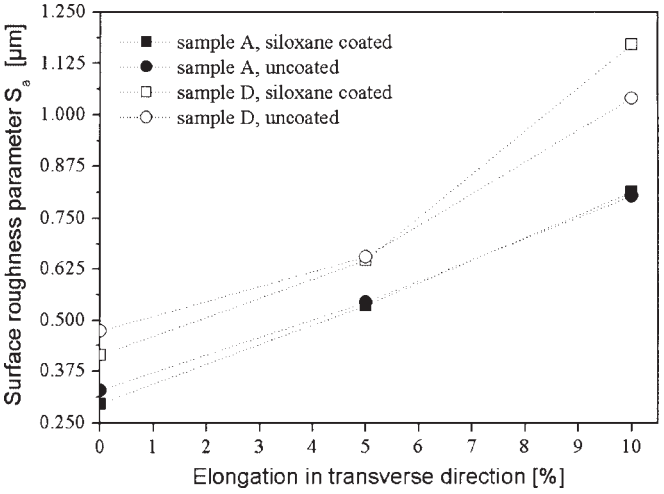

Fig. 6. Development of the surface roughness as a function of plastic strain for coated and uncoated samples A and D (flat tensile test).

nium substrate. Such recovery process might lead to stronger orange peel and ridging effects when compared to the uncoated sheets.

These experimental observations of sheet roughening during forming allow us to draw some important conclusions. First, when judging the micromechanical behavior of coatings during subsequent plastic deformation their roughness must be carefully investigated as a function of strain. In other words coated sheets can show larger strain-induced roughness than uncoated sheets of the same material. Second, changes in intrinsic surface topography during plastic straining can in detail be understood in terms of the distribution of the accumulated plastic microstrains, which, in turn depends on the in-plane and through-thickness microstructure. The determination of microstrains gives a clearer picture of surface micromechanics than texture measurements alone. The spatial distribution of Cube- and Goss-oriented crystals can explain the observed accumulated plastic microstrains and banded surface topographies of uncoated aluminium sheets.[2] In particular the presence of grain clusters consisting of the above-mentioned components, i.e. the occurrence of soft and hard clusters, stimulates strong heterogeneity of surface strains and entails ridging. Orange peel can be explained in terms of the individual deformation behavior of the crystals.

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Fabrication and Mechanical Properties of Ternary Compound Ti_3SiC_2: Application of Pulse Discharge Sintering Technique**

By *Zhe-Feng Zhang*,* *Zheng-Ming Sun*, and *Hitoshi Hashimoto*

Recently, Barsoum[1] summarized the fabrication and characterization of the ternary compound Ti_3SiC_2, which is a novel material with many of the best attributes of both metals and ceramics. Like metals, it is a good electrical and thermal conductor, readily machinable, relatively soft, and highly thermal-shock resistant. Like ceramics, it is very stiff, oxidation resistant, and stable to at least 1700 °C. As far as we are aware, this combination of strength and ductility at elevated temperatures, resistance to thermal shock, and good machinability has not been observed in other materials.[2] Therefore, it is important to make bulk Ti_3SiC_2 samples with high purity and develop new synthesis techniques for the wide application of this novel material in industry. The early chemical synthesis of Ti_3SiC_2 was carried out by Jeitschko and Nowotny[3] in 1967, followed by Goto and Hirai[4] using a CVD method in 1987. Barsoum et al.[5,6] successfully synthesized this material with high purity (about 98 vol.-%) by a hot-isostatic pressing (HIP) method from Ti/SiC/C mixtures. There are some other successful examples of synthesis from Ti/Si/C and Ti/Si/TiC mixtures using a HIP technique or other methods.[7–18] However, the sintering processes were often conducted at a relatively high temperature (1400–1600 °C) for a long time. Recently, an innovative technique for rapid sintering, pulse discharge sintering (PDS), was developed for sintering ceramics and metallic materials.[19–21] With this method metals and ceramics can be rapidly sintered at relatively low temperatures for short times, with fine grains and high performances. However, this new technique has not been used for the synthesis of Ti_3SiC_2. The main purpose of the present research was to apply the PDS technique to the rapid fabrication of Ti_3SiC_2 samples by using different start-

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ing powder mixtures at relatively low temperatures. High-temperature mechanical tests were carried out to identify the properties of the Ti_3SiC_2 samples made by the PDS technique.

