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Effect of Al addition on the synthesis of Ti_3SiC_2 bulk material by pulse discharge sintering process

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Abstract

Ti_3SiC_2 bulk materials were synthesized from the starting powders of 1Ti/1Si/2TiC–xAl and 3Ti/1SiC/1C–xAl (molar ratios, x ranges from 0.05 to 0.15) at temperatures between 1100 and 1400 °C for 15 min by pulse discharge sintering technique. X-ray diffraction and scanning electron microscopy were used to characterize the synthesized materials. It was found that the addition of Al decreases the content of TiC in the sintered samples and expands the optimal temperature range for the synthesis of Ti_3SiC_2 bulk materials. By addition of Al, Ti_3SiC_2 bulk materials of high phase-purity have been synthesized at 1100 and 1200 °C from 1Ti/1Si/2TiC and 3Ti/1SiC/1C starting powders, respectively.

Keywords: Sintering; Ti_3SiC_2

1. Introduction

Ti_3SiC_2 is the representative of a novel ternary compound family, called MAX phases (viz. $M_{n+1}AX_n$, where M: early transition metal, A: group A element, X: C and/or N, $n = 1$–3). It has been attracting attention from both the material scientists and physicists, due to its unusual combination of both metallic and ceramic merits, including high electrical ($\sim 4.5 \times 10^6\ \Omega^{-1}\ m^{-1}$) and thermal ($\sim 37$ W/m K) conductivities,[1,2] relatively low hardness (~ 4 GPa), high damage tolerance and thermal shock resistance,[2,3] machinability,[4] relatively low density (~ 4.52 g/cm^3) and high stability at high temperatures (~ 1700 °C).[5]

The synthesis of Ti_3SiC_2 was first reported in 1967 by Jeitschko and Nowotny using chemical reaction.[6] Even though various methods, such as arc-melting,[7] hot isostatic pressing(HIP) or self-propagating high-temperature synthesis (SHS)-HIP,[8–12] reactive sintering,[13,14] and pulse discharge sintering (PDS),[20–22] have been applied for the synthesis of Ti_3SiC_2 bulk material using Ti/Si/C,[8–11,13–15] Ti/SiC/C[11,12] and Ti/Si/TiC[18–22] as starting powders, the synthesis of Ti_3SiC_2 bulk materials with high phase-purity is still difficult. Concomitant impurity phases like TiC and/or titanium silicides, such as Ti_5Si_3 and $TiSi_2$, frequently co-exist in the final product.[7–22] Furthermore, a relatively high temperature (e.g. 1600 °C by reactive hot-pressing[11]) is required for the synthesis of Ti_3SiC_2 with high phase-purity and the optimal temperature range for Ti_3SiC_2 sintering is very narrow, less than 50 °C.[20,22] The lower temperature synthesis of highly phase-pure Ti_3SiC_2 bulk material with wider optimal sintering temperature range is, therefore, desirable for the development and wide applications of this material.

In 2005, Li et al.[23] reported that with an addition of Al into the 3Ti/1Si/2C starting powders, the optimal temperature for the synthesis of highly phase-pure Ti_3SiC_2 was decreased from 1450 to 1350 °C using vacuum sintering. Our previous results suggested that the PDS technique can rapidly synthesize fully dense Ti_3SiC_2 bulk material at lower temperatures[19–22] (e.g. 15 min at 1250–1300 °C using starting powders of 1Ti/1Si/2TiC[20]). In the present work, we investi-

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gated the synthesis of Ti_3SiC_2 by addition of Al to Ti/Si/2TiC and 3Ti/1SiC/1C starting powders using PDS technique.

2. Experimental procedures

Commercial powders of Ti (average diameter (dm): ca. 10 μm, 99.9% pure), Si (dm: 2–3 μm, 99% pure), TiC (dm: 2–5 μm, 99% pure), SiC (dm: 2–5 μm, 99% pure) and Al (dm: 3 μm, 99.9% pure), made by Kojundo Chemical Lab. Co. Ltd. Saitama, Japan, with a molar ratio of Ti:Si:TiC:Al = 1:1:2:*x* and Ti:SiC:C:Al = 3:1:1:*x* (*x* = 0.05, 0.10, 0.15), were used as the starting powders and mixed by a Tubular shaker mixer in argon atmosphere for 24 h. The mixed powders were compacted into a graphite mold, and sintered in vacuum using PDS technique at 1100–1400 °C for 15 min under a constant axial pressure of 50 MPa. The synthesized samples, 20 mm in diameter and 4–5 mm in thickness, were then analyzed by X-ray diffractometry (XRD) with Cu Kα radiation. Some samples, polished and etched using a solution of H_2O:HNO_3:HF = 2:1:1, were observed using scanning electron microscopy (SEM) equipped with an energy-dispersive spectroscopy (EDS). The densities of the synthesized samples were measured by means of the Archimedes method.

