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Letter

Synthesis of Ti_3SiC_2 by infiltration of molten Si

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ABSTRACT

High-purity Ti_3SiC_2 compounds have been fabricated by infiltration of molten Si into a precursor, a partially sintered TiC_x ($x = 0.67$) preform. The Si source and the TiC_x preform were placed side by side on carbon cloth, and the system was heated to 1550 °C. Molten Si infiltrated the preform through the carbon cloth, and a direct reaction between TiC_x and molten Si immediately occurred at the reaction temperature to yield pure Ti_3SiC_2. We could observe phase formation and the microstructure of the bulk products with time, which were investigated by X-ray diffraction (XRD) and scanning electron microscopy (SEM) equipped with energy-dispersive spectroscopy (EDS). Pure Ti_3SiC_2 compounds were formed on the exterior of the TiC_x preform at 1550 °C when the sintered TiC_x:Si ingot molar ratio was 3:1.4. At 1550 °C, no other minor phases were detected for any of the sintering time ranges.

1. Introduction

The ternary compound Ti_3SiC_2 is a representative of materials that exhibit the characteristics of both metals and ceramics. Similar to metals, Ti_3SiC_2 shows high electrical and thermal conductivity, thermal shock resistance, damage tolerance, low hardness, and good machinability without cooling or lubrication. Further, similar to a ceramic, Ti_3SiC_2 has a high Young's modulus, high-temperature strength, and oxidation resistance. The chemical vapor deposition (CVD) technique has most commonly been employed to fabricate pure Ti_3SiC_2, by a solid-state reaction between TiH_2, Si, and graphite at 2000 °C, as originally suggested by Jeitschko and Nowotny [1]. However, the CVD technique is limited to the bulk synthesis of Ti_3SiC_2. Recently, several methods have been reported for the bulk synthesis of Ti_3SiC_2: powder metallurgy methods to synthesize single-phase bulk Ti_3SiC_2 by hot pressing [2–4]; self-propagating high-temperature synthesis (SHS) [5]; hot isostatic pressing (HIP) [4,6,7]; gas-pressure combustion synthesis (GPCS) [8]; arc melting [9]; solid–liquid reactions [10]; and pulse discharge sintering [11–15]. In addition, Ti_3SiC_2 has been synthesized using starting material mixtures such as Ti/SiC/C [4,7,12–14,16], Ti/Si/C [17], TiH_2/Si/C [3], and Ti/Si/TiC [15,18]. Recently, Hwang et al. [19] and Panigrahi et al. [20] reported pressureless technique to fabricate Ti_3SiC_2. And, Shan et al. [21] also used a similar method used in this study that infiltration of molten Si into a TiC/Ti precursor could produce Ti_3SiC_2 with various Si contents. However, not all impurities, such as SiC and Ti_8C_5, could be removed in this case. In this study, we also used the Si melt infiltration method, but we used a partially dense TiC_x ($x = 0.67$) preform to synthesize bulk Ti_3SiC_2, instead of the TiC/Ti precursor and we observed how the microstructure evolved with reaction time. Microstructures were analyzed, and the possible reaction mechanisms for the synthesis of pure Ti_3SiC_2 were discussed.

2. Experimental

Commercially available Ti powder (<45 μm, 99.7% pure, Sumitomo Co. Ltd., Japan) and graphite powder (~10 μm, 99.95% pure, SGP, Japan) were used to form a partially dense TiC_x preform. A high-purity Si ingot (99.999% pure, LG Siltron, Korea) was used for infiltration into the TiC_x preform, and thus, Ti_3SiC_2 was synthesized. For the preparation of the TiC_x preform, Ti and graphite powders were dry-mixed in a 3:2 molar ratio. Cold-pressing of the mixed powder under 40 MPa was then performed to produce 30 mm × 10 mm × 10 mm bars, followed by a thermal reaction under a vacuum of about 0.1 Torr at 1550 °C for 3 h. The partially sintered TiC_x was then cut into cube-shaped specimens with dimensions of 10 mm × 10 mm × 10 mm. The density of the partially sintered TiC_x was only about 60% of that of fully sintered TiC. A schematic in Fig. 1 shows the experimental setup for the Si melt infiltration process used in this study. The specimen to be infiltrated by the Si melt was placed on the carbon cloth, and the Si ingot was placed on the same carbon cloth at a certain distance away from the specimen. The weight of the Si ingot used in this experiment was about 4 g, which was approximately 140% of the amount of the Si required to synthesize stoichiometric Ti_3SiC_2 by evaporation of the Si melt above the Si melting temperature [22].