To make Ti_3SiC_2, the possible starting powders can be determined from the Ti–Si–C ternary phase diagram.[22] It is found that there are five possible reaction paths for the synthesis of Ti_3SiC_2 and the possible reactions are listed as follows.

$$Ti + Si + C \rightarrow Ti_3SiC_2 \quad (A)$$

$$Ti + SiC + C \rightarrow Ti_3SiC_2 \quad (B)$$

$$Ti + Si + TiC \rightarrow Ti_3SiC_2 \quad (C)$$

$$Ti + SiC + TiC \rightarrow Ti_3SiC_2 \quad (D)$$

$$Ti + TiSi_2 + TiC \rightarrow Ti_3SiC_2 \quad (E)$$

Reactions A and B have been used for the HIP synthesis.[5–17] Recently, Li et al.[18] made Ti_3SiC_2 through reactive sintering of a Ti/Si/TiC mixture. Reactions D and E were newly developed in our recent investigations.[23,24] In the present experiment, commercially available Ti, Si, C, SiC, $TiSi_2$, and TiC powders were prepared and five sets of powder mixtures, Ti/Si/C, Ti/SiC/C, Ti/Si/TiC, Ti/SiC/TiC, and Ti/$TiSi_2$/TiC, were mixed in a Turbula shaker mixer under Ar for 24 h. Before sintering, the powder mixtures were compacted into a graphite mold (20 or 50 mm diameter) and sintered in vacuum (10^{-3} Pa) in a temperature range of 1200–1450 °C for various times using the PDS technique. The heating rate was controlled in the range 50–60 °C/min and the applied pressure was maintained constant at 50 MPa during sintering. The synthesized samples were analyzed by X-ray diffractometry (XRD) and observed by scanning electron microscopy (SEM) and optical microscopy (OM). The density of the synthesized samples was measured by the Archimedes method. The specimens were machined and polished to 2 mm × 2 mm × 6 mm for compressive tests and 2 mm × 4 mm × 40 mm for four-point bending tests. The mechanical tests were performed on an Instron 8562 universal testing machine from room temperature to elevated temperatures (930 °C for compressive and 1300 °C for bending tests) in vacuum (10^{-3} Pa). The flexural stresses of the specimens were calculated from the equation[25,26]

$$\sigma = (3P\Delta L)/(2BW^2)$$

where P is the load applied to the specimen, ΔL is the inner span, B and W are the thickness and width.

After sintering of all the mixtures, it was found that Ti_3SiC_2 is the main phase in most of samples and the content of secondary TiC (sometimes $TiSi_2$) depends on the mixtures: the detailed results can be seen elsewhere.[23,24,27,28] Figure 1 shows the XRD patterns of the synthesized samples from all five sets of powder mixtures sintered at 1300 or 1350 °C for 15 min. Each XRD pattern in the figure represents the sample with the highest purity of Ti_3SiC_2 in each set. From the figure, it can be seen that all the main peaks correspond to Ti_3SiC_2 and the peak intensities of impurity TiC decrease substantially to a low level for all the samples. It is noted that the relative peak intensities of impurity TiC synthesized from Ti/Si/C, Ti/SiC/C, Ti/SiC/TiC, and Ti/$TiSi_2$/TiC are nearly the same, however, the TiC peaks became too weak to be identified in the XRD patterns of the sample synthesized from Ti/Si/TiC mixture. This indicates that all the powder mixtures could be used to synthesize Ti_3SiC_2 containing a small amount of TiC impurity after sintering. Figure 2a summarizes the temperature dependence of the TiC impurity content in the samples sintered for 15 min from the five sets of mixtures. Clearly, all the synthesized samples have the highest Ti_3SiC_2 content near 1300 °C except for the samples sintered from the Ti/SiC/TiC mixture, for which the optimum sintering temperature was near 1350 °C.[23] This indicates that the present sintering temperature is lower than that for the HIP technique. Meanwhile, it is interesting to find that the samples synthesized from Ti/Si/TiC always have the lowest content of TiC impurity compared with the samples made from the other four sets of mixtures. Figure 2b gives the lowest TiC content achieved from each group of mixtures. It is seen that the lowest TiC content increases in the order of samples C (1.0 wt.-%), E (4.8 wt.-%), A (6.7 wt.-%), B (7.3 wt.-%), and D (8.2 wt.-%). Therefore, it can be concluded that the purity of Ti_3SiC_2 samples synthesized through the PDS technique strongly depends on the type of starting powder in the mixtures. Ti_3SiC_2 samples with the highest purity are synthesized from the Ti/Si/TiC mixture. Meanwhile, the PDS technique can effectively decrease sintering temperature and shorten sintering time in comparison with the HIP technique.

