on the Ti particles. The undistorted core of the particles is progressively reduced in size until after 90 minutes of milling discrete Ti particles are hard to define in Figure 5(f). The particles remain approximately equiaxed until, between 45 and 60 minutes of milling, lamellar structures within the Ti matrix are formed. These structures are identified by the

- 26 -

elongated layering of the un-deformed and deformed Ti regions, more readily observed in Figures 5(d) and 5(e):

Unlike Ti, the SiC particles remain qualitatively the same size and shape with increased
5 milling. Clearly the more ductile Ti phase absorbs the majority of the milling energy as it plastically deforms about the SiC particles. There is an accompanying systematic change in the SiC distribution. Initially the SiC particles merely fill the interstices between the much larger Ti particles (Figure 5(a)). Later, there is considerable mixing of highly deformed Ti and relatively un-deformed SiC in the weld seams (Figures 5(b-
10 f)). At very long milling times (e.g. 90 min, Figure 5(f)) the larger SiC particles are finally broken down.

Within the weld seams between pure Ti particles, the interfacial contact area between Ti and SiC has increased by many orders of magnitude over the initial state. Overall, the
15 mixing induced by high-energy milling appears to occur through the deformation of ductile Ti as it is conformed about the harder SiC particles. The rate of mixing, as judged by pure Ti particle size estimates, reduces as a function of milling time. After 90 minutes, mixing is nearly complete; however the rate is very slow. The trends in Figure 5, suggest that reactant homogeneity is relatively high after 107 minutes milling, at
20 which time combustion occurs spontaneously in the mill.

The partial XRD patterns included in Figures 5(g-l) illustrate several interesting features. The first is that, although the peaks rapidly broaden as crystallite sizes are reduced and internal strains around dislocations accumulate, the apparent broadening does not
25 increase significantly for additional milling beyond 15 minutes. This is contrary to

expectation, given the large changes in the observed ratio of deformed to un-deformed Ti in Figures 5(a-f). This observation is thought to be a sampling problem i.e. the X-rays are absorbed within a few microns of the surface and hence sample mostly the deformed exterior of any milled agglomerates that they encounter. The second interesting feature is that the Ti peaks shift to lower 2θ . This is most readily evident in the (002) Ti peak which is initially at $38.5^\circ 2\theta$ and partially resolved from the adjacent (013) SiC peak (see Figure 5(g)). After an additional 15 min of milling, the two peaks have merged.

The peak shifts were quantified in the form of refined lattice parameters from the Rietveld analyses. Results are shown in Figure 4 where it is apparent that both the a -axis and c -axis expand linearly with increased milling. This may be due either to Ti forming a solid solution with either C or Si, or as a result of increased defect densities formed during the milling process. SiC exhibits similar lattice parameter trends, however the relationship is not linear.

THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:-

1. A method of forming $M_{n+1}AX_n$, where M is an early transition metal or mixtures thereof, A is a group III or IV element or mixtures thereof and X is C, N or mixtures thereof, the method comprising the steps of :
5 providing a precursor of formula $M_{n+1}X_n$ and
reacting the $M_{n+1}X_n$ with A to provide $M_{n+1}AX_n$.
2. A method according to claim 1 wherein the $M_{n+1}X_n$ is ordered and/or twinned
10 prior to reacting with A.
3. A method according to claim 2 wherein the $M_{n+1}X_n$ is ordered and/or twinned during its formation from M and X.
- 15 4. A method according to claim 3 wherein A is present during the formation of $M_{n+1}X_n$ from M and X.
5. A method according to claim 3 wherein $M_{n+1}X_n$ is ordered and/or twinned by treatment of disordered $M_{n+1}X_n$.
20
6. A method according to claim 5 wherein A is present during the ordering and/or twinning of disordered $M_{n+1}X_n$.
7. A method according to any one of the preceding claims wherein A is Al, Si, P, S,
25 Ga, Ge, As, Cd, In, Sn, Tl or Pb.

