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Synthesis and mechanical properties of Ti_3AlC_2 by spark plasma sintering

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In this paper, spark plasma sintering (SPS), after hot isostatically pressing (HIP) method was reported as a new approach to prepare bulk polycrystalline samples of Ti_3AlC_2. The ternary carbide was fabricated by spark plasma sintering (SPS) at a pressure of 22 MPa and temperature of 1250°C. The raw materials, elemental powders of Ti, Al and activated carbon, were pretreated in the following different ways prior to SPS: one way was to obtain porous Ti_3AlC_2 by self-propagating high-temperature synthesis (SHS) from mixture of Ti, Al and C, and then densify the product by SPS; the second way was to synthesize Al_4C_3 from Al and C firstly, and then mix powders of Ti and C with synthesized Al_4C_3 to fabricate bulk Ti_3AlC_2 by SPS. Obtained polycrystalline Ti_3AlC_2 ceramics had excellent mechanical properties: density was 4.24 ± 0.02 g/cm^3, flexural strength was 552 ± 30 MPa and fracture toughness (K_{IC}) was 9.1 ± 0.3 MPa $\cdot$ m$^{1/2}$. It could be concluded that SPS method was a useful method to synthesize bulk Ti_3AlC_2 with excellent properties in a very short time and easily sintering process. The optimal conditions to synthesize Ti_3AlC_2 were also discussed.
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1. Introduction

Titanium aluminum carbide (Ti_3AlC_2) is a member of a class of ternary carbides that recently have been shown to possess an unusual combination of properties. It combines the merits of both metals and ceramics. Like metals, Ti_3AlC_2 is thermal and electrical conductive, easy to machine with conventional tools, and resistant to thermal shock; like ceramics, it has high strength, high melting point and thermal stability. Especially, Ti_3AlC_2 has a unique property in ceramics of some compressive plasticity at room temperature [1]. Those properties make Ti_3AlC_2 useful in many fields [1–3]. For example, it can be used as a high-temperature structural material instead of expensive high-temperature alloys.

Even though Ti_3AlC_2 has so many excellent properties, it has not obtained many attentions until recent years because it is difficult to synthesize bulk samples of Ti_3AlC_2 with high-purity. There are only two methods reported to synthesize this material. Ti_3AlC_2 was first synthesized by Pietzka and Schuster [4] in 1994 and found to be isostructural with Ti_3SiC_2. They synthesized Ti_3AlC_2 by sintering cold-compacted powder mixtures of titanium, TiAl, Al_4C_3, and carbon in pure hydrogen for 20 h. Recently Tzeonov and Barsoum [1] first prepared bulk polycrystalline samples of Ti_3AlC_2 by reactively hot isostatically pressing (HIP) mixtures of titanium, graphite, and Al_4C_3 powders at 1400°C for 16 h.

Because Al will start to melt at ~650°C, both of the above methods used Al_4C_3, instead of metal Al, as aluminum source. Al_4C_3, however, can generate Al_2O_3 impurity coexisting with Ti_3AlC_2 for the following reaction [1]:

$$Al_4C_3 + 6H_2O = 2Al_2O_3 + 3CH_4 \uparrow \qquad (1)$$

In our previous work [2], porous Ti_3AlC_2 was synthesized from powder mixtures of Ti, Al and C by self-propagating high-temperature synthesis (SHS). If there is a suitable way to densify it as well as avoiding its decomposition, it must be another good way to prepare bulk polycrystalline samples of Ti_3AlC_2 besides HIP method.

Spark plasma sintering (SPS) is a new process to synthesize or sinter ceramic powders very fast to full density [5–7]. It is similar to hot-pressing which is carried out in a graphite die, but the most difference for SPS is that the heating is accomplished by spark discharges in voids between particles generated by an instantaneous pulsed direct current applied through electrodes at the top and bottom punches of the graphite die. Due to these discharges, the particle surface is activated and purified, and a self-heat phenomenon is generated between the particles, thus the heat-transfer and mass-transfer can be completed instantaneously.

