JOURNAL OF MATERIALS SCIENCE **38** (2003) 2661 – 2666

Fabrication of highly dense Ti_3SiC_2 ceramics by pressureless sintering of mechanically alloyed elemental powders

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Pressureless sintering of Ti_3SiC_2 ceramics has been investigated by using mechanically alloyed elemental Ti, Si and C powder mixture as the starting materials. It has been found that mechanical alloying enhanced both the formation of Ti_3SiC_2 phase and the densification during sintering process. Highly dense Ti_3SiC_2 ceramics with a relative density up to 99% and a phase purity of ~80% Ti_3SiC_2 (TiC_x as the secondary phase) were obtained by sintering the mechanically alloyed powders at relatively low temperatures near 1773 K in an argon atmosphere of 0.1 MPa. The physical properties of the present pressureless-sintered Ti_3SiC_2-based ceramics are comparable to those of nearly single phase Ti_3SiC_2 ceramics fabricated by the reactive hot-isostatic pressing (HIP) that had been used so far. © *2003 Kluwer Academic Publishers*

1. Introduction

Titanium silicon carbide (Ti_3SiC_2) is an interesting material that exhibits an unusual combination of functional and mechanical properties, such as good electric conductivity, high crack propagation resistance and elevated-temperature strength, and good oxidation resistance [1, 2]. Recently, there are increased numbers of investigations devoted to the processing and characterization of Ti_3SiC_2 ceramics [3–16]. Among the previous investigations, Ti_3SiC_2 ceramics were often fabricated by using pressure-assisted processes, such as, hot pressing (HP) or hot-isostatic pressing (HIP) for the purpose to prepare high density and high phase-purity Ti_3SiC_2 samples and to explore the intrinsic properties of this new material. From an industrial point of view, pressureless sintering is much more attractive because of its advantages such as shape-forming flexibility and cost effectiveness as compared with HP or HIP. The applications of Ti_3SiC_2 ceramics may be facilitated greatly, if its pressureless sintering process of Ti_3SiC_2 ceramics is established. However, according to our best knowledge, no work about the normal sintering of Ti_3SiC_2 has been reported in the literature so far. Hence, the motivation of this study is to fabricate Ti_3SiC_2 ceramics by pressureless sintering process.

In our previous study [15], we have found that high phase-purity Ti_3SiC_2 powder can be synthesized by mechanical alloying (MA) of elemental Ti, Si and C powders and post-annealing treatment. Therefore, in this study, the mechanically alloyed elemental powder mixtures were used as the starting powders so that the overall fabrication process can be simplified. This paper focuses on the phase evaluation during the mechanical alloying and the following sintering processes, sintering densification behavior, sintered microstructure and some physical properties of the pressureless-sintered samples.

2. Experimental

Commercial Ti (average particle size: 16 μm, >99.6% purity, Toho Titanium Co., Japan), Si (average particle size: 70 μm, >99.9% purity, Rare Metallic Co., Japan) and C (average particle size: 5 μm, >99.7% purity, High Purity Chemicals Co., Japan) powders were used in the present study. These powders were weighed in a mass ratio calculated from the stoichiometic composition of Ti_3SiC_2, and milled in the form of MA as reported previously [15]. The MA process was conducted using a vibratory mill (MB-0, Chu-ou Kakoki Co., Japan) with cylindrical jars (inner diameter: 140 mm, capacity: 1400 mL) made from stainless steel (JIS, SUS304) and chrome-steel balls (12.7 mm diameter). The vibration amplitude was 4 mm and the frequency of vibration was 1440 rpm. The Ti, Si and C powders were charged into the jar in a glove box filled with argon gas, and the weight ratio of ball to powder was 100 to 1. The MA process was conducted for different durations ranging from 6 to 800 h. The milled powders were formed to billets 10 mm in diameter and ~10 mm in height, by die pressing at 130–150 MPa and subsequent cold-isostatic pressing at 200 MPa. The green compacts of the mixed powders were placed in a BN crucible and sintered in Ar (99.9995% purity, $O_2 < 0.2$ ppm) of 0.1 MPa in an electric furnace with a carbon heater. The heating and cooling rates were 15 K/min and 20 K/min, respectively. The soaking time at the sintering temperature was 1 h.