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8. A method according to claim 7 wherein A is Si, Ge or Al.
9. A method according to claim 8 wherein A is Si.
- 5 10. A method according to any one of the preceding claims wherein M is Sc Ti V Cr, Zr, Nb, Mo, Hf, Ta or W.
11. A method according to claim 10 wherein M is Ti.
- 10 12. A method according to any one of the preceding claims wherein X is C.
13. A method according to any one of the preceding claims wherein n is an integer.
- 15 14. A method according to claim 13 wherein n is 1, 2, or 3.
- 15 15. A method according to claim 14 wherein n is 2.
16. A method according to any one of the preceding claims wherein $M_{n+1}AX_n$ is a
- 20 Ti-Si-C, Ti-Ge-C, Ti-Al-C, Ti-Al-N or Ti-Si-N system.
17. A method according to claim 16 wherein $M_{n+1}AX_n$ is a Ti-Si-C system.
18. A method according to claim 17 wherein the Ti-Si-C system is Ti_3SiC_2 .

- 30 -

19. A method according to claim 18 wherein $M_{n+1}AX_n$ is a Ti-Al-C system.
20. A method according to claim 19 wherein $M_{n+1}AX_n$ is a $Ti_{n+1}AlC_n$ system.
- 5 21. A method according to claim 20 wherein the $Ti_{n+1}AlC_n$ system is Ti_2AlC , Ti_3AlC_2 or Ti_4AlC_3 .
22. A method according to any one of claims 2 to 21 wherein A is added to the ordered $M_{n+1}X_n$ phase by mixing the two in powdered form.
- 10 23. A method according to any one of claims 2 to 21 wherein A is added to the ordered $M_{n+1}X_n$ phase by gaseous phase or liquid phase mixing.
24. A method according to any one of the preceding claims wherein any or all of the
- 15 M, A and X crystallographic sites are occupied by multiple elements.
25. A method according to any one of the preceding claims wherein M is any combination of early transition metals.
- 20 26. A method according to claim 25 wherein M is a combination of Ti and V.
27. A method according to claim 24 wherein A is a combination of Si and Al.
28. A method according to claim 24 wherein X is a combination of C and N.

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29. A method according to claim 24 wherein $M_{n+1}AX_n$ is $Ti_3Si_mAl_{1-m}C_2$, $Ti_yV_{3-y}AlC_2$ or $Ti_3SiC_xN_{2-x}$.
30. A method according to any one of the preceding claims wherein $M_{n+1}X_n$ is
5 mechanically treated to provide an ordered and/or twinned $M_{n+1}X_n$ phase.
31. A method according to claim 30 wherein the mechanical treatment is mechanical alloying.
- 10 32. A method according to claim 31 wherein the mechanical alloying is milling.
33. A method according to claim 32 wherein the mechanical alloying is milling of graphite and any suitable source of M.
- 15 34. A method according to any one of the preceding claims wherein $M_{n+1}X_n$ is thermally treated to provide an ordered and/or twinned $M_{n+1}X_n$ phase.
35. A method according to any one of the preceding claims wherein reacting the $M_{n+1}X_n$ with A to provide $M_{n+1}AX_n$ takes place with thermal treatment.
- 20 36. A method according to claim 35 wherein reacting the $M_{n+1}X_n$ with A to provide $M_{n+1}AX_n$ is insertion of Si into twinned Ti_3C_2 .
37. A method according to claim 35 or 36 wherein the thermal treatment is carried
25 out at temperatures less than about 1100°C.

38. A method according to claim 35 wherein the thermal treatment is carried out at temperatures less than about 500°C.

5 39. A method of forming $M_{n+1}AX_n$, where M is an early transition metal or mixtures thereof, A is a group III or IV element or mixtures thereof and X is C, N or mixtures thereof, comprising:

providing a precursor of formula $M_{n+1}X_n$;

treating $M_{n+1}X_n$ if required to provide an ordered and/or twinned $M_{n+1}X_n$

10 phase;

adding element A to the ordered $M_{n+1}X_n$ phase; and

treating the mixture of A and $M_{n+1}X_n$ to provide $M_{n+1}AX_n$.

40 A method of forming $M_{n+1}AX_n$ where M is an early transition metal or mixtures
15 thereof, A is Si, Ge, Al or mixtures thereof and X is C, N or mixtures thereof, comprising:

treating a mixture of $n+1M$ and nX to provide an ordered and/or twinned $M_{n+1}X_n$ phase

adding element A to the ordered $M_{n+1}X_n$ phase

treating the mixture of A and $M_{n+1}X_n$ to provide a $M_{n+1}AX_n$.

