

Synthesis and Characterization of a Metallic Ceramic Material—Ti₃SiC₂

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Various powder mixtures from the starting powders of Ti/Si/C, Ti/SiC/C, Ti/Si/TiC, Ti/SiC/TiC and Ti/TiSi₂/TiC were used for the synthesis of ternary compound titanium silicon carbide (Ti₃SiC₂) by using a pulse discharge sintering (PDS) process. The Ti/Si/TiC powder was found to be the best among the five powder mixtures for Ti₃SiC₂ synthesis. Phase purity of Ti₃SiC₂ can be improved to ≈99 mass% at the sintering temperature of 1300°C for 15 min. The relative density of all the synthesized samples is higher than 98–99% at the sintering temperature above 1275°C. The nearly single phase Ti₃SiC₂ was found to show plastic deformation at room temperature and good machinability. Both electrical and thermal conductivity were found to be greater than two times of the values of a control pure Ti sample fabricated by the same sintering process. The thermopower of the synthesized Ti₃SiC₂ was measured to be nearly zero in the testing temperature range, much lower than some common low thermopower substances such as gold or carbon. Their mechanical properties at ambient and elevated temperatures were also examined. The ternary compound Ti₃SiC₂ is referred to as a “metallic ceramic” according to its physical and mechanical behavior representing both metals and ceramics.

(Received August 26, 2005; Accepted November 8, 2005; Published January 15, 2006)

Keywords: pulse discharge sintering, titanium silicon carbide, conductivity, thermopower, machinability, mechanical property, high temperature

1. Introduction

As a representative compound of the ternary M_{n+1}AX_n phases (or MAX phases), where M is an early transition metal such as Ti, Cr, A an A group element such as Al and Si, X carbon and/or nitrogen, and $n = 1-3$, titanium silicon carbide (Ti₃SiC₂) has received considerable attention in the last decade.¹⁻¹⁶ Its crystal structure is comprised of hexagonal nets of Si atoms separated by three nearly close-packed Ti layers that accommodate C atoms in the octahedral sites between them.¹⁷ This compound is a promising lightweight (density of 4.52 g/cm³) candidate for high temperature applications as structural and functional materials.¹ It is relatively soft (HV 4 GPa) and unusually thermal shock resistant.¹ At the 29th international conference on advanced ceramics and composites (Cocoa Beach, Florida, January 2005), a special session was organized for this compound and the other MAX phases, on their synthesis, physical properties, mechanical properties, oxidation resistance and also the industrialization. Whereas the field of MAX phases are growing to the stage of commercialization in the United States and also in Europe,¹⁻⁵ it is in a recession stage in Japan after some limited research activities as we can trace from the open literature,^{6,7,17} in addition to the work in our group.⁸⁻¹⁴

Barsoum¹ summarized the fabrication and characterization of Ti₃SiC₂. The early synthesis of Ti₃SiC₂ was carried out by Jeitschko and Nowotny¹⁶ via chemical reaction in 1967. Goto and Hirai¹⁷ reported the synthesis of this compound through CVD method in 1987. Barsoum *et al.*^{2,3} successfully synthesized this material with high Ti₃SiC₂ content (≈ 98 vol%) through hot-isostatic pressing (HIP) method from Ti/SiC/C mixtures. Besides, there are some other successful examples from Ti/Si/C and Ti/Si/TiC mixtures through the HIP technique or other methods.^{6,10,18} However, the sintering processes available were often conducted at relatively high temperature (1400–1600°C) for long time. Recently, an innovative technique for rapid reactive sintering, *i.e.* pulse discharge sintering (PDS), also called spark

plasma sintering (SPS), was developed for sintering ceramics and intermetallic materials.¹⁹ Recently we have applied this new technique to the synthesis of Ti₃SiC₂; fairly plausible results were obtained. The main purpose of this article is to report the rapid synthesis of Ti₃SiC₂ samples by using different starting powder mixtures at relatively low temperature. Furthermore, the deformation at room temperature, machinability, thermal and electrical properties as well as high-temperature mechanical properties were examined, and all these results are indicating this compound to be typically a ceramic material, with many metallic characteristics.