The phases of the milled powders and the sintered samples were identified using X-ray diffraction (XRD) with Ni-filtered Cu K_α radiation. The contents of Ti_3SiC_2 were quantified according to the calibrated relationship between the diffraction intensity ratio and volume fraction of Ti_3SiC_2 and TiC_x, as TiC was a major secondary phase mixed with Ti_3SiC_2. the microstructure was observed by scanning electron microscopy (SEM). Density was determined using the Archimedes method. Fracture strength was measured with a 4-point bending test with lower and upper spans of 20 and 10 mm, respectively. The bending tests were performed at a crosshead speed of 0.5 mm/min by using the specimens of nominal dimensions 24 mm × 2.0 mm × 1.5 mm. The prospective tensile surfaces were ground and polished to achieve a mirrorlike surface finish prior to mechanical testing. Vickers microhardness was measured under a load of 4.9 N. Electrical conductivity and the thermal conductivity were measured by using the two-probe method and the laser flash method, respectively.

3. Results and discussion

Fig. 1 shows the XRD patterns of the powder mixtures subjected to MA for various durations. The peaks belonging to carbon disappeared first at a short time due to the formation of amorphous carbon [17]. The peaks of silicon and titanium became significantly weak when the MA time was increased to 48 h, at which two main broad peaks were formed at the diffraction angles corresponding to that of {111} and {200} peaks of TiC phase. The peaks of the starting elemental powders almost disappeared the powders being milled for more than 200 h. The features of the XRD patterns show that the powders became amorphous-like after being mechanically alloyed for more than 400 h.

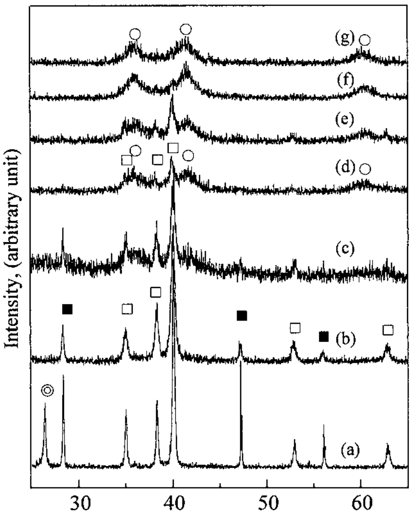

Figure 1 XRD patterns of the Ti, Si and C powder mixtures subjected to mechanical alloying for different times: (a) 0 h, (b) 6 h, (c) 24 h, (d) 48 h, (e) 100 h, (f) 200 h, and (g) 400 h. (◎: C, ■: Si, □: Ti, ○: TiC_x).

Fig. 2 compares the appearances of the powder mixtures subjected to the MA for different times. The reduction of particle sizes can be clearly seen from the SEM micrographs. Many coarse particles or agglomerates

