Synthesis of TiB2-Ti3SiC2 Composites by Reactive Hot Pressing of B4C-SiC-Ti Powder Mixtures

Hitoshi Taimatsu1, Shigeaki Sugiyama2 and Shuhou Koseki1,*

1Department of Materials Science and Engineering, Faculty of Engineering and Resource Science, Akita University, Akita 010-8502, Japan
2Akita Prefectural Research and Development Center, Akita 010-1623, Japan

TiB2-TiC-Ti3SiC2 composites were reaction-sintered from B4C-xSiC-(3 + 2x)Ti (x = 0 to 1) powder mixtures using reactive hot pressing, and the phase relation of reaction products and sintering behavior were investigated. The reaction B4C + xSiC + (3 + 2x)Ti → 2TiB2 + (1 – x)TiC + xTi3SiC2 proceeded fundamentally during hot pressing. Although the reaction demands no production of TiC phase at x = 1, TiC phase was formed due to the nonstoichiometry of TiC and Ti3SiC2 phases produced. The hot-pressed composites containing the layered compound Ti3SiC2 had no preferential texture. Both TiB2 and TiC were first produced near 960°C during heating, and then Ti3SiC2 near 1200°C. The product Ti3SiC2 contributed effectively to the densification of the composites above 1450°C.

[doi:10.2320/matertrans.MRA2008174]

(Rceived May 30, 2008; Accepted July 10, 2008; Published August 20, 2008)

Keywords: titanium boride, titanium carbide, titanium silicon carbide, reaction sintering, solid state reactions

1. Introduction

Titanium boride and carbide, TiB2 and TiC, are very hard and chemically stable compounds with good electrical conductivity like WC. If they can be consolidated easily, their use will increase as hard engineering ceramics possible to be readily formed using electro-discharge machining. Unfortunately their sinterability is so bad that they can not be easily sintered even by hot pressing. For TiB2-TiC composites, however, a reactive hot pressing technique can be applied. Barsoum et al.1) and Brodkin et al.2) obtained dense TiB2-TiC composites at 1600°C using the reactive hot-pressing of B4C and Ti powder mixtures, in which the displacement reaction B4C + 3Ti → 2TiB2 + TiC proceeded. This sintering temperature is much lower than that in the ordinary hot pressing of TiB2 and TiC powder mixtures.4) We also successfully applied basically the same technique to prepare dense composites of TiB2-TiC,3) B4C-TiB2-TiC5) and TiB2-TiC(C, N).6) Thus the reactive hot pressing accompanying by the solid state reaction is very effective for the consolidation of TiB2-TiC ceramics.

Titanium silicon carbide, Ti3SiC2, have been drawn attention as a machinable ceramic.8,9) This ceramic, which is a layered compound with a hexagonal crystal structure, is deformable at high temperatures and resistant to thermal shock.10–12) Because of these properties, Ti3SiC2 addition to improve fracture toughness of ceramics has been investigated.13–15) However, these properties also propose a use of Ti3SiC2 as a ceramic sintering aid for the hot pressing of difficultly sinterable ceramics. When B4C-SiC-Ti powder mixtures are used as the starting powder and the reaction B4C + xSiC + (3 + 2x)Ti → 2TiB2 + (1 – x)TiC + xTi3SiC2 is allowed to proceed during hot pressing, TiB2-TiC-base ceramics may be consolidated at lower temperatures because of the displacement reaction and the deformable product Ti3SiC2. Furthermore, these ceramics probably promise to have better properties in oxidation resistance as well as in fracture toughness, because Ti3SiC2 is much more oxidation-resistant than TiC.16) In this study, therefore, we intended to prepare dense TiB2-TiC-Ti3SiC2 ceramics by the reactive hot pressing of the B4C-SiC-Ti powder mixtures. Reaction products and microstructure were measured for sintered bodies, and the phase relation of the reaction products and sintering behavior were investigated.

2. Experimental

The starting materials for reaction sintering were B4C powder (Rare Metallic, average particle diameter 1.05 μm, purity 99 mass%, B/C molar ratio 4.0), SiC powder (Ibiden, average particle diameter 0.31 μm, impurities (mass%): free SiO2 0.39, free C 1.08, total Al 0.0153, total Fe 0.0173, H2O 0.20) and Ti powder (Rare Metallic, average particle diameter 24.5 μm, purity 99.5 mass%). These powders were weighed and mixed in an Al2O3 mortar at ratios to produce TiB2-TiC-Ti3SiC2 composites in accordance with the reaction

\[
\begin{align*}
B_4C + xSiC + (3 + 2x)Ti &\rightarrow 2TiB_2 + (1 - x)TiC + xTi_3SiC_2 \quad (x = 0 \text{ to } 1)
\end{align*}
\]

during reactive hot pressing. Since both the TiC and Ti3SiC2 practically have nonstoichiometry as described later, precise quantity of each product does not obey eq. (1). The mole fractions of the reactants are 1/(4 + 3x) for B4C, x/(4 + 3x) for SiC and (3 + 2x)/(4 + 3x) for Ti.