2. Experimental Procedures

Based on the commercially available element or compound powders, we can find five possible reaction paths for the synthesis of Ti₃SiC₂, that is, (A) Ti + Si + C → Ti₃SiC₂, (B) Ti + SiC + C → Ti₃SiC₂, (C) Ti + Si + TiC → Ti₃SiC₂, (D) Ti + SiC + TiC → Ti₃SiC₂, (E) Ti + TiSi₂ + TiC → Ti₃SiC₂. The reactions (A) and (B) were widely employed for the synthesis of Ti₃SiC₂ by HIP technique.^{2,3,18} Recently, Li *et al.*⁶ fabricated Ti₃SiC₂ through reactive sintering Ti/Si/TiC mixture. The reactions (D) and (E) were newly developed in our recent investigations.¹⁰⁻¹² In the present experiment, commercially available Ti, Si, C, SiC, TiSi₂ and TiC powders were used and five groups of powder mixtures, *i.e.* Ti/Si/C, Ti/SiC/C, Ti/Si/TiC, Ti/SiC/TiC and Ti/TiSi₂/TiC at various molar ratios, were respectively mixed in a Turbular shaker mixer in Ar atmosphere for 24 h. The powder mixtures were sintered in vacuum (10⁻³ Pa) in a temperature range of 1200–1450°C for different duration by using the PDS technique. The heating rate was 50°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 optical microscope (OM) and scanning electron microscope (SEM) equipped with energy dispersive spectrum analyzer (EDS). The electrical conductivity and thermopower (Seebeck

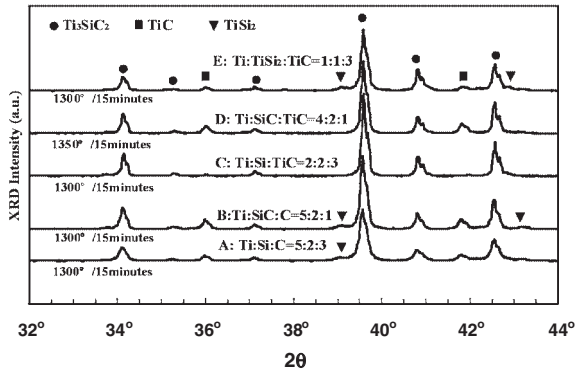


Fig. 1 X-ray diffraction patterns of the samples sintered at 1300 or 1350°C for 15 min from the five groups of powders. The molar ratios of the constitutive powders are indicated in the figure.

coefficient) were measured (ULVAC ZEM-1) and the thermal conductivity were determined by measuring the thermal diffusivity (ULVAC TC-7000), heat capacity (SEIKO DSC-6200) and the density, for the nearly single phase Ti₃SiC₂ and for a pure Ti control sample, which was sintered with the same sintering processes as for the tested Ti₃SiC₂. 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).

3. Results and Discussion

3.1 Characterization of the synthesized materials

Ti₃SiC₂ was found to be the main phase in most of the sintered samples and the content of secondary phase TiC (sometimes there is TiSi₂ phase) depends on the starting powder mixtures and the detailed results can be seen elsewhere.^{8,10–13} Figure 1 shows the XRD patterns of the synthesized samples from the five groups of powder mixtures sintered at 1300 or 1350°C for 15 min. Each XRD pattern in the figure represents the sample with the highest Ti₃SiC₂ content in the group of the materials synthesized from the respective powder mixture. It can be seen that all the strong peaks correspond to Ti₃SiC₂ phase, while the peak intensities of TiC are decreased substantially to a low level for all the samples. Besides, it is noted that the relative peak intensities of TiC synthesized from Ti/Si/C, Ti/SiC/C, Ti/SiC/TiC and Ti/TiSi₂/TiC are nearly the same, however, the TiC peaks were found to be in negligibly low intensities in XRD patterns of the sample synthesized from Ti/Si/TiC mixture. The TiC content in the synthesized materials can be calculated from the integrated XRD peak intensities according to our experimental calibration, assuming a (Ti₃SiC₂ + TiC) two-phase composite:¹⁰

