A TEM study on TiB$_2$–20\%MoSi$_2$ composite: Microstructure development and densification mechanism

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Abstract

We report the results of transmission electron microscopy (TEM) study, carried out on a hot-pressed TiB$_2$–20 wt.\%MoSi$_2$ composite. One of the important microstructural observations includes the detection of crystalline TiSi$_2$ at triple grain junctions. The densification mechanism is discussed, based on experimental observations and thermodynamic analysis.

Keywords: TiB$_2$; MoSi$_2$; Hot pressing; TEM

1. Introduction

Non-oxide ceramics, in particular TiB$_2$, are candidate materials for high temperature structural applications due to their attractive properties like high melting point, superior thermal and electrical conductivities, high elastic modulus, high hardness and good corrosion resistance [1]. Despite possessing useful properties, the engineering applications of monolithic TiB$_2$ are rather limited because of poor sinterability. To obtain dense borides, various metallic and non-metallic binders have been explored [2–6]. However, for high temperature applications, the use of ceramic sinter-additives is preferred. In recent times, we have been able to demonstrate that MoSi$_2$ addition improves the sinterability of TiB$_2$ and that dense TiB$_2$–20 wt.\%MoSi$_2$ composite can be obtained through hot pressing at 1700 $^\circ$C for 1 h [7]. Higher hardness of $\sim$25–26 GPa along with moderate fracture toughness of 4–5 MPa m$^{1/2}$ is measured with TiB$_2$–20 wt.\% MoSi$_2$ composites. These novel materials also exhibit better wear resistance properties than monolithic TiB$_2$ [8]. In the present work, we examine the microstructure development in TiB$_2$–MoSi$_2$ composites in order to gain an insight into the densification mechanism during hot pressing.

Transmission electron microscopy (TEM) is a powerful tool to explore microstructure at small length scale, essentially for revealing process mechanisms. Torizuka et al. [3,4], using the TEM technique, observed the formation of grain boundary liquid phase (amorphous SiO$_2$) when SiC is used as an additive to TiB$_2$. Moreover, they identified the presence of a liquid phase (Ti,Zr)$_5$Si$_3$ at triple points in TiB$_2$–19.5 wt.%ZrO$_2$–2.5/5.0 wt.%SiC composite processed via the hot isostatic pressing route. Li et al. [5] identified the formation of BN, TiN, Al$_2$O$_3$ phases in TiB$_2$–20 wt.%AlN composite fabricated by hot pressing at 1800 $^\circ$C. In another work, Park et al. [6] reported the formation of different reaction products like TiN and BN in TiB$_2$–2.5–10 wt.%Si$_3$N$_4$ composites (sintered at 1800 $^\circ$C) and observed that Si$_3$N$_4$ acts as a grain growth inhibitor.

A critical literature analysis reveals that neither any detailed TEM work, nor any report on densification mechanism is available for TiB$_2$–MoSi$_2$ composites. In view of its excellent mechanical and tribological properties, further study has been conducted to characterize in detail the
microstructure evolution in TiB₂–MoSi₂ composites. Additionally, in order to further optimize the sintering aid content and sintering parameters, it is necessary to understand the mechanisms of sintering through a detailed analysis of the microstructure. The present contribution aims to meet this goal.

2. Experimental

The in-house processed TiB₂ and MoSi₂ powders were selected as starting powders for composite production. TiB₂ powder had been obtained by borothermic reaction between TiO₂ (Merck, Germany), B₄C (in-house processed) and carbon (99% purity, M/S Assam Carbon, India). B₄C powders were processed using carbothermic reduction of boric acid (HBO₃). The major impurities of as synthesized TiB₂ include oxygen (0.5 wt.%) and carbon (0.6 wt.%), as determined by the vacuum fusion analysis technique (Leco Industries, USA). The TiB₂ powders have an average particle size around 1.1 µm (ASTM standard, D₅₀). MoSi₂ was synthesized from elemental powders of Mo (>99% purity, supplier Leco Industries, USA) and Si (>99% purity, supplier Merck, Germany). Mechanical grinding was employed to reduce the size of the MoSi₂ powder after synthesis to yield finer particle size with D₅₀ (mean particle diameter) around 1.4 µm.