The powder mixture was pressed at 50 MPa in a graphite die with an inner diameter of 20 mm and outer diameter of 50 mm. The powder compact was sintered in the die using a resistance-heated hot-pressing system (the Spark-Plasma Sintering Machine, Sumitomo Coal Mining, SPS-2080) in a vacuum under the following conditions: sintering temperature 2000°C for x = 0, 1600°C for x = 0.1 to 0.5 and 1500°C for x = 0.5 to 1; heating rate 50°C min⁻¹; applied pressure 50 MPa; holding time at each sintering temperature...
10 min. The temperature was measured 10 mm inside the outer surface of the die (5 mm outside the sample) through a small hole using an optical pyrometer. The displacement of a pressing ram was monitored during heating. The decrease in length per unit length of a sample for a temperature rise of 1°C, i.e., the shrinkage coefficient of the sample, was calculated from net displacement obtained by correcting measured displacement for the expansion of load train spacers and work punches during heating. Sintered bodies were examined for reaction products and microstructure using a high-power X-ray diffractometer (Rigaku, RINT-2500VHF, output 18 kW, Cu Kα) and an electron probe microanalyzer (JEOL, JXA-8200), respectively. Their bulk density was measured by the Archimedean method.

3. Results and Discussion

3.1 Reaction products

X-ray diffraction (XRD) patterns for the sintered bodies, which were obtained from their polished surfaces perpendicular to the compression direction in hot pressing, showed that TiB₂, TiC and Ti₃SiC₂ were produced as expected in eq. (1) and that any unreacted B₂C, Ti and SiC did not remain. The XRD patterns of the composites of x = 0.3 and 1 are shown in Fig. 1. The lattice plane having the strongest reflection peak listed in the JCPDS file is (101) for TiB₂, (200) for TiC and (008) for Ti₃SiC₂. The relative intensities of diffraction peaks were very close to those in the JCPDS file for both TiB₂ and TiC, but were not for Ti₃SiC₂. In the JCPDS file, the firstly, secondly and thirdly strongest intensities for Ti₃SiC₂ are reflected from (008), (104) and (105) planes, respectively. In this study, the strongest intensity for Ti₃SiC₂ was obtained from (104) plane and the relative intensities agreed well with calculated ones based on its crystal structure. Such inconsistency with the JCPDS file in the relative intensities for Ti₃SiC₂ was found in many XRD analyses, e.g., Ti₃SiC₂ powder prepared by the reactive hotpressing of Ti, SiC and C powders showed clearly that they had no preferential texture. Tang et al. examined the effect of the glass-mounting of Ti₃SiC₂ powder samples for XRD on the change in orientation of crystallites, and pointed out that the powder samples easily formed {001} texture in the preparation because of the planner structure of Ti₃SiC₂ crystallites and that the relative intensities for a powder prepared to have randomly distributed crystal planes were in agreement with calculated ones. These facts strongly suggest that such hot pressing as that used in this study did not bring about a particular texture in a polycrystalline Ti₃SiC₂ due to applied pressure. According to Murugaiah et al., crystal grains at free surfaces of pressureless-sintered Ti₃SiC₂ easily have (008) orientation.

The relative intensity of each product, Iᵢ / ΣIᵢ, was calculated as a measure of the product concentration, where Iᵢ is the peak intensity of the strongest reflection for a product X and ΣIᵢ the sum of those for the all products. The Ti₃SiC₂ phase increased with x in eq. (1), and correspondingly the TiB₂ and TiC phases decreased, as shown in Fig. 2. Although eq. (1) demands no existence of TiC phase at x = 1, an unignorable amount of TiC was detected. TiC has wide nonstoichiometry for carbon as widely known, and Ti₃SiC₂ also is nonstoichiometric. Their nonstoichiometry requires a modification in eq. (1).