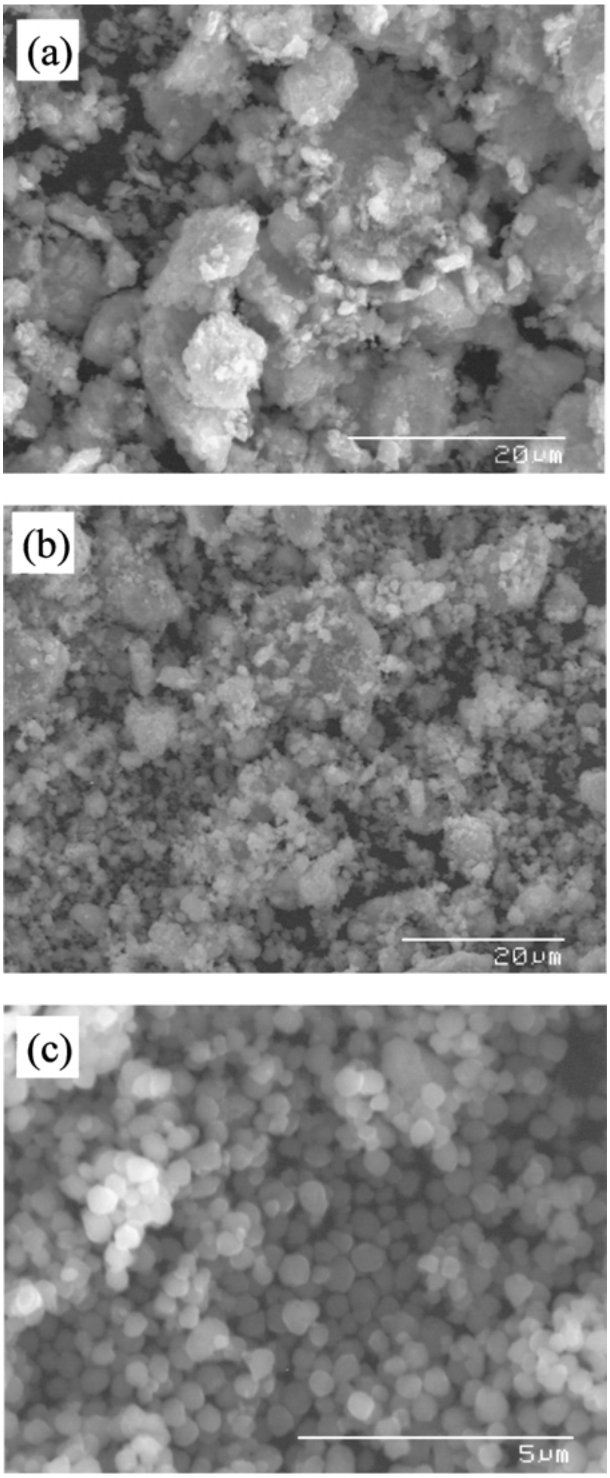

Figure 2 SEM micrographs of the powder mixtures subjected to the mechanical alloying for different periods: (a) 6 h, (b) 12 h, and (c) 400 h.

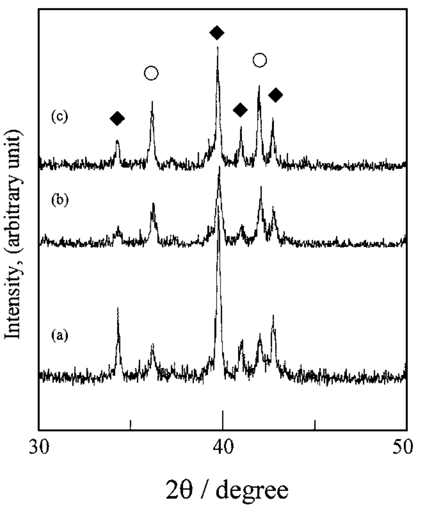

Figure 3 XRD patterns of the Ti, Si and C powder compacts that were mechanically alloyed for 400 h and subsequently sintered at different temperatures: (a) 1373 K, (b) 1573 K, and (c) 1773 K. (○: TiC_x, ◆: Ti_3SiC_2).

with fine particles on their surfaces were observed in the samples after being milled for 6 h, whereas the powders were uniformly pulverized after the extensive MA of 400 h. The average particle sizes of the powders mechanically alloyed for 100, 200, 400 and 800 h were measured to 1.29, 1.03, 0.85 and 0.64 μm, respectively.

Fig. 3 shows the XRD patterns of the samples sintered at different temperatures using the powder mixtures subjected to MA of 400 h as an example. Ti_3SiC_2 was formed as the main phase in the sintered powder compacts at all the temperatures investigated, although the amount of TiC_x secondary phase increased with increasing sintering temperature. As shown in Fig. 3a, a considerable amount of Ti_3SiC_2 phase was formed at a relatively low temperature near 1373 K, because of the MA-assisting effects as reported previously [15]. If the powders were mixed by conventional procedures such as wet ball milling or hand mixing, Ti_3SiC_2 phase was formed above 1673 K by a different mechanism as discussed elsewhere [13].

The phase purity of Ti_3SiC_2 was calculated from the diffraction peak intensity, and the results are shown in Fig. 4. The Ti_3SiC_2 contents in the sintered samples are greatly affected by MA time. When the MA was extended from 100 to 400 h, the Ti_3SiC_2 content was significantly increased, particularly in the samples sintered at the high temperatures; however, the Ti_3SiC_2 content tended to decrease when the MA time exceeded 400 h. This result suggests that there exists an optimum MA time for the synthesis of Ti_3SiC_2 derived from the mechanically alloyed elemental powder mixtures. The highest Ti_3SiC_2 content obtained at 1773 K was nearly 80% for the sample with 400 h MA time. Although the phase purity is not as high as in the samples prepared by the reactive hot-isostatic pressing (HIP) process, highly dense Ti_3SiC_2 ceramics were successfully fabricated for the first time in the present study.

