

## Formation of High-Density TiN/Ti<sub>5</sub>Si<sub>3</sub> Ceramic Composites Using Preceramic Polymer

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The formation, microstructure and properties of high-density TiN/Ti<sub>5</sub>Si<sub>3</sub> ceramic composites created by the pyrolysis of preceramic polymer with filler were investigated. Methylpolysiloxane was mixed with TiH<sub>2</sub> as filler and ceramic composites prepared by pyrolysis at 1200 °C to 1600 °C under N<sub>2</sub>, Ar and vacuum were studied. When a specimen with 70 vol.% TiH<sub>2</sub> was pyrolyzed up to 1600 °C in a vacuum after a preheat treatment at 850 °C in a N<sub>2</sub> atmosphere and subsequently heat-treated at 1600 °C for 1 h under Ar at a pressure of 2 MPa, a ceramic composite with full density was obtained. The microstructure of the ceramic composite was composed of TiN and Ti<sub>5</sub>Si<sub>3</sub> phases. Under specific pyrolysis conditions, a ceramic composite with a density of 99.2 TD%, a Vickers hardness of 18 GPa, a fracture toughness of 3.5 MPam<sup>1/2</sup>, a flexural strength of 270 MPa and a electrical conductivity of 6200 ohm<sup>-1</sup>·cm<sup>-1</sup> was obtained.

**Keywords:** ceramic, composites, sintering, mechanical properties, microstructure

### 1. INTRODUCTION

Titanium nitride has attracted a great deal of interest due to its exceptional physical and chemical properties. High hardness, good wear resistance, chemical inertness and high thermal stability are some of the excellent properties that allow it to be used as an additive and a coating on other metals and ceramics to improve their wear resistance [1,2]. Moreover, the good electrical conductivity of titanium nitride makes it a useful additive for use with other ceramic matrices to achieve conducting ceramics. However, bulk titanium nitrides have been used very little in industrial applications because of the difficulties involved in densifying them as a monolithic ceramic. The pressureless sintering of TiN requires a high temperature, which results in exaggerated grain growth and the deterioration of the mechanical properties. Moreover, the hot pressing (HP) of TiN is limited to the production of simple shapes [3,4].

Recently, the manufacturing of ceramic materials from preceramic silicon containing polymers such as polysilanes, carbosilanes, silazanes, or siloxanes has attracted interest. [5-8]. Preceramic polymers have good shaping and processing ability and can be easily changed to a ceramic at a low temperature. However, the significant shrinkage that occurs due to the increase in the density during the pyro-

lytic polymer-ceramic conversion process causes the formation of defects such as pores and cracks. Accordingly, active filler materials such as Ti, Cr, or Zr must be added to ceramic composites. [9]. The dispersion of the filler materials in the polymer precursor offers the possibility of reducing the shrinkage and porosity. Many investigations have been carried out with the goal of developing a ceramic material containing TiN using polymer pyrolysis [10-14]. However, almost all of the investigations focused only on controlling the microstructures through the regulation of the composition. They did not obtain TiN-based ceramic composites with full density by polymer pyrolysis.

The aim of this study is to develop high-density TiN based ceramic composites by the pyrolysis of preceramic polymers with an active filler.

### 2. EXPERIMENTAL PROCEDURE

Methylsiloxane (MK, Wacker, Germany) with an average molecular weight of 9,400 g/mol was chosen as the preceramic polymer precursor, and TiH<sub>2</sub> was used as the filler. Polymer/filler mixtures with an initial filler fraction of 40 vol.% to 70 vol.% and a catalyst (Aluminumacetylacetonate, C<sub>15</sub>H<sub>21</sub>AlO<sub>6</sub>) loading of 2 wt.% of the total polymer amount were prepared by the dry ball milling method for 15 h. The polymer-filler mixture powders were molded at an axial pressure of 30 MPa at 230 °C for 45 min in a metal die with a diameter of 20 mm. The compact was pre-

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heated to 850 °C at a low heating rate of 0.5 °C/min in an N<sub>2</sub> atmosphere. The preheated specimen was kept in various atmospheres at pyrolysis temperatures between 1200 °C and 1600 °C and gas pressure sintering was then carried out at a pressure of 2 MPa for 1 h.

