A Concurrent Process for the Synthesis and Fabrication into Rods of the Ternary Compound Ti_3SiC_2 by means of a Traveling-Zone Sintering Method

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A Concurrent process for the synthesis and fabrication into rods of the machinable ceramic Ti_3SiC_2 by using a traveling-zone sintering method was investigated. Two different powder mixtures were prepared for the synthesis of Ti_3SiC_2 . The first (TSC1) had the stoichiometric composition of $\text{Ti}/\text{Si}/\text{C} = 3:1:2$. In the second (TSC2), TiC was used instead of C to give a molar composition $\text{Ti}/\text{Si}/\text{TiC} = 2:2:3$. In the production of Ti_3SiC_2 rod from TSC1, there was a tendency for the cylindrical mold to become cracked during the sintering, because the synthesis of Ti_3SiC_2 from the simple mixture of Ti , Si and C occurred by a tandem process and the primary exothermic reaction of Ti with C to form TiC caused a large thermal expansion of the material compact. On the other hand, Ti_3SiC_2 rod was successfully produced from the TSC2 mixture. Their density was elevated as increasing the sintering temperature and reducing the rate of movement of the stage, but employing too high temperature caused a reaction between the material powder and the mold, resulting in the product having unsatisfactory properties. The Ti_3SiC_2 rod produced contained varying amounts of TiC phase, the percentage of which showed a tendency to decrease under the same sintering conditions required to obtain a high density. We concluded that a well-densified, homogeneous Ti_3SiC_2 rod with high purity can be produced by the traveling-zone sintering method under the sintering conditions of a high temperature and a prolonged sintering time, if attention is paid to preventing reaction between the material compact and the mold.

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1. Introduction

The ternary compound Ti_3SiC_2 is a relatively new material¹⁾ that combines some of the desirable engineering properties of both metals and ceramics, such as high thermal and electrical conductivities, a high thermal stability, and good corrosion resistance. More remarkable is the fact that Ti_3SiC_2 exhibits excellent machinability. The material is therefore expected to be an interesting material that could be used in high-temperature and corrosive environments.

Many studies²⁻⁵⁾ have been devoted to the synthesis of Ti_3SiC_2 . An effective and practical process for the synthesis of Ti_3SiC_2 , however, has yet to be established, because current processes for the synthesis of Ti_3SiC_2 require treatment at high temperatures for long times,³⁾ and are often accompanied by the formation of other, undesirable phases.²⁾ Recently, rapid sintering techniques called pulse discharge sintering (PDS) and spark plasma sintering (SPS) have been used in synthesis of Ti_3SiC_2 .⁶⁻¹⁰⁾ These approaches can decrease the optimum sintering temperature to below 1600 K⁹⁾ and have increased the content of the Ti_3SiC_2 phase to over 99%.¹⁰⁾

The PDS process, however, places severe restrictions on applicable product forms, as it is very difficult to maintain a uniform the sintering temperature in the production of long rods or components with irregular sectional profiles. In view of this problem, the authors have proposed a traveling-zone sintering method,¹¹⁻¹³⁾ in which the equivalent sintering temperature can be provided over the entire body of a product form, even a problematic form such as a rod or an irregularly shaped profile. In present study, a concurrent process for

synthesizing Ti_3SiC_2 and forming it into a long rod by means of a traveling-zone sintering method was investigated.¹⁴⁾

2. Experimental Procedure

Two different material powder mixtures were prepared for the synthesis of Ti_3SiC_2 . The first (TSC1) had a stoichiometric composition of $\text{Ti}/\text{Si}/\text{C} = 3:1:2$, whereas the second (TSC2), in which TiC was substituted for C , had a molar composition of $\text{Ti}/\text{Si}/\text{TiC} = 2:2:3$. All the material powders used in this study had purities of over 99% and particle sizes in the range 2–45 μm . Both TSC1 and TSC2 were prepared by mixing in air with a Turbula mixer for 86.4 ks.

Figure 1 shows the graphite cylinder used in this study. The bore diameter and the length of this cylinder were $\phi 8$ and 160 mm, respectively. As much as possible of each material powder was loaded into the cylinder, but because of the difference in their tap densities, the actual amount of material powders loaded were 10.0 g for TSC1 and 12.0 g for TSC2. When the material powder had been pre-compacted under a load of about 2 kN, the graphite cylinder was placed in the traveling-zone sintering machine and the lower end of the electrode was matched to the bottom of the material powder in the cylinder. The thickness of the electrode was 20 mm.

