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Scripta Materialia 45 (2001) 1461–1467

Scripta MATERIALIA

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A new synthesis reaction of Ti_3SiC_2 through pulse discharge sintering Ti/SiC/TiC powder

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Received 8 May 2001; received in revised form 5 September 2001

Abstract

Ti_3SiC_2 was synthesized by pulse discharge sintering 4Ti/2SiC/TiC mixture powder in a temperature range of 1250–1450 °C. The purity of Ti_3SiC_2 was improved to 92 vol% at a sintering temperature of 1350 °C. The microstructure in the synthesized samples was controlled to be fine, coarse and duplex grains, depending on the sintering temperature and time.

Keywords: Ti_3SiC_2; Pulse discharge sintering; Synthesis; Microstructure

Introduction

Ti_3SiC_2 is a remarkable material that combines many of the best attributes of both metals and ceramics, such as low density (4.53 g/cm^3), high melting point, good electrical and thermal conductivity [1,2], easy machinability [3], good resistance to oxidation [4] and thermal shock [5]. Besides, it can maintain its strength to the temperature that renders the best superalloys available today unusable. When large-grained, oriented Ti_3SiC_2 polycrystalline samples were compressed at room temperature, it could display plastic behavior by a combination of shear and kink-band formation [6]. Therefore, this material is very damage tolerant and is capable of locally absorbing a lot of energy at room temperature. In recent decade, various processes were employed to synthesize bulk Ti_3SiC_2 samples mainly by the three reactions, i.e. (1) $3Ti + Si + 2C \rightarrow Ti_3SiC_2$; (2) $3Ti + SiC + C \rightarrow Ti_3SiC_2$ and (3) $Ti + Si + 2TiC \rightarrow Ti_3SiC_2$. The first

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1359-6462/01/$ - see front matter
PII: S1359-6462(01)01184-8

reaction has been widely used through the mixture powders of Ti/Si/C by many investigators, such as Racault et al. [7], Lis et al. [8,9], Radhakrishnan et al. [10], Gao et al. [11,12], Li et al. [13,14], Sun and Zhou [15]; while Barsoum and El-Raghy [16,17], Gao et al. [11] employed the second reaction. Recently, Ti_3SiC_2 was synthesized from Ti/Si/TiC powder through reactive sintering method [18], and pulse discharge sintering (PDS) technique [19,20]. However, another possible reaction, i.e. $2Ti + SiC + TiC \rightarrow Ti_3SiC_2$ has never been reported for synthesizing Ti_3SiC_2. Therefore, in the present study, the Ti/SiC/TiC powder was prepared to fabricate Ti_3SiC_2 by using the PDS technique [21] for rapid sintering and densification.

Experimental procedures

Commercially available Ti/SiC/TiC were selected as raw powders and mixed by a Tubular shaker mixer in Ar atmosphere for 24 h. The sizes and purities are 10 μm and 99.9% for Ti, 2–3 μm and 99% for SiC, 2–5 μm and 99% for TiC, respectively. The molar ratios of Ti:SiC:TiC were chosen to be 4:2:1, in which the molar ratios of Ti:Si:C were 5:2:3. In our previous work [20], high purity Ti_3SiC_2 samples was synthesized by Ti/Si/TiC powder with the molar ratios of 2:2:3. The present molar ratios of Ti:Si:C was chosen in accordance with the previous one. The mixed powder was compacted into a graphite mold and sintered in vacuum (10^{-3} Pa) at the temperature range of 1250–1450 °C for 15–120 min by using the PDS technique. The heating rate was controlled in the range of 50–60 °C/min and the applied pressure was maintained constant of 50 MPa during reaction sintering. After sintering, the size of the samples is 20 mm in diameter and 4–5 mm in thickness. The samples can be easily removed from the die without inducing any crack in the samples. The surfaces of the samples were ground to remove the graphite layer and analyzed by X-ray diffractometry with CuKα radiation at 30 kV and 40 mA to determine the purity of Ti_3SiC_2 by means of standard additive method [18]. After that, the samples were mechanically polished and etched by a solution of H_2O:HNO_3:HF (2:1:1) to expose the Ti_3SiC_2 grains. With the help of scanning electron microscopy (SEM), the microstructures of the synthesized samples were observed and analyzed.