On the other hand, the price factor of the starting powders should be considered for the industrial application. Figure 3a and Figure 3b compare the relative prices of the powders and their mixtures. All the prices of the starting powders are se-

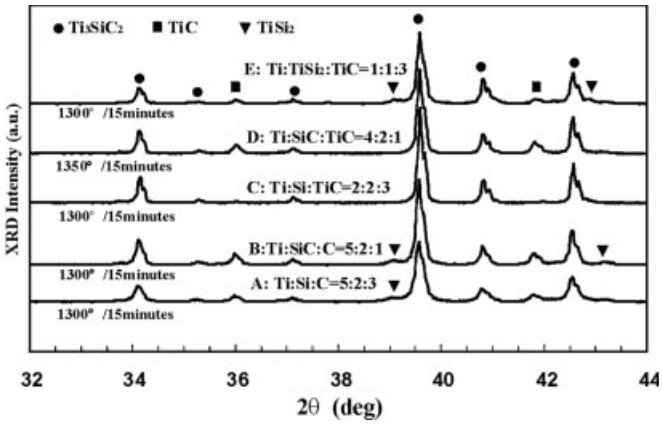

Fig. 1. X-ray diffraction patterns of samples from the five powder sets sintered at 1300 or 1350 °C for 15 min.

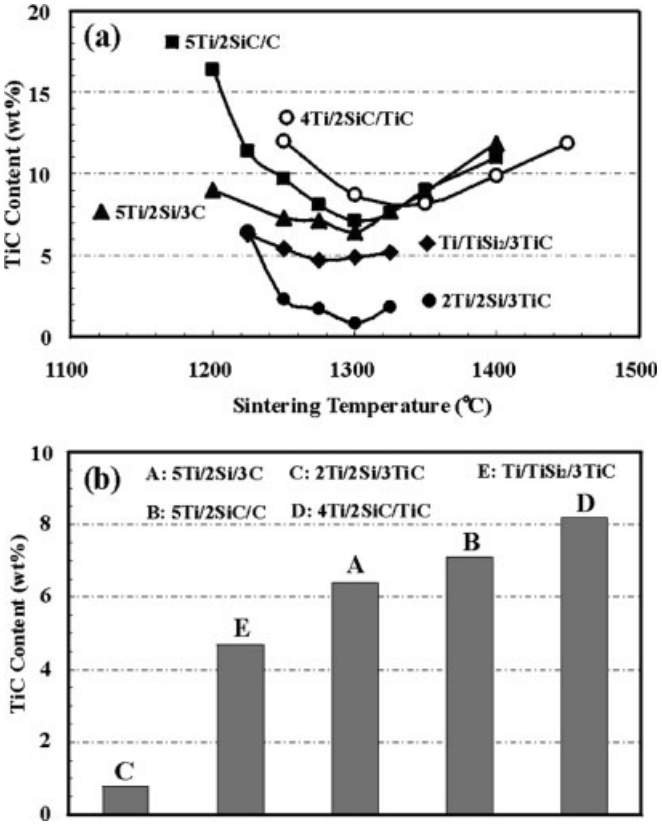

Fig. 2. a) Dependence of TiC contents on the sintering temperature; b) comparison of lowest TiC content in the samples synthesized from the five powder sets.

lected from the *Aldrich Handbook of Fine Chemicals and Laboratory Equipment 2000–2001*. It is noted that the relative price of Ti and $TiSi_2$ powders is higher than the other four powders. When these powders are mixed into A, B, C, D, and E mixtures, the relative price increases in the following order: C < E < D < B < A. The present results indicates that mixture C has lowest price in comparison with the other four sets of mixtures. Therefore, it can be concluded that the Ti/Si/TiC is the best mixture among the five sets of mixtures for the synthesis of the Ti_3SiC_2 products if considering the factors of purity and powder cost.

After sintering, the samples were mechanically polished and etched with a solution of H_2O:HNO_3:HF (2:1:1) to expose the Ti_3SiC_2 grains. Microstructural observations for all the samples by SEM and OM show that the microstructure of the Ti_3SiC_2 samples mainly exhibit the following features:[23,24,27,28]

- at a sintering temperature below 1250 °C, the grains in the samples are very fine (about 5 μm in length and 2–3 μm in width);
- at a sintering temperature above 1250 °C, some grains became coarse and were embedded in the homogenous fine grains, the volume fraction and size of the coarse grains increase with sintering temperature;
- the Ti_3SiC_2 grains did not grow to a large size even at the highest sintering temperature of 1400 °C (or 1450 °C) due to the rapid sintering process in the PDS technique.