3. Results and discussion

X-ray diffraction results indicated that the addition of small amount of Al favors the formation of Ti_3SiC_2 phase and lowers the synthesis temperature of highly phase-pure Ti_3SiC_2 materials. Fig. 1a–d shows the X-ray diffraction patterns of samples synthesized at different temperatures from the starting powders of 1Ti/Si/2TiC–*x*Al. All the patterns are composed mainly of Ti_3SiC_2 peaks with weak peaks of TiC (with main peak at 41.7°). The relative intensity of TiC peaks varies with the synthesis temperature and the Al content in the starting powders. At synthesis temperatures below 1200 °C, the relative intensity of TiC peaks decreases with increasing Al content. At higher synthesis temperatures, the TiC peaks in all patterns are negligible or hard

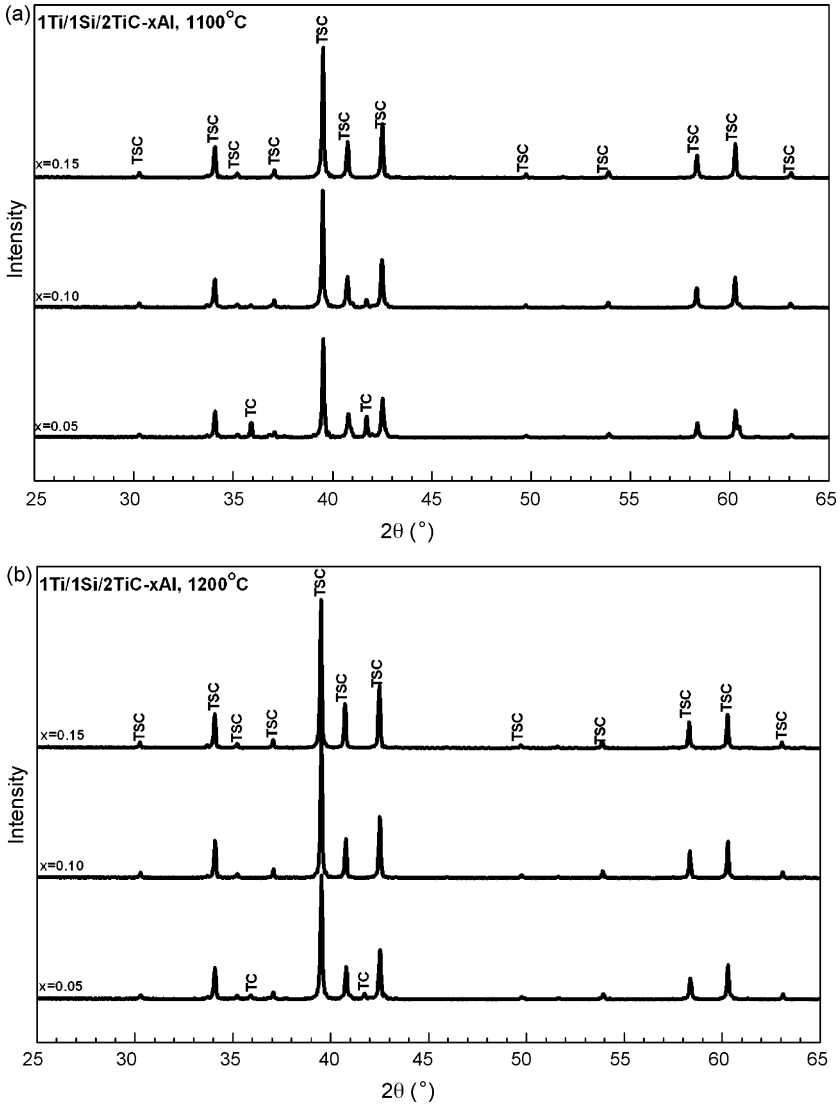

Fig. 1. X-ray diffraction patterns of 1Ti/1Si/2TiC/*x*Al samples synthesized at (a) 1100 °C, (b) 1200 °C, (c) 1300 °C and (d) 1400 °C for 15 min.