In this paper, SPS was chosen to prepare bulk polycrystalline samples of Ti_3AlC_2 from porous Ti_3AlC_2 obtained by SHS, which was called as *SHS-SPS* method. For the sake of comparison with HIP process [1], we also prepared bulk Ti_3AlC_2 by SPS from the same mixture of Ti, Al_4C_3 and C as that used in the HIP

process. The Al_4C_3 used here was obtained by pressureless sintering the mixture of Al powder and C powder in advance. This method was called as *in situ-SPS* method. All the methods were compared and discussed to find the optimal conditions to fabricate Ti_3AlC_2.

Even though it is clear that Ti_3AlC_2 has many excellent properties, the understanding to this material is still far from complete. For example, the most valuable merit of Ti_3AlC_2 is its machinability, which mainly depends on its excellent property of damage-tolerance. Tzenov and Barsoum characterized the property by its post-indentation flexural strengths, which were almost independent of the indentation loads [1]. However, fracture toughness (K_{IC}) of Ti_3AlC_2 was not reported, which was often used to characterize damage-tolerance property of ceramics. In this paper, we firstly measured and reported the very high fracture toughness (K_{IC}) of Ti_3AlC_2 ceramic, which verified that Ti_3AlC_2 has a good damage-tolerance property.

2. Experimental procedure

The starting materials were powders of titanium (99.4% pure, Beijing Research Institute of Nonferrous Metal, −400 mesh), Al (99.5% pure, Beijing Xizhong Chemical Plant, −200 mesh) and activated carbon (98% pure, Beijing Dali Activated Carbon Factory). These powders were mixed by several different molar ratios, and then ball-milled with absolute alcohol for 24 h. The slurries were vacuum dried and then sieved with 100-mesh screen. These mixtures were cold-pressed into bars with dimensions of 50 mm × 10 mm × 10 mm, followed by SHS reactions. The reactions were ignited by reaction heat between titanium and carbon at one end of the bars, which were heated for several seconds by passing an electric current through a tungsten filament. To avoid the influence of oxygen, the reactions took place in vacuums. Obtained porous products were crushed with agate mortars and pestles, and then sieved with 100-mesh screens.

Spark plasma sintering (SPS), also known as pulsed electric current sintering (PECS), was carried out in vacuum using Dr Sinter 1020 SPS apparatus (Sumitomo Coal Mining Co., Ltd., Japan). The prepared powder was carefully placed into a 35 × 35 mm^2 square graphite die coated with graphite foil, and heated to 1250°C at a rate of 600°C/min. After 5 min at the temperature, the sintering sample was cooled to near room temperature in about 40 min. A pressure of 22 MPa was applied during the whole process. This process was called *SHS-SPS* method.

Another method to prepare Ti_3AlC_2, namely *in situ-SPS* method, was to sinter the mixture of Ti, Al_4C_3 and C by SPS. Firstly, Al_4C_3 was synthesized by sintering the mixture of Al and C with a stoichiometric ratio at 1400°C for 1 h in Ar atmosphere. The yellow Al_4C_3 powder was obtained with a little residual aluminum according to its XRD pattern. Thereafter, the powders of Ti, C and Al_4C_3 were mixed with Ti:Al:C molar ratio of 3:1.2:2. Because of weight loss of aluminum at elevated temperature, a little excess aluminum was added. Finally, the mixture was treated and sintered by the same SPS procedure as that of *SHS-SPS* method.

Hot pressing (HP) is a very convenient method to synthesize Ti_3SiC_2 and many other ceramics [3]. However, there were few reports about the preparation of Ti_3AlC_2 by hot pressing. For the purpose of comparison, Ti_3AlC_2 was also synthesized by hot-pressing process in this paper. The mixture of Ti, Al_4C_3 and C powders with Ti:Al:C molar ratios = 3:1.2:2 was cold pressed. Then the green body was wrapped in graphite foil and placed in a graphite die with diameter of 50 mm, thereafter hot pressed at 1400°C for 3 h under pressure of 25 MPa and in Ar atmosphere.