The sintering temperature, the sintering load, and the rate of movement of the stage were changed to examine their effects on the density and composition of Ti_3SiC_2 rod that was formed. All sintering conditions are listed in Table 1. T is the sintering temperature, F the applied load, v the rate of movement of the stage, and l the distance traveled by the stage. The sintering temperature was controlled by an infrared thermometer that was focused on the cylinder surface at the center level of the electrode. Graphite sheets

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Fig. 1 Initial settings for a traveling-zone sintering experiment.

Table 1 Traveling-zone sintering conditions for the production of Ti_3SiC_2 rods.

Sample	T (K)	F (N)	v (mm/s)	l (mm)
TSC1-1	1623	3519	0.012	45
TSC1-2	1623	3519	0.012	36
TSC1-3	1643	3519	0.012	36
TSC1-4	1643	3519	0.012	36
TSC1-5	1643	3519	0.012	36
TSC1-6	1643	3519	0.012	36
TSC1-7	1643	3267	0.012	36
TSC1-8	1643	3519	0.012	45
TSC1-9	1643	2514	0.012	45
TSC2-1	1653	3016	0.012	45
TSC2-2	1643	3519	0.012	45
TSC2-3	1623	3519	0.012	45
TSC2-4	1653	3519	0.012	45
TSC2-5	1643	3519	0.012	45
TSC2-6	1643	3519	0.010	45
TSC2-7	1643	4021	0.010	45
TSC2-8	1623	4021	0.010	45
TSC2-9	1623	4021	0.010	45

were inserted between an electrode and a cylinder for both sides to ensure those stable contact under the moving of the heating zone. All sintering tests were carried out in vacuum. The density of the sintered samples was measured by the Archimedes method. X-ray diffraction was carried out with Cu $K\alpha$ radiation at 30 kV and 40 mA for phase analysis.

3. Results and Discussion

The graphite cylinders were frequently cracked on increasing the temperature in the sintering of powder TSC1.

Fig. 2 X-ray diffraction pattern for a Ti_3SiC_2 rod produced from the TSC1 powder mixture.

This cracking originated in the central section where the material powder was placed. TSC1 consists simply of Ti, Si, and C. The synthesis of Ti_3SiC_2 from these elements is considered to occur by a tandem process. The first stage is the formation of titanium silicide (TiSi_2 or Ti_5Si_3) and titanium carbide (TiC). Ti_3SiC_2 is then synthesized from these phases. Figure 2 shows an X-ray diffraction pattern for a TSC1 sample that had caused cracking of the graphite cylinder. It can clearly be seen that the sample contained not only Ti_3SiC_2 , but also TiC. The reaction $\text{Ti} + \text{C} \rightarrow \text{TiC}$ is exothermic and generates a large amount of heat, equivalent to about 165 kJ/mol. We believe that this generated heat caused a large thermal expansion of the sample body, resulting in the fracture of the cylinder. This problem could be avoided by using a stronger cylinder with a thicker wall, but this measure would also reduce the energy efficiency of the process. It is therefore better to use a powder in which Ti and C are already combined to form TiC, rather than a simple stoichiometric mixture of Ti, Si, and C, for the synthesis of Ti_3SiC_2 by the traveling-zone sintering method, as this reduces the stresses on the mold.

Unlike the case of TSC1, no breakage failure of the cylindrical molds occurred during sintering of TSC2, even when the temperature was raised to 1653 K. Figure 3 shows the density distributions of Ti_3SiC_2 rods produced under a loading of 3519 N (70 MPa) at various temperatures. The density was generally higher near the both ends of the rods, but it remained relatively low near the central sections of each sample. The density was increased by raising the sintering temperature, but when the temperature was set to

Fig. 3 The effect of sintering temperature on the density distribution in a Ti_3SiC_2 rod produced from TSC2 powder mixture.

Fig. 4 The improvement in the homogeneity of a Ti_3SiC_2 rod by prolonging the sintering time.

1653 K, the material powder compact was becoming stuck to the mold surface as a result of a chemical reaction, resulting in prevention of its densification. It is therefore important to set the sintering temperature as high as possible while paying attention to the prevention of any reaction between the material compact and the mold.

It was not possible to obtain a homogeneous density distribution in rods produced by sintering at the highest temperature that no chemical reaction occurred between the material compact and the mold. For this reason, the sintering time was changed. The sintering time was prolonged by decreasing the rate of movement of the stage from 0.012 to 0.010 mm/s. Figure 4 shows the density distributions of Ti_3SiC_2 rods produced at 1643 K and 3519 N (70 MPa). It can clearly be seen that the density near the central section was considerably increased, and the density of the rod became more homogeneous on prolonging the sintering time. The theoretical density of Ti_3SiC_2 is $4.52 \times 10^3 \text{ kg/m}^3$. It was anticipated that the produced rod would contain some residual TiC phase with a theoretical density of $4.8 \times 10^3 \text{ kg/m}^3$, but the Ti_3SiC_2 rods produced in this study had satisfactory densities, even when this effect was taken into consideration.

