Effect of Si Content on Melt Infiltration Method of SiCf/SiC-Ti3SiC2

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Abstract. SiCf/SiC composites have attracted wide attention as thermo-structural materials owing to its extraordinary properties at elevated temperature. To further improve the toughness of SiCf/SiC, Ti3SiC2 is used as the reinforcement of SiC matrix. In this study, the effect of Si content on the formation of Ti3SiC2 was discussed. The melt Si infiltration method was used to prepare the SiC matrix, which Ti3SiC2 phase was in-situ formed from the reaction between TiC, C and Si during the infiltration process. X-ray diffractometry (XRD), scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS) were determined to characterize the phase constitution and microstructure of the matrix. The results demonstrate that the synthesis of Ti3SiC2 was depended on the amount of Si during the molten Si infiltration. The small amount of Si could resulted in the incomplete infiltration reaction. TiSi2 was obtained at the presence of excessive Si. Thus appropriate amount of Si promotes the formation of Ti3SiC2 and improves the purity.

1. Introduction
SiCf/SiC composites have attracted wide attention as thermo-structural materials owing to its extraordinary properties at elevated temperature [1-2]. To overcome the brittleness of SiC matrix, the new toughening phase is considered to introduce to the matrix. As one of the representative MAX phases, Ti3SiC2 has unique properties due to its special structure. The Ti3SiC2 of lamellar structure can increase the fracture toughness of materials by delaminating along the weak basal plane and forming debonding, knot, bending and pullout during the fracture process. Hence, Ti3SiC2 is used as the reinforcement of SiC matrix due to the good match between the thermal expansion coefficients of Ti3SiC2 and SiC [3]. SiCf/SiC-Ti3SiC2 composites can be fabricated via polymer impregnation and pyrolysis (PIP), chemical vapour deposition (CVD), melt infiltration (MI) and hot pressing (HP). Among these methods, melt infiltration is considered as a cost effective, near net-shape forming process [4]. But the purity of Ti3SiC2 was the main problem during the infiltration process, because the byproducts TiSi2 or Ti5Si3 can also be formed in SiC matrix through the Si melt infiltration of a TiC-C preform. These byproducts are harmful to the toughening promotion of SiC matrix because of their high hardness and low fracture toughness.
In this work, Ti$_3$SiC$_2$ was \textit{in-situ} generated in the SiC matrix through melt Si infiltration method. And we discussed the effect of Si content on the formation of Ti$_3$SiC$_2$ by characterizing the phase constitution and microstructure of obtained composites using XRD, SEM and EDS.

2. Experimental
TiC powder(5 $\mu$m, 99.9 % pure), phenolic resin were used to fabricate a C-TiC preform. The synthesis procedures were as follows: The mixture of TiC and phenolic resin (the mass ratio of TiC to phenolic resin was 4:10) was ball-milled for 2 h at 1000r/h. The mixture was hot-pressed in vacuum at 220$^\circ$C for 30min and then pyrolyzed in an argon atmosphere up to 1000$^\circ$C for 1h to form a porous C-TiC preform. After that, the preform was infiltrated by different amount of Si(5$\mu$m, 99.99% pure)melt at 1450$^\circ$C for 30min under a vacuum atmosphere. And samples were synthesized by the infiltration of C-TiC preform with 20 wt.% , 30 wt.% , 40 wt.% , 45 wt.% Si melt were named as S1, S2, S3 and S4. It is worth to notice that the infiltration reaction was not complete in S1 from the appearance.

The phase constitution and microstructure of the infiltrated samples were investigated by SEM (Nova Nano450, FEI, USA) which equipped with back-scattered electron (BSE) detector and EDS. And the samples were analyzed by XRD (D8 Advance, Bruker, German) with CuK$\alpha$ radiation.

![Figure 1. XRD patterns of the samples infiltrated in various Si content.](image)

3. Results and Discussion
X-ray diffraction patterns of samples infiltrated with various Si contents are given in figure 1. It is obvious that the peaks of SiC or TiC can be detected in all the samples. Due to the overlapping of the peaks of TiC and SiC, it was difficult to identify SiC and TiC based on the XRD results [5]. It can be found that, in S1, the weak peaks attributed to TiSi$_2$ and Ti$_3$SiC$_2$ phase are showed in the matrix and an unreacted amorphous C can also be detected. Furthermore, there is no Si phase left which indicating that all introduced Si was consumed completely. It is probable that the infiltration reaction is not fully processed in the absence of sufficient Si content. The related reactions taken place in this stage are as follows [6-7]:

\[
\begin{align*}
\text{Si} + \text{C} &= \text{SiC} \quad (1) \\
\text{TiC} + 3\text{Si} &= \text{TiSi}_2 + \text{SiC} \quad (2) \\
3\text{TiC} + 2\text{Si} &= \text{Ti}_3\text{SiC}_2 + \text{SiC} \quad (3)
\end{align*}
\]