All the obtained samples were examined by D/MAX-IIIB X-ray diffractometer (XRD) with Cu K_α radiation. The microstructure was observed by scanning electron microscopy (SEM) (OPTON, CSM 950, Germany). Density of the materials was measured by Archimedes' method. Flexural strength was measured by a three-point bending method with a span length of 30 mm and a crosshead speed of 0.5 mm/min. Sintered samples were cut and ground to test bars with a dimension of 4 mm × 3 mm × 35 mm, and then polished with diamond pastes down to 3.5 μm on the side that would experience tension stress during testing. The two corners on the tension surface were rounded with a 15 mm diamond-grinding wheel. Fracture toughness was measured by single edge notched beam (SENB) method with a specimen dimension of 6 mm × 4 mm × 35 mm and a span length of 24 mm. The widths and lengths of notches were ∼0.20 mm and ∼2.8 mm respectively.

3. Results and discussion

3.1. Synthesis and microstructure of Ti_3AlC_2

XRD patterns of prepared materials were shown in Fig. 1. In the figure, it can be seen that three phases, Ti_3AlC_2, Ti_2AlC and TiC, were generally synthesized in this paper. Many peaks corresponding to the three phases, however, are coincidence. The characteristic peaks are 9.5° for Ti_3AlC_2, 13.0° for Ti_2AlC, and 35.9° for TiC, respectively.

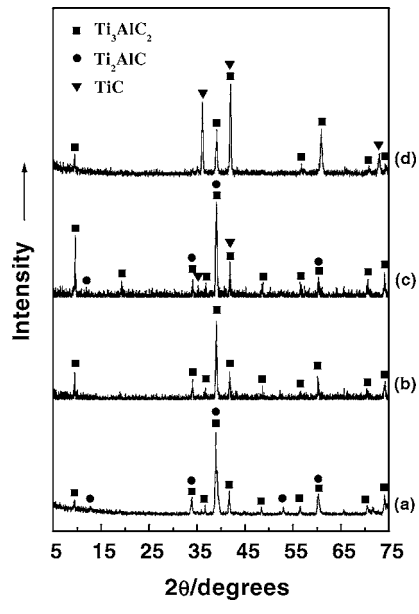

Figure 1 XRD pattern of Ti_3AlC_2 synthesized by different methods: (a) Ti_3AlC_2 powder prepared by SHS, (b) Product of *SHS-SPS*, (c) Product of *in situ-SPS*, and (d) Product of HP.

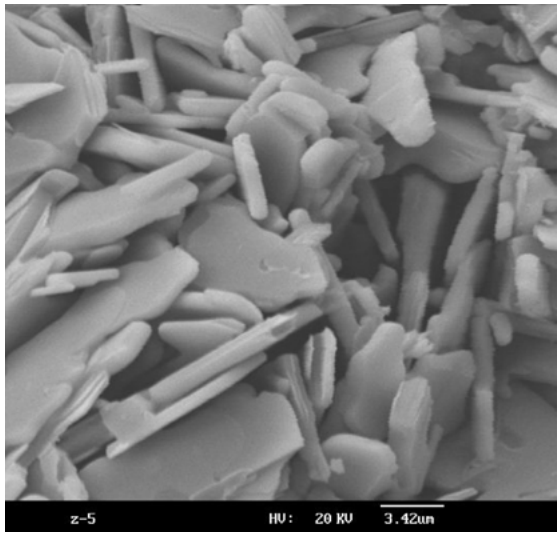

Figure 2 SEM micrograph of Ti_3AlC_2 obtained by SHS.