20

41 A method of forming a $M_{n+1}AX_n$ compound, where M is an early transition metal or mixtures thereof, A is Si, Ge, Al or mixtures thereof and X is C, N or mixtures thereof, comprising:

treating a mixture of $n+1M$ and nX in the presence of A to provide an ordered and/or

25 twinned $M_{n+1}X_n$ phase

- 33 -

and

treating the mixture of A and $M_{n+1}X_n$ to provide a $M_{n+1}AX_n$.

42. The use of $M_{n+1}X_n$ as a precursor in the preparation of $M_{n+1}AX_n$.

5

43. The use according to claim 42 wherein Ti_3C_2 ($TiC_{0.67}$) is a precursor in the preparation of Ti_3SiC_2 .

44. $M_{n+1}AX_n$ substantially free from MX and or other residual phases.

10

45. $M_{n+1}AX_n$ according to claim 44 wherein MX is <5 mole % of the total.

46. $M_{n+1}AX_n$ according to claim 45 wherein MX is <1 mole % of the total.

15 47. $M_{n+1}AX_n$ according to claim 44 wherein MX is <0.5 mole % of the total.

48. Ti_3SiC_2 substantially free from TiC, Ti_5Si_3 or other impurity phases.

49. Ti_3SiC_2 containing a no more than a predetermined amount of another phase.

20

50. Ti_3SiC_2 according to claim 495 containing a no more than a predetermined amount of TiC.

51. An ordered $M_{n+1}X_n$ phase.

25

- 34 -

52. A twinned $M_{n+1}X_n$ phase.

53. A composite material based on $M_{n+1}AX_n$ substantially free from MX and or other residual phases.

5

54. A composite material according to claim 53 comprising a matrix of Ti_3SiC_2 with embedded TiC particles.

55. A composite material according to claim 53 in the form of oxide ceramics which
10 have a layered structure.

15

FIGURE 1

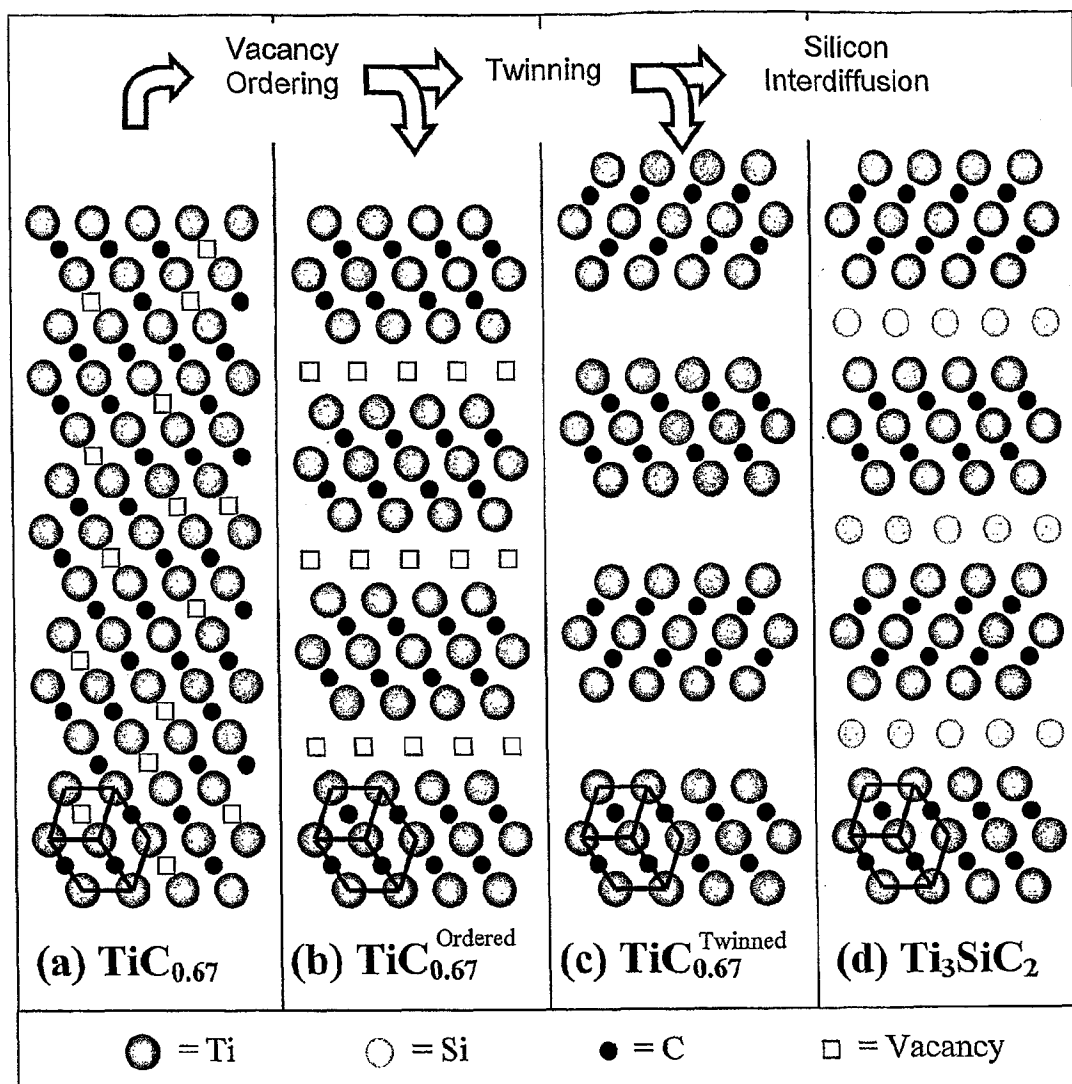


Figure 1: Structural engineering of Ti_3SiC_2 from a $\text{TiC}_{0.67}$ precursor, detailing the mechanisms used to control the reaction pathway for ceramic synthesis.

FIGURE 2

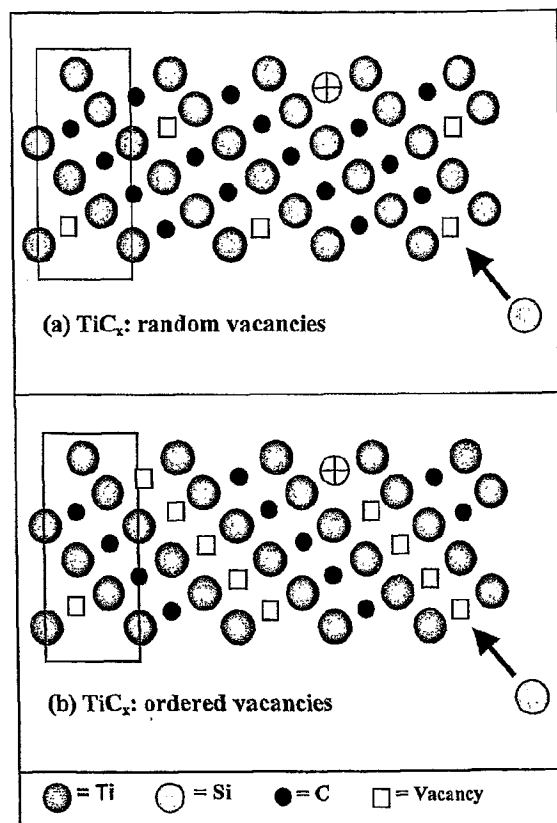


Figure 2: Si diffusion through TiC_x , in which the vacancy sites are (a) random, and then (b) ordered.

