Synthesis of Ti$_3$SiC$_2$ MAX phase ceramic materials using macrosized non-powder forms of titanium metal

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Abstract. A novel approach to the synthesis of Ti$_3$SiC$_2$ MAX phase ceramic materials using macrosized non-powder forms of titanium metal, such as foils, sheets, rods, tubes, etc., as a reactant was developed. According to this method, dispersions of SiC particles in slurries or pastes as well as tape casted polymer films filled with SiC particles can be used as a second component of the reaction system. Heat treatment under oxygen-free conditions at 1350–1500°C enables the SHS and RMI processes to occur in the reactive assemblies, allowing them to be sintered into a dense ceramic composites with a damage tolerant Ti$_3$SiC$_2$-based matrix reinforced with hard SiC particles. It was demonstrated that the proposed approach can be applied for fabricating Ti$_3$SiC$_2$/SiC ceramic matrix composites with specified internal structures including cellular and cannular ones. Since there is no need for a high pressure assistance during the sintering process, the method is expected to provide the Ti$_3$SiC$_2$ MAX phase ceramic materials with important competitive advantages through an increase in manufacturing productivity.

Various methods for high-temperature synthesis are presently used to obtain bulk Ti$_3$SiC$_2$ MAX phase ceramics and ceramic composites. They include furnace synthesis, hot pressing, spark plasma sintering, self-propagating high-temperature synthesis (SHS), microwave sintering, etc. [1–3]. Most of them are often combined with mechanical activation of starting materials. It is important to note that all these methods, regardless of particular technical and technological details, are commonly associated with reaction sintering of powder mixtures of elements as well as binary compounds of the Ti–Si–C system. This ensures both a good homogeneity of the powder reactant mixtures and high rates of solid-state reactions due to the small size of the reactant particles. However, an external pressure assistance is usually required in order to obtain a fully dense material. Commonly, a rather high loading pressure of several tens of MPa is needed to be used for this purpose. Such a requirement implies a significant decrease in productivity and makes the final products more expensive than competing materials. This, in large part, explains why Ti$_3$SiC$_2$-based materials, in spite of their promising properties, have not yet found wide application beyond laboratory scale.

An alternative way for the synthesis of Ti$_3$SiC$_2$-based ceramic materials is through the use of macrosized non-powder forms of titanium metal, such as foils, sheets, rods, tubes, etc., whose characteristic sizes are larger than 50–100 μm. In this case, titanium items can be manipulated individually, allowing them to be positioned at a desired orientation and distance with respect to each other, and thereby giving opportunities to build reaction assemblies with a specific spatial arrangement of the reactants. This makes it possible to design materials with complex internal structures (cellular,
cannular, tubular, annular, lamellar, granular, etc.) as well as gradient and spatially modulated materials. Another advantage of using non-powder titanium metal items is that due to their high strength and good stiffness, they can act as a kind of load-bearing component, which significantly reduces the risk of damage to the green body under mechanical stresses. This point becomes of crucial importance when Ti$_3$SiC$_2$-based ceramic parts of large size and complex shape have to be produced. Besides, the use of the macrosized titanium metal items, which originally contain no pores, minimizes total pore volume in the reaction assemblies, thereby making their sintering to full density more facile.

However, there is a serious obstacle for solid non-powder reactants with a characteristic size larger than 50–100 μm to be used in the synthesis of ceramic materials. In this case, the product layer can grow up to several tens of micrometers in thickness, making diffusion path of the reactants too long. As a result, rates of the solid state reactions decrease dramatically. So, in order to overcome this limitation an alternative path has to be provided for mass transfer. To address this problem, a kind of reactive melt infiltration (RMI) process comprising rapid in situ melting of the titanium metal non-powder reactants followed by capillary spreading of the melt over other components of the reaction system can be employed. In addition, some exothermic SHS reaction is desirable to assist the RMI process, since a large amount of heat energy is needed to melt titanium metal items.

![Figure 1.](image)