Figure 4a and Figure 4b show the typical microstructure of the Ti_3SiC_2 samples sintered from Ti/SiC/C and Ti/Si/TiC mixtures at 1300 °C for 15 min. The white particles in Figure 4a are the typical TiC phase, however, the amount of TiC particles in Figure 4b can be ignored, indicating the purity of the samples should be high enough. The observed microstructures are identical with those observed by El-Raghy and Barsoum.[6] Besides, it is found that when the sintering temperature is below 1250 °C, the density is lower than 4.50 g/cm^3. When the sintering temperature rose to above 1275 °C, the measured density was improved to 4.50–4.52 g/cm^3, which is quite close to the theoretical density 4.53 g/cm^3 of Ti_3SiC_2.

The present results reveal that the Ti_3SiC_2 samples synthesized at relatively low temperature for short times by PDS have good densities.

The Ti_3SiC_2 specimens used in this study were synthesized from a Ti/Si/TiC mixture at 1300 °C for 15 min. A mixed microstructure is found, with plate-shaped large grains of 20–50 μm and equiaxed small grains of around 5 μm. The Ti_3SiC_2 phase content was calculated from the XRD data to be about 99 wt.-%. Figure 5a shows the stress–strain curves of the Ti_3SiC_2 specimen under a constant compression strain rate of 5.6×10^{-4} s^{-1} at various testing temperatures. At temperatures lower than 800 °C, the stress–strain relationship shows almost linearity until failure. Compared with this brittle fracture behavior, when tested at a temperature higher than 850 °C the specimen demonstrates plastic deformation, as shown by the distinct nonlinearity in the stress–strain curves. After the linear part of the stress–strain curves at high temperatures, an increase in stress with increasing strain was observed, similar to the strain-hardening behavior of metals. Further increase in strain, however, causes a decrease in

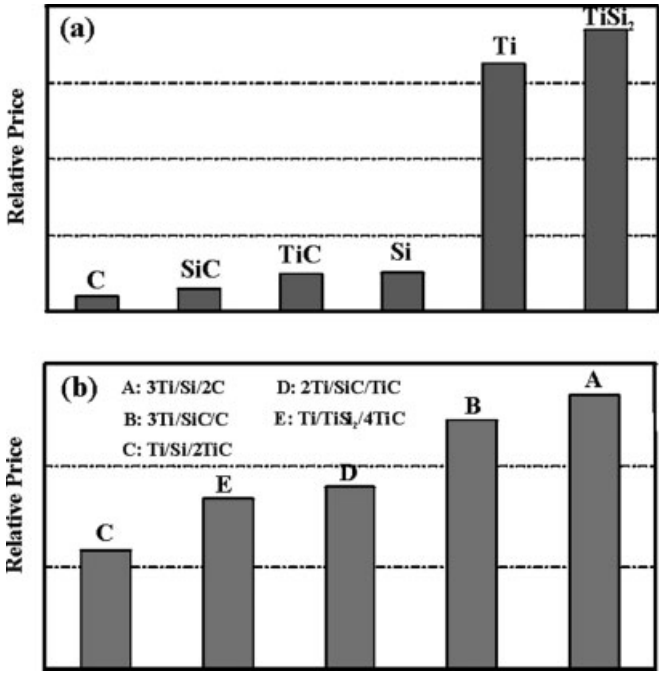

Fig. 3. Comparison of the relative price of: a) the powders used, b) their mixtures.