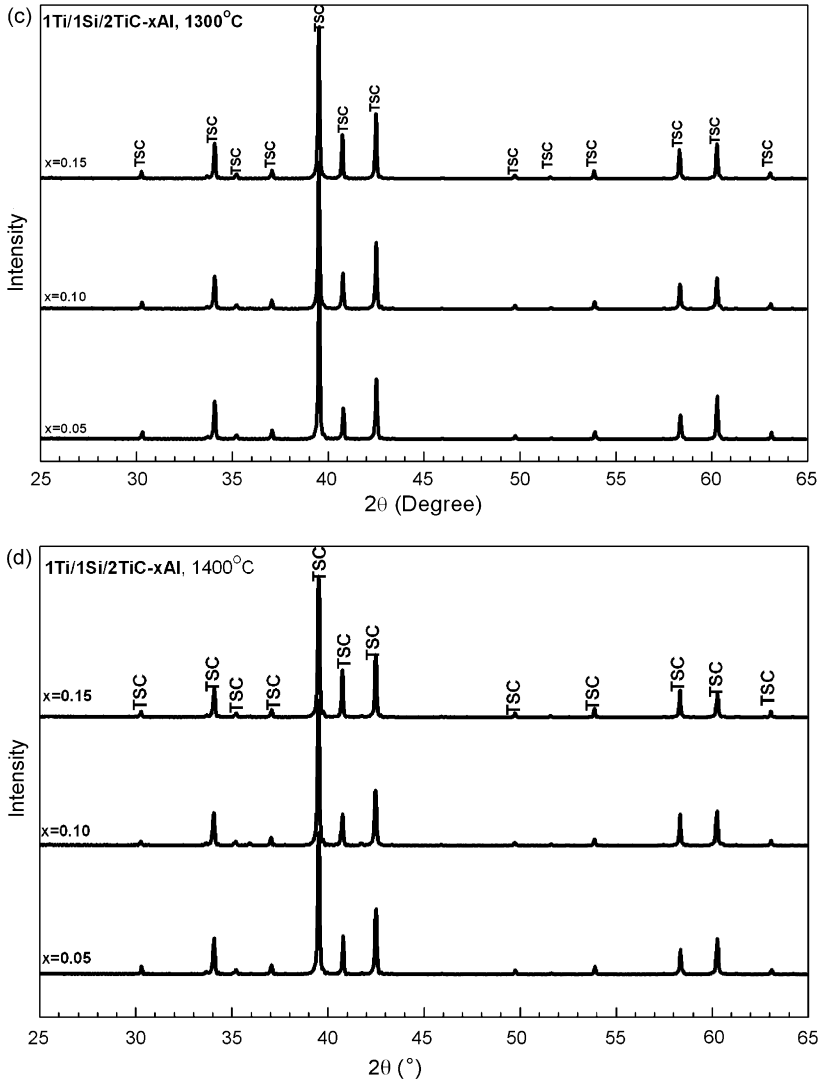

Fig. 1. (*Continued*).

to be detected, indicating the synthesized samples contain high phase-purity of Ti_3SiC_2. It should be pointed out that there are no peaks from Al or Al-containing compounds seen in the XRD patterns. This is probably due to the relative low content of Al (the weight content of Al is 2.0% at x of 0.15).

Assuming a Ti_3SiC_2–TiC two-phase system, the weight percentage of the TiC phase, W_{TC}, in the samples can be estimated from the following equation[20]:

