

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

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Abstract. Titanium silicon carbide (Ti_3SiC_2) is a kind of ceramic that has physical property value similar with metal. Ti_3SiC_2 has been synthesized through various methods based on solid state reaction. Although Ti_3SiC_2 has been synthesized through various methods by using various starting materials consisting titanium (Ti), silicon (Si), and carbon (C) the mechanism of Ti_3SiC_2 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, $2\text{Ti}/2\text{Si}/3\text{TiC}$ and $5\text{Ti}/2\text{Si}/3\text{C}$. The analysis through XRD and SEM-EDS shows that the formation of intermediate phases, TiC and Ti_5Si_3 , takes place prior to the formation of Ti_3SiC_2 . In other words, Ti_3SiC_2 can only be formed through solid state reaction between TiC and Ti_5Si_3 . Since TiC has already available in the system $2\text{Ti}/2\text{Si}/3\text{TiC}$, the phase purity of Ti_3SiC_2 in $2\text{Ti}/2\text{Si}/3\text{TiC}$ is always higher than that of $5\text{Ti}/2\text{Si}/3\text{C}$.

1. Introduction

Titanium silicon carbide (Ti_3SiC_2) is a ceramic compound that behaves like metal. Unlike ordinary ceramics, the hardness of Ti_3SiC_2 is extremely low and its thermal/electrical conductivity is relatively high. The detail properties of Ti_3SiC_2 had been reported by Barsoum et al [1]. Since it was found, Ti_3SiC_2 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 Ti_3SiC_2 . 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/TiSi₂/TiC [13].

The utilization of various starting materials results in the formation of intermediate compounds as well as Ti_3SiC_2 . The melting of elemental powder (Ti/Si/C) at 1200-1400 °C for 100 hours results in the formation Ti_3SiC_2 , TiC, TiSi_2 , and $\text{Ti}_5\text{Si}_3\text{C}_x$ [4,5,7,8]. The excess of silicon in the process that used elemental powder as starting material leads to the formation of TiSi_2 [4]. Depending on process temperature, other combination of other starting materials such as Ti/Si/TiC also results in the formation of TiC, TiSi_2 as well as Ti_3SiC_2 [11]. The phase purity of Ti_3SiC_2 sample depends on the combination of starting materials. By using Ti/Si/TiC as starting material, the phase purity of Ti_3SiC_2 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 Ti_3SiC_2 synthesis usually focuses on the characterization of Ti_3SiC_2 after being sintered at single temperature. There is no firm explanation on



the mechanism of Ti_3SiC_2 formation and the actual reactions takes place at lower temperature prior to the formation of Ti_3SiC_2 . Therefore, the aim of this research is to reveal the mechanism of Ti_3SiC_2 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 Ti_3SiC_2 at relatively lower temperature, that is, the starting powders with composition and ratio $2\text{Ti}/2\text{Si}/3\text{TiC}$ and $5\text{Ti}/2\text{Si}/3\text{C}$. 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 Ti_3SiC_2 at lowest temperature and shortest time [11].

2. Experimental Procedure

Commercial Ti, Si and TiC powders at mol ratio of $2\text{Ti}/2\text{Si}/3\text{TiC}$ 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 $^{\circ}\text{C}$ 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 $\text{CuK}\alpha$ 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 $5\text{Ti}/2\text{Si}/3\text{C}$ was also prepared by using the same procedure with that of $2\text{Ti}/2\text{Si}/3\text{TiC}$.

3. Result and Discussion

The XRD patterns for $2\text{Ti}/2\text{Si}/3\text{TiC}$ samples sintered at various temperatures are summarized in figure 1. The XRD pattern of sample sintered at 700 $^{\circ}\text{C}$ 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 $^{\circ}\text{C}$, a new phase, Ti_5Si_3 , which is an indication that a reaction has taken place, can be found. The formation of Ti_5Si_3 becomes rapid at 900-1000 $^{\circ}\text{C}$. It is indicated by the increasing of the diffraction intensity corresponding to Ti_5Si_3 and the decreasing of diffraction intensity corresponding to Ti and Si. Ti_5Si_3 is one the phases in binary phase diagram of Ti-Si, as well as TiSi , Ti_3Si , Ti_5Si_4 , and TiSi_2 [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 Ti_5Si_3 [15,16,17]. Therefore, based on these facts, the formation of Ti_5Si_3 can be written as follows.



The new set of diffraction intensity corresponding to Ti_3SiC_2 starts to appear at 1000 $^{\circ}\text{C}$. The 2 θ s of the diffraction intensity corresponding to Ti_3SiC_2 in our sample are 39.59, 40.81 and 42.57. These are almost the same with 2 θ s of Ti_3SiC_2 in ICDD database (39.58, 40.86, and 42.57). Other researcher that deals with Ti_3SiC_2 synthesis also reported that 2 θ s of their Ti_3SiC_2 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 $^{\circ}\text{C}$. 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 Ti_5Si_3 decrease and finally disappear, the intensity of the diffraction intensity corresponding Ti_3SiC_2 is getting higher. Thus, the formation of Ti_3SiC_2 must be the cumulative result of solid state reaction between TiC and Ti_5Si_3 .