Infiltration of the Si melts into the partially sintered TiC_x was performed at 1550 °C under vacuum (~10^{-1} Torr) for periods of time ranging from 1 min to 2 h in a graphite furnace, at a heating rate of 10 °C/min. After completing the infiltration process, phase identification was accomplished by X-ray diffraction (XRD) analysis with Cu Kα radiation at a scanning rate of 10° min^{-1}. For microstructural observations,

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Fig. 1. A schematic of the experimental setup used in this study.

the infiltrated samples were cut parallel to the direction of the Si melt infiltration and polished down to 1 μm using diamond paste. The polished samples were etched using an $HF:HNO_3:H_2O$ solution (0.5:1:2 ratio by volume) and then characterized by scanning electron microscopy (SEM).

3. Results and discussion

The results of the microstructural evaluations are shown in Fig. 2. A schematic, Fig. 2(a), describes how the molten Si infiltrates the TiC_x preform. Fig. 2(b) shows the representative microstructures (1st, 2nd, and 3rd), which correspond to the areas indicated by 1, 2, and 3 in Fig. 2(a), on the cross section of a specimen synthesized after the infiltration of the Si melt into the partially sintered TiC_x preform. Detailed examinations of the microstructures indicated by the letters "a," "b," and "c" will be depicted later. As shown in Fig. 2(b), the Si melts did not infiltrate completely into the TiC_x preform. The infiltration depth of the Si melt into the specimen increased with the infiltration time. As the infiltration time increased from 1 min to 2 h, the infiltration depth proportionately increased from 0.8 mm to 2 mm. The interior of the TiC_x preform remained unaffected, even though the samples had been held for 2 h at the infiltration temperature of 1550 °C. This was presumably due to the deficiency of the Si melt caused by consumption during the reaction with the TiC_x preform and the evaporation of the Si melt at the reaction temperature. The evaporation of the Si melt was confirmed by the formation of the $TiSi_2$ phase after holding for more than 2 h in the presence of excess Si. It was assumed that the 40% excess Si used was not sufficient for continuous infiltration into a TiC_x preform of the dimensions used in this study, because Si could be sublimated under vacuum even before reaching the melting temperature of 1414 °C [23]. In addition, the infiltrated parts were uniformly thick in all directions, as indicated in the schematic in Fig. 2. The relationship between the infiltration time and the infiltration depth is plotted in Fig. 3. As infiltration time increased from 1 min to 30 min, the infiltrated depth rapidly increased. Thereafter, infiltration depth was saturated, which was due to the depletion of the Si source. After sintering for up to 2 h at 1550 °C, the relative density of the partially sintered TiC_x specimen changed from 60.8% to 78.7%.