Another technical factor relating to the sintering process, the effect of the sintering load, was also examined. A Ti_3SiC_2 rod was produced with an increased sintering load of 4021 N (80 MPa), while the temperature and the rate of movement of the stage were held at the optimum conditions of $T = 1643 \text{ K}$ and $v = 0.010 \text{ mm/s}$, respectively. These sintering conditions, unfortunately, brought about a chemical reaction between the material and the mold, causing deterioration in the homogeneity of the Ti_3SiC_2 rod produced. This showed that an increase in the sintering load promotes the chemical reaction, even though the same sintering temperature was used. These results show that the sintering temperature and the sintering load must be set to the highest possible values that do not lead to a reaction between the material powder compact and the mold, and that an extended processing time should be used to produce well-densified, homogeneous Ti_3SiC_2 rods by the traveling-zone sintering process.

In the production of a Ti_3SiC_2 rod, the purity of the product is important in addition to its density. Unfortunately, a

Fig. 5 An example of an X-ray diffraction pattern for a Ti_3SiC_2 rod produced from the TSC2 powder mixture.

Table 2 The effect of the sintering conditions on the TiC phase content.

T (K)	F (N)	v (mm/s)	I_{TSC} (counts)	I_{TC} (counts)	W_{TSC} (%)	W_{TC} (%)
1643	3519	0.012	312.00	176.00	76.14	23.86
1643	3519	0.010	486.20	114.75	88.41	11.59
1643	4021	0.010	436.57	104.07	88.31	11.69
1623	4021	0.010	508.52	147.56	86.12	13.88

residual TiC phase was present in all the Ti_3SiC_2 rods produced from the TSC2 powder mixture. Figure 5 shows an example of an X-ray diffraction pattern for one of these rods. The pattern clearly shows main peaks for Ti_3SiC_2 (104) and TiC(200). The relative mass fractions of Ti_3SiC_2 (W_{TSC}) and TiC (W_{TC}) in a Ti_3SiC_2 -TiC two-phase material are calculated according to the following equations:⁸⁾

$$W_{\text{TSC}} = K / (K + I_{\text{TC}} / I_{\text{TSC}}), \text{ and}$$

$$W_{\text{TC}} = (I_{\text{TC}} / I_{\text{TSC}}) / (K + I_{\text{TC}} / I_{\text{TSC}}),$$

where I_{TSC} and I_{TC} are the integrated diffraction intensities of Ti_3SiC_2 (104) and TiC(200), respectively. K is a constant that is equal to 1.8 in this case. Table 2 summarizes the correlation between sintering conditions and the mass fraction of residual TiC. The amount of residual TiC decreased with increasing sintering time and increasing sintering temperature, but was not affected by the sintering load.

It is desirable that no TiC phase, which causes a deterioration in the machinability, is retained in the final rod. In fact, TSC2 did not have the stoichiometric composition of $\text{Ti/Si/C} = 3:1:2$. The stoichiometric composition, including TiC, is Ti/Si/2TiC . However, it has been reported¹⁰⁾ that the Ti_3SiC_2 content in sintered product is improved by changing the material composition from Ti/Si/2TiC to 2Ti/2Si/3TiC . More-precise adjustment of the material composition might improve the Ti_3SiC_2 phase purity.

4. Concluding Remarks

In this study, a concurrent process for the synthesis of Ti_3SiC_2 and its fabrication into a rod by using the traveling-zone sintering method was examined. Guidelines for the successful production of a Ti_3SiC_2 rod are summarized as follows.

- (1) It is better to prepare a material powder mixture containing preformed TiC to reduce the load on the mold during sintering.
- (2) The density of the Ti_3SiC_2 rod increases with increasing sintering temperature and increasing sintering time; however, employing too high a sintering temperature sometimes leads to a chemical reaction between the material compact and the mold. It is important to prevent this reaction in order to produce a homogeneous Ti_3SiC_2 rod by the traveling-zone sintering method.
- (3) The amount of residual TiC phase in the Ti_3SiC_2 rods is decreased by adopting the same sintering conditions as those required to improve the density. Well-densified, homogeneous Ti_3SiC_2 rods with smaller amounts of TiC phase can be produced by the traveling-zone sintering method under the sintering conditions of a high temperature and a long sintering time, paying attention to the prevention of reaction between the mold and the material compact.

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