FIGURE 3

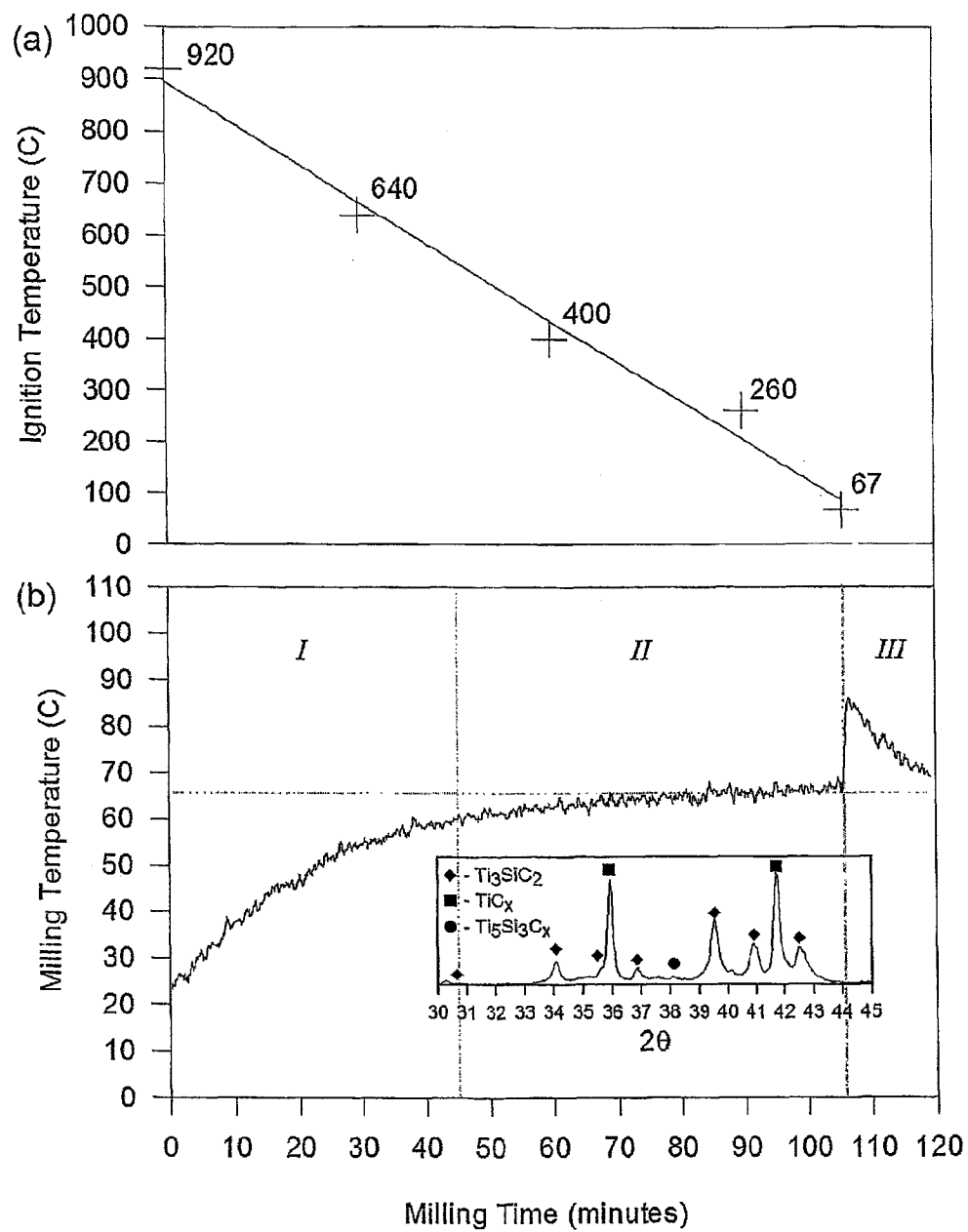
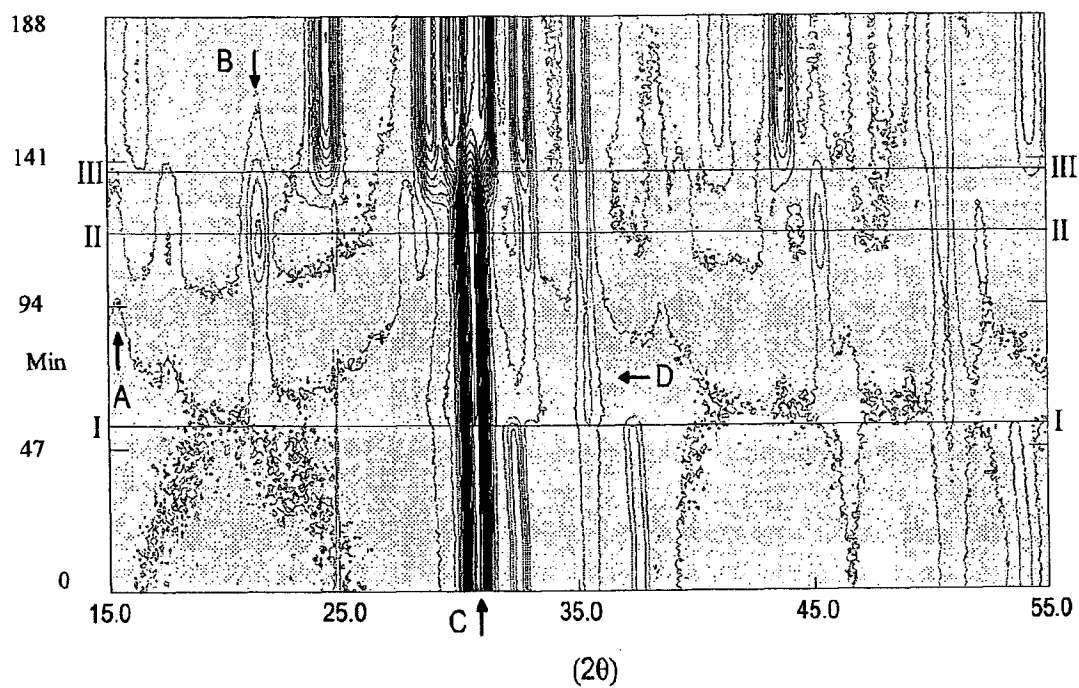


