Formation Mechanism of Titanium Silicon Carbide: The Effect of Different Composition of Starting Materials

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Abstract. Titanium silicon carbide (Ti₃SiC₂) is a kind of ceramic that has physical property value similar with metal. Ti₃SiC₂ has been synthesized through various methods based on solid state reaction. Although Ti₃SiC₂ has been synthesized through various methods by using various starting materials consisting titanium (Ti), silicon (Si), and carbon (C) the mechanism of Ti₃SiC₂ formation through sintering has not fully understood. The aim of this research is to reveal the mechanism happening during sintering. Two composition of starting material was used, 2Ti/2Si/3TiC and 5Ti/2Si/3C. The analysis through XRD and SEM-EDS shows that the formation of intermediate phases, TiC and Ti₅Si₃, takes place prior to the formation of Ti₃SiC₂. In other words, Ti₃SiC₂ can only be formed through solid state reaction between TiC and Ti₅Si₃. Since TiC has already available in the system 2Ti/2Si/3TiC, the phase purity of Ti₃SiC₂ in 2Ti/2Si/3TiC is always higher than that of 5Ti/2Si/3C.

1. Introduction
Titanium silicon carbide (Ti₃SiC₂) is a ceramic compound that behaves like metal. Unlike ordinary ceramics, the hardness of Ti₃SiC₂ is extremely low and its thermal/electrical conductivity is relatively high. The detail properties of Ti₃SiC₂ had been reported by Barsoum et al [1]. Since it was found, Ti₃SiC₂ has been synthesized through various methods such as chemical reaction (CR) [2], chemical vapor deposition (CVD) [3], reactive sintering (RS) [4], hot isostatic pressing (HIP) [5,6,7], arc melting (AM) [8] solid-state synthesis (SSS) [9,10] and pulse discharge sintering (PDS) [11,12,13]. Various starting materials combinations have been used to synthesize Ti₃SiC₂. Some of them are Ti/Si/C [4,5,7,8] Ti/SiC/C [1,6,9] Ti/Si/TiC [11], Ti/SiC/TiC [12] and Ti/TiS₂/TiC [13].

The utilization of various starting materials results in the formation of intermediate compounds as well as Ti₃SiC₂. The melting of elemental powder (Ti/Si/C) at 1200-1400 °C for 100 hours results in the formation Ti₃SiC₂, TiC, TiSi₂, and Ti₅Si₃Cx [4,5,7,8]. The excess of silicon in the process that used elemental powder as starting material leads to the formation of TiSi₂ [4]. Depending on process temperature, other combination of other starting materials such as Ti/Si/TiC also results in the formation of TiC, TiS₂ as well as Ti₃SiC₂ [11]. The phase purity of Ti₃SiC₂ sample depends on the combination of starting materials. By using Ti/Si/TiC as starting material, the phase purity of Ti₃SiC₂ was more than 99 %, whereas by using the elemental powder (Ti/Si/C), the phase purity is lower than that of Ti/Si/TiC. The previous works deal with Ti₃SiC₂ synthesis usually focuses on the characterization of Ti₃SiC₂ after being sintered at single temperature. There is no firm explanation on
the mechanism of Ti5SiC2 formation and the actual reactions takes place at lower temperature prior to the formation of Ti5SiC2. Therefore, the aim of this research is to reveal the mechanism of Ti5SiC2 formation through calcinations at various temperatures. A series of sintering experiment from low to high temperature has been done to reveal the intermediate phases in the sample sintered at various temperatures. Based on previous research [4,5,7,8,11], we concluded that only two kinds of starting material that can produce Ti5SiC2 at relatively lower temperature, that is, the starting powders with composition and ratio 2Ti/2Si/3TiC and 5Ti/2Si/3C. Therefore, in this experiment we used similar composition and atomic ratio. The technique chosen was Plasma Discharge Sintering (PDS) technique, since it can synthesize highest phase purity of Ti5SiC2 at lowest temperature and shortest time [11].

2. Experimental Procedure
Commercial Ti, Si and TiC powders at mol ratio of 2Ti/2Si/3TiC were mixed by tubular shaker for 24 hours in argon atmosphere. The average particle size and purity of the powders are 10 µm and 99.9 % for Ti, 2-5 µm and 99 % for TiC, 10 µm and 99 % for Si, respectively. The mixed powder were compacted and sintered in vacuum using PDS technique at 700 – 1300 °C with a constant mechanical pressure of 50 MPa. After being sintered, the sample was ground and polished to remove the graphite layer on the surface of the sample. X-ray diffractometer, with CuKα radiation at 30 kV and 40 mA, was used to analyze the sample. The back scattering electron (BSE) image of each sample was observed by using Scanning Electron Microscope (SEM). The phase in the BSE image was analyzed through Energy-Dispersive X-ray Spectroscopy (EDS). Another starting powder consisting of commercial Ti, Si and C powders at mol ratio of 5Ti/2Si/3C was also prepared by using the same procedure with that of 2Ti/2Si/3TiC.