Results and discussion

Fig. 1 shows the X-ray diffraction profiles of the mixed 4Ti/2SiC/TiC powder and the samples sintered at 1250–1450 °C for 15 min. Ti, SiC and TiC peaks can be clearly seen in the diffraction profile of the mixture powder. After sintering at different temperatures, all the Ti and SiC peaks disappeared, and the TiC peaks at $2\theta = 36°$ and 41.8° was decreased to lower intensity, with all the other peaks corresponding to Ti_3SiC_2 phase. When the mixture powder was sintered at 1350 °C, the intensities of TiC peaks were found to be lowest in all the samples. Therefore, the powder was further sintered at this temperature for different times in order to compare the effect of sintering time on

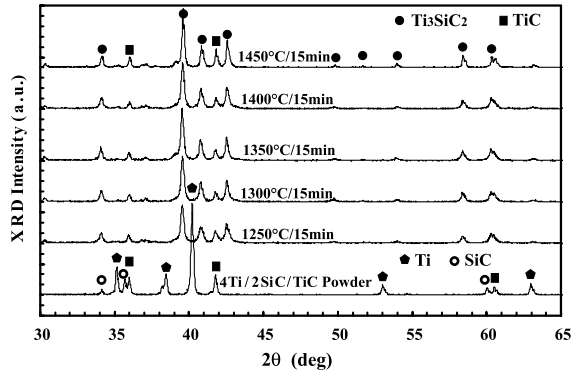


Fig. 1. X-ray diffraction profiles of the mixed 4TiC/2SiC/TiC powder and the samples sintered at 1250–1450 °C.

the purity. The X-ray diffraction profiles of the samples sintered for different times nearly had the same peak intensities for TiC. The results indicate that there should be only two phases, i.e. main phase of Ti_3SiC_2 and impurity phase of TiC, in all the samples, implying that the present Ti/SiC/TiC powder could be regarded as a new mixture for the synthesis of Ti_3SiC_2 by using the PDS technique.

In the present study, the following equation, obtained by the standard addition method [20], was used to calculate the purity of Ti_3SiC_2:

$$V_{TC} = \frac{I_{TC}/I_{TSC}}{1.95 + I_{TC}/I_{TSC}}$$

wherein, V_{TC} is the volume fraction of TiC, I_{TC}/I_{TSC} is the integrated diffraction intensity ratio of TiC to Ti_3SiC_2 main peaks, which were obtained from the X-ray diffraction profiles scanned in a narrower diffraction range of 32–44 at a scanning speed of one fourth that used for the results in Fig. 1. The purity of Ti_3SiC_2 in all the samples was calculated in this way and is summarized in Fig. 2. It can be seen that TiC content

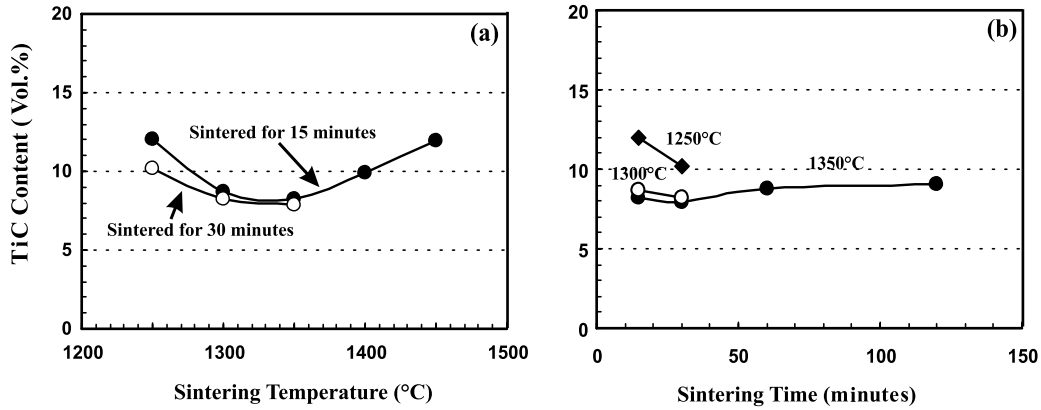


Fig. 2. TiC content in the samples sintered at (a) 1250–1450 °C and (b) 1250–1350 °C.

decreased with increasing sintering temperature and had the lowest value of about 8 vol% at 1350 °C (see Fig. 2(a)), followed by an increase in TiC content with further increasing the sintering temperature. When the samples were sintered for 30 min, TiC content in the samples is slightly lower than that sintered for 15 min at low sintering temperature. Fig. 2(b) shows the effect of sintering time on the purity of Ti_3SiC_2. At low sintering temperature of 1250 °C, the effect of sintering time on the purity of Ti_3SiC_2 seems to be obvious. At 1350 °C, the TiC content nearly maintained constant value of 8–9 vol% in the sintering time range of 15–120 min, indicating that the PDS technique could rapidly synthesize Ti_3SiC_2. Even though the purity of Ti_3SiC_2 in the present synthesis process was not very high, it is possible to further purify the products by optimizing sintering conditions, such as by using fluctuation method [15] or further adjusting the molar ratios of Ti:SiC:TiC.