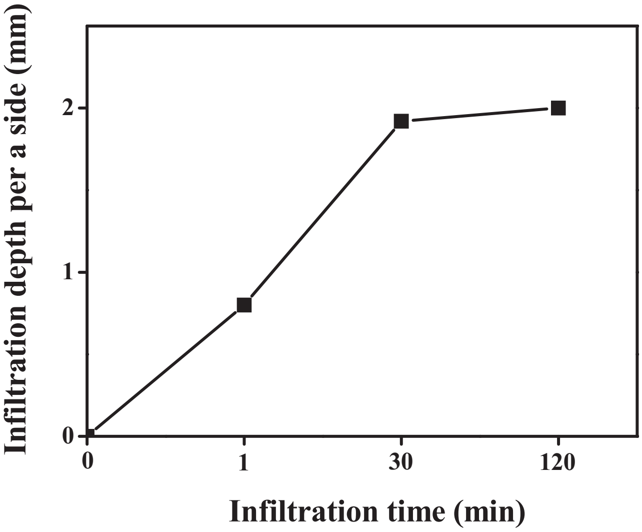
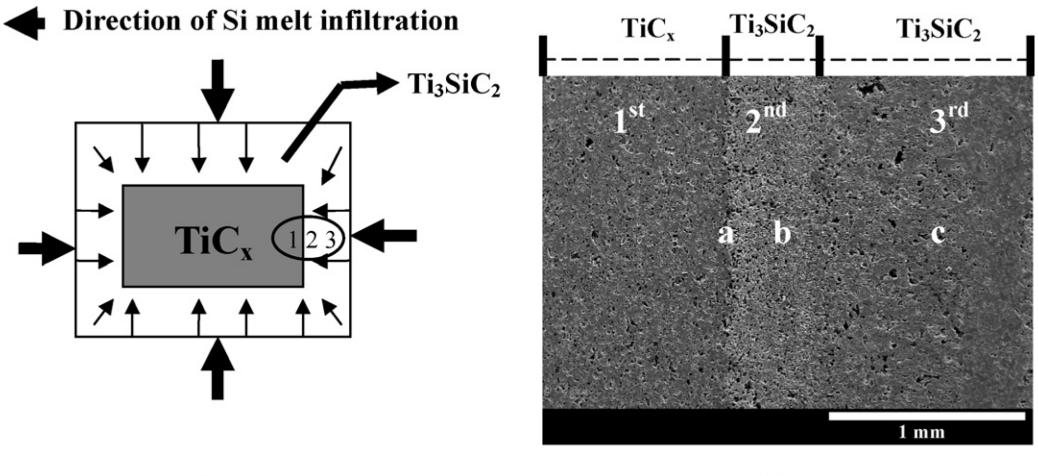


Fig. 3. A plot of infiltration depth vs. infiltration time. The reaction was performed to synthesize samples at 1550 °C. The infiltration depth was saturated over time because of depletion of the Si source.

Fig. 4 shows the XRD patterns of Ti_3SiC_2 synthesized by the infiltration of the Si melt into the partially sintered TiC_x specimens. Fig. 4(a) depicts the TiC_x preform synthesized for 3 h at 1550 °C with a 3Ti:2C powder mixture. Fig. 4(b), (c), and (d) shows the XRD patterns of the specimens after the infiltration of the Si melt for 1 min, 30 min, and 2 h, respectively, at 1550 °C for a sintered TiC_x:Si ingot molar ratio of 3:1.4. The exterior of the TiC_x specimen after reaction for 1 min was found to consist of mostly Ti_3SiC_2 and a small amount of TiC_x. After a longer reaction time, pure Ti_3SiC_2 was formed on the TiC_x preform. No other minor phases were detected for any of the sintering time ranges when sintering was performed at 1550 °C. These results are somewhat comparable to those of previous studies in which Ti_3SiC_2 was synthesized by hot pressing



(a) (b)

Fig. 2. (a) A schematic and (b) SEM micrograph of the cross section of a specimen synthesized using partially sintered TiC_x by Si melt infiltration. The regions numbered in the schematic have different microstructures, and the arrows indicate the infiltration direction of the Si melt. The areas numbered 1st, 2nd, and 3rd show the unreacted TiC_x, final Ti_3SiC_2 (synthesized in the last stage of the reaction), and initial Ti_3SiC_2 (synthesized in the early stage of the reaction), respectively; the difference in the microstructures in these regions is due to the infiltration direction of the Si melt.