or

\[
9\text{TiC} + 8\text{Si} + 2\text{C} = 3\text{Ti}_3\text{SiC}_2 + 5\text{SiC} \quad (4)
\]
The Ti₃SiC₂ was more favorable formed through the reaction (4), due to the thermodynamic calculation [8-9]. With the amount of Si increased, in S2, the peaks of TiSi₂, Ti₃SiC₂ increased and amorphous C peak disappeared, indicating an incomplete reaction of TiC with molten Si. As the Si content reaches to 40 wt.%, Ti₃SiC₂ becomes the dominant phase. With further increase of the Si content, the residual Si phase are found in S4. And TiSi₂ becomes the main phase by displacement of Ti₃SiC₂. TiSi₂ was easy to form by reacting TiC with excess Si. The excessive Si would have accelerated the phase transition from TiSi₂ to Ti₃SiC₂. Based on the past researches [10-12], in the Ti-Si-C ternary phase system, the standard Gibbs free energy of formation of Ti₅Si₃ shows more negative value than that of TiSi₂ at this infiltration temperature, indicating a higher thermodynamic stability of Ti₅Si₃. But in our research, it seems that there is no Ti₅Si₃ phase exists in the matrix. It could be that Ti₃SiC₂ was consumed completely to form Ti₃SiC₂ in this synthesized temperature [9, 13-14]. In addition, the peak intensity of TiSi₂ and Ti₃SiC₂ were affected by many factors. The main reason should be attributed that the existence of these two phases restrain the grain growth of each other.

Figure 2 shows the BSE images and EDS analysis of the cross-section of samples infiltrated by various Si content. It is noticeable that different phases are found in all these samples. The deep gray area is the domains of SiC phase and bright area might be composed of titanium compounds. In order to clarify the phase composition of the bright area in the matrix, the EDS analysis was detected (figure 2(e)~(h)). As shown in figure 2(a), the black area is a region of unreacted C in the matrix. The bright area marked in A and B might be associate with the unreacted TiC phase and mixture of titanium compounds respectively, as it was confirmed by the EDS result (figure 2(e)). From figure 2(f), the bright area can be considered as the mixture of TiSi₂ and Ti₃SiC₂ which was also confirmed by the XRD result. It is clear that the phase marked in S3 (figure 2(g)) is composed of 54.05 at.% Ti, 15.13 at.% Si and 30.83 at.% C. This atom percentage is quite accordance with Ti₃SiC₂, which becomes the dominant phase in this area. This result is also agreed with the XRD. It is worth to notice that the BSE image of S4 reveals different phases in bright area (figure 2(d)). And the EDS analysis marked in S4 are shown in figure 2(h). We can see that region C contains the mixture of titanium compounds in which TiSi₂ may be the dominate phase. From the spectrum in region D, it is observed that Ti content is much higher than any of the other elements. The presence of such a phase is not detected by XRD. But the reason is yet unclear. While the spectrum in region E presents the content ratio of Ti to C is close to 1, which demonstrate that TiC may be the main phase in this region. TiC phase existing in S4 may be attributed to the decomposition of Ti₃SiC₂ [12], the main reason will be discussed in our future work.

The fracture surfaces of SiC-Ti₃SiC₂ infiltrated with different Si melt content are observed by SEM. As shown in figure 3(a), it is clear that the unreacted C exists in the matrix due to the uncomplicated infiltration process. Besides, there also be other grains exists in the unreacted C phase. The MAX phase Ti₃SiC₂ is characterized by its lamellar structure. The Ti₃SiC₂ phase can be obviously observed in S2 and S3. And it seems that the lamellar structure presents more abundant in S3 than S2. When the amount of Si increases to 45 wt.%, in S4, the lamellar structure almost disappeared. According to the results of XRD, the new phase is considered as Ti₃SiC₂. In general, the SEM results are consistent with the XRD and EDS results.

4. Conclusion was successfully synthesized
The in-situ synthesized SiC-Ti₃SiC₂ matrix was prepared by using melt Si infiltration method. The formation of Ti₃SiC₂ was controlled by using various Si content during the infiltration process. We found that the infiltration reaction is not fully processed in the absence of sufficient Si content. Moreover, TiSi₂ was obtained when TiC reacted with excess Si. It is suggested that a proper Si content is required for the formation of Ti₃SiC₂. And the more pure Ti₃SiC₂ phase can be synthesized at 40 wt.% of Si. In our future work, the reaction mechanism and infiltration process based on TiC, Si and C during the Si melt infiltration should be investigated. And further research should be done to control the purity of Ti₃SiC₂.
Figure 2. BSE images (a) ~ (d) of polished-surface of samples infiltrated in various Si content, and the EDS analysis (e) ~ (h) of the marked phase in (a) ~ (d).
Figure 3. The fracture surfaces of samples infiltrated in various Si content (a) S1, (b) S2, (c) S3 and (d) S4.

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