Figure 2 presents the back scattering electron (BSE) image of mixed and sintered $2\text{Ti}/2\text{Si}/3\text{TiC}$ powder at 900, 1100 and 1300 $^{\circ}\text{C}$. The selection of these temperatures for SEM-EDS evaluation was based on XRD profile of sintered sample, presented in Figure1, which shows that the lowest temperature where Ti_3SiC_2 can be formed, one among temperatures where all product can be found,

and one among temperatures where the sample consisting only Ti_3SiC_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_5Si_3 . Meanwhile, at 1100 °C, Si has disappeared and Ti_3SiC_2 can be found, as well as TiC and Ti_5Si_3 . Finally at 1300 °C in the entire image, other phases have disappeared, leaving Ti_3SiC_2 as the only phase in the sample. These result is agree with the XRD result that shows the formation of Ti_5Si_3 at 800-900 °C, the disappearance of Si and the formation of Ti_3SiC_2 at 1000 °C, and Ti_3SiC_2 as single phase at 1300 °C.

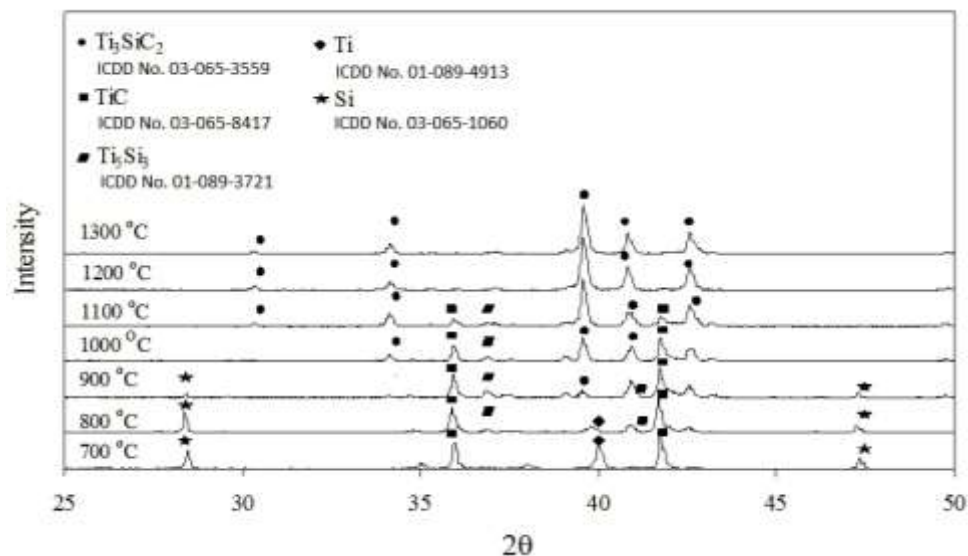


Figure 1. XRD profile of mixed 2Ti/2Si/3TiC sintered at 700-1300°C for 15 minutes.

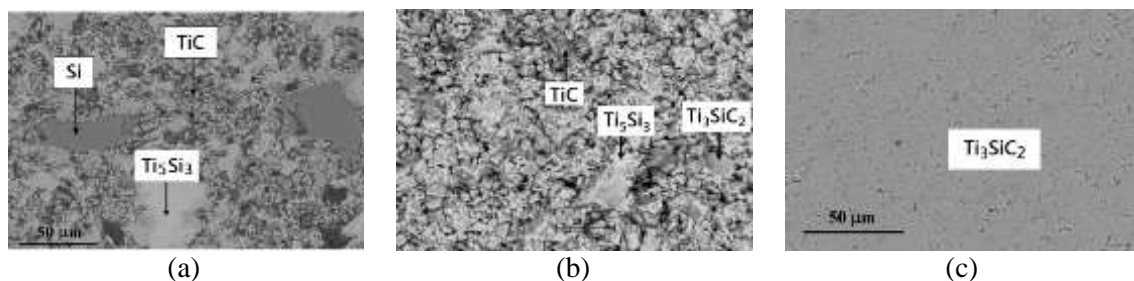


Figure 2. BSE image of mixed 2Ti/2Si/3TiC sintered at (a) 900 °C, (b) 1100 °C, (c) 1300 °C for 15 minutes.

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_5Si_3 , another intermediate compound, Ti_8C_5 , was formed during sintering. The diffraction intensity of Ti_8C_5 , increases with an increasing in temperature until it disappears at 1000 °C. As Ti_8C_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_5C_8 . Therefore, the reaction of TiC formation can be written as follows.