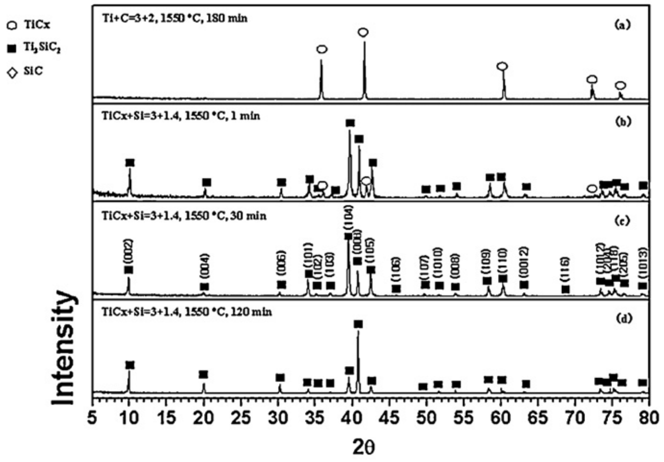
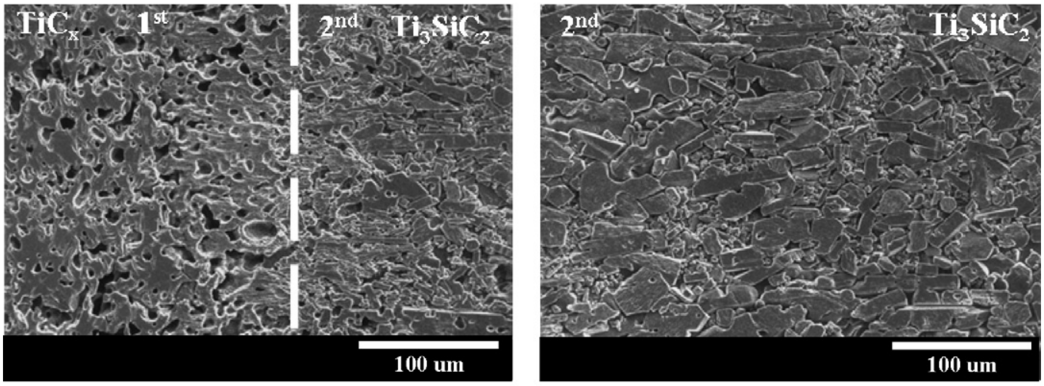


Fig. 4. X-ray diffraction patterns of the samples: (a) TiC_x preform synthesized for 3 h at 1550 °C with a 3Ti:2C powder mixture; (b) specimen after 1 min of Si melt infiltration; (c) specimen after 30 min of Si melt infiltration; and (d) specimen after 2 h of Si melt infiltration at 1550 °C with a sintered TiC_x:Si ingot molar ratio of 3:1.4.

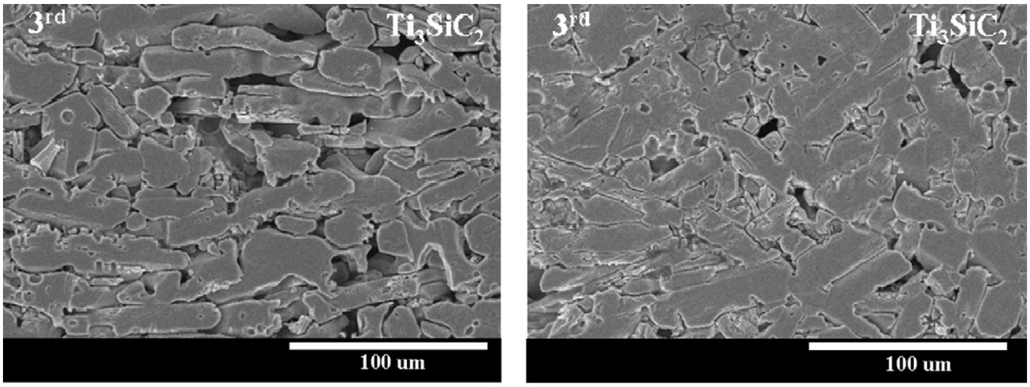
using Ti–Si–C powder mixtures as starting materials [4] or Si melt infiltration into a TiC/C precursor [21]; both these approaches, however, afforded small amounts of TiC_x, SiC, and Ti_8C_5 as minor phases. In this study, most of the excess carbon source was eliminated by producing partially sintered TiC_x, which could give pure Ti_3SiC_2 without any other phases. In the XRD patterns of Ti_3SiC_2, as the Si infiltration time was increased, the crystalline plane with the highest intensity changed from (1 0 4) to (0 0 8) (see Fig. 4(c) and (d)). We speculate that the grain orientation of the specimen might have changed with the reaction time. The dependence of the microstructure on the reaction time at 1550 °C will be discussed later in this paper.