**Figure 1.** Mechanism for the formation of the Ti$_3$SiC$_2$/SiC ceramic matrix composites.

In line with this concept, we have recently developed a novel approach to fabricate Ti$_3$SiC$_2$/SiC ceramic matrix composites through the use of macrosized non-powder forms of titanium metal as a reactant [4–9]. Dispersions of SiC particles in slurries or pastes as well as tape casted polymer films filled with SiC particles can be used as a second component of the reaction system. These dispersions and films can optionally contain TiC and carbon additions acting as chemical modifiers. For the synthesis, the reactant components are assembled into a green body comprising of regularly arranged macrosized titanium metal items with a space between which is filled with SiC particles as well as TiC and carbon additions (if required). Heat treatment under oxygen-free conditions at 1350–1500°C enables the SHS and RMI processes to occur in the reactive assembly thus prepared, allowing it to be sintered into a dense ceramic composite with a damage tolerant Ti$_3$SiC$_2$-based matrix reinforced with hard SiC particles. Beside these major constituents, a minor amount of TiSi$_2$ inclusions are also present in the matrix. It is worthy to note that the presence of TiSi$_2$ in the composite is not desirable because of its poor mechanical properties. In order to decrease TiSi$_2$ content, carbon-containing
Compounds (e.g. carbon black or TiC particles) should be added to the reaction system. Thus, the phase composition of the obtained materials corresponds to the overall reaction:

$$(3 + y - z)Ti + (1 + x + 2y)SiC + (1 - 2y - z)C + zTiC = [Ti_3SiC_2 + yTiSi_2]_{\text{matrix}} + xSiC_p$$

The mechanism for the formation of the $Ti_3SiC_2/SiC$ composites, as shown in figure 1, can be described in the following stages: i) a primary diffusion-controlled solid-state exothermic reaction between the initial reactants above 1100°C giving rise to the formation of intermediate product layer consisting of TiC$_x$ and Ti$_5$Si$_3$C$_x$; ii) triggering the SHS reaction above 1340°C, corresponding to the Ti–Ti$_5$Si$_3$ eutectic temperature in the binary Ti–Si system, resulting in rapid melting of the titanium metal items; iii) rapid infiltration of the entire area occupied by SiC particles with the titanium melt due to the capillary effect; iv) crystallization of Ti$_3$SiC$_2$ MAX phase together with a minor amount of TiSi$_2$ by a peritectic reaction of the melt with SiC particles resulting in the formation of a dense ceramic matrix enclosing the SiC particles that remained after the previous stages. SEM image and XRD pattern of a typical sample of the $Ti_3SiC_2/SiC$ composite are illustrated in figures 2 and 3, respectively.

**Figure 2.** Cross-sectional SEM images of the $Ti_3SiC_2/SiC$ ceramic matrix composite synthesized using non-powder titanium metal items.

**Figure 3.** XRD pattern of the $Ti_3SiC_2/SiC$ ceramic matrix composite synthesized using non-powder titanium metal items.

Based on the proposed approach, particular techniques for fabricating $Ti_3SiC_2/SiC$ ceramic matrix composites with specified internal structures, some of which are given in figure 4, have been developed.

*Solid plates and sheets.* The $Ti_3SiC_2/SiC$ ceramic composites in a shape of solid flat plates, sheets, slabs and other similar ones can be fabricated by low pressure assisted reactive sintering of multilayer sandwich-like assemblies consisting of titanium foils and tape casted polymer films filled with SiC particles, as shown in figure 4a.

*Hollow-core plates.* The $Ti_3SiC_2/SiC$ ceramic composites in a shape of hollow-core flat plates, slabs and other similar ones can be fabricated by low pressure assisted reactive sintering of sandwich assemblies consisting of titanium foils, array of parallel spaced titanium rods and tape casted polymer films filled with SiC particles, as shown in figure 4b.

*Blocks with arrayed hollow channels.* The $Ti_3SiC_2/SiC$ ceramic composites in a shape of blocks, slabs and other similar ones containing arrayed hollow channels can be fabricated by pressureless reactive sintering of assemblies consisting of an array of parallel aligned titanium rods with a space between which is filled with a slurry of SiC particles, as shown in figure 4c.

*Cellular blocks.* The $Ti_3SiC_2/SiC$ ceramic composites in a shape of cellular blocks, slabs and other similar ones can be fabricated by pressureless reactive sintering of assemblies consisting of thin-walled titanium tubes of different cross-sections including rectangular ones, bound together with a paste of SiC particles, as shown in figure 4d.

It is especially important that all the proposed techniques do not require high loading pressure to be applied during the sintering process. In fact, there is needed only a small uniaxial load commonly less
than 1–2 MPa that suppresses the warping deformation of thin titanium metal items in the first stage of heat treatment. Such a decrease in the requirement for pressure assistance during the synthesis is expected to enable the Ti$_3$SiC$_2$ MAX phase ceramic materials to gain competitive advantages through an increase in productivity of manufacturing processes.

**Figure 4.** Schematic sketches of the initial reactive assemblies (left) and photographs of the prepared samples of the Ti$_3$SiC$_2$/SiC ceramic matrix composites (right): (a) solid flat plates, (b) hollow-core flat plates, (c) blocks containing arrayed hollow channels, and (d) cellular block.

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