Appropriate amount of powders with TiB₂:MoSi₂ in 80:20 (wt.%) ratio were mixed using a WC grinder. The densification was performed by hot pressing under vacuum (10⁻⁵ Pa) and 32 MPa pressure, using a 10 mm diameter graphite die. The samples were hot-pressed at 1700 °C for 1 h. A heating rate of 15 °C/min was used to achieve the temperature. The crystalline phases in the starting powders and hot pressed samples were analyzed using powder X-ray diffraction (XRD) (Rich-Seifert 2000D). The detailed microstructural analysis was performed using a scanning electron microscope (SEM, FEI model SIRION), operated at 20 kV and TEM (JEOL 2000 FXII) operated at 200 kV. Compositional measurements on the flat polished sections of the hot pressed composites were performed using an energy dispersive spectroscopy (EDS) detector (ultrathin window, capable of detecting boron), attached to a SIRION FEG-SEM. The volume fraction of various ceramic phases was calculated using SigmaScan Pro image processing software (Version 4, Jandel Scientific, USA). Thin foil for TEM was prepared following standard ion beam thinning procedure.

3. Results

XRD patterns acquired from the hot-pressed composite as well as from the starting powders are shown in Fig. 1. XRD results indicate the predominant presence of TiB₂, MoSi₂ and a small amount of TiSi₂ in the composite. The formation of TiSi₂ originates from sintering reaction, which will be discussed in detail later. No sign of TiO₂ or SiO₂ is observed within the detection limit of XRD.

Fig. 1. XRD spectra showing the phase analysis of the starting powder and hot-pressed TiB₂–20 wt.%MoSi₂. The different crystalline phases are also indexed.

Fig. 2 is a back scattered scanning electron (BSE) micrograph showing the distribution of the TiB₂ and MoSi₂. One can note the distribution of MoSi₂ (5 µm or coarser) which appears in brighter contrast in the TiB₂ matrix. As will be evident from the TEM observations, described later, the observed MoSi₂ phase on SEM image is in fact agglomerates of finer MoSi₂ particulates. From low magnification BSE images, the volume fractions of the MoSi₂ and TiB₂ were calculated using commercial image analysis software (SigmaScan Pro image processing, version 4, Jandel Scientific, USA). The average volume fractions of the two phases, as calculated by random sampling, were: MoSi₂ = 16% and TiB₂ = 84%. Using the known density of these two phases (densities of MoSi₂ = 5.57 gm/cc and TiB₂ = 4.52 gm/cc), the amount (in wt.%) of MoSi₂ was found to be 19.1%, which is consistent with the compositional analysis using EDS.

A detailed microstructural characterization of the sintered TiB₂–20% MoSi₂ samples was carried out using TEM. Fig. 3a and b are bright field and dark field pair from a typical grain. Selected area diffraction pattern
(SADP) analysis from the same grain is shown in Fig. 3c. The diffraction analysis confirms these to be TiB₂ with a hexagonal close-packed (hcp) structure. It may be noted that the room temperature lattice parameters of hcp TiB₂ are: \( a = 0.303 \) nm and \( c = 0.3229 \) nm. The grain size of TiB₂ varies between 1 and 1.2 \( \mu \)m. The dark field image (Fig. 3b) shows a clean grain in the present case and the absence of dislocations. The absence of any defect substructure was noticed in most of the investigated TiB₂ grains.

Fig. 4 presents the morphology of a MoSi₂ grain, as recorded under different imaging conditions. The bright field image (Fig. 4a) reveals an elongated MoSi₂ grain with a few faceted grain boundaries. The strong beam dark field image using (001) reflection is shown in Fig. 4c. The grain size of MoSi₂ particles (as measured using dark field
images) varies between 1.2 and 2 µm and the typical aspect ratio of elongated MoSi$_2$ particles is about 4. The SADP pattern (Fig. 4d), obtained with beam orientation along one of the mutually orthogonal zone axis [010], confirms the tetragonal structure of MoSi$_2$. The crystal structure analysis indicates that the lattice parameters (at room temperature) of MoSi$_2$ are: $a = 0.3204$ nm and $c = 0.7844$ nm.

Considering the initial particle sizes of TiB$_2$ ($D_{50} \sim 1.1$ µm) and MoSi$_2$ ($D_{50} \sim 1.4$ µm), the above observation indicates that hot pressing at 1700 °C did not promote any significant grain growth. In an earlier study, Torizuka et al. [3] had observed extensive grain growth when 20 wt.%ZrO$_2$ was used as a sintering additive to densify TiB$_2$ at 1700 °C. The present observation is in contrast to this result and indicates that MoSi$_2$ could potentially act as a grain growth inhibitor for TiB$_2$.