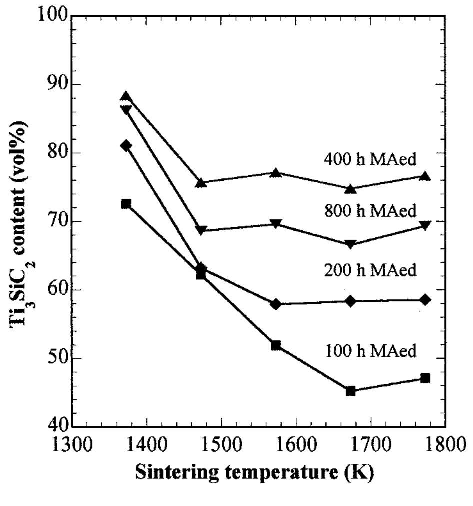

Figure 4 Volume fraction of Ti_3SiC_2 in the presureless-sintered powder compacts as a function of sintering temperature.

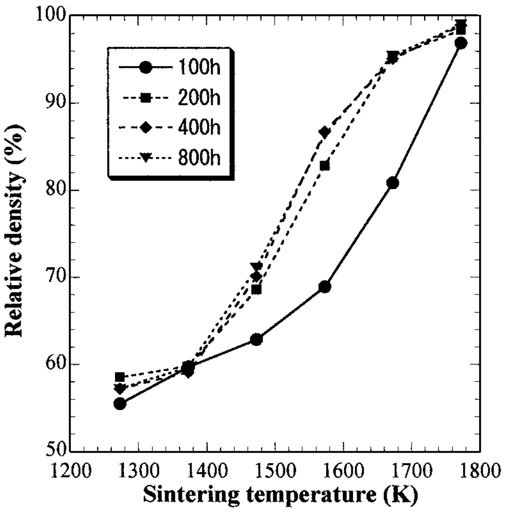

Figure 5 Relative density of the pressureless-sintered Ti_3SiC_2-based ceramics with different MA durations shown in the figure as a function of sintering temperature.

Fig. 5 shows the relative density of the pressureless-sintered compacts of the mechanically alloyed powder mixtures as a function of sintering temperature. The relative density was calculated according to the Ti_3SiC_2 content shown in Fig. 4 and the theoretical densities of Ti_3SiC_2 and TiC_x, being 4.52 g/cm^3 and 4.68 g/cm^3, respectively. It was confirmed that almost no sintering densification was observed in the non-MA samples (wet-mixed powder) even after being sintered at temperature as high as 1773 K, whereas all the samples subjected to the MA treatment of more than 100 h were sintered to high density as shown in Fig. 5. It is clear that the MA treatment not only promoted the densification but also enhanced the formation of Ti_3SiC_2 at low temperature. Although the powder mixtures that were mechanically alloyed for 100 h had lower density within intermediate sintering temperature ranges, its density increased finally with increasing temperature and reached at the same level as the other samples with longer MA times. The powders subjected to the MA of 100 h showed lower density below 1773 K probably because of their relatively large particle sizes.

As shown in Fig. 6a, the microstructure near the surface was apparently different from that inside. In addition, it was found that the surface was much harder than the interior. This suggests that more TiC_x phase was formed at and near the surface. In fact, the XRD (the patterns is not shown here) confirmed that the content