3. Result and Discussion
The XRD patterns for 2Ti/2Si/3TiC samples sintered at various temperatures are summarized in figure 1. The XRD pattern of sample sintered at 700 °C shows that this sample still contains only starting materials, which indicates Ti, Si and TiC has not reacted at this temperature. But in the sample sintered at 800 °C, a new phase, Ti2Si3, which is an indication that a reaction has taken place, can be found. The formation of Ti2Si3 becomes rapid at 900-1000 °C. It is indicated by the increasing of the diffraction intensity corresponding to Ti2Si3 and the decreasing of diffraction intensity corresponding to Ti and Si. Ti5Si3 is one the phases in binary phase diagram of Ti-Si, as well as TiSi, Ti3Si, Ti5Si4, and TiSi2 [14]. Although there are various phases in binary phase diagram of Ti-Si, the reaction takes place between Ti and Si always results in the formation of single phase Ti5Si3 [15,16,17]. Therefore, based on these facts, the formation of Ti5Si3 can be written as follows.

\[ 5Ti + 3Si \rightarrow Ti_5Si_3 \]  \hspace{1cm} (1)

The new set of diffraction intensity corresponding to Ti5SiC2 starts to appear at 1000 °C. The 2θs of the diffraction intensity corresponding to Ti5SiC2 in our sample are 39.59, 40.81 and 42.57. These are almost the same with 2θs of Ti3SiC2 in ICDD database (39.58, 40.86, and 42.57). Other researcher that deals with Ti3SiC2 synthesis also reported that 2θs of their Ti3SiC2 sample are almost similar with that of our sample [18,19,20,21].

Meanwhile, the diffraction intensity corresponding to TiC decrease with an increasing of temperature, and then they finally disappear at 1200 °C. The disappearance of the diffraction intensity corresponding to TiC obviously indicates that a reaction involving TiC has taken place. It is interesting to see that as the diffraction intensity corresponding to TiC and Ti5Si3 decrease and finally disappear, the intensity of the diffraction intensity corresponding Ti5SiC2 is getting higher. Thus, the formation of Ti5SiC2 must be the cumulative result of solid state reaction between TiC and Ti5Si3.

Figure 2 presents the back scattering electron (BSE) image of mixed and sintered 2Ti/2Si/3TiC powder at 900, 1100 and 1300 °C. The selection of these temperatures for SEM-EDS evaluation was based on XRD profile of sintered sample, presented in Figure 1, which shows that the lowest temperature where Ti5SiC2 can be formed, one among temperatures where all product can be found,
and one among temperatures where the sample consisting only Ti$_3$SiC$_2$ are 900, 1100, and 1300 °C, respectively. At 900 °C, three phases can be distinguished and identified through Energy-Dispersive X-ray Spectroscopy (EDS), they are Si, TiC and Ti$_5$Si$_3$. Meanwhile, at 1100 °C, Si has disappeared and Ti$_3$SiC$_2$ can be found, as well as TiC and Ti$_5$Si$_3$. Finally at 1300 °C in the entire image, other phases have disappeared, leaving Ti$_3$SiC$_2$ as the only phase in the sample. These result is agree with the XRD result that shows the formation of Ti$_5$Si$_3$ at 800-900 °C, the disappearance of Si and the formation of Ti$_3$SiC$_2$ at 1000 °C, and Ti$_3$SiC$_2$ as single phase at 1300 °C.

Figure 1. XRD profile of mixed 2Ti/2Si/3TiC sintered at 700-300°C for 15 minutes.

Figure 2. BSE image of mixed 2Ti/2Si/3TiC sintered at (a) 900 °C, (b) 1100 °C, (c) 1300 °C for 15 minutes.