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

or Ti₃SiC₂ content by

$$W_{\text{TSC}} = \frac{K}{K + I_{\text{TC}}/I_{\text{TSC}}} \quad (2)$$

where W_{TC} and W_{TSC} represent the mass content of TiC and

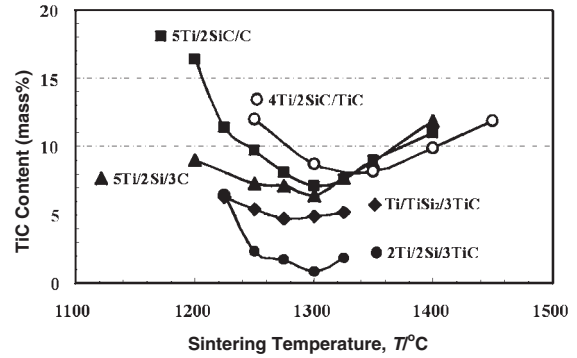


Fig. 2 Dependence of TiC contents on the sintering temperature in the samples synthesized from the five powder mixtures.

Ti₃SiC₂, respectively; I_{TC} and I_{TSC} represent the integrated diffraction peak intensities of TiC and Ti₃SiC₂, respectively; K is a constant which is calibrated to be

$$K = 1.80, \quad \text{for TiC}(200)/\text{Ti}_3\text{SiC}_2(104) \quad (3)$$

or

$$K = 1.20, \quad \text{for TiC}(111)/\text{Ti}_3\text{SiC}_2(104) \quad (4)$$

Figure 2 summarizes the temperature dependence of the TiC content in the samples sintered for 15 min from the five groups of mixtures. Obviously, all the synthesized samples have the highest Ti₃SiC₂ content near 1300°C except for the samples sintered from the Ti/SiC/TiC mixture, by which the optimum sintering temperature was near 1350°C. It is interesting to find that the samples synthesized from Ti/Si/TiC powder mixture always have the lowest TiC content in comparison with the samples made from the other 4 groups of mixtures in the testing temperature range. The lowest TiC content achieved from each group of mixtures increases in the order of samples C (1.0 mass%), E (4.8 mass%), A (6.7 mass%), B (7.3 mass%) and D (8.2 mass%).

3.2 Microstructure and densification

SEM and OM observations show that the microstructure of the Ti₃SiC₂ samples mainly exhibit the following features:^{8,10–13} (1) at the sintering temperature below 1250°C, the grains in the samples are very fine (about 5 μm in length and 2–3 μm in width); (2) at the 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; (3) the Ti₃SiC₂ grains did not grow to a large size even at the highest sintering temperature of 1400°C (or 1450°C). Figure 3 shows the typical microstructure of the Ti₃SiC₂ samples sintered from Ti/Si/TiC mixtures at 1275°C for 15 min, showing nearly single phase Ti₃SiC₂ microstructure. Besides, it is found that when the sintering temperature is below 1250°C, the density is lower than 4.50 g/cm³. When the sintering temperature rose to above 1275°C, the measured density was improved to 4.50–4.52 g/cm³, which is quite close to the theoretical density 4.52 g/cm³ of Ti₃SiC₂. The present results reveal that the Ti₃SiC₂ samples synthesized at relatively low temperature for short time have a good densification effect due to the application of PDS technique.