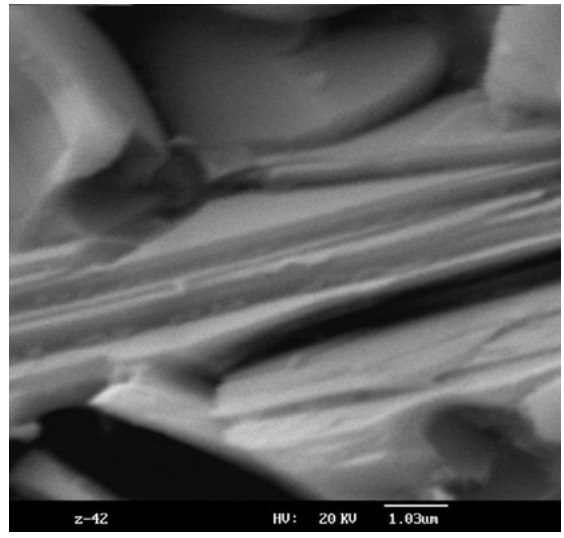

Figure 3 SEM microphotograph of Ti_3AlC_2 obtained by *SHS-SPS*.

3.1.1. SHS process

In most cases, only TiC and Al were obtained from reactions among elemental powders of Ti, Al and C at elevated temperature [8–10]. However, in the previous work by the present authors [2], Ti_3AlC_2 and Ti_2AlC were obtained from those powders by SHS process. Among several powder mixtures with different atomic ratios, the mixture with Ti:Al:C molar ratio of 2:1:1 was most easy to be ignited and a self-sustaining SHS process can continue to proceed. Therefore, the SHS process discussed below was referred to the process from a raw material with Ti:Al:C molar ratio of 2:1:1. According to the XRD pattern shown in Fig. 1a, Ti_3AlC_2 was the main phase synthesized in this process. Some Ti_2AlC and small quality of TiC were also synthesized. A SEM micrograph of that sample is shown in Fig. 2. Grains of Ti_3AlC_2 are plate-like with average diameters in the range of 5–10 μm. The fully discussion can be seen in our previous work [2].

Titanium and carbon are easy to react with each other to synthesize TiC and gives out a lot of heat. Existence of aluminum is favorable to this reaction because molten Al at elevated temperature provides a route for the move of Ti and C [9–11]. However, if heating rate for the reaction is as high as to avoid aluminum to melt in a wide-ranging field, ternary carbides, namely Ti_3AlC_2 and Ti_2AlC, will be synthesized. Those Ti_3AlC_2 and Ti_2AlC samples were porous rather than dense materials, as shown in Fig. 2.

3.1.2. SHS-SPS process

Dense Ti_3AlC_2 sample was prepared from the SHS product by SPS. From the comparison between the XRD patterns shown in Fig. 1a and 1b, it can be seen that *SHS-SPSed* Ti_3AlC_2 was purer than only *SHSed* Ti_3AlC_2 since the peaks corresponding to Ti_2AlC were weakened and those corresponding to Ti_3AlC_2 became stronger. There is a purification effect in SPS process, which should be the contribution of a short period at high temperature. The soaking temperature of SPS was measured as 1250°C by an optical pyrometer focused on a small hole in the die containing the sintered sample. In fact, the sintering temperature in the reacting field is much higher than measured 1250°C, because reacting heat is generated by spark discharge in the reacting field. The high temperature was favorable to the synthesis of Ti_3AlC_2. Aluminum and titanium are apt to evaporate and loss at high temperature. This is the reason why Ti_3AlC_2 was synthesized from the initial Ti:Al:C molar ratio of 2:1:1 instead of 3:1:2, and is also favorable to the phase transformation from Ti_2AlC to Ti_3AlC_2. Compared with the several-hour sintering time of hot pressing, the soaking time of SPS was very short, which was only several minutes. Because of the very short soaking time at high-temperature, there was not enough time for Ti_3AlC_2 to decompose.

Fig. 3 is a SEM micrograph of the fracture surface of *SHS-SPSed* Ti_3AlC_2. In this figure, the layered structure of the compound is apparent to be seen, which is the characteristics of Ti_3AlC_2 materials. The thickness of a grain-layer is about 100 nm.

3.1.3. In situ-SPS process

As shown in Fig. 1c, the product of SPS from mixture of Ti, Al_4C_3 and C, viz. product of *in situ-SPS*, was also mainly Ti_3AlC_2. However, its purity is less than the product of *SHS-SPS* and some TiC coexisted with Ti_3AlC_2.