XRD patterns for the samples sintered from the powder mixture of 5Ti/2Si/3C are shown in figure 3. It was found that except the intermediate compounds of Ti$_5$Si$_3$, another intermediate compound, Ti$_8$C$_5$, was formed during sintering. The diffraction intensity of Ti$_8$C$_5$, increases with an increasing in temperature until it disappears at 1000 °C. As Ti$_8$C$_5$ disappears at 1000 °C, TiC has been formed and it still can be found until 1200 °C. The formation of TiC was at the same time with the disappearance of C and Ti$_5$C$_8$. Therefore, the reaction of TiC formation can be written as follows.

\[ 8\text{Ti} + 5\text{C} \rightarrow \text{Ti}_8\text{C}_5 \]  
\[ \text{Ti}_8\text{C}_5 + 3\text{C} \rightarrow 8\text{TiC} \]

Meanwhile, diffraction intensity corresponding to Ti$_3$SiC$_2$ can be found significantly for the first time in the XRD pattern of sample sintered at 1000 and it continues to exist until 1200 °C. At these
temperatures, silicon and titanium has been reacted to form Ti₅Si₃ and TiC has also been formed through mechanism as shown in equation (2) and (3). Thus, the reaction takes place during sintering should be happen between TiC and Ti₅Si₃.

![XRD profile](image)

**Figure 3.** XRD profile of the mixed 5Ti/2Si/3C sintered at temperature 700–1200 °C for 15 minutes.

![BSE image](image)

**Figure 4.** BSE image of mixed 5Ti/2Si/3C sintered (a) 700 °C, (b) 1000 °C, (b) 1200 °C for 15 minutes.

Figure 4 shows the BSE image of mixed 5Ti/2Si/3C powder sintered at 700, 1000, and 1200 °C. The phases within this image were also identified through Energy-Dispersive X-ray Spectroscopy (EDS). At 700 °C the phases that can be found are C, Si, Ti₅C₅, and Ti₅Si₃. Obviously, the reactions among Ti, Si and C have taken place, resulted in the formation of Ti₅C₅ and Ti₅Si₃. The SEM-EDS analysis results quite similar with the result obtained through XRD analysis that shows the formation of Ti₅C₅ and Ti₅Si₃. The SEM-EDS analysis to the sample sintered at 1000 °C is also quite similar with the analysis obtained through XRD, which shows that Ti, C and Si have been reacted to form Ti₅C₅ and Ti₅Si₃. Finally at 1200 °C, Ti₅SiC₂ becomes the matrix phase in the image with TiC as dispersed phase. This result is also similar with the result obtained through XRD which shows that at this temperature the sintered powder consist of Ti₅SiC₂ with TiC.

The fraction of Ti₅SiC₂ to TiC is the representation of phase purity of Ti₅SiC₂ in the sintered
sample. It was calculated by using integrated intensity ratio method, in which the integrated intensity of Ti₃SiC₂ was compared to the sum of the integrated intensity of Ti₃SiC₂ (104) and TiC (200). The result of calculation is presented in Figure 5. The figure clearly shows that at any temperature, the phase purity of 2Ti/2Si/3TiC is always higher than that of 5Ti/2Si/3C. The previous XRD and SEM-EDS analysis can be summarized that the formation of TiC and Ti₃Si₂ takes place prior to the formation of TSC. In other words, TiC and Ti₃Si₂ are the necessary reactant for Ti₃SiC₂ formation. Since in the 2Ti/2Si/3TiC, the TiC was already available in the starting material, there was no energy needed to form TiC in 2Ti/2Si/3TiC. Therefore, the rapidity of Ti₃SiC₂ formation in 2Ti/2Si/3TiC is higher than that of 5Ti/2Si/3C.

![Integrated intensity ratio for Ti₃SiC₂ in 2Ti/2Si/3TiC and 5Ti/2Si/3C sintered at temperatures of 700-1200 °C for 15 minutes.](image)

**Figure 5.** Integrated intensity ratio for Ti₃SiC₂ in 2Ti/2Si/3TiC and 5Ti/2Si/3C sintered at temperatures of 700-1200 °C for 15 minutes.

4. Summary

Ti₃SiC₂ can be formed through plasma discharge sintering method by using molar composition and ratio Ti/2Si/3TiC or 5Ti/2Si/3C. XRD and SEM-EDS analysis shows that formation of certain intermediate phases takes place prior to the formation of Ti₃SiC₂. Some intermediate phases are Ti₈C₅ and Ti₃Si₄, and TiC, Ti₃C₂ gradually converts to TiC at 1000 °C, whereas Ti₅Si₃ did not convert to another intermediate phase. The analysis through XRD and SEM-EDS combined with the calculation fraction of Ti₃SiC₂ to TiC shows that TiC and Ti₅Si₃ is needed in the formation of Ti₃SiC₂, and therefore, the sample that already posses those phases TiC (2Ti/2Si/3TiC) can produce more Ti₃SiC₂ than that of 5Ti/2Si/3C.

5. Reference

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