$$W_{TC} = \frac{I_{TC}/I_{TSC}}{1.8 + I_{TC}/I_{TSC}} \quad (1)$$

where I_{TC} and I_{TSC} are the integrated diffraction intensity of main peaks for TiC (at 2θ of 41.7°) and Ti_3SiC_2 (at 2θ of 39.5°), respectively. The calculated results are described in Fig. 2. With an increase of Al content, the TiC content in the samples synthesized from 1Ti/1Si/2TiC–xAl starting powders at temperatures below 1200 °C (Fig. 2a) and all the samples synthesized from 3Ti/1Si/1SiC–xAl starting powders (Fig. 2b) decreases remarkably. The addition of small amount of Al into the starting powders decreases the lower limit of the temperature for the synthesis of Ti_3SiC_2 with high phase-purity. By addition of 2.0% of Al, the lowest temperature for the synthesis of highly phase-pure (>99.9 wt.%) Ti_3SiC_2 from 1Ti/1Si/2TiC–0.15Al and 3Ti/1SiC/1C–0.15Al is 1100 and 1200 °C, respectively, which is much lower than that without Al addition.[22] In addition, the optimal temperature range for the synthesis of Ti_3SiC_2 with high phase-purity is greatly enlarged by the Al addition. This range is greater than 300 °C using 1Ti/1Si/2TiC–0.15Al as the starting powders, much larger than 50 °C without Al additiont.[22] By comparing Fig. 2a with b, we can also see that, Ti_3SiC_2 samples synthesized from 1Ti/1Si/2TiC–xAl have higher phase-purity than those synthesized from 3Ti/1SiC/1C–xAl. This might be attributed to the different reaction processes. It has been reported that intermediate phases, TiC_x and $Ti_5Si_3C_x$, formed during the synthesis of Ti_3SiC_2 bulk materials from Ti/SiC/C mixture.[12,24] The formation of TiC_x and $Ti_5Si_3C_x$ is a result of reaction between Ti, SiC, and C. While using 1Ti/1Si/2TiC–xAl as starting powders, TiC is a starting powder, and Ti_5Si_3 may form from Ti and Si at temperature below 800 °C through[25]:

$$5Ti + 3Si \rightarrow Ti_5Si_3 \quad (2)$$

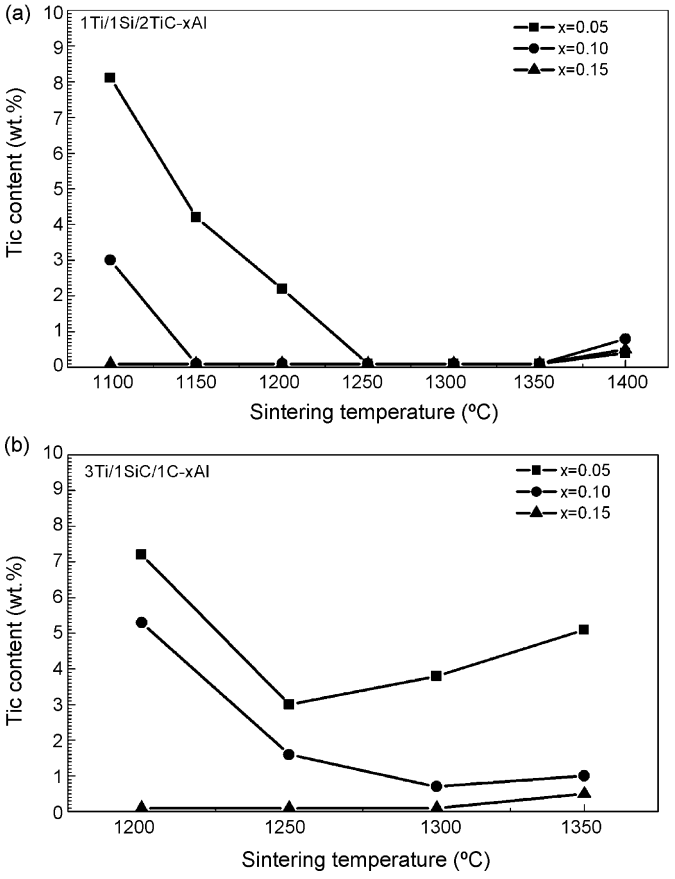

Fig. 2. Weight percentage of TiC phase in the samples synthesized from (a) 1Ti/1Si/2TiC–*x*Al and (b) 3Ti/1SiC/1C–*x*Al powder mixtures.