In Fig. 1c, the relative intensity of a Ti_3AlC_2 peak with $2\theta = 9.5^\circ$ is 66.2. It is obvious higher than that in Fig. 1b, which is 34.7. However, the calculated relative intensity of this peak should be 44 according to Tzenov *et al.* [1]. Therefore, a strong preferred orientation must exist in the *in situ-SPSed* samples and there is no strong preferred orientation in the *SHS-SPSed* samples. In the *in situ-SPS* process, Ti_3AlC_2 was obtained by chemical reaction among Ti, Al_4C_3 and C. Seed crystallites of Ti_3AlC_2 were firstly nucleated and then grew to Ti_3AlC_2 crystals. Ti_3AlC_2 belongs to hexagonal crystal system and it forms platelet-like crystals having basal planes perpendicular to the (unique) hexagonal axis of Ti_3AlC_2. It is easy to reorientate the

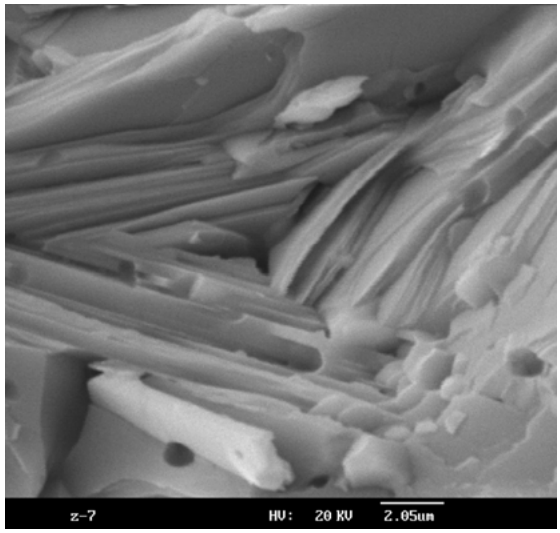

Figure 4 SEM microphotograph of Ti_3AlC_2 obtained by *in situ-SPS*.

platelet-like crystals as they are in a liquid-phase surround. Thus some platelet crystals change their orientation and their basal planes become perpendicular to the direction of pressing. That is the reason why a strong preferred orientation is obtained in an *in situ-SPS* process. In the *SHS-SPS* process, however, there was no obvious chemical reaction and nucleation of seed crystallites during SPS processing. This process is only a physical sintering process. It is difficult for basal planes to change their original orientation. So the preferred orientation in *SHS-SPSed* samples was not obvious, compared to that in *in situ-SPSed* samples.

A SEM micrograph of the fracture surface of *in situ-SPSed* Ti_3AlC_2 is shown in Fig. 4. The micrograph confirms the layered nature of the material. Some little holes shown in this figure should be the vestiges of weight loss of Al at high temperature.

3.1.4. HP process

As sown in Fig. 1d, a lot of TiC was obtained when Ti_3AlC_2 was attempted to synthesize by hot pressing. Previous researches [1, 8–11] drew the similar conclusion that TiC was easy to be obtained from reactions among Ti, Al and C by conventional methods. It is believed that HP method is not a suitable way to synthesize pure Ti_3AlC_2 even though it is a good method to synthesize Ti_3SiC_2 and other ceramics.