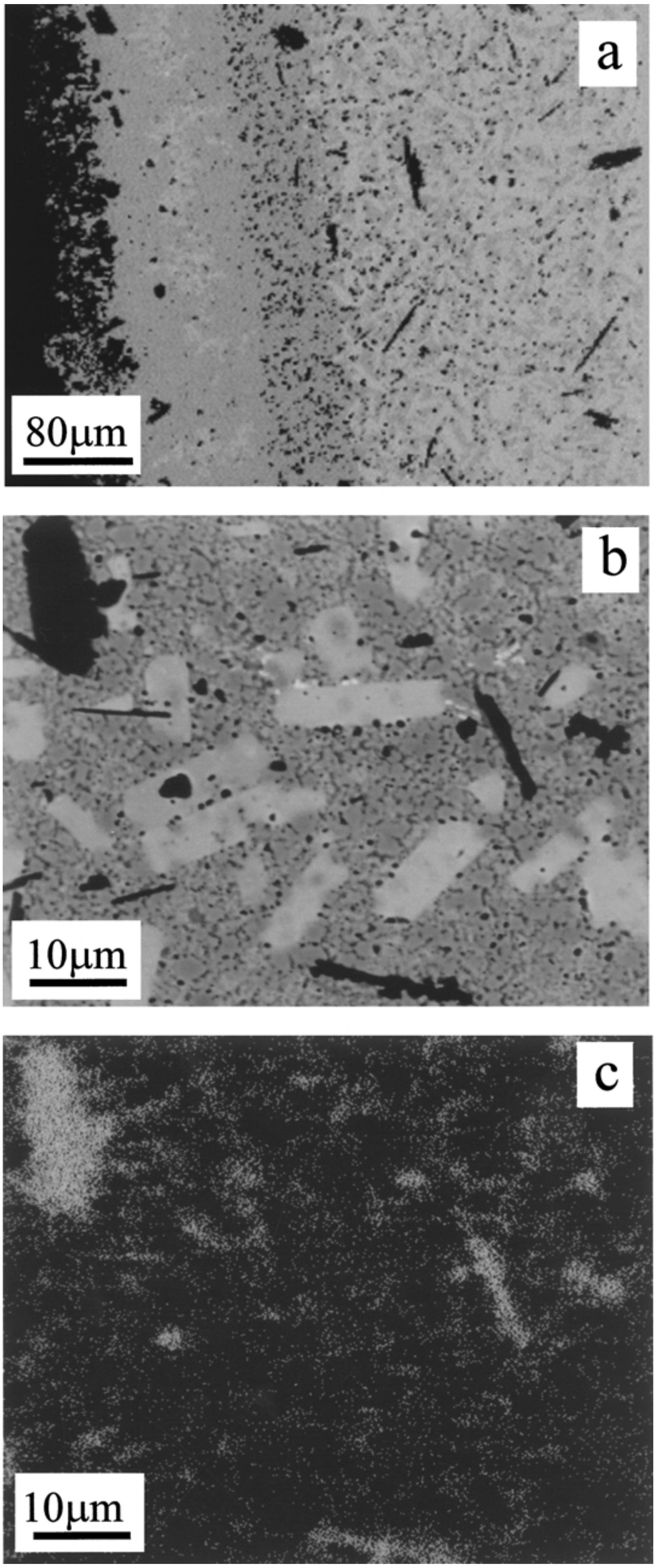

Figure 6 SEM micrographs of the polished surfaces of pressureless-sintered Ti_3SiC_2-based ceramics: (a) BSE image near the surface, (b) BSE image inside the sample, and (c) Si distribution map at the area corresponding to (b).

of TiC_x phases was much higher than that inside. The formation of the TiC_x phase on the surface was probably due to the decomposition of Ti_3SiC_2, via a reaction to be discussed later. On the other hand, as shown in Fig. 6b at large magnification, large plate-like grains are dispersed in the fine-grained matrix, being similar to the bimodal microstructure obtained in the Ti_3SiC_2 ceramics fabricated by reactive hot-isostatic pressing [14]. Some dark spots, where the Si elements were concentrated as shown by Fig. 6c, were observed on the

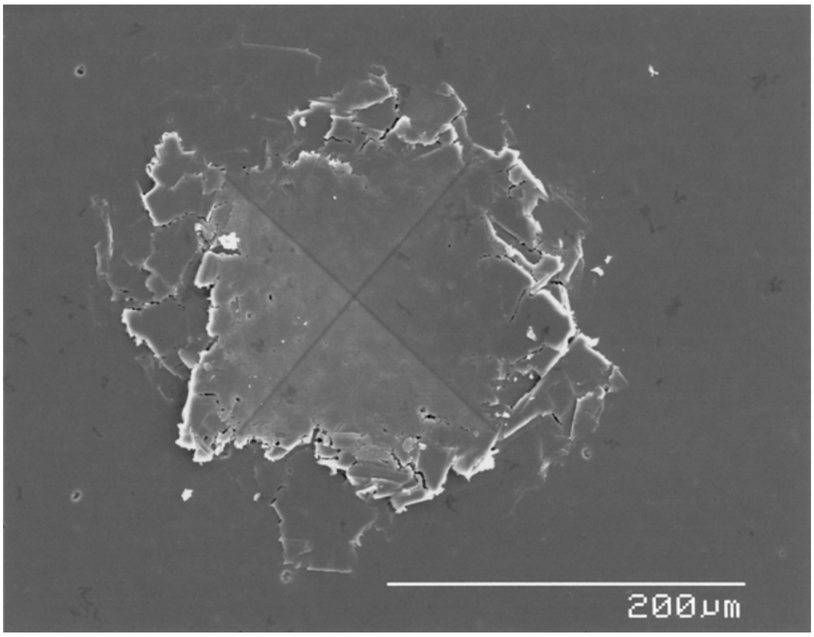

Figure 7 SEM micrograph of Vickers indentation (load = 98 N) made on the polished surface of the pressureless-sintered Ti_3SiC_2-based ceramics from the powder mixture subjected to mechanical alloying for 400 h.