TiC can have a large carbon deficiency: δ in TiC₃ ranges from 1 to about 0.5. Storms summarized many lattice constant data of TiC₃, and concluded that the lattice constant of oxygen-free TiC increases a little with decreasing δ down to 0.8 and below this value greatly decreases with decreasing δ. Oxygen soluble in TiC lowers the lattice constant. Oxygen is an inevitable impurity in TiC under such an ordinarily-controlled atmosphere as in this work. The lattice constant of TiC phase formed in the sintered bodies is shown in Fig 3. The lattice constant slightly increased with x below x = 0.1, and above this value decreased. The lattice constant of TiC phase at x = 0, where TiC of δ = 1 must be produced, is smaller than that of oxygen-free TiC of δ = 1. This fact

![Fig. 1 X-ray diffraction patterns of the composites of x = 0.3 and 1.](image1)

![Fig. 2 Relative intensities of the reaction products TiB₂, TiC and Ti₃SiC₂.](image2)
means that TiC phase contained oxygen and its carbon content decreased with x. The lattice constants \(a\) and \(c\) of Ti\(_3\)SiC\(_2\) phase formed in the sintered bodies were not changed with x as shown in Fig. 4. The constants \(a\) and \(c\) are in agreement with the values reported by Jeitschko and Nowtony.\(^{30}\)

### 3.2 Sintering behavior

The bulk density of sintered bodies was shown in Fig. 5. Fully dense bodies were prepared at 2000\(^\circ\)C for \(x = 0\), at 1600\(^\circ\)C for \(x = 0.1\) and 0.3 and at 1500\(^\circ\)C for \(x = 0.5\) to 1. In the previous study,\(^{5}\) the powder mixture of \(x = 0\), which produced only TiB\(_2\) and TiC, requires a sintering temperature above 1800\(^\circ\)C for full densification by the reactive hot pressing. The formation of Ti\(_3\)SiC\(_2\) significantly improves the sinterability of TiB\(_2\) and TiC.

In every shrinkage coefficient curve during heating, several peaks were observed. Shrinkage coefficient curves during heating are shown in Fig. 6. There are two local maximum points \(A\) and \(C\) in the coefficient curve for \(x = 0\), where TiB\(_2\) and TiC were only produced as reaction products, and three local maximum points \(C\), \(D\) and \(E\) in the curves for \(x \geq 0.3\), where TiB\(_2\), TiC and Ti\(_3\)SiC\(_2\) were produced. The points \(A\) and \(C\) are located at the same temperature. According to the study of the solid-state reactions between B\(_4\)C and Ti powders,\(^{31}\) TiB\(_2\) and TiC are substantially produced at 1000\(^\circ\)C. In our study, temperature was measured for a graphite die. Although real sample temperature becomes higher than die temperature with increasing temperature in the resistance-heated hot-pressing system used in this study, the temperature differences is small below 1200\(^\circ\)C, e.g., 1231\(^\circ\)C at a die temperatures of 1200\(^\circ\)C.\(^{32}\) Points \(A\) and \(C\) are both located near 960\(^\circ\)C. The reaction of eq. (1) accompanies a volume reduction.
Although TiC was in fact produced more than in eq. (1), a volume reduction must occur because the molar volume of the product TiC is the smallest in the reactants and products. Hence, the shrinkage in points A and C was caused by the production of TiB$_2$ and TiC mixtures, and that in point B near 1700°C resulted from their densification.

In the synthesis of Ti$_3$SiC$_2$ from a Ti-Si-TiC powder mixture, Ti$_3$SiC$_2$ is not produced at 1000°C, but at 1100°C. 23) Gao et al. 24) reported that, in the synthesis of Ti$_3$SiC$_2$ from a Ti-Si-C powder mixture by the same hot-pressing system as in this study, a large sample volume change due to the production of Ti$_3$SiC$_2$ occurred at 1170°C during heating. These facts suggest that the shrinkage in point D near 1200°C is due to the formation of Ti$_3$SiC$_2$. The samples of $x = 0.1$ and 0.3 were fully consolidated at 1600°C, and those of $x = 0.5$ to 1 at 1500°C. Consequently, the shrinkage near point E is caused by the densification of TiB$_2$, TiC and Ti$_3$SiC$_2$ mixtures. Ti$_3$SiC$_2$ contributes to the densification of the composites above 1450°C.