3.1.5. Mechanisms on Ti_3AlC_2 ceramics synthesis

Pietzka and Schuster reported that Ti_3AlC_2 is decomposed at ∼1360°C [4]; Tzenov and Barsoum considered that Ti_3AlC_2 is unstable above 1400°C [1]. In this paper, the reacting temperature of SHS was above 1700°C. Therefore Ti_3AlC_2 is thermodynamically unstable at this temperature. The reacting time, however, was short enough to avoid the decomposition of Ti_3AlC_2. Thus the reason for obtaining Ti_3AlC_2 by SHS is kinetic rather than thermodynamic. It is conceivable that the short reaction time is favorable to synthesize ternary carbides, include Ti_3AlC_2 and Ti_2AlC. The reacting time of HP or HIP is usually several hours, while the reacting time of SPS is several minutes and that of SHS is only several seconds. Thus it can be concluded that a large amount of Ti_2AlC and Ti_3AlC_2 can be obtained by SHS and almost no TiC is generated, as shown in Fig. 1a. If a SPS process follows a SHS process, viz. an *SHS-SPS* process, Ti_2AlC transform to Ti_3AlC_2 and the amount of TiC does not increase, as shown in Fig. 1b. Therefore, Ti_3AlC_2 purity of *SHS-SPSed* samples is the highest. However, *in situ-SPS* process can generate a little TiC and HP process generates more TiC, as shown in Fig. 1c and d. A necessary condition for SHS is that raw materials are elemental powders of Ti, Al and C in order to generate a large amount of heat. However, TiC rather than Ti_3AlC_2 is easy to be obtained from those elemental powders [8–11]. A rapid reaction is necessary to prepare ternary carbides. SHS process usually finishes in several seconds and can meet the condition. The main reactions in this SHS process are:

$$\text{Step 1: Ti} + \text{C} \xrightarrow{\text{Al}} \text{TiC seed crystals} \quad (2)$$

$$\text{Step 2: TiC seed crystals} + \text{molten Al} \rightarrow \text{Ti}_3\text{AlC}_2 \text{ crystals} \quad (3)$$

In Step 1, TiC seed crystals are formed. The TiC seed crystals, however, cannot grow bigger because no enough Ti or C can migrate to the reacting field in a very short reacting time. In Step 2, TiC seed crystals react with nearby molten Al to form Ti_3AlC_2. That is not because Ti_3AlC_2 is more stable than TiC at that temperature but because the amount of Al in the reacting field is very large and the formation of Ti_3AlC_2 is quicker than its decomposition.

Almost pure TiC is obtained by hot-pressing mixture of Ti, Al and C powders even with the stoichiometric molar ratio of 3:1:2 [2]. However, if aluminum powder is replaced by Al_4C_3 powder, the synthesis of Ti_3AlC_2 becomes easy and the formation of TiC becomes difficult. In this paper, a considerable Ti_3AlC_2 can be obtained by HP process when Al is replaced by Al_4C_3 in the starting materials.

3.2. Mechanical properties of Ti_3AlC_2

As discussed above, both *SHS-SPS* and *in situ-SPS* methods can be used to fabricate dense samples of Ti_3AlC_2 within a short soaking time. Compared with samples fabricated by *in situ-SPS* method, samples fabricated by *SHS-SPS* have higher purity and less preferred orientation. Thus, the mechanical properties of *SHS-SPSed* samples are discussed below as typical properties of Ti_3AlC_2.

The unit cell of Ti_3AlC_2 is hexagonal, with a theoretical density of 4.25 g/cm^3 [4]. In the *SHS-SPSed* samples, the density is measured as 4.24 ± 0.02 g/cm^3, which is very close to the theoretical density. This is also a proof that nearly full dense bulk Ti_3AlC_2 ceramics were obtained by *SHS-SPS* in this paper.

The fracture toughness, K_{IC}, of Ti_3AlC_2 was measured as 9.1 ± 0.3 MPa $\cdot$ m$^{1/2}$, which is never reported

in any previous work, as we know. That value is very high in monolithic ceramics. Tzenov and Barsoum [1] reported a unique post-indentation flexural strength of Ti_3AlC_2, which was corresponding to its excellent property of damage tolerance. The high K_{IC} of the material measured in this paper also indicates the good damage-tolerance property of Ti_3AlC_2.

The high fracture toughness of Ti_3AlC_2 may be derived from its layered nature. As shown in Figs 3 and 4, the fracture surface of Ti_3AlC_2 is very similar to that of layered ceramics. Layered ceramics, usually with high fracture toughness, consist of alterative hard ceramic layers and soft interlayers with thickness of several microns to several dozen microns. Ti_3AlC_2 has layered nature similar to layered ceramics. Ti_6C layers are hard layers, and Al layers are soft layers. Ti_6C layers and Al layers are bound together by metallic bonding of Ti—Al. The difference between Ti_3AlC_2 and general layered ceramics is that the layer thickness in Ti_3AlC_2 is only several nanometers. Therefore, Ti_3AlC_2 can be considered as a natural nano-layered ceramic material.