FIGURE 4



- 5 Figure 4 Contour plots of scattered neutron intensity as a function of scattering angle (2θ) and time (y-axis).

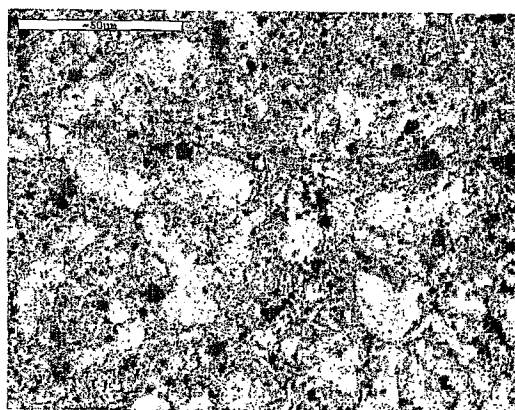
FIGURE 5



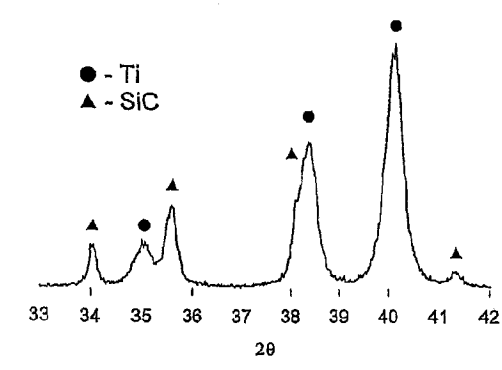
(a)



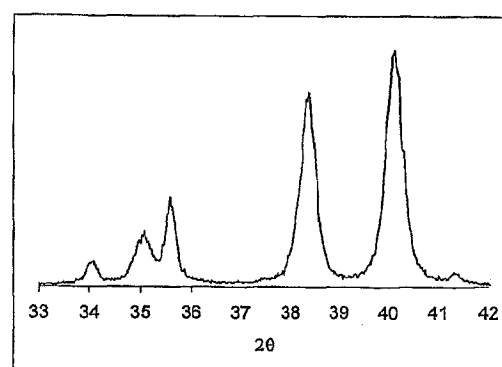
(b)



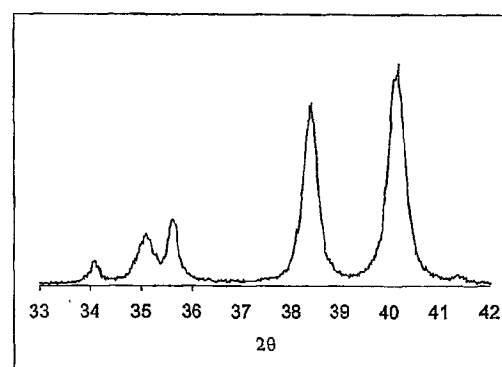
(c)



