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Synthesis of Ti_3SiC_2 by spark plasma sintering(SPS) of elemental powders①

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Abstract: Ti_3SiC_2 materials have been fabricated by spark plasma sintering of the elemental powders with the addition of Al. At the heating rate of 80 ℃/min and under the pressure of 30 MPa, the ideal synthesis temperature of Ti_3SiC_2 is in the range of 1 150－1 250 ℃. The addition of Al is in favor of the formation of Ti_3SiC_2. The synthesized compound has the molecular of $Ti_3Si_{0.8}Al_{0.2}C_2$ and lattice parameters of a= 0.306 9 nm, c= 1.767 0 nm. Its grain is plane-shape with a size of about 50 μm in the elongated dimension. The prepared material has Vickers hardness of 3.5－5.5 GPa(at 1 N and 15 s) and is as readily machinable as graphite's.

Key words: Ti_3SiC_2; synthesis; spark plasma sintering
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1 INTRODUCTION

Recently, titanium silicon carbide(Ti_3SiC_2) has received considerable attention because of the unusual combination of good properties that makes it a candidate for many high temperature applications[1]. It has excellent machinability, and it is not sensitive to thermal shock. At room temperature, it has electrical and thermal conductivities of 4.5×10^6 $s\cdot m^{-1}$ and 37 W/(m·K), respectively[1, 3]. Ti_3SiC_2 has a Vickers hardness of 4 GPa, elastic modulus of 325 GPa and a room temperature fracture toughness of 7 $MPa\cdot m^{1/2}$[2]. Its coefficient of thermal expansion is 9.2×10^{-6} K^{-1}[1, 3]. Ti_3SiC_2 is also a damage-tolerant material and has a brittle-to-plastic transition at 1 200 ℃. At 1 300 ℃, the material is plastic with 'yield' points of 100 and 500 MPa in flexure and compression, respectively[4]. When samples with large oriented grains(2－4 mm) are tested under compression, the material exhibits macro-plasticity at room temperature by forming shear and kink bands[5]. It shows parabolic oxidation behavior in air in the temperature range of 900－1 400 ℃ with an activation energy of 370±20 J/mol[6]. Additionally, Ti_3SiC_2 is an exceptional solid lubricant with an ultra-friction of $(2-5)\times10^{-3}$[7].

While there is general agreement regarding the attractive attributes of Ti_3SiC_2, its synthesis with both high purity and density is difficult. Although the ternary has been synthesized by CVD[8, 9], the gaseous reaction method is limited in a small-scale production. Many solid-state synthesis methods via different starting powders have been investigated in order to fabricate bulk monolithic Ti_3SiC_2. However, the solid-state synthesized Ti_3SiC_2 usually contains a small amount of TiC and/or SiC as impurities. Recently, Ranghy and Barsoum[10] successfully fabricated high-purity Ti_3SiC_2 polycrystsls by reactively hot-pressing the mixture of Ti, graphite and SiC powders, but the fabricating process was very complex. Thus further work is needed to develop new methods for the synthesis of Ti_3SiC_2. In the present research, synthesis of Ti_3SiC_2 by spark plasma sintering of the elemental powders is reported. And because Ti_3AlC_2 has the same structure and similar properties as those of Ti_3SiC_2[11], the effect of Al on the formation of Ti_3SiC_2 is especially investigated.

2 EXPERIMENTAL

Commercially available Ti, Si, Al and graphite powders were used as raw materials to synthesize Ti_3SiC_2 by spark plasma sintering. The characteristics of starting powders are listed in Table 1. The mixture with a designed composition was firstly mixed in ethanol for 24 h and then was filled into graphite crucibles with 20 mm in diameter and finally sintered in Spark Plasma Sintering System(Dr SINTER1020, Izumi Technology Co. Ltd.).

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Fig. 1 shows the schematic diagram of the system. The samples were heated at a rate of 80 ℃/min, in vacuum of 0.5 Pa, and under the pressure of 30 MPa in the preparing process. When the temperatures reached the designed sintering one, soak the sample at that temperature for 10 min. The sintering temperature ranges from 1 100 ℃ to 1 300 ℃.

Table 1 Characteristics of starting powders

Starting powder	Content/%	Average size/μm
Ti	99.0	35
Si	99.5	28
Al	99.8	40
C	99.0	2