Meanwhile, diffraction intensity corresponding to Ti_3SiC_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 Ti_5Si_3 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 Ti_5Si_3 .

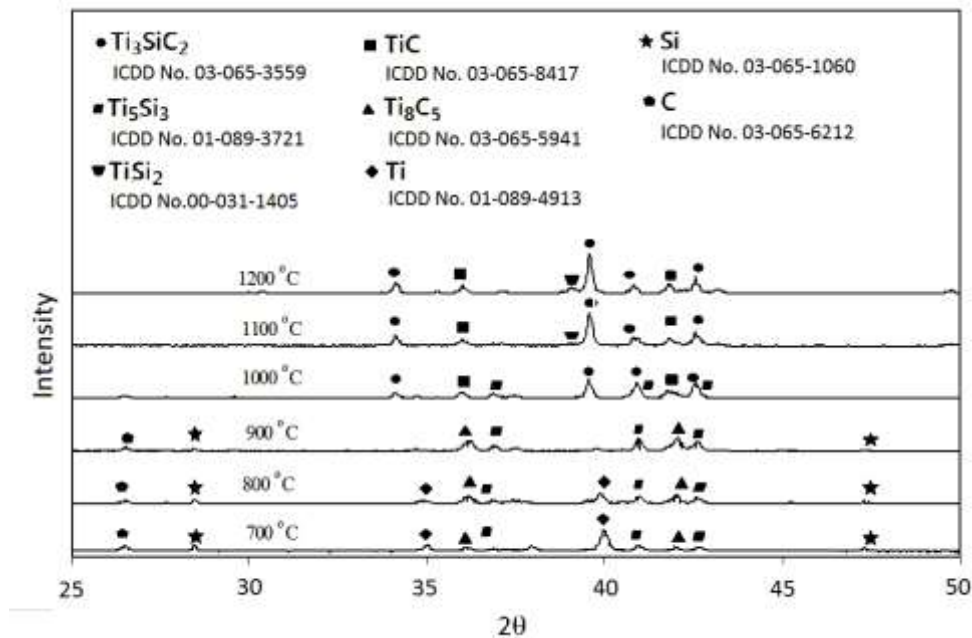


Figure 3. XRD profile of the mixed 5Ti/2Si/3C sintered at temperature 700–1200 °C for 15 minutes.

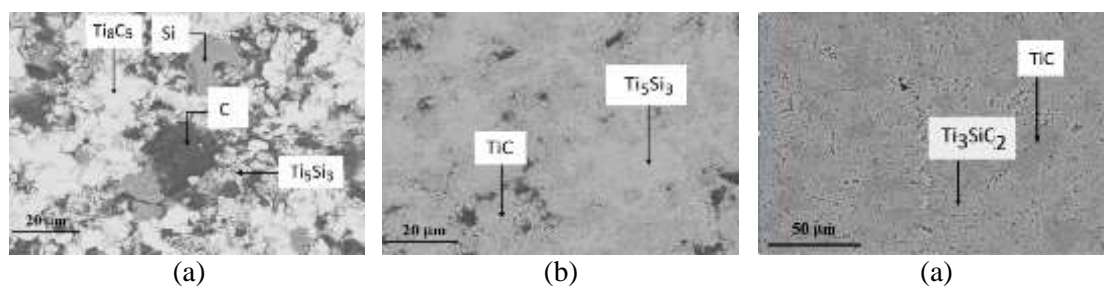


Figure 4. BSE image of mixed 5Ti/2Si/3C sintered (a) 700 °C, (b) 1000 °C, (c) 1200 °C for 15 minutes.

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, Ti_8C_5 , and Ti_5Si_3 . Obviously, the reactions among Ti, Si and C have taken place, resulted in the formation of Ti_8C_5 and Ti_5Si_3 . The SEM-EDS analysis results quite similar with the result obtained through XRD analysis that shows the formation of Ti_8C_5 and Ti_5Si_3 . 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 Ti_8C_5 and Ti_5Si_3 . Finally at 1200 °C, Ti_3SiC_2 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 Ti_3SiC_2 with TiC.

The fraction of Ti_3SiC_2 to TiC is the representation of phase purity of Ti_3SiC_2 in the sintered

sample. It was calculated by using integrated intensity ratio method, in which the integrated intensity of Ti_3SiC_2 was compared to the sum of the integrated intensity of Ti_3SiC_2 (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 Ti_5Si_3 takes place prior to the formation of Ti_3SiC_2 . In other words, TiC and Ti_5Si_3 are the necessary reactant for Ti_3SiC_2 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 Ti_3SiC_2 formation in 2Ti/2Si/3TiC is higher than that of 5Ti/2Si/3C.