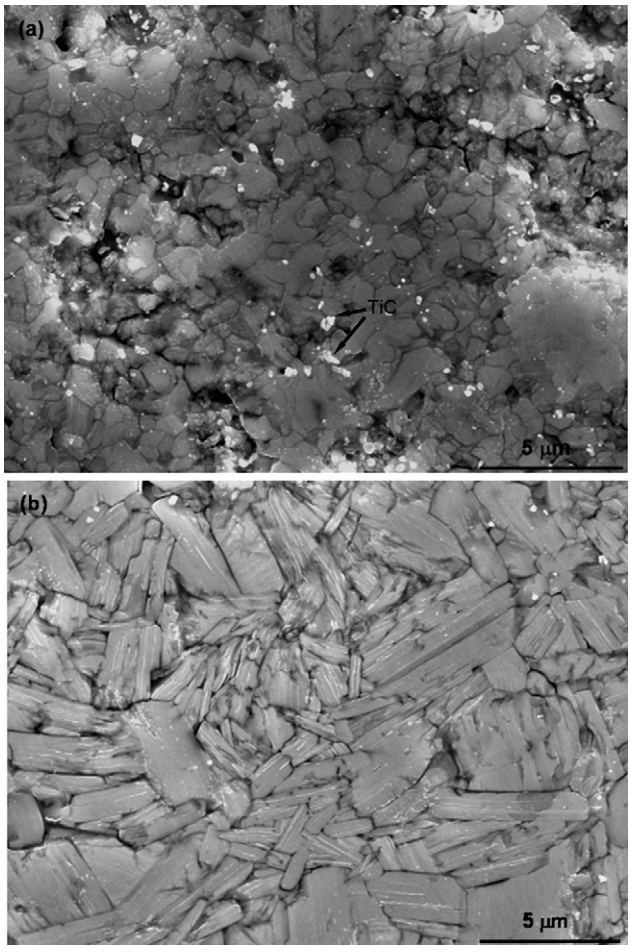

Fig. 3. SEM morphologies of samples synthesized at 1100 °C for 15 min from starting powders of (a) 1Ti/1Si/2TiC–0.05Al and (b) 1Ti/1Si/2TiC–0.15Al.

Then, Ti_3SiC_2 may form at higher temperature through[25]:

$$Ti_5Si_3 + 10TiC + 2Si \rightarrow 5Ti_3SiC_2 \quad (3)$$

Fig. 3 shows the SEM micrographs of samples synthesized at 1100 °C from the starting powders of 1Ti/1Si/2TiC–0.05Al and 1Ti/1Si/2TiC–0.15Al, respectively. The sample synthesized from 1Ti/1Si/2TiC–0.05Al consists of high content of ancillary TiC phases, as indicated by arrows in Fig. 3a, while only several white spots (TiC particles) can be seen at the top right corner of Fig. 3b, image taken from the sample synthesized from 1Ti/1Si/2TiC–0.15Al. It is evident that the increase in Al content significantly increases the phase-purity of Ti_3SiC_2, in consistence with the XRD results.

Fig. 4 shows the relative density, ρ_m/ρ_t, of the samples synthesized from starting powders of 1Ti/1Si/2TiC–xAl at temperatures ranging from 1150 to 1400 °C, where ρ_m is the measured density, and ρ_t is the theoretical density of the samples. ρ_t can be calculated through the following equation:

$$\rho_t = \frac{1}{\text{TSC wt.\%}/\rho_{tsc} + \text{TiC wt.\%}/\rho_{tic}} \quad (4)$$

where TSC wt.% and TiC wt.% are the weight percentages of Ti_3SiC_2 and TiC in the sintered samples, respectively. And ρ_{tsc} is the theoretical density of Ti_3SiC_2, being 4.52 g/cm^3, ρ_{tic} is the theoretical density of TiC, being 4.94 g/cm^3. We can see that the density increases with increasing synthesis temperature, and the relative density increases from 95 to 99% when synthesis temperature increased from 1150 to 1400 °C with x of 0.05. At temperatures below 1200 °C, the sample density increases with increasing Al content. However, at temperatures above 1250 °C (the critical temperature for synthesis of highly phase-

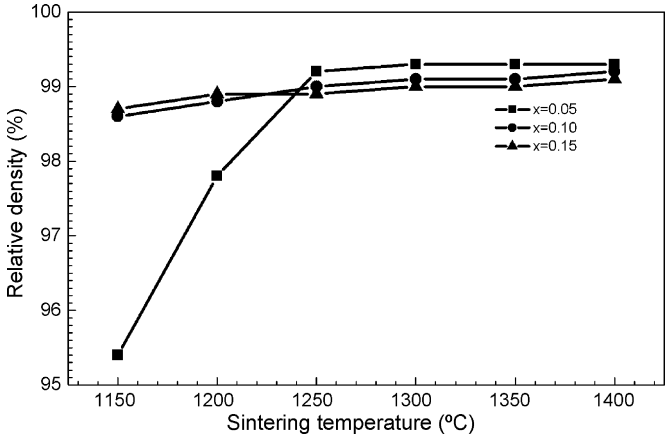

Fig. 4. Relative density of the samples synthesized from 1Ti/1Si/2TiC–*x*Al starting powders at different temperatures ranging from 1150 to1400 °C.