The microstructure of the synthesized samples observed by SEM can be seen in Fig. 3. When the sintering was conducted at relatively low temperature of 1250 °C for 15 min, the synthesized Ti_3SiC_2 grains are very fine and plate-like. As shown in Fig. 3(a), the average grain size is about 5 μm in length and 2 μm in width. Besides, there are some white particles marked by arrows. By EDX analysis, they were determined as TiC, which is in consistent with the X-ray diffraction results in Fig. 1. With increasing sintering temperature to 1300 °C, the grain was coarsened, but still homogeneous. When the sample was sintered at 1350 °C for 15 min, as shown in Fig. 3(b), there appeared some coarse grains with the size of about 20 μm, which were embedded in a homogeneous matrix of fine grains. With extending sintering time at 1350 °C, the size and volume fraction of the coarse grains increased gradually. As shown in Fig. 3(c), the grain size could grow into more than 50 μm; accordingly, these coarse grains nearly

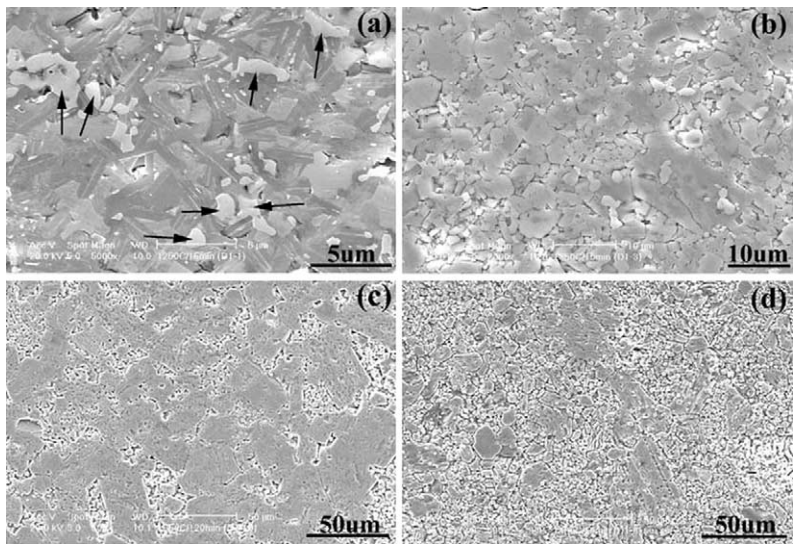
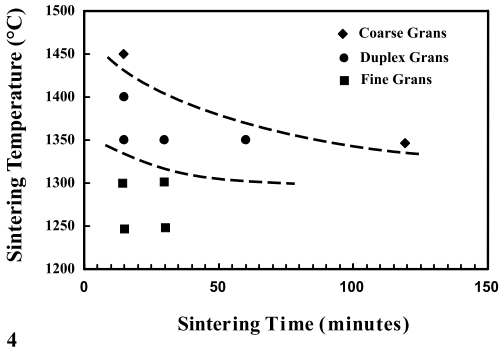


Fig. 3. Microstructure of the samples sintered at 1250–1450 °C observed by SEM: (a) 1250 °C/15 min, (b) 1350 °C/15 min, (c) 1350 °C/120 min and (d) 1450 °C/15 min.

occupied all the area of the sample when sintering was conducted for 120 min. At higher sintering temperatures of 1400 and 1450 °C, as shown in Fig. 3(d), the grain size continued to increase in comparison with that in Fig. 3(b), while the volume fraction of the coarse grains did not raise to a high value due to the short sintering time of 15 min. Meanwhile, the grain size of the sample sintered at 1450 °C for 15 min is smaller than that sintered at 1350 °C for 120 min, indicating that sintering time might play a distinct role in grain growth. From the microstructures above, it can be seen that both sintering temperature and time can affect the microstructure of Ti_3SiC_2 and the grain size could be controlled to a variation with a factor of 10 from fine to coarse grains. Fig. 4 summarized the microstructure characterization of Ti_3SiC_2, and the microstructure of Ti_3SiC_2 was classified into three types, i.e. fine ($d \leqslant 10$ μm), coarse ($d \geqslant 50$ μm) and duplex ($10 \leqslant d \leqslant 50$ μm) grains, depending on the sintering temperature and time. From this illustration, it can be found that the duplex grains could be obtained mainly in the temperature range of 1350–1400 °C, which exactly corresponds to the optimized sintering temperature.