The defect sub-structure, i.e. the presence of dislocation, is clearly visible in the MoSi$_2$ grains. Weak beam dark field imaging was used for the observation of the defect structure (Fig. 4c). The presence of dislocations in the central region of MoSi$_2$ grain is clearer under the weak beam condition. Dislocation activity could be seen in all the MoSi$_2$ grains. In some cases, the presence of dislocation tangles (not shown) is observed within MoSi$_2$ grains. This type of dislocation tangle was observed earlier [9] in MoSi$_2$–1 at.%Nb alloy, compressed at 1600 °C. Dislocation cell-structures, i.e. subgrain formation, was also reported [10] earlier in MoSi$_2$ monoliths following compressive deformation at temperatures above 1300 °C.

The detailed TEM observations of the phase at a grain boundary triple point are presented in Figs. 5 and 6. Fig. 5 shows two different grain configurations in which...
TiSi₂ has been found to be formed at the triple junction point. Fig. 5a illustrates that TiSi₂ is surrounded by two TiB₂ and one MoSi₂ grains whereas Fig. 5b reveals that TiSi₂ is surrounded by two MoSi₂ grains and one TiB₂ grain. One can see that the size of the TiSi₂ is much smaller in the former case as compared to the second one. More importantly, the interfaces are either planar or curved with concaveness towards the TiSi₂ phase suggesting a wetting tendency of this phase. Fig. 6a shows a typical bright field image of a TiSi₂ grain surrounded by two TiB₂ grains and one MoSi₂ grain. The SAD pattern taken from the surrounding TiB₂ and MoSi₂ grains are shown as insets of Fig. 6a. The micro diffraction pattern obtained from the phase at the triple junction point along [001] is shown in Fig. 6c. The analysis of the recorded pattern confirms the presence of orthorhombic TiSi₂ phase at the triple junction (a = 0.8268 nm, b = 0.8553 nm and c = 0.4798 nm). Bright field TEM images reveal that the size of the crystalline phase at a triple pocket varies between 30 and 400 nm. The faceted crystalline morphology of this phase is clearer in the dark field image, presented in Fig. 6b.

4. Discussion

We will first summarize the important facts that have emerged from the present investigation as they are relevant for developing an understanding of the sintering process. Besides MoSi₂ and TiB₂, the sintered ceramic composite contains a small amount of TiSi₂. TiSi₂ has a melting point of 1500 °C (1773 K) and hence must be molten at the sintering temperature (1700 °C). TEM studies indicate that this phase exists at the triple points with at least one of the surrounding grains being MoSi₂. Thus, the microstructural observations strongly suggest that densification of TiB₂–MoSi₂ composite occurred by liquid phase sintering, involving rearrangement of grains by capillary action in the presence of wetting liquid phase TiSi₂. However, the reaction path leading to formation of TiSi₂ phase remains to be determined. Let us now discuss the possible ways TiSi₂ could be formed.

It is reported in the literature that surface layers of TiO₂ and B₂O₃ can exist on the surfaces of TiB₂ particles [12]. Literature report also indicates that B₂O₃ vaporizes rapidly above 1127 °C (1400 K) [12]. In our hot pressing experiment, 4–6% weight loss is measured and this is attributed to the evaporation of the volatile oxides (B₂O₃, MoO₃). In the presence of surface oxides, TiSi₂ can be formed by a reaction between TiO₂ and MoSi₂:

\[
\text{TiO}_2 + \text{MoSi}_2 \rightarrow \text{TiSi}_2 + \text{MoO}_3(g)
\]

Based on the available thermodynamic data of the energy of formation of different compounds, this reaction is not thermodynamically feasible at and below the sintering temperature of 1973 K (Fig. 7).

Although the experiments have been carried out inside a vacuum chamber (10⁻³ Pa), residual oxygen will be present during the hot pressing experiment. In the case where oxy-

The overall free energy change for this reaction to proceed in the forward direction is negative at and below 1973 K. For example, \(\Delta G\) at 1800 K is estimated to be \(-183.10\) kcal. Hence this reaction leading to formation of TiSi₂ is thermodynamically feasible.

There exist other alternative possibilities for the formation of TiSi₂. It is reported that the MoSi₂ grains are often covered by a SiO₂ layer due to low temperature oxidation [11]. This layer co-exists with MoO₃, which vaporizes at higher temperatures [13]. The presence of SiO₂ at the interface between MoSi₂ and TiB₂ grains can promote the following possible sintering reactions:

\[
\text{MoSi}_2 + 7\text{TiB}_2 + 12\text{SiO}_2 \rightarrow 7\text{TiSi}_2 + 7\text{B}_2\text{O}_3(g) + \text{MoO}_3(g)
\]

\[
\text{5MoSi}_2 + 14\text{TiB}_2 + 21\text{SiO}_2 \rightarrow \text{Mo}_5\text{Si}_3 + 14\text{TiSi}_2 + 14\text{B}_2\text{O}_3(g)
\]

The free energy calculations for these two reactions indicate a positive free energy change for the reactions to proceed from left to right at the sintering temperature. However, these reactions may be feasible at temperatures higher than the hot pressing temperature. The fact that the presence of Mo₅Si₃ has neither been detected by XRD nor observed during the TEM investigation rules out the reaction (4) in the present case. It can be noted that Mo₅Si₃ phase is reported to form during high temperature oxidation of MoSi₂ [11]. The changes in Gibbs energy values as a function of temperature for all the above reactions are summarized in Fig. 7.