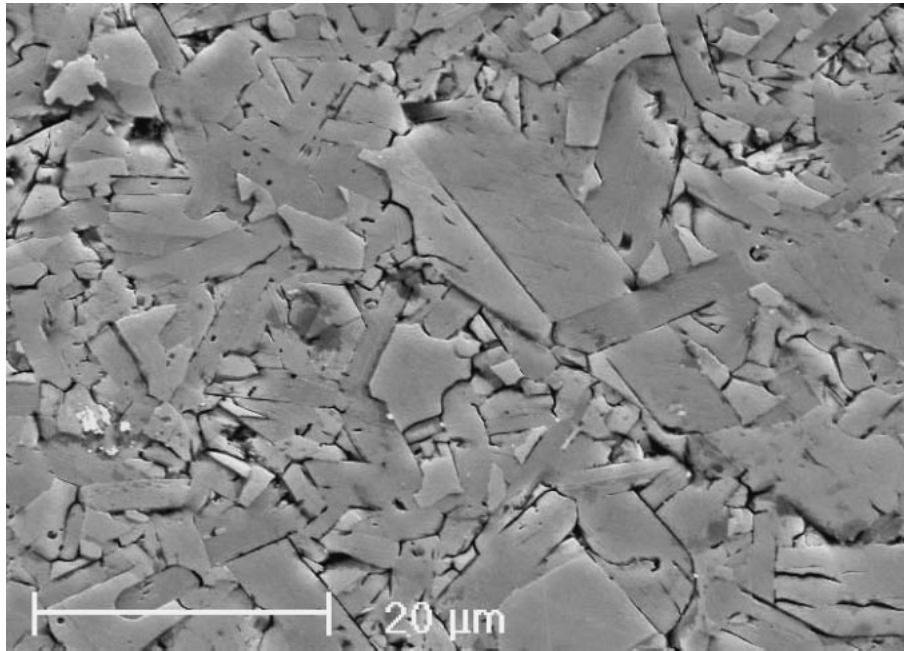


Fig. 3 Microstructure of a Ti_3SiC_2 sample synthesized from 2Ti/2Si/3TiC mixture at 1275°C for 15 min.

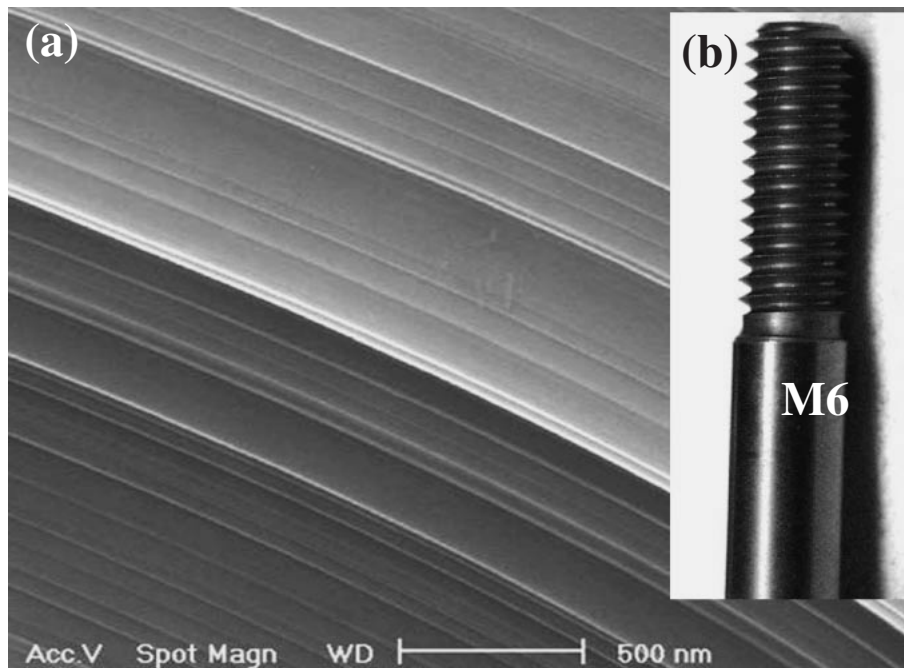


Fig. 4 (a) Room temperature plastic deformation in a Ti_3SiC_2 grain, and (b) a bolt cut from the Ti_3SiC_2 compound (no cooling, no lubricant for the machining).