polished surface. This result gave us a hint to presume that a gaseous phase is involved in the Ti_3SiC_2 decomposition reaction, and the composition of the gaseous phase is Si, as shown in the following equation:

$$Ti_3SiC_2\ (\text{solid}) \rightarrow TiC_x\ (\text{solid}) + Si\ (\text{vapor}) \qquad (1)$$

The gaseous Si phase was formed and entrapped in the interior of the sintered body at elevated temperatures, and then became amorphous during cooling process and deposited on the surfaces of some pores or between some grains. Therefore, for the pressureless sintering of Ti_3SiC_2 powder compacts, the decomposition and densification occur simultaneously and competitively during the sintering process of Ti_3SiC_2. In considering the nature of the decomposition reaction accompanied by gaseous Si phase, it is not difficult to understand why the decomposition occurs more easily near free surfaces than inside. Before the densification, the decomposition is easy to occur in the porous powder compacts, but it is increasingly suppressed when the compacts become increasingly densified with increasing sintering temperature. That may account for the fact that the Ti_3SiC_2 contents decreased significantly within the temperature range from 1373 to 1473 K, during which the density is not high enough as shown in Fig. 4, whereas further temperature increase did not reduce the Ti_3SiC_2 content, except for the sample with 100 h MA time. The Ti_3SiC_2 content decreased more significantly in the sample with 100 h MA time as compared with the others, because the density increased much more slowly with increasing temperature, as shown in Fig. 5.

Table 1 summarizes some physical properties of the pressureless-sintered Ti_3SiC_2 ceramics and the referential high-purity Ti_3SiC_2 ceramics prepared by reactive hot-isostatic pressing. It is worthy noting that the pressureless-sintered Ti_3SiC_2 ceramics show almost the same electrical and thermal conductivities as the HIP-sintered high-purity Ti_3SiC_2 ceramics. In addition, the bending strength is also equal to that obtained in the HIPed Ti_3SiC_2 ceramics; of course, higher bending strengths can be obtained in the fine-grained Ti_3SiC_2 ceramics prepared by reactive HIP [18]. Because the present Ti_3SiC_2 based ceramics contain more TiC_x phase, which is much harder than Ti_3SiC_2 phase, the Vickers hardness is somewhat higher than the HIP-sintered high-purity Ti_3SiC_2. Nevertheless, their physical properties are not inferior to the HIP-sintered high-purity Ti_3SiC_2, even though the present pressureless-sintered Ti_3SiC_2 ceramics contain about 20% TiC_x as the secondary phase. As shown in Fig. 7, no straight indentation cracks were formed from the corners even under a load as high as 98 N, indicating that the present pressureless-sintered Ti_3SiC_2 ceramics show high indentation damage resistance as the high-purity Ti_3SiC_2 ceramics prepared by reactive HIP process [19].

TABLE I Property comparison between the present pressureless-sintered Ti_3SiC_2-based ceramics and high-purity Ti_3SiC_2 ceramics prepared by HIP

Property	The present Ti_3SiC_2	High-purity Ti_3SiC_2 [8]
Density (g/cm^3)	4.52	4.46
Vickers hardness (GPa) (at 4.9 N)	6.42	5.77
Bending strength (GPa)	336	360
Electrical conductivity (S/m) (at 25°C)	3.54×10^6	4.7×10^6
Thermal conductivity (W/mK) (at 25°C)	34.1	33.5

4. Conclusion

Highly dense Ti_3SiC_2 based ceramics can be fabricated by pressureless sintering of mechanically alloyed elemental Ti, Si and C powder mixture at relatively low temperatures around 1773 K.

The mechanically alloyed elemental powders convert to Ti_3SiC_2 at temperatures as low as 1373 K and then densification occurs subsequently with increasing sintering temperature up to 1773 K. By the combination of mechanical alloying and pressureless sintering, highly dense Ti_3SiC_2 ceramics with a relative density over 98% and near 80% Ti_3SiC_2 (TiC_x as the secondary phase) are obtained in the present study. The TiC_x phase forms during the sintering process mainly due to the decomposition of Ti_3SiC_2.

The physical properties of the present pressureless-sintered Ti_3SiC_2-based ceramics are comparable to that of nearly single phase Ti_3SiC_2 ceramics fabricated by hot-isostatic pressing (HIP). By optimizing the presureless sintering conditions, it is possible to further increase the phase purity and the resultant properties.

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Received 29 July 2002
and accepted 26 February 2003