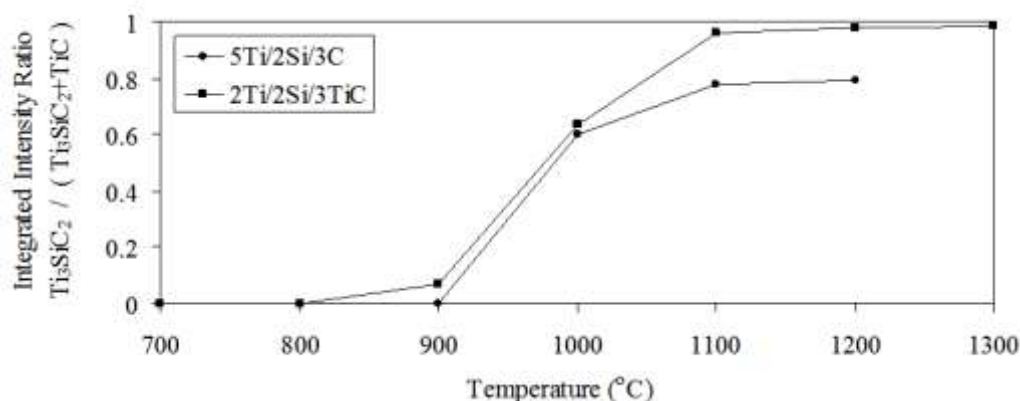


Figure 5. Integrated intensity ratio for Ti_3SiC_2 in 2Ti/2Si/3TiC and 5Ti/2Si/3C sintered at temperatures of 700-1200 °C for 15 minutes.

4. Summary

Ti_3SiC_2 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 Ti_3SiC_2 . Some intermediate phases are Ti_8C_5 and Ti_5Si_3 , and TiC , Ti_8C_5 gradually converts to TiC at 1000 °C, whereas Ti_5Si_3 did not convert to another intermediate phase. The analysis through XRD and SEM-EDS combined with the calculation fraction of Ti_3SiC_2 to TiC shows that TiC and Ti_5Si_3 is needed in the formation of Ti_3SiC_2 , and therefore, the sample that already possesses those phases TiC (2Ti/2Si/3TiC) can produce more Ti_3SiC_2 than that of 5Ti/2Si/3C.

5. Reference

- [1] Barsoum M W and El-Raghy T 1996 *J. Am. Ceramic Soc.* **79** 1953
- [2] Jeitschko W and Nowotny H 1967 *Monath. Chem.* **98** 329
- [3] Goto T and Hirai T 1987 *Mater. Res. Bull.* **22** 1195
- [4] Radhakrishnan J, William JJ, and Akinc M 1999 *J. of Alloy and Compound* **85** 285
- [5] Lis J, Miyamoto Y, Pampuch R, and Tanihata K 1995 *Material Letters* **22** 163
- [6] Hong X, Okano T, Iseki T, and Yano T 1995 *J. of Material Science Letters* **30** 3087
- [7] Li J F, Sato F, and Watanabe R 1999 *J. of Material Science Letters* 1595
- [8] Arunajatesan S, and Carim AH 1995 *J. Am. Ceramic Soc.* **78** 667
- [9] Goesmann F, Wenzel R, and Fetzer R S 1998 *J. Am. Ceram. Soc.* **81** 3025
- [10] Racault C, Langlais F, and Naslain R 1994 *J. of Mat. Sci.* **29** 3384
- [11] Sun Z M, Zhang Z F, Hashimoto H and Abe T 2002 *Mater. Trans.* **43** 428
- [12] Zhang Z F, Sun Z M, Hashimoto H, and Abe T 2001 *Scripta Materialia* **45** 1461
- [13] Zhang Z F, Sun Z M, Hashimoto H, and Abe T 2002 *Mat Res Innovat.* **5** 185
- [14] Massalski T B, Okamoto H, Subramanian P R, Kacprzak L 1990 *Binary Alloy Phase Diagrams*, ASM International, Materials Park, OH
- [15] Vishnyakov V, Lu J, Eklund P, Hultman L, Colligon J 2013 *Vacuum*, (93), 56-59
- [16] Kachelmyer C R, Khomenko IO, Rogachev AS, Varma A 1997 *J. Mater. Res.* **12** 12

- [17] Sabooni S, Karimzadeh F, Abbasi M H 2012 *Bull. Mater. Sci.* **35** 439
- [18] Zou Y, Sun Z M, Tada S, Hashimoto H 2006 *Materials Transactions* **47** 2987
- [19] Tang K, Wang C, Huang Y, Xia J 2001 *J. European Ceramic Soc.* **21** 617
- [20] Tang K Wang C, Xu X, Huang Y 2002 *Materials Letters* **55** 50
- [21] Wang L, Jiang W, Chen I, Bai B 2004 *J. Mater. Res.* **19** 3004