3.3 A metallic ceramic?—room temperature deformation, machinability, thermal and electrical properties

As carbide, a typical ceramic in common sense, Ti_3SiC_2 was hardly believed to be able to deform plastically at room temperature. However, as shown in Fig. 4(a), apparent plastic deformation features were characterized by the slip traces on the deformed sample surface, though macroscopic plastic deformation is still difficult due to the lack of sufficient independent slip systems. This locally occurred plastic deformation, however, is believed to play a decisive role in the good machinability and the good damage tolerance

of this material. The machinability of the manufactured nearly single phase Ti_3SiC_2 compound was approved. For example, Fig. 4(b) shows an M6 bolt machined by the author using an old lathe with a high speed steel cutting tool without cooling, without lubricant, from the compound sintered from the Ti/Si/TiC powder mixture with the PDS process at 1300°C for 15 min.

Table 1 shows the thermal and electrical properties of the single phase Ti_3SiC_2 fabricated with PDS process and those of a pure titanium sample fabricated with the same sintering process. It can be seen that thermal diffusivity of the Ti_3SiC_2

Table 1 Comparison of the room temperature (25°C) thermal and electrical properties between the Ti₃SiC₂ and a pure titanium specimen, both fabricated with a PDS process.

Material	Specific Heat (J kg ⁻¹ K ⁻¹)	Thermal Diffusivity (m ² s ⁻¹)	Thermal Conductivity (W m ⁻¹ K ⁻¹)	Electrical Conductivity (Ω ⁻¹ m ⁻¹)
Ti ₃ SiC ₂	591	14.99 × 10 ⁻⁶	39.92	4.30 × 10 ⁶
Pure Ti	573	6.37 × 10 ⁻⁶	16.45	1.30 × 10 ⁶

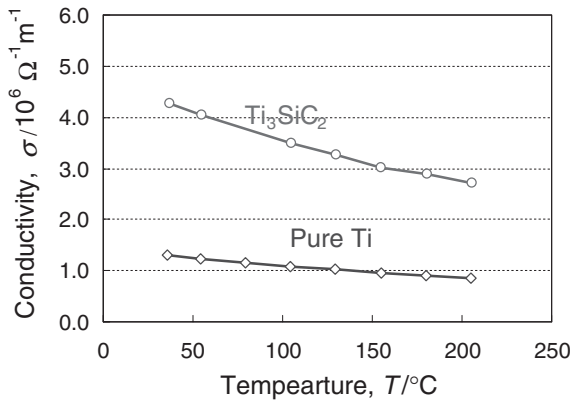


Fig. 5 Electrical conductivity of Ti₃SiC₂ in the temperature range of RT to 210°C, in comparison with a pure Ti sample prepared with the same process as for Ti₃SiC₂.

sample is two times of that of the pure Ti sample. The density and heat capacity of the two materials are comparable and therefore the thermal conductivity of the Ti₃SiC₂ is about 2–3 times of that of Ti. The electrical conductivity was also measured to be about 3 times of that of Ti.

As shown in Fig. 5, the electrical conductivity of the Ti₃SiC₂ decreases with increasing testing temperature in the measured range of RT to 210°C. The temperature dependence of conductivity for Ti₃SiC₂ is more prominent than the pure Ti sample. The thermal conductivity of Ti₃SiC₂ decreases with temperature with a coefficient of -9.4×10^3 (Ω⁻¹ m⁻¹ K⁻¹), whereas that of Ti decreases with a coefficient of -2.7×10^3 (Ω⁻¹ m⁻¹ K⁻¹) in the testing temperature range.

