Fabrication of Functionally Graded Ti_3SiC_2 -TiC Binary-Phase Material

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Ti_3SiC_2 -TiC binary-phase material was investigated with the aim of developing a new hard product. The starting material for the synthesis was prepared by compounding raw powders of Ti, Si and TiC at molar ratios of 1:1: x ($x = 1.8$ – 7.0). The products were synthesized by sintering and the structures of the samples produced were examined. The product obtained was single-phase Ti_3SiC_2 when x was 2.0 or less and a Ti_3SiC_2 -TiC binary-phase structure when x was more than 2.0. The mass fraction of TiC in the binary-phase structure increased with increasing x . The optimum sintering temperatures for densification were different for the different synthesized structures: the Ti_3SiC_2 single-phase structure was well densified at up to 1673 K, whereas higher temperature was required to densify the Ti_3SiC_2 -TiC binary-phase structure. These results suggest the possibility of producing Ti_3SiC_2 -TiC functionally graded materials. The traveling-zone sintering method permits integrated sintering of materials at variable temperatures. Powder mixtures with TiC contents from 1.8 to 7.0 mole were layered in the same mold and sintered at variable temperatures from 1643 to 1733 K. The synthesized structure was successfully graded, as in the case of individual synthesis of each of the compounds. The hardness of the produced sample showed a tendency to increase with increasing mass fraction of TiC. These results prove that the traveling-zone sintering method has the potential to fabricate functionally graded materials that require variable sintering temperatures. [doi:10.2320/matertrans.48.139]

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1. Introduction

Tungsten carbide is now widely used in industry to produce super-hard tools because of its excellent hardness, and it is one of the most important materials in sustaining Japanese industry. However, almost all the tungsten that is used has to be imported into Japan, and its uneven distribution as a mineral resource is a major problem for the country. Worries over the stability of future supplies of tungsten necessitate the urgent development of new hard materials as replacements for tungsten carbide.

Titanium carbide is one candidate for replacing tungsten carbide, and it has already been put into practical use as a cermet. It has, however, not yet completely replaced tungsten carbide as a super-hard material because of problems of thermal shock and high-temperature plasticity. It is therefore necessary to develop better binder systems to improve the performance of TiC-based hard materials.

The ternary-phase compound Ti_3SiC_2 , which combines the good engineering properties of both metals and ceramics, has been recently discovered.¹⁾ This relatively new material shows high thermal and electric conductivities, a high thermal stability, good corrosion resistance, and excellent machinability, and is therefore expected to be useful as an engineering material. Several studies^{2–5)} have been made on the synthesis of Ti_3SiC_2 , and it has been reported^{6–10)} that the pulse discharge sintering (PDS) process is effective in the synthesis of high-purity Ti_3SiC_2 . It has been also reported¹¹⁾ that the structure of synthesized Ti_3SiC_2 is sensitive to the compounding ratio of the raw material powder mixture of Ti, Si, and TiC. Insufficient TiC in the compound left some titanium sulfide in the structure, whereas single-phase Ti_3SiC_2 was successfully synthesized from mixtures of Ti/Si/TiC in ratios of 1.0:1.0:1.6–1.8. These results suggest that

larger ratios of TiC in the formulation would give Ti_3SiC_2 -TiC binary-phase material.

With the aim of developing a new hard product, we examined the relationship between the mixing ratio of the raw material powder and the structure of the synthesized Ti_3SiC_2 -TiC binary phase.¹²⁾ The effect of the mass fraction of TiC in the Ti_3SiC_2 -TiC binary-phase material on its hardness was examined. We also examined the functional grading of Ti_3SiC_2 -TiC binary-phase material to give it interesting properties, such as a combination of a high hardness from a TiC-rich structure and excellent machinability from the presence of Ti_3SiC_2 , by utilizing the ability of the traveling-zone sintering method^{13–15)} to sinter materials with a variable temperature distribution.

2. Experimental Procedure

Ti, Si, and TiC powders were used to synthesize the Ti_3SiC_2 -TiC two-phase material. All the material powders used had purities of over 99% and particle sizes in the range 2–45 μm . The stoichiometry of the reaction between the three raw material powders is as follows:

According to this equation, single-phase Ti_3SiC_2 will be obtained from a mixture of Ti, Si, and TiC in a molar ratio of 1:1:2, whereas a Ti_3SiC_2 -TiC binary-phase structure will be produced from mixtures with higher contents of TiC. Therefore, several powder mixtures with fixed Ti/Si molar ratios of 1.0 and variable TiC molar ratios of 1.8–7.0 were prepared, as shown in Table 1. Each powder mixture was sintered individually in the temperature range 1643–1733 K to examine the effects of the mixing ratio on the structure of the product. As shown in Fig. 1, integrated sintering of layered material powders was also carried out to produce a functionally graded Ti_3SiC_2 -TiC rod by a traveling-zone

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Table 1 Compounding conditions for raw material powder mixtures.