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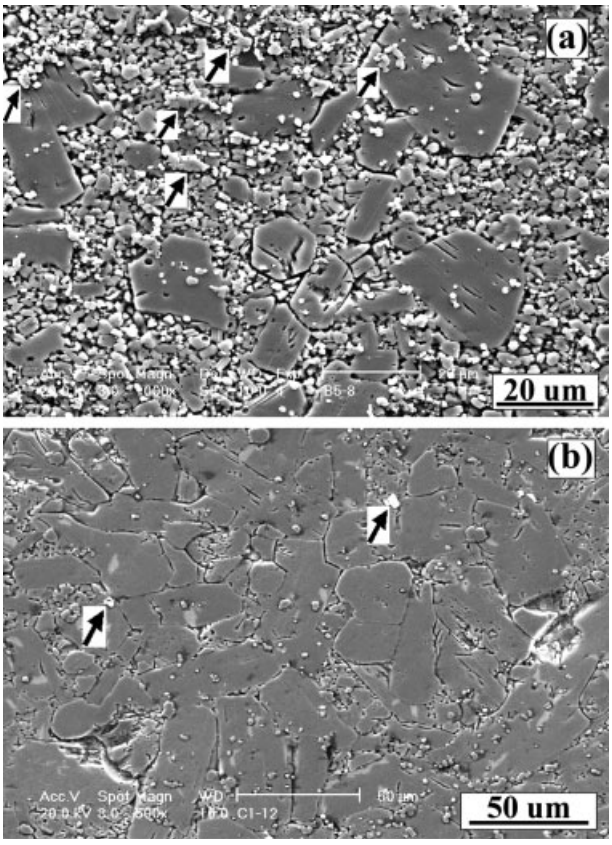

Fig. 4. Microstructure of Ti_3SiC_2 samples synthesized from: a) Ti/SiC/C mixture, b) Ti/Si/TiC mixture, both at 1300 °C for 15 min. (The etching solution is $2H_2O$:HNO_3:HF, the etching time is about 10 sec).

stress. The pseudo-strain-hardening and softening observed in Figure 5a at temperatures above 900 °C is then attributed to the formation of shear bands along the basal planes, kink-band-formation, and microcrack formation, rather than yielding.[29–31]

The compressive strength of Ti_3SiC_2 specimens is plotted in Figure 5b as a function of testing temperature, which shows a monotonic decrease with increasing testing temperature. As well as the data of the present investigation, some literature data were also plotted in the figure for comparison. The data marked with FG (fine grained, a few microns) and CG (coarse grained, 100–200 μm) are the materials made from Ti/SiC/C by the HIP technique at the temperatures of 1600 °C for a few hours.[25] It can be seen that the strength of the present Ti_3SiC_2 specimens is located between the strength values of CG and FG compounds. Since the microstructure of the present Ti_3SiC_2 specimen is a mixed structure consisting of coarse and fine grains, the strength of the present specimen is comparable to those synthesized by HIP. Also plotted in the figure are data marked with TSC^{Z610} and TSC^{Z510}, made by in-situ solid–liquid reaction of Ti_3SiC_2 from Ti/Si/C powder mixture[32] with purity of 93 and 87 wt.-%, respectively. Compared with the data of the literature, it has been found that the ductile–brittle transition temperature for the present Ti_3SiC_2 specimen is about 200–300 °C lower than that of the samples sintered from Ti/Si/C and Ti/SiC/C powders.[25,26,29–32]

Figure 6a shows the four-point bending deformation curves of the same group of Ti_3SiC_2 specimens under a constant crosshead speed of 0.05 mm/min at different temperatures. At room temperature and 1100 °C, the specimens did not exhibit obvious plastic deformation and fractured abruptly. With increasing temperature to 1150 and 1200 °C, obvious plastic deformation can be seen from its deformation curves. The deformed specimens can be seen in Figure 6b, it is apparent that specimen D deformed at 1200 °C begins to bend. At higher temperature, the specimen can display larger plasticity and did not fracture. As shown in Figure 6b, the three specimens E, F, and G can be bent to be bow-like without fracture, indicating that the Ti_3SiC_2 specimens have a good plasticity at temperatures above 1200 °C. Observations on deformed Ti_3SiC_2 specimens revealed that the large plastic deformation at the temperature above 1200 °C can be attributed to the formation of shear bands, grain buckling, kink bands, and microcracks, which will be reported elsewhere. Therefore, it can be concluded that the present Ti_3SiC_2 specimens synthesized by the PDS technique also possess good plasticity, which is identical with the samples made by HIP.[29–31]

The purity of the Ti_3SiC_2 samples depends on the starting mixtures. For Ti/Si/C, Ti/SiC/C, Ti/SiC/TiC, and Ti/$TiSi_2$/

