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Microstructure, Mechanical and Wear Properties of Hot-pressed Si_3N_4-TiC Composites

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Si_3N_4-TiC composites have been known as electrically conductive ceramics Si_3N_4-TiC composites with 2 wt% Al_2O_3 and 4 wt% Y_2O_3 were hot pressed in N_2 environment. The mechanical properties including hardness, fracture toughness, and flexural strength and tribological properties were investigated as a function of TiC content. Si_3N_4-40 vol% TiC composite was hot pressed at 1,750°C, 1,800°C, and 1,850°C for 1, 3 and 5 hours in N_2 gas. Mechanical and tribological properties depended on microstructures, which were controlled by the TiC content, hot press temperature, and hot press holding time. However, mechanical properties and tribological behaviors were degraded by the chemical reaction between TiC and N. The chemically reacted products such as TiCN, SiC, and SiO_2 were detected by the X-ray diffraction analysis.

Key words: Silicon nitride, Titanium carbide (TiC), Electrically conductive ceramics, Hot press, Tribology

I. Introduction

Silicon nitride ceramic is one of the most attractive engineering materials for high-temperature applications, because of its excellent properties such as high strength, oxidation resistance, thermal shock resistance, wear and creep resistance. However, low fracture toughness and high cost for machining limit its application .[1]

Particulate reinforcements such as SiC, BN, TiB_2 or TiN are incorporated into Si_3N_4 ceramics in order to improve mechanical properties.[2-9]

TiC has been used as a cutting tool material because of its high melting point, hardness, strength, and chemical stability. TiC powder has been added to enhance fracture toughness of the ceramics including alumina and silicon nitride.[10-12] Another advantage of Si_3N_4-TiC composite is that it can be electrical discharge machinable.[13] For brittle materials, such as Si_3N_4, wear behavior was reported to depend on inverse function of hardness and fracture toughness .[15] In this study, the mechanical and tribological properties of Si_3N_4-TiC composite were studied. Various hot pressing conditions (sintering time: 1, 3, 5 hours, sintering temperature: 1,750, 1,800, 1,850°C) were employed to find out the effect of microstructure on the mechanical and tribological properties of Si_3N_4 ceramics. The aim of this study was to find the optimum sintering condition for the mechanical and tribological properties when TiC particulates were incorporated into Si_3N_4.

II. Experimental Procedure

2.1. Specimens and apparatus

In this study, the specimens were prepared by the proce-

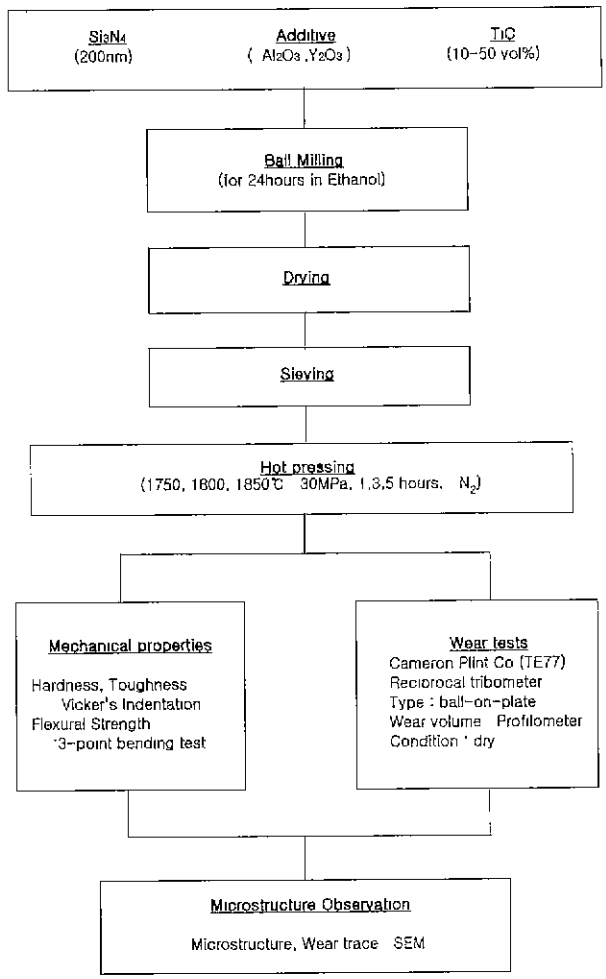

Fig. 1. Flow diagram of the experimental procedure.