Figure 6 summarizes the testing temperature dependence of thermopower (Seebeck coefficient) of Ti₃SiC₂ and the control Ti sample. Also plotted in the figure are the room temperature thermopower of some low thermopower substances such as pure gold and carbon. It is interesting to note that the thermopower of the Ti₃SiC₂ prepared in this study is not only much lower than the control Ti samples, but also much lower than the value of the known values of existing low thermopower substances, and showing virtually zero thermopower in the testing temperature range used in this study. This is consistent with an early report.²⁰⁾ The negligible thermopower of Ti₃SiC₂ is not only evidence showing its metallic ceramic characterization, but also providing the possibility for this novel material to find applications as functional materials, such as lead wire for precise thermoelectric properties measurements.

The plastic deformability, good machinability, good thermal and electrical conductivity are indicating that the

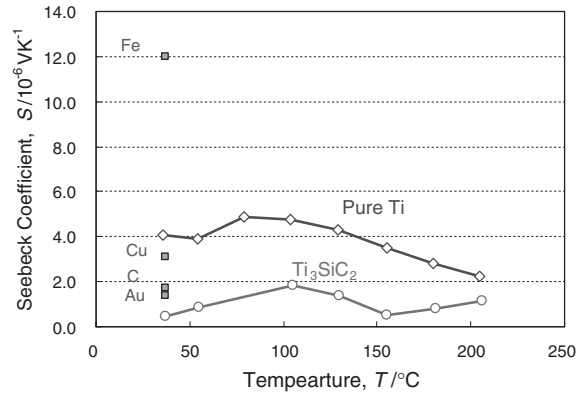


Fig. 6 Thermopower (Seebeck coefficient) of Ti₃SiC₂ in the temperature range of RT to 210°C, in comparison with a pure Ti sample prepared with the same process as for Ti₃SiC₂. Also plotted in the figure are the room temperature thermopower values of a few low thermopower substances.

Ti₃SiC₂ is quite similar to a metal, and we are therefore referring this material a metallic ceramic.

3.4 Mechanical properties

The Ti₃SiC₂ specimens used for mechanical property evaluation were synthesized from Ti/Si/TiC mixture at 1300°C for 15 min with the Ti₃SiC₂ phase content to be 99 mass%, possessing a mixed microstructure of coarse and fine grains. Figure 7 shows the stress–strain curves of the Ti₃SiC₂ specimen under compression (strain rate $\approx 5.6 \times 10^{-4}$ s⁻¹) at various testing temperatures. At temperatures below 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 non-linearity 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 stress. The Ti₃SiC₂ compound fabricated in this study shows comparable strength with the materials fabricated with other processes *e.g.*^{4,9)} The pseudo-strain-hardening and softening observed in Fig. 7 at elevated temperatures above 900°C is then attributed to, rather than yielding, the formation of shear bands along the basal planes, kink-band-formation, micro-crack formation.^{4,9)}

Figure 8(a) shows the four-point bending deformation curves of the same group of Ti₃SiC₂ 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 Fig. 8(b); it is apparent that the specimen D deformed at 1200°C begins to bend. The three specimens E, F and G were bent to be bow-like without fracture, indicating the good plasticity of Ti₃SiC₂ specimens at the temperature above 1200°C. Observations on deformed Ti₃SiC₂ specimens revealed that the large plastic deformation at the temperature

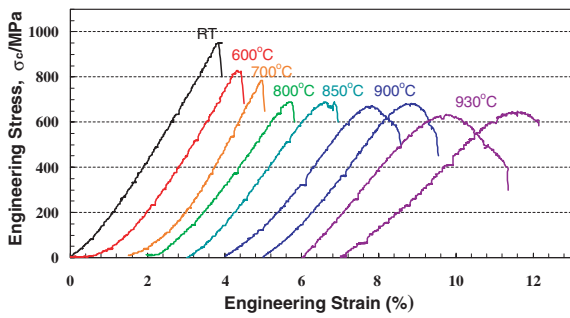


Fig. 7 Compressive stress–strain curves of Ti_3SiC_2 samples at various temperatures.