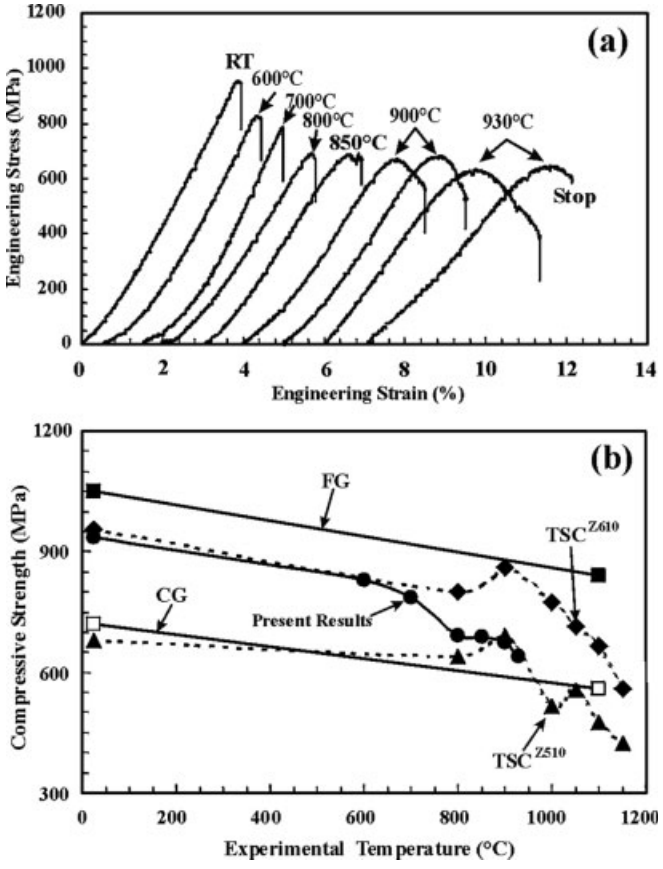

Fig. 5. a) Compressive stress–strain curves of Ti_3SiC_2 samples at various temperatures; b) variation of compressive strength of Ti_3SiC_2 with testing temperature. TSC^{Z610} and TSC^{Z510} were sintered from Ti/Si/C powder mixture and have purities of 93 wt.-% and 87 wt.-%, respectively.

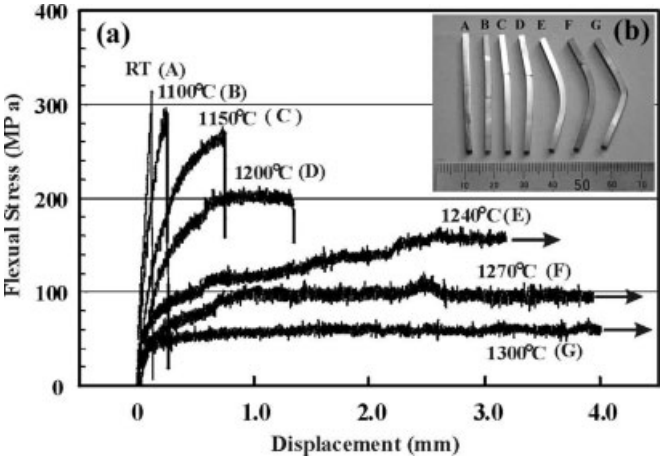

Fig. 6. a) Four-point bending deformation curves; b) the deformed Ti_3SiC_2 samples, both at various temperatures.

TiC mixtures, the purity of Ti_3SiC_2 can only be improved to 93–95 wt.-%. However, the Ti/Si/TiC mixture can be successfully sintered to Ti_3SiC_2 samples with purity of 98–99 wt.-%. Besides, the optimized sintering temperature of the PDS technique is near 1300 °C, which is a relatively low temperature compared with HIP. The synthesized Ti_3SiC_2 samples have a good density (more than 98–99 %). Meanwhile, the relative price of the Ti/Si/TiC mixture is the lowest among the five sets of mixtures. Therefore, it is suggested that the Ti/Si/TiC is the best for the synthesis of Ti_3SiC_2 products by PDS if considering the factors of purity and powder cost.

Mechanical tests on Ti_3SiC_2 specimens made from the Ti/Si/TiC mixture showed a good performance at elevated temperatures. Under compressive loading, Ti_3SiC_2 exhibits obvious plastic deformation in the stress–strain curves at the temperature near 900 °C, where pseudo-strain-hardening was observed followed by strain softening. Under four-point bending loads, Ti_3SiC_2 can display a larger plastic deformation without fracture at temperatures above 1200 °C. The mechanical properties of the present Ti_3SiC_2 specimens demonstrated that the PDS technique is applicable for the rapid synthesis of Ti_3SiC_2 products with good performance.

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