The density of the specimens was measured by the Archimedes method. The theoretical density of the pyrolyzed specimens was determined by the pycnometric measurement of the powdered specimens. The phases were analyzed by x-ray diffraction using monochromated Cu-K $\alpha$ -radiation. The microstructures of the specimens were examined by scanning electron microscopy (SEM; S-2150, Hitachi) and transmission electron microscopy (TEM; JSM-35CF, Jeol).

The Vickers hardness (HV 112, Akashi, Japan) was measured by 10 point measurements under the conditions of a 98 N load for 20 s and the average value of eight points (excluding the maximum and minimum values) was calculated. The fracture toughness of the specimen, K<sub>IC</sub>, was measured by the Indentation Fracture (IF) method at a loading of 98 N for 20 s. The flexural strength was measured in a three-point bending test with a span length of 16 mm from rectangular bars whose surface was finished by diamond polishing. The DC-4 probe method with a Keithley 224 programmable current source meter and a Keithley 2000 multimeter was used to obtain the electrical conductivity of the specimens at room temperature.

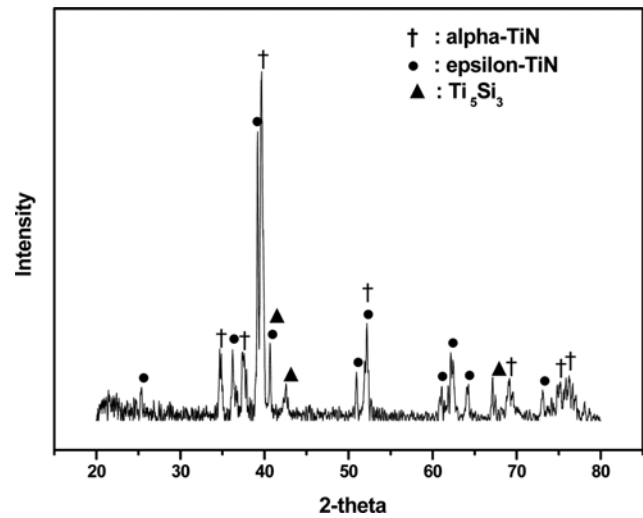
### 3. RESULTS AND DISCUSSION

Specimens with 70 vol.% TiH<sub>2</sub> were reacted first at 850 °C in an N<sub>2</sub> atmosphere and then heated to 1600 in various atmospheres. The results are summarized in Table 1. The density of the specimens depends strongly on the atmosphere during the heating process. The density of the specimens pyrolyzed in N<sub>2</sub> and Ar atmospheres was much lower than that of a specimen pyrolyzed in a vacuum, viz. 97.3 TD%.

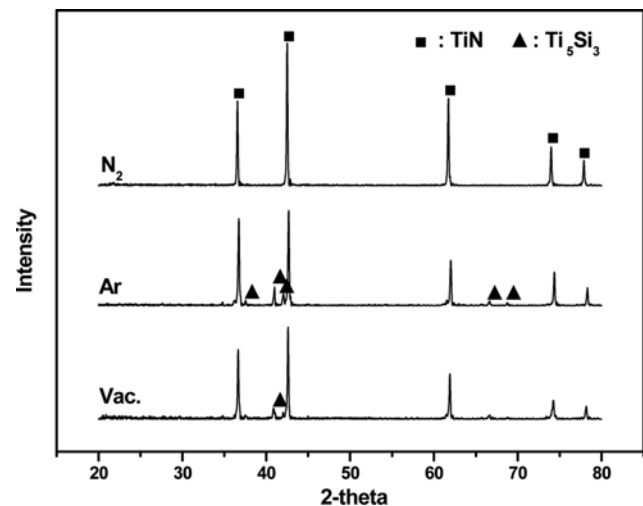
Figure 1 shows the XRD pattern of the specimen with 70 vol.% TiH<sub>2</sub> pyrolyzed at 850 °C in an N<sub>2</sub> atmosphere. During the heating process, the decomposition of the polymer started above 400 °C and was almost completed at 800 °C [15]. At 650 °C, TiH<sub>2</sub> as a filler was decomposed into titanium and hydrogen gas by an endothermic reaction. Ti from the filler reacted with the introduced N<sub>2</sub> gas and silicon derived from the polymer, forming polymorph TiN and Ti<sub>5</sub>Si<sub>3</sub> phases at 850 °C.