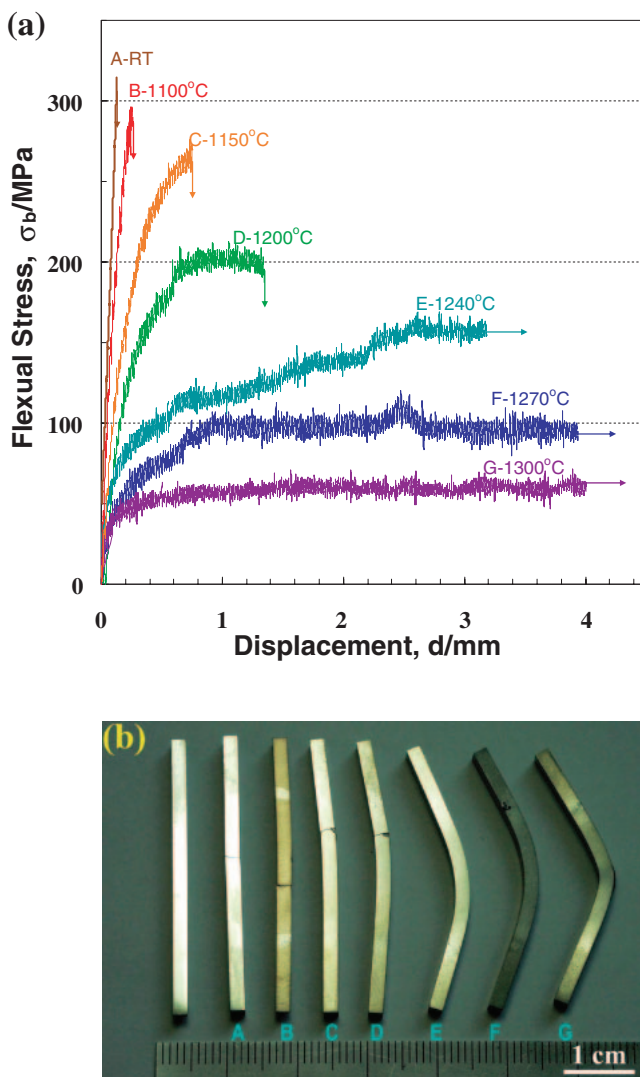


Fig. 8 (a) Four-point bending deformation curves, and (b) the deformed Ti_3SiC_2 samples at various temperatures. The leftmost is a sample before testing.

above 1200°C can be attributed to the formation of shear bands, grain buckling, kink bands and micro-cracks, which will be reported elsewhere.

4. Conclusions

(1) The Ti_3SiC_2 content in the synthesized samples

depends on the type of the starting powder. For Ti/Si/C, Ti/SiC/C, Ti/SiC/TiC and Ti/TiSi₂/TiC mixtures, the Ti_3SiC_2 content can only be improved to 93–95 mass%. However, the Ti/Si/TiC mixture was reactively sintered to compacts with 99 mass% Ti_3SiC_2 with nearly full density.

- (2) The nearly single phase Ti_3SiC_2 shows local plastic deformation at room temperature and good machinability. Both the electrical and the thermal conductivity were measured to be 2–3 times of the value of pure Ti. The thermopower of the synthesized Ti_3SiC_2 was found to be negligible in the testing temperature range, much lower than the known existing low thermopower substances such as gold and carbon.
- (3) Ti_3SiC_2 specimens fabricated 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 a pseudo-strain-hardening was observed followed by a strain softening. Under four-point bending loads, Ti_3SiC_2 can display a larger plastic deformation without fracture at the temperatures above 1200°C .
- (4) The ternary compound Ti_3SiC_2 is referred to as a “metallic ceramic” according to its physical and mechanical behavior representing both metals and ceramics.

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