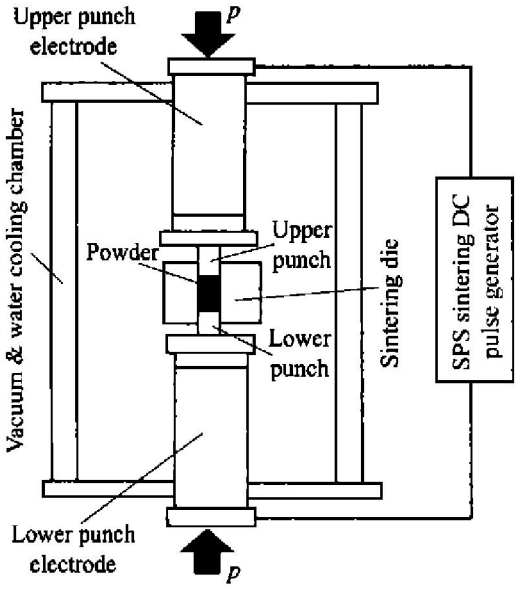

Fig. 1 Schematic of spark plasma sintering system

The sintered product was characterized by XRD method to determine the phases and lattice parameters. The lattice parameters were calculated by Rietveld analysis and measured with Si as a standard additive. The density of the sintered product was measured by Archimedes' method and compared with the theoretical density derived from the lattice constants. The measurement of its Vickers hardness was carried out at 1 N for 15 s by using a large polarizing microscope. Their chemical analyses of minerals were performed in a JEOL JCXA-733 electron-probe microanalysis (EPMA) with three wavelength-dispersive spectrometers. A scanning electronic microscope(SEM) was used to investigate the microstructure of the material.

3 RESULTS AND DISCUSSION

3.1 Effect of addition of Al on synthesis of Ti_3SiC_2

It has been reported that the purity of Ti_3SiC_2 synthesized from Ti/Si/C powders was very sensitive to the discrepancy from its stoichiometric composition. The deficiency of Si usually favors the formation of TiC[12, 13]. The loss of Si might occur by evaporation as the sample fired in Ar or vacuum, resulting in product containing quite a large amount of TiC. Li[13] synthesized high pure Ti_3SiC_2 material by using a starting composition with 20% Si more than that suggested by stoichiometry of Ti_3SiC_2. In the present research, samples with three different starting composition in molar fraction ratio (a) $x(Ti):x(Si):x(C)=3:1:2$; (b) $x(Ti):x(Si):x(C)=3:1.2:2$; (c) $x(Ti):x(Si):x(Al):x(C)=3:1:0.2:2$, were investigated. The powder mixtures were sintered in the spark plasma sintering system at 1 250 ℃ for 10 min. Fig. 2 shows the X-ray diffraction patterns of resultant products. The main phase of the samples was Ti_3SiC_2. No second phase was identified by X-ray diffraction in sample (c), but both sample(a) and sample(b) contained quite a large amount of TiC and the content of TiC in sample(a) was much higher than that in sample(b). The results confirmed our initial expectation that the addition of Al would be in favor of the synthesis of Ti_3SiC_2. Therefore, the composition of sample(c) was chosen as that of the samples used in the following experiments.

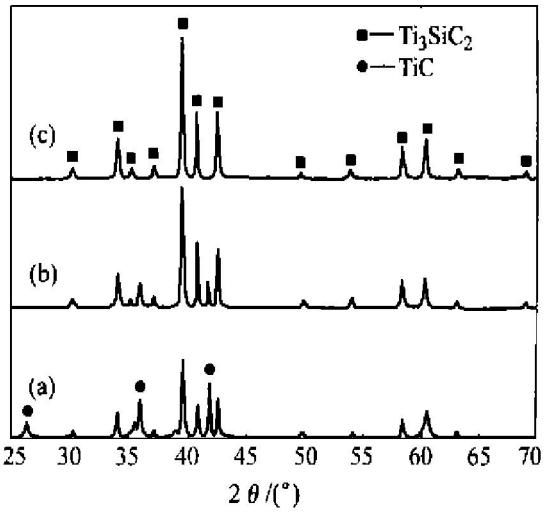

Fig. 2 X-ray diffraction patterns of resultant products sintered at 1250 ℃ from different starting compositions
(a) —$x(Ti):x(Si):x(C)=3:1:2$;
(b) —$x(Ti):x(Si):x(C)=3:1.2:2$;
(c) —$x(Ti):x(Si):x(Al):x(C)=3:1:0.2:2$

3.2 Influence of sintering temperature

Fig. 3 shows the X-ray diffraction patterns of the resultant products sintered at different temperatures. When sintered at 1 100 ℃, the product mainly consisted of Ti_3SiC_2 and TiC, which suggested that Ti_3SiC_2 formed in large quantity at that temperature, but there was still a great amount of TiC. When a sample was sintered at 1 150 ℃, the formation of Ti_3SiC_2 almost completely finished and only a very weak peak of TiC($2\theta=41.82°$)

was identified by X-ray diffraction. When sintering temperature reached at 1 200 ℃ or 1 250 ℃, no phase but Ti_3SiC_2 was identified by X-ray diffraction, which indicated that the products were pure Ti_3SiC_2. But at 1 300 ℃, TiC appeared again, and the X-ray diffraction peaks of Ti_3SiC_2 became weaken at the same time. That the appearance of TiC at 1 300 ℃ is due to eithor the decomposition of Ti_3SiC_2, or the rapid loss of Si causing the decrease of the content of Ti_3SiC_2 by evaporation in large quantities at high heating rate, is still unclear.