Enlarged SEM micrographs of the regions indicated as “a,” “b,” and “c” in Fig. 2(b) are shown in Figs. 5 and 6. Fig. 5(a) and (b) corresponds to regions “a” and “b” in Fig. 2(b), respectively. In Fig. 5(a), one can observe a relatively dense layer identified as Ti_3SiC_2 on the right side of the micrograph, which is clearly separated from the unreacted TiC_x on the left side. Interestingly, Fig. 5(b) shows that crystallized Ti_3SiC_2 grains are directionally grown in a certain orientation: the synthesized Ti_3SiC_2 grains from the partially sintered TiC_x specimen seemed to have grown in the direction of infiltration of the Si melt. Fig. 6 shows the SEM microstructures of the synthesized Ti_3SiC_2 in the 3rd region of the reaction layer, “c” in Fig. 2(b); Ti_3SiC_2 was synthesized from the partially sintered TiC_x preform by Si melt infiltration at 1550 °C for up to 2 h. As shown in Fig. 6(a) and (b), the average grain size of the synthesized Ti_3SiC_2 was about 30 μm (length) × 10 μm (width). We could observe a slight change of the shape and size of grains with reaction time. Furthermore, as shown in Fig. 6, it was found that the alignment of the Ti_3SiC_2 grains in a certain direction changed slightly with an increase in the infiltration time. This could be one of the reasons for the change in the highest-intensity plane of the synthesized Ti_3SiC_2 from (1 0 4) to (0 0 8), as mentioned in the discussion of Fig. 4.



(a) (b)

Fig. 5. SEM micrographs of the specimen synthesized by Si melt infiltration into the porous TiC_x preform. The reaction was performed for 30 min at 1550 °C with a sintered TiC_x:Si ingot molar ratio of 3:1.4 by Si melt infiltration: (a) an enlarged micrograph of the interface between the 1st part and the 2nd part of Fig. 2(b); (b) interior of the 2nd part.



(a) (b)

Fig. 6. SEM micrographs of the synthesized Ti_3SiC_2 sections with a sintered TiC_x:Si ingot molar ratio of 3:1.4 by Si melt infiltration at 1550 °C for (a) 30 min and (b) 2 h.

4. Conclusions

In conclusion, high-purity Ti_3SiC_2 was synthesized using partially sintered TiC_x ($x = 0.67$) as a starting material by Si melt infiltration at 1550 °C. The TiC_x preform was synthesized by partial sintering for 3 h at 1550 °C with a 3:2 Ti:C mixture. Pure Ti_3SiC_2 was formed on the exterior of the TiC_x preform at 1550 °C with a sintered TiC_x:Si ingot molar ratio of 3:1.4. When sintering at 1550 °C, no other minor phases were detected during any of the time ranges. Ti_3SiC_2 could be synthesized by a direct reaction between TiC_x and molten Si without the need for employing a complex reaction to synthesize thermodynamically stable Ti_3SiC_2, as suggested in previous studies. Presumably, producing the TiC_x preform helps avoid the accumulation of excess carbon and aids the formation of pure Ti_3SiC_2.

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