On the basis of the thermodynamic calculations, there is only one possibility for the formation of TiSi₂ phase at the
sintering temperature (1973 K). From Fig. 7, it is evident that the TiSi₂ phase forms and grows during the sintering primarily through reaction (2). The equilibrium partial pressure \( p_{O_2} \) required for reaction (2) is calculated to be \( 2.5 \times 10^{-14} \) Torr, which is much lower than the \( p_{O_2} \) level of \( 2.7 \times 10^{-5} \) Torr, estimated to be present in the hot press chamber during sintering. This estimation of \( p_{O_2} \) is done by considering a vacuum level of \( 10^{-5} \) Pa (see Section 2) to be present in the hot press chamber and assuming that the \( O_2:N_2 \) ratio in the vacuum is the same as that in ambient air. Therefore, the formation of TiSi₂ is highly likely even in the weak oxidizing condition that is present in the hot press chamber. At the sintering temperature, TiSi₂ is molten and aids the sintering process that is present in the hot press chamber by grain rotations, necessary for densification. This process is also accompanied by wetting the grain boundaries enabling enhanced capillary driven mass transport. This process is also accompanied by grain rotations, necessary for densification.

The TEM analysis indicates the absence of any dislocation activity in TiB₂ and a significant presence of dislocations in MoSi₂ grains. The observation of finer TiB₂ grain sizes is also important. In the case of TiB₂, the anisotropic thermal contraction behavior is reported to the formation of microcracks during post-fabrication cooling in the case of grain size exceeding the critical grain size of 20 µm [7]. Thus, a finer TiB₂ starting powder as well as lower densification temperature, as employed in the present work, is useful to obtain finer grain size and crack free dense material. The presence of such finer TiB₂ grains also leads to the attainment of high hardness (25 GPa). However, the fracture toughness of these novel materials remains moderate and around 5 MPa m\(^{1/2}\). Further investigation is under way to improve the toughness properties.

Another important result of the present study is the evidence for the presence of TiSi₂ at the grain boundary triple pocket. It is possible that TiSi₂ can form due to solid-state reaction between TiB₂ and MoSi₂ during heating of the powder compact at lower temperature by reaction (2). From a study of relevant binary and ternary phase diagrams of systems based on Mo, Ti and Si, [15] it is evident that TiSi₂, even if formed in solid-state, would melt (melted temperature: 1733–1753 K) and form a sintering liquid at the hot pressing temperature of 1973 K. TEM investigation further reveals that TiSi₂ is present only at the grain boundary triple pockets in the sintered microstructure. This has most likely occurred due to the migration of the liquid during sintering. The migration of all the TiSi₂ in the solid-state to the triple points is unlikely due to the limited diffusion in the solid-state. Therefore, we conclude that the densification mechanism is dominated by liquid phase sintering in the presence of a sintering liquid i.e. TiSi₂ phase (\( T_m \sim 1773 \) K).

5. Conclusions

Based on the present results and discussion, we can arrive at the following conclusions:

(a) The presence of MoSi₂ aids in the sintering of TiB₂–20 wt.%MoSi₂ composites through the formation of small amount of TiSi₂ phase, which is liquid at a hot pressing temperature of 1700 °C. The morphology of this phase at the triple points suggests that it can wet the TiB₂–MoSi₂ interface. The densification is assisted by liquid phase sintering.

(b) The hot-pressed microstructure is characterized by the presence of finer TiB₂ grains. None of the investigated boride grains show any observable dislocation activity. On the other hand, MoSi₂ particulates are coarser (>1 µm) and the presence of significant dislocation activity is critically noted.

(c) Thermodynamic analysis of the various possible reactions indicates that the most likely reaction pathway for the formation of TiSi₂ is

\[
\text{TiB}_2 + 3\text{O}_2(g) + \text{MoSi}_2 \rightarrow \text{TiSi}_2 + \text{B}_2\text{O}_3(g) + \text{MoO}_3(g)
\]

This reaction can take place at a partial pressure of oxygen as low as \( 2.5 \times 10^{-14} \) Torr.

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