**Table 1.** Results of the specimen with 70 vol.% TiH<sub>2</sub> pyrolyzed at 1600 °C for 1 h in various atmospheres

Properties	Atmospheres	Nitrogen	Argon	Vacuum
Relative density (%)		82.7	83.7	97.3

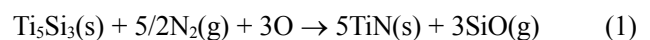


**Fig. 1.** XRD patterns of the specimen with 70 vol.% TiH<sub>2</sub> pyrolyzed at 850 °C in N<sub>2</sub> atmosphere.



**Fig. 2.** XRD patterns of the specimens with 70 vol.% TiH<sub>2</sub> pyrolyzed at 1600 °C in various atmospheres.

The XRD results of the specimen with 70 vol.% TiH<sub>2</sub> pyrolyzed at 1600 °C in various atmospheres after a pre-heat treatment at 850 °C in N<sub>2</sub> are shown in Figure 2. Only TiN phase was observed in the N<sub>2</sub> atmosphere. The alpha- and epsilon-TiN, which had formed at 850 °C, were transformed into stable TiN with a cubic structure at higher temperatures. The Ti<sub>5</sub>Si<sub>3</sub> phase reacted with the introduced N<sub>2</sub> gas and oxygen from the amorphous Si-O-C phase derived from the polymer, which resulted in the formation of TiN and SiO gas.



However, Ti<sub>5</sub>Si<sub>3</sub> phases were conserved up to 1600 °C in the Ar and vacuum atmospheres. In other works, TiC was found in an Ar atmosphere during the pyrolysis of the polysiloxane/

Ti mixture [10,11]. TiC was formed by the reaction of Ti with the hydrocarbon fragments derived during polymer pyrolysis in an Ar atmosphere. However, Ti<sub>5</sub>Si<sub>3</sub> and TiN are thermodynamically more stable than TiC [16]. It is believed that most of Ti had previously reacted with the N<sub>2</sub> and Si derived from the polymer during the preheat treatment at 850 °C in N<sub>2</sub> in our experiment. Therefore, TiC could not be formed in the subsequent treatment in the Ar atmosphere. Although the same phases were formed in the Ar and vacuum atmospheres, the density of the specimen pyrolyzed in a vacuum was higher than that of the specimen pyrolyzed in an Ar atmosphere. It is considered that the extraction of the reaction and pyrolyzed product gases from the specimen played an important role in the densification process; moreover, it is likely that a specimen with full density can be obtained through the elimination of the gases present in the specimen in a vacuum atmosphere. The gas entrapped within the pores inhibits the densification of the specimen [17].

We subsequently heat-treated the specimen, which was pyrolyzed at 1600 °C in a vacuum, at 1600 for 1 h under N<sub>2</sub> or Ar at a pressure of 2 MPa in order to achieve a much higher density. In the case of the specimens heat-treated in N<sub>2</sub>, the reaction corresponding to Eq. 1 also occurred and the relative density was consequently decreased to 84.5 % due to the larger formation of the SiO gas phase. However, there was no chemical reaction leading to the formation of other phases in the specimen pressurized by Ar gas. The relative density was increased, and a specimen with a density of 99.2 % was ultimately obtained.