The flexural strength of Ti_3AlC_2 synthesized by *SHS-SPS* was 552 ± 30 MPa. This value is much higher than that of the HIP Ti_3AlC_2 reported by Tzenov and Barsoum [1], which was 375 ± 15 MPa. It agrees with the reports that samples sintered by SPS have better properties than samples obtained by routine methods [5–7].

For the sake of comparison, the fracture toughness and flexural strength of HPed Ti_3AlC_2 were also measured, which were 5.7 ± 0.3 MPa $\cdot$ m$^{1/2}$ and 212 ± 15 MPa, respectively. Because of existence of a considerable amount of TiC in the HPed Ti_3AlC_2, both of fracture toughness and flexural strength of the sample decreased substantively.

Fracture toughness and flexural strength are two important mechanical properties for ceramics to be applied as structural materials. In Table I, the fracture toughness and flexure strength of Ti_3AlC_2 were compared with those of other ceramics. From the table, we can see that fracture toughness of *SHS-SPSed* Ti_3AlC_2 is much higher than most monolithic ceramics and its flexural strength is also relative high. Since brittleness is the most obvious shortcoming of structural ceramics, the very high fracture toughness of Ti_3AlC_2 indicates the material is a very promising material to research further.

TABLE I Fracture toughness and flexural strength of our samples and other ceramics

Samples	Fracture toughness (MPa $\cdot$ m$^{1/2}$)	Flexural strength (MPa)
SHS-SPSed Ti_3AlC_2 in this paper	9.1 ± 0.3	552 ± 30
HPed $TiAlC_2$ in this paper	5.7 ± 0.2	212 ± 10
HIPed Ti_3AlC_2 [1]	Not reported	375 ± 15
Ti_3SiC_2	4.52 ± 0.15 [13] or 6.9 [12]	300 [13] or 580 [12]
Al_2O_3, $\lambda = 3$ μm [14]	3.9	488
Al_2O_3, $\lambda = 3$ μm [14]	3.3	400
Al_2O_3, $\lambda = 3$ μm [14]	4.6	302
SiC [14]	4.1	600
Si_3N [14]	4.4	520

4. Conclusion

1. *SHS-SPS* method is an economical and simple way to fabricate fully dense and almost single-phase Ti_3AlC_2 from elemental powders of Ti, Al and C. *In situ-SPS* method is also a good way to synthesis high pure Ti_3AlC_2 with a strong preferred orientation.

2. The fabrication of Ti_3AlC_2 is more depend on a kinetic reason rather than a thermodynamic reason. The optimal condition of synthesis Ti_3AlC_2 is sintering at high temperature in a short time. SHS method can be used to synthesize pure Ti_3AlC_2 from elemental powders of Ti, Al and C. If Al_4C_3 replaces Al as starting material, Ti reacts with Al and C together instead of with C individually, thus, the formation of TiC is more difficult and the formation of Ti_3AlC_2 is easer. As a result, SPS can be used to fabricate bulk Ti_3AlC_2 from powders of Ti, Al_4C_3 and C. Compared with HIP, SPS can be carried out in a short time and easy process.

3. The fracture toughness (K_{IC}) of bulk polycrystalline Ti_3AlC_2 ceramic was firstly measured as 9.1 ± 0.3 MPa $\cdot$ m$^{1/2}$, which is much higher than most common structural ceramics. The high fracture toughness gives high damage-tolerance proprieties of Ti_3AlC_2. The reason for the high fracture toughness is that Ti_3AlC_2 can be considered as a natural nano-layered ceramic material.

4. With very high fracture toughness, relative high flexural strength and other unique properties, full dense bulk Ti_3AlC_2 fabricated economically by our method will be a promising material in diverse fields.

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