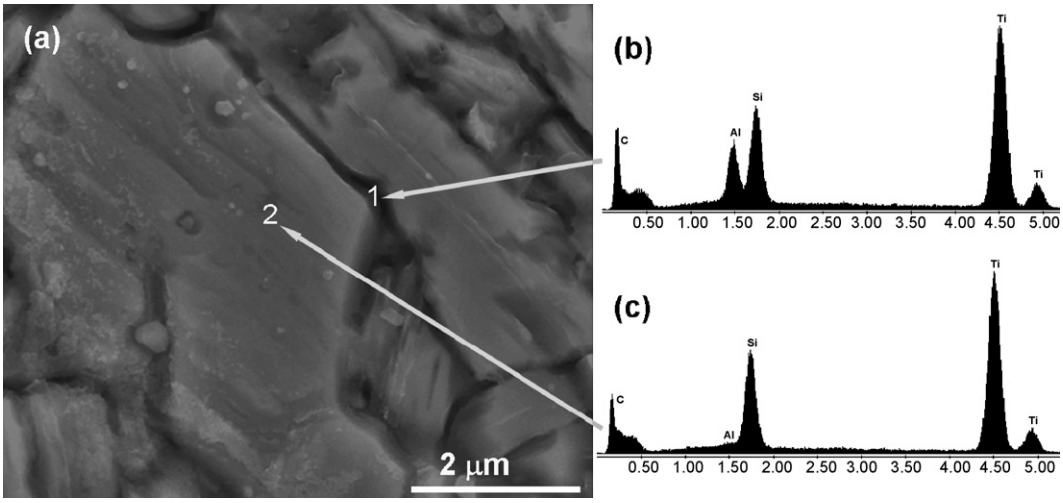

Fig. 5. (a) Microstructure of Ti_3SiC_2 synthesized from 1Ti/1Si/2TiC–0.15Al at 1300 °C for 15 min. (b) and (c) Energy-dispersive spectra obtained at spot 1 and spot 2, as marked in (a).

pure Ti_3SiC_2 in all the cases), the sample density decreases with increasing Al content. Similar results were found when 3Ti/SiC/C–*x*Al were used as the starting powders (not shown). At lower synthesis temperatures, the increase of the density with Al addition could be attributed to sintering densification effect. The addition of Al accelerates the sintering and densification process, and thus reduces the porosity and increase the density. The decrease of density with increasing Al content should be attributed to the much lower density of Al (2.7 g/cm^3) than Ti_3SiC_2. Assuming a Ti_3SiC_2–Al two-phase composite, the relative density would be 99.1% if Al with *x* of 0.15 is added to the powders. Actually, the decrease of density with Al addition as shown in Fig. 4 is within this range.

EDS analysis indicated that Al preferably distributes at the grain boundaries, as shown in Fig. 5. It is reasonable to believe that Al acts as melting pool during the synthesis, and Ti_3SiC_2 nucleates and grows inside the pool. It has been reported that the twin grain boundaries of TiC are good sites for Ti_3SiC_2 nucleation[25,26] and that the addition of Al can effectively reduce the twin boundary energy of TiC to stabilize its twin structures.[27] The addition of Al would be beneficial to the nucleation of Ti_3SiC_2 and thus accelerates the synthesis of Ti_3SiC_2 with high phase-purity.

Parallel to the present work, similar effect of another low-melting-point metal element, Sn, on the synthesis of another important member in MAX family, Ti_3AlC_2, was reported recently by Ai et al.[28] The addition of Sn also improves the phase-purity of the final product, reduces the lower limit of the optimal synthesis temperature and expands the optimal sintering temperature range.

4. Conclusions

The effects of Al addition on the synthesis of Ti_3SiC_2 from 1Ti/1Si/2TiC–*x*Al and 3Ti/1SiC/1C–*x*Al starting powders were investigated and the results have demonstrated that the addition of Al can decrease the lower limit of the optimal temperature and expand the optimal temperature range for the synthesis of highly phase-pure Ti_3SiC_2. Highly pure dense Ti_3SiC_2 bulk material has been synthesized rapidly (15 min) by PDS from 1Ti/1Si/2TiC–0.15Al and 3Ti/1SiC/1C–0.20Al powder mixtures at temperature as low as 1100 and 1200 °C, respectively.

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