Figure 3 shows the XRD analysis results of the specimen pressurized under an N<sub>2</sub> or Ar atmosphere at a pressure of 2 MPa. Only the TiN phase was observed in the N<sub>2</sub> environment. However, in the case of the specimen pressurized by Ar gas, the TiN and Ti<sub>5</sub>Si<sub>3</sub> phases were conserved.

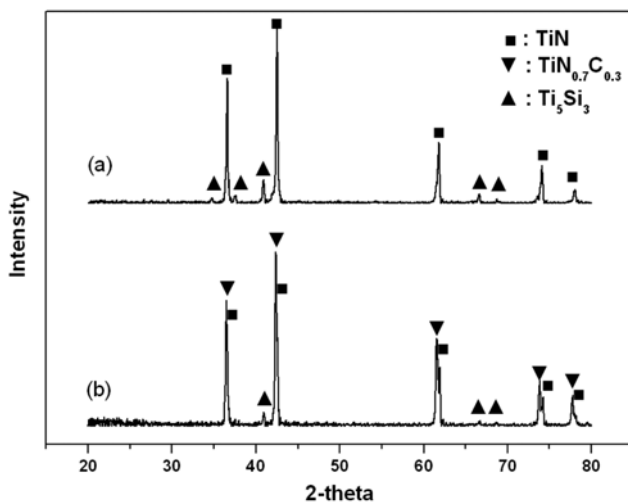
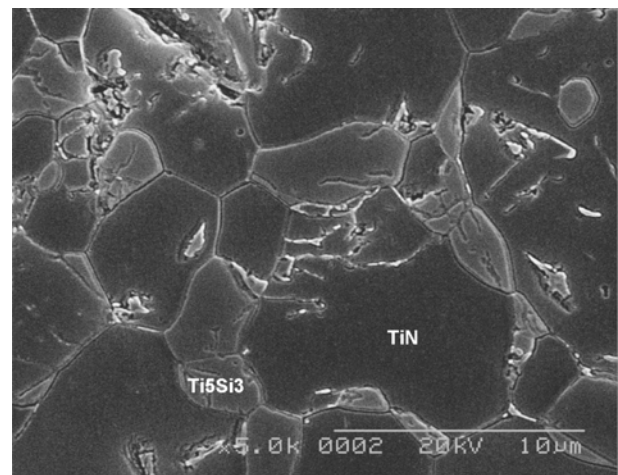


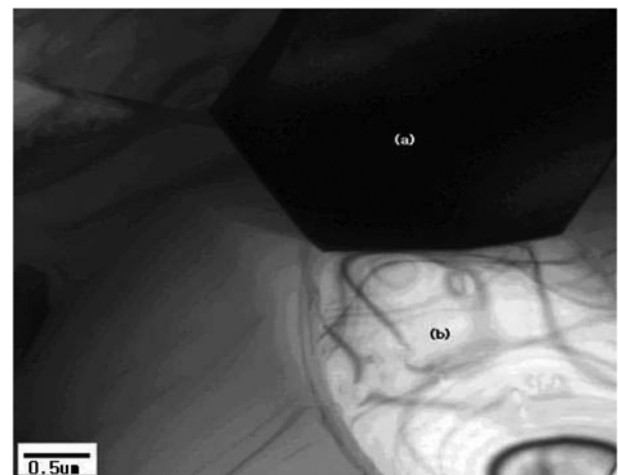
Fig. 3. XRD patterns of the specimens treated at 1600 °C for 1 h under Ar (a) and N<sub>2</sub> (b) at a pressure of 2 MPa.