Powder	Compounding ratio			Stoichiometric synthesis	
	Ti, mol	Si, mol	TiC, mol	Ti ₃ SiC ₂ , mol	TiC, mol
TSC18	1.0	1.0	1.8	1.0	
TSC20	1.0	1.0	2.0	1.0	0.0
TSC25	1.0	1.0	2.5	1.0	0.5
TSC30	1.0	1.0	3.0	1.0	1.0
TSC35	1.0	1.0	3.5	1.0	1.5
TSC40	1.0	1.0	4.0	1.0	2.0
TSC45	1.0	1.0	4.5	1.0	2.5
TSC50	1.0	1.0	5.0	1.0	3.0
TSC55	1.0	1.0	5.5	1.0	3.5
TSC60	1.0	1.0	6.0	1.0	4.0
TSC65	1.0	1.0	6.5	1.0	4.5
TSC70	1.0	1.0	7.0	1.0	5.0

Fig. 1 Schematic illustration of powder loading to produce a functionally graded Ti₃SiC₂-TiC binary-phase material.

sintering method, as previously proposed.^{13–15)} A mold was charged with 4.5 g of TSC18 (see Table 1) at first and 0.5 g of each of the other raw material powders, from TSC20 to TSC70, was stacked sequentially on top of it. The raw material mixtures were subjected to different sintering temperatures: TSC18 and TSC20 were sintered at 1643 K, whereas other mixtures were sintered at 1733 K. The rate of movement of the stage was set at 0.01 mm/s.

All the sintering tests were carried out in a vacuum of about 5 Pa. The graphite mold used for the sintering had a bore diameter of $\phi 8$ mm. The density of the sintered samples was measured by the Archimedes method. The hardness was measured by using a Vickers hardness tester under a load of 9.8 N with a holding time of 15 s. X-ray diffraction studies for phase analysis were carried out with Cu K α radiation at 30 kV and 40 mA.

3. Results and Discussion

Figure 2 shows the X-ray diffraction patterns for the structures obtained by sintering of the individual powder mixture. It is obvious that single-phase Ti₃SiC₂ was obtained when x , the molar proportion of TiC, was 2.0 or less, whereas a Ti₃SiC₂-TiC binary-phase structure was obtained when x exceeded 2.0. The peak intensity of TiC rose with increasing

Fig. 2 X-ray diffraction patterns of Ti₃SiC₂-TiC binary-phase materials. Fig. 3 TiC mass fraction of Ti₃SiC₂-TiC binary-phase materials synthesized from various material powder mixtures.

x , as expected from eq. (1). The relative mass fractions of Ti₃SiC₂ (W_{TSC}) and TiC (W_{TC}) in a Ti₃SiC₂-TiC binary-phase material can be calculated according to the following equations,⁸⁾

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

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

where I_{TSC} and I_{TC} are the intensities of the Ti₃SiC₂(104) and TiC(200) peaks, respectively. K is a constant, equal to 1.8 in this case. Figure 3 shows the TiC mass fraction calculated from eq. (2) plotted against the molar ratio of TiC in the material powder mixture. The solid line is a least-square approximate curve, and the broken curve is the stoichiometric estimate from eq. (1). It can be seen that the experimental values fall slightly below those predicted from the stoichiometric calculation. This discrepancy has not yet been clearly explained, but it is possible that it is a result of

Fig. 4 The relation between the sintering temperature and the density of synthesized Ti_3SiC_2 -TiC binary-phase materials.

Fig. 5 The effect of the proportion of TiC in the material powder mixture on the Vickers hardness.

the partial formation of a solid solution. In any case, it was confirmed that the mass fraction of TiC in the synthesized binary-phase structure can be controlled by adjusting the proportion of TiC in the raw material powder.

Figure 4 shows the relation between the sintering temperature and the density of the synthesized body. Single-phase Ti_3SiC_2 ($x = 1.8$) was satisfactorily densified at up to 1673 K, whereas the sintering temperature had to be increased to 1733 K to obtain a fully densified Ti_3SiC_2 -TiC binary-phase ($x = 2.5$) structure. Other Ti_3SiC_2 -TiC binary-phase materials synthesized from TSC30 to TSC70 mixtures were also fully densified at 1733 K. We therefore recommend this sintering temperature for the synthesis of Ti_3SiC_2 -TiC binary-phase materials, regardless of their phase ratio. The effect of the molar proportion of TiC in the initial powder mixture on the Vickers hardness of the product is shown in Fig. 5. The hardness generally increased with increasing proportions of TiC in the powder mixture, although some dispersion was observed.