Table 1. Composition and Sintering Conditions

Si_3N_4+2 wt% Al_2O_3+4 wt% Y_2O_3+TiB_2		Hot pressing conditions	
SNTB 10	10 vol% TiC	SNTB10~SNTB50	1,850°C , 30 MPa, 1 hour
SNTB 20	20 vol% TiC	SNTB 40	Variation of temperature (1,750, 1.800, 1,850°C)
SNTB 30	30 vol% TiC		
SNTB 40	40 vol% TiC		Variation of holding time (1. 3, 5 hours)
SNTB 50	50 vol% TiC		

dure shown in Fig. 1. The average particle size of silicon nitride powder (UBE E-10, Ube Ind, Tokyo, Japan) with high (-fraction was about 0.2 μm. Sintering additives were 2wt% Al_2O_3 powder (HP-DBN grade, Leynold, Philadelphia, U.S.A.) and 4wt% Y_2O_3 powder (fine grade, Hermann C. Starck Co, Berlin, Germany). Sintering conditions are shown in Table 1.

Each powder was weighed and mixed in a polyethylene bottle with high purity silicon nitride balls and ethanol, and ball milled for 24 hours. The slurry was dried using a rotary evaporator. After drying, the mixed powders were passed through a 45-mesh screen.

The mixed powders (as shown in Table 1) were hot pressed at 1,850°C for 1 hour under 30 MPa in a flowing nitrogen atmosphere. Si_3N_4-40 vol% TiC specimen was hot pressed at 1,750°C, 1,800°C and 1,850°C for 1 hour. The holding time at 1,850°C for Si_3N_4-40vol% TiC specimen were 1, 3, and 5 hours. Hot pressing temperature and pressure profiles are shown in Fig. 2. Bulk density of sample was measured by Archimedes method, and relative density of the materials was calculated according to the mixture rule. Hardness and fracture toughness of sintered samples was measured by indentation method. Indentation load was 200 N, and the duration time was 15 seconds. Fracture toughness was calculated by Evans and Charles' equation.[15] The average values of hardness and fracture toughness were obtained from 10 measurements.

For the flexural strength measurements, samples were cut into 3 mm×4 mm×35 mm dimensions. The edges of the tensile side of the fracture strength bars were chamfered at 45° using a diamond wheel. The crosshead speed was 0.5 mm/min and the span was 20 mm. All data points are averaged of at least 10 measurements. For observing microstructures, plasma etching was performed and etched samples were coated with gold. The wear track and the

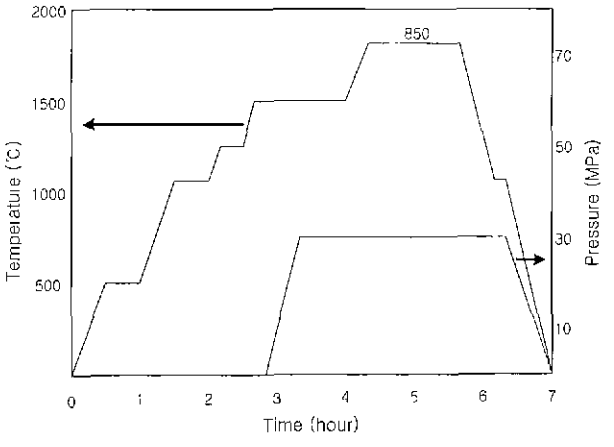

Fig. 2. Hot pressing temperature and pressure profiles.