### 3.3 Microstructure

The sintered bodies had characteristic morphology for microstructure, in which the shapes of starting large Ti particles remained strongly. The microstructure is shown in Fig. 7, where dark phases are TiB$_2$, grey ones TiC and white ones Ti$_3$SiC$_2$. There are Ti$_3$SiC$_2$ phases outside and inside of rings composed of very fine TiB$_2$ grains. As shown in Fig. 7(b), contacts between grains in TiB$_2$ rings are not necessarily complete. There are very thin Ti$_3$SiC$_2$ layers at interfaces between grains in many places. Many angular TiB$_2$ grains are also formed inside of TiB$_2$ rings. Most TiC phases are formed near centers of TiB$_2$ rings. As mentioned above, TiB$_2$ and TiC phases were first produced. The TiB$_2$ phases were probably formed first on the peripheries of Ti particles, and the TiC phases inside the TiB$_2$ phases forming rings. The outer diffusion of Ti through the TiB$_2$ rings, the inner diffusion of C and Si through the rings and the inner diffusion of B through the rings are needed for the respective formation of Ti$_3$SiC$_2$ outside the rings, Ti$_3$SiC$_2$ inside the rings and angular TiB$_2$ grains inside the rings.

The analysis of TiB$_2$ phases by EPMA scarcely showed solubility of Si and C. The nonstoichiometry of TiB$_2$ is small: 65.6 to 66.7 mol% B. 23) Assuming that TiB$_2$ is stoichiometric, the average composition of the total TiC and Ti$_3$SiC$_2$ phases is given by the rational formula Ti$_{0.5}$Si$_{x/2}$C$_{(1+x)/(2+4x)}$ because the equation

$$\text{B}_4\text{C} + (3 + 2x)\text{Ti} + x\text{SiC}$$

$$= 2\text{TiB}_2 + (1 + 2x)\text{Ti} + x\text{Si} + (1 + x)\text{C}$$

(2)

holds. The experimental points estimated in the Ti-Si-C phase diagram 34) are shown in Fig. 8. This diagram well explains the fact that a large amount of Ti$_3$SiC$_2$ and a small amount of TiC were formed at $x = 1$. In the diagram, a very slight amount of SiC should coexist in the composite of $x = 0.1$. In fact, any SiC phases were not detected by XRD. As the $x$ value approaches 1 in the diagram, the corresponding tie line between the Ti$_3$SiC$_2$ and TiC phases at equilibrium moves to the high carbon-deficient TiC side.

---

**Fig. 7** Microstructures (backscattered electron images) of the composites. (a): $x = 0.5$, 1500°C; (b): enlarged view of (a); (c): $x = 0.1$, 1600°C; (d): $x = 0.8$, 1600°C.
carbon content of TiC phase formed in a sintered body decreases with increasing $x$. This is consistent with the experimental results. The phase diagrams\textsuperscript{35,36} different in the constitutional range of Ti$_3$SiC$_2$ phase from the diagram shown in Fig. 8 were also presented. In these diagrams, Ti$_3$SiC$_2$ phase only must be produced at $x = 1$. This is incoherent from the results shown in Fig. 2.

4. Conclusions

The Ti$_3$SiC$_2$ phase in the TiB$_2$-TiC-Ti$_3$SiC$_2$ composites which were prepared by the reactive hotpressing of B$_4$C-Ti$_{x}$SiC$_{1-x}$Ti (x = 0 to 1) powder mixtures increased with $x$, and correspondingly the TiB$_2$ and TiC phases in the composites decreased fundamentally in accordance with the reaction B$_4$C + xSiC + (3 + 2x)Ti $\rightarrow$ 2TiB$_2$ + (1 - x)TiC + xTi$_3$SiC$_2$. At $x = 1$, however, TiC was formed due to the nonstoichiometry of TiC and Ti$_3$SiC$_2$ phases. The powder mixtures of $x \geq 0.1$ which produced Ti$_3$SiC$_2$ were fully densified by hot pressing at much lower temperatures than that producing TiB$_2$ and TiC only. No preferential texture existed in the hot-pressed composites containing Ti$_3$SiC$_2$ phase. Both TiB$_2$ and TiC were first produced near 960°C during heating, and their densification without Ti$_3$SiC$_2$ formation occurred near 1700°C. Ti$_3$SiC$_2$ phase was produced near 1200°C, and it contributed to the densification of the composites above 1450°C. The carbon deficiency of the product TiC phase was increased with $x$ because the tie line between the Ti$_3$SiC$_2$ and TiC phases at equilibrium in the Ti-Si-C phase diagram moves to the high carbon-deficient TiC side.

REFERENCES

22) A. Murugaiah, A. Souchet, T. El-Ragy, M. Radovic, M. Sundburg and
2340

H. Taimatsu, S. Sugiyama and S. Koseki