These results suggest the possibility of producing a functionally graded Ti_3SiC_2 -TiC binary-phase material. Such a material would combine the properties of a high hardness, as a result of the TiC-rich structure, and excellent machinability, as a result of the presence of Ti_3SiC_2 , making it useful in industry. For example, a functionally graded Ti_3SiC_2 -TiC rod with a very hard tip combined with an easily machinable body could be useful as a cutting tool.

Functionally graded materials have been produced by sintering processes, but it is very difficult to achieve

Fig. 6 The transition in TiC mass fraction in a synthesized functionally graded Ti_3SiC_2 -TiC rod.

Fig. 7 The density distribution in a functionally graded Ti_3SiC_2 -TiC rod.

intentional temperature differences within a material powder compact during sintering by conventional processes because during such processes the entire compact body is heated at the same time. However, the traveling-zone sintering method,¹³⁻¹⁵ in which a limited heating zone is moved through a mold, permits the precise control of the sintering temperature at any position within the mold and enables sintering to be performed with a variable temperature distribution.

Figure 6 shows the changes in the mass fraction of TiC in a synthesized functionally graded Ti_3SiC_2 -TiC rod. The abscissa of this figure represents the distance from the end of the TSC18 side. The rod was 43-mm long, and it was estimated that 4.5 g of TSC18 accounted for nearly 20 mm of this length, and 0.5 g portions of the other material powders (TSC20-70) each corresponded to a 2.1-mm long segment. It can be seen that nearly all the first 20 mm of the rod consisted of single-phase Ti_3SiC_2 , but subsequently a TiC structure appeared; the proportion of TiC increased with approaching to the other end of the rod. The broken curve shows a least-squares approximation of the results from individual syntheses from each raw material powder. We consider that the two series of results correspond well with each other. We therefore concluded that the traveling-zone sintering method enables the integral production of a functionally graded material that requires a varying sintering temperature.

The density distribution of the functionally graded Ti_3SiC_2 -TiC rod is shown in Fig. 7. The Ti_3SiC_2 -TiC rod was cut in widths that were nearly equivalent to each of the

Fig. 8 The distribution of the Vickers hardness within a functionally graded Ti_3SiC_2 -TiC rod.

raw material powders and the density was measured for each fraction. The broken curve in this figure indicates the estimated density, calculated by the rule of mixtures from the theoretical densities of Ti_3SiC_2 ($4.52 \times 10^3 \text{ kg/m}^3$) and TiC ($4.92 \times 10^3 \text{ kg/m}^3$). The experimental results generally correspond to the calculated values, although some dispersion is observed. This dispersion might be caused by a chemical reaction between the raw material powder compact and the graphite mold, leading to sticking to the mold, since a rather high sintering temperature (1733 K) was employed in this synthesis. It is possible that this chemical reaction may have hampered the densification of the rod, especially near its central section.

Figure 8 shows the Vickers hardness measured for each fraction cut from a Ti_3SiC_2 -TiC functionally graded rod, produced as described above. The broken curve was calculated by the rule of mixtures for the individual hardness values for Ti_3SiC_2 (4 GPa) and TiC (31 GPa), as in the case of Fig. 7. It can be seen that the hardness values near the two ends were close to the calculated values, and the hardness attained the same value as that of tungsten carbide near the TiC-rich end, where the mass fraction of TiC was about 56%. However, the hardness remained relatively low in the central section, where the molar proportion of TiC in the raw material powder was between about 4.0 and 6.0. It is possible that the mechanical properties of the binary-phase material are dominated by the Ti_3SiC_2 structure, which is not so hard, and that the rule of mixing does not apply in this range, but the details are not yet clear. An unsatisfactory density distribution may be another influencing factor. It will be necessary to produce a well-densified functionally graded Ti_3SiC_2 -TiC rod in order to evaluate its mechanical properties properly. For the sake of improving the quality, it will be important to employ better sintering conditions that do not cause sticking between the mold and the material powder compact during sintering.

4. Concluding Remarks

In this study, Ti_3SiC_2 -TiC binary-phase material was

examined as a possible new hard material and the traveling-zone sintering method was used to produce a functionally graded material. The principal results are summarized as follows.

- 1) A Ti_3SiC_2 -TiC binary-phase structure was obtained by sintering of a powder mixture consisting of Ti, Si and TiC. The mass fraction of TiC in the binary-phase sintered product could be controlled by adjusting the proportion of TiC in the raw material powder mixture.
- 2) The traveling-zone sintering method enabled the integral sintering of the raw material powders that required different sintering temperatures. A functionally graded rod comprising both a Ti_3SiC_2 single-phase and a graded Ti_3SiC_2 -TiC binary-phase in the same body was successfully produced by this process.
- 3) The hardness of the functionally graded rod that was obtained increased as the mass fraction of TiC in the structure increased, and it attained to the same level as that of tungsten carbide near the end of the rod, where the mass fraction of TiC was about 56%.

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