Fig. 5 shows the variation of the measured density (ρ_M), theoretical density (ρ_T) and relative density (ρ_M/ρ_T) with sintering temperature of the samples sintered for 15 min with the PDS technique. It can be seen that the measured density of the samples increased from 4.47 to 4.54 g/cm^3 at the temperature range of 1250–1450 °C. It was reported that the theoretical densities of Ti_3SiC_2 and TiC are equal to 4.53 and 4.90 g/cm^3, respectively. Accordingly, the theoretical densities of the synthesized samples were calculated from the densities of Ti_3SiC_2 and TiC along with the purity of Ti_3SiC_2 shown in Fig. 2. It is apparent that the relative density of the samples is quite high (97.7–99.4%) at all the sintering temperatures. When the sintering temperature is higher than 1350 °C, the relative density of the samples could be higher than 99%, indicating that a good densification effect of the PDS process conducted at a pressure of 50 MPa for 15 min.

Concerning the synthesis reactions of Ti_3SiC_2 from Ti/SiC/TiC, it is suggested that there might be two possible reaction paths during sintering. It was reported by Naka et al. [22] that Ti_3SiC_2 could form between Ti/SiC diffuse couples through several



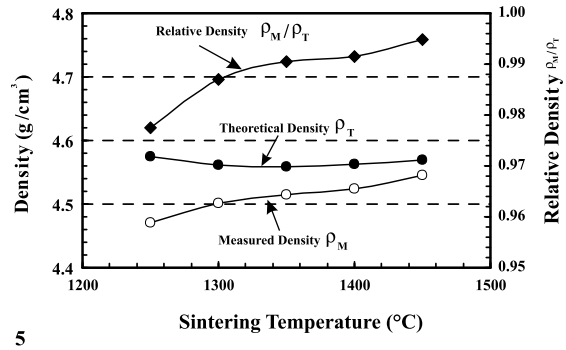


Fig. 4. Dependence of microstructure of Ti_3SiC_2 on the sintering temperature and time.
Fig. 5. Dependence of density of synthesized samples on the sintering temperature.

phases, i.e. $Ti/Ti_5Si_3C_x/Ti_5Si_3C_x + TiC_x/Ti_3SiC_2/SiC$ when the bonding was conducted at 1100–1500 °C. Therefore, the first possible synthesis reaction of Ti_3SiC_2 might occur between Ti and SiC particles through the above reaction paths. Additionally, Kooi et al. [23] reported another reaction between Ti and SiC to form TiC and Si, i.e. $SiC + Ti \rightarrow TiC + Si$. It is known that TiC has an octahedral structure; while Ti_3SiC_2 is a layered hexagonal structure, in which two octahedral TiC are connected by Ti and Si layers [24,25]. Meanwhile, Ti–Si system has two eutectic reactions for the $Si–TiSi_2$ and $Ti–Ti_5Si_3$ compositions both at the temperature of 1333 °C [14,18]. When the sintering temperature reached this eutectic point, the eutectic liquid phase would begin to appear between Ti and Si particles. Therefore, it is possible to form Ti_3SiC_2 at the interfaces between the Ti–Si liquid phase and TiC particles, i.e. $2TiC + Ti - Si\ (liquid) \Rightarrow Ti_3SiC_2$. Recently, it has been proved that high purity Ti_3SiC_2 (>98 wt.%) could be rapidly synthesized from Ti/Si/TiC powders [18–20], which might provide indirect evidence on the discussed synthesis reaction. When the PDS technique was applied on the Ti/SiC/TiC powder, pulse electric field may activate the surface of the powder particles resulting in an easy sintering process. Meanwhile, possible plasma occurred between the particles may locally increase the temperature to much higher a level than the controlled average temperature, which could effectively promote the synthesis reaction of Ti_3SiC_2 [21].

Summary

Ti_3SiC_2 could be synthesized from Ti/SiC/TiC powder at 1250–1450 °C by using the PDS technique. The purity of Ti_3SiC_2 was improved to higher than 92 vol% and the relative density of the synthesized samples was higher than 99% at the temperature higher than 1350 °C. The microstructure of Ti_3SiC_2 was found to have three types, i.e. fine, coarse and duplex grains, depending on the sintering temperature and time. It is suggested that Ti/SiC/TiC powder can be regarded as a new mixture for the synthesis of Ti_3SiC_2 by using the PDS technique.

Acknowledgements

One of authors (Dr. Zhang, Z.F.) wishes to acknowledge the Japan Science and Technology Agency (STA) providing for a postdoctoral fellowship.

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