(g)



(h)



(i)

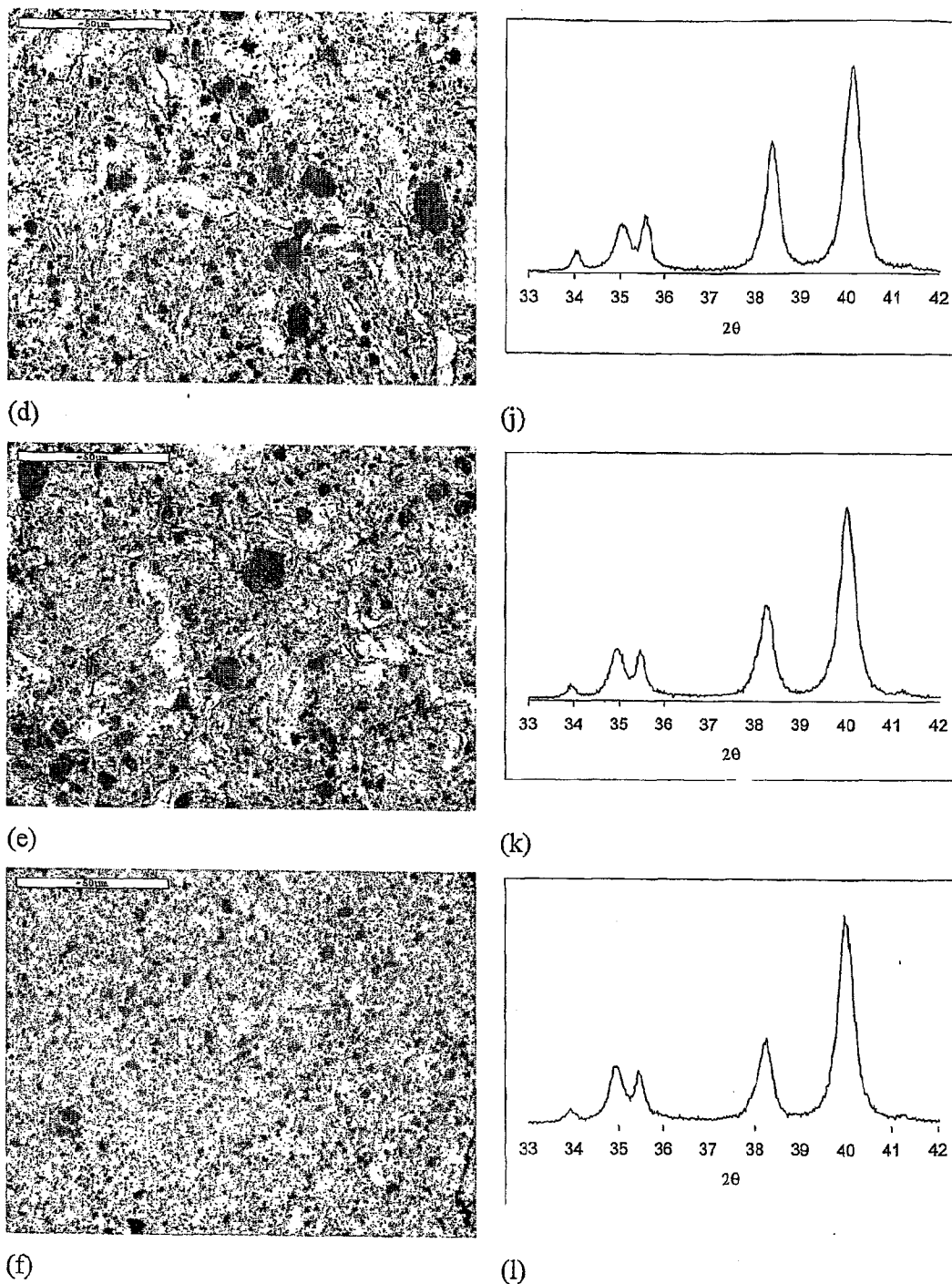


Figure 5 Backscattered electron images of sectioned agglomerates after milling for (a) 15 min, (b) 30 min, (c) 45 min, (d) 60 min, (e) 75 min, (f) 90 min and a small region of their corresponding XRD patterns (g)-(l).