Figure 4 shows SEM and TEM microphotographs of the specimen pressurized by Ar gas. Coarsened TiN and Ti<sub>5</sub>Si<sub>3</sub> particles were found in this specimen. In the TEM image, darker large TiN (a) and bright Ti<sub>5</sub>Si<sub>3</sub> particles (b) with a clear boundary were observed by EDS spectroscopy. To measure of their volume fraction, the areas of the Ti<sub>5</sub>Si<sub>3</sub> phases were calculated by an image analyzer. The presence of Ti<sub>5</sub>Si<sub>3</sub> phases with a volume fraction of 25 vol.% was confirmed in the SEM microstructures. The content of silicon of 25 vol.% Ti<sub>5</sub>Si<sub>3</sub> approximately coincided with the initial silicon content of 30 vol.% polysiloxane. This implies that the Si present in the polysiloxane was completely consumed to form Ti<sub>5</sub>Si<sub>3</sub> phases.

Various TiH<sub>2</sub> contents were studied in this experiment. However, the final density decreased with decreasing TiH<sub>2</sub> content. The amount of Ti<sub>5</sub>Si<sub>3</sub> formed also decreased with decreasing TiH<sub>2</sub> content, although the initial amount of Si was larger, due to the higher polymer content. The unreacted



(a)



(b)

Fig. 4. Microstructure of the specimen treated at 1600 °C for 1 h under Ar at a pressure of 2 MPa observed with SEM (a) and TEM (b).

**Table 2.** Properties of the TiN/Ti<sub>5</sub>Si<sub>3</sub> ceramic composite

Compositions	Properties	Flexural strength (MPa)	Fracture toughness (MPam <sup>1/2</sup> )	Vickers hardness (GPa)	Electrical conductivity (ohm <sup>-1</sup> ·cm <sup>-1</sup> )
30 vol.% Polymer 70 vol.%TiH <sub>2</sub>		270 ± 30	3.5 ± 0.3	18 ± 0.5	6200

Si-O-C phase derived from the polymer can be decomposed by carbothermal reduction at temperatures over 1400 °C, which causes a substantial increase in the porosity. It is believed that the optimum initial TiH<sub>2</sub> content for high-density TiN-Ti<sub>5</sub>Si<sub>3</sub> is achieved when the Si in the polysiloxane reacts completely with the Ti derived from TiH<sub>2</sub>.

The mechanical properties and electrical conductivity of the TiN/Ti<sub>5</sub>Si<sub>3</sub> ceramic composite are given in Table 2. A Vickers hardness of 18 GPa, a Young's modulus of 232 GPa, a flexural strength of 270 MPa and a fracture toughness of 3.5 MPam<sup>1/2</sup> were achieved. It was reported that the bending strength of Ti<sub>5</sub>Si<sub>3</sub> ceramics was 94 MPa, which is much lower than that of TiN [18]. It is considered that the lower mechanical properties of the TiN/Ti<sub>5</sub>Si<sub>3</sub> ceramic composite compared to those of TiN ceramics may be associated with the existence of the soft Ti<sub>5</sub>Si<sub>3</sub> phase. The electrical conductivity was 6200 ohm<sup>-1</sup>·cm<sup>-1</sup> at room temperature, which is also slightly lower than that of TiN (7692 ohm<sup>-1</sup>·cm<sup>-1</sup>) [19].

#### 4. CONCLUSION

TiN/Ti<sub>5</sub>Si<sub>3</sub> ceramic composites with full density were obtained from a mixture of TiH<sub>2</sub> and methylpolysiloxane. When a specimen with 70 vol.% TiH<sub>2</sub> was pyrolyzed at temperatures of up to 1600 °C in a vacuum after a preheat treatment at 850 °C in an N<sub>2</sub> atmosphere and subsequently heat-treated at 1600 for 1 h under Ar at a pressure of 2 MPa, a specimen with full density could be obtained by the extraction of the reaction gas from the pore. In this process, the TiH<sub>2</sub> content and pyrolyzing atmospheres played an important role in the densification process. The microstructures of the composites were composed only of TiN and Ti<sub>5</sub>Si<sub>3</sub> particles. Their physical properties were slightly lower than those of pure TiN due to the existence of Ti<sub>5</sub>Si<sub>3</sub> phase.

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