The measured lattice parameters of Ti_3SiC_2 solid solution were a = 0.306 9 nm, c = 1.767 0 nm, respectively, being very close to those reported by other authors[6, 7]. It was clear that the solid solution of Al in Ti_3SiC_2 barely changed the lattice parameters. The measured densities of bulk materials sintered at 1 200 ℃ and 1 300 ℃ were 4.40 and 4.43 g/cm^3, that were 97.2% and 97.9% of theoretic density of Ti_3SiC_2, respectively. It can be concluded that high pure Ti_3SiC_2 material can be synthesized by SPS from the starting powders mixtures with a molar fraction ratio x(Ti)∶x(Si)∶x(Al)∶x(C) = 3∶1∶0.2∶2.

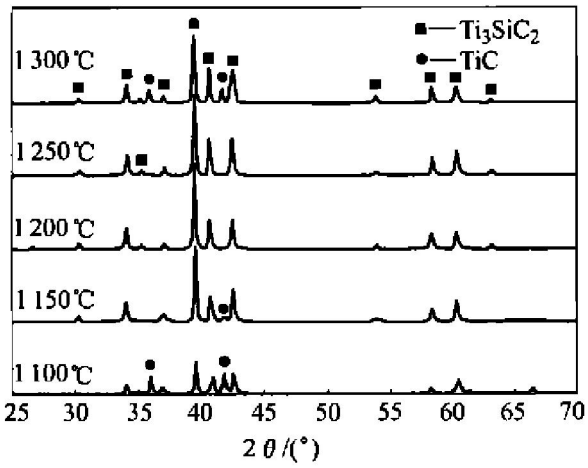

Fig. 3 X-ray diffraction patterns of resultant products sintered at different temperatures

3.3 Composition and microstructure

The sample synthesized at 1 200 ℃ was examined by EPMA. Its composition analysis was performed at 15 different positions. The results showed that x(Si)∶x(Al) (mole fraction, %) in the sample ranged from 75.6∶24.4 to 87.2∶12.8 and the average result is 80.8∶19.2, which indicated the synthesized mineral has the molecular of $Ti_3Si_{0.8}Al_{0.2}C_2$. Fig. 4 showed the SEM fractograph of samples sintered at 1 200 ℃ and 1 250 ℃, respectively, which revealed the materials consist of densely packed plane-shape grains and the maximum size in the plane of these grains is about 50 μm and the processing temperature affected the plane-shape grain size of Ti_3SiC_2.

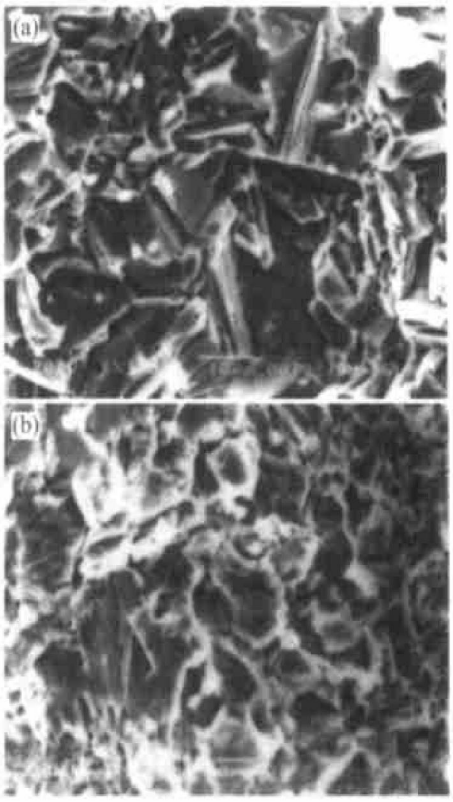

Fig. 4 SEM fractographs of Ti_3SiC_2 material synthesized by SPS
(a) —1 200 ℃; (b) —1 250 ℃

3.4 Vickers hardness and machinability

The measured Vickers hardness of the products sintered at the temperatures of 1 200 ℃ and 1 250 ℃ was in the range of 3.5 ~ 5.5 GPa, which is slightly smaller than other reported results. It is perhaps the solid solution of Al in Ti_3SiC_2 reduced its hardness. More importantly, the material has the same machinability as graphite's. It could easily be machined with ordinary machining tools, and holes could readily be drilled by using common steel drills without lubrication.

4 CONCLUSIONS

1) The addition of Al is in favor of the synthesis of Ti_3SiC_2. Pure Ti_3SiC_2 solid solution is synthesized by spark plasma sintering an elemental powder mixture with a composition of x(Ti)∶x(Si)∶x(Al)∶x(C) = 3∶1∶0.2∶2 in molar fraction ratio. The ideal synthesis temperature ranged from 1 150 ℃ to 1 250 ℃, which is the lowest temperature for fabricating pure Ti_3SiC_2 material so far.

2) The lattice parameters of Ti_3SiC_2 solid solution are a = 0.306 6 nm, c = 1.767 0 nm, respectively. The synthesized mineral has the molecular of $Ti_3Si_{0.8}Al_{0.2}C_2$. The grain is plane-shape with a maximum size in the plane of about 50 μm.

3) The obtained material has Vickers hardness of 3.

5 – 5.5 GPa and could be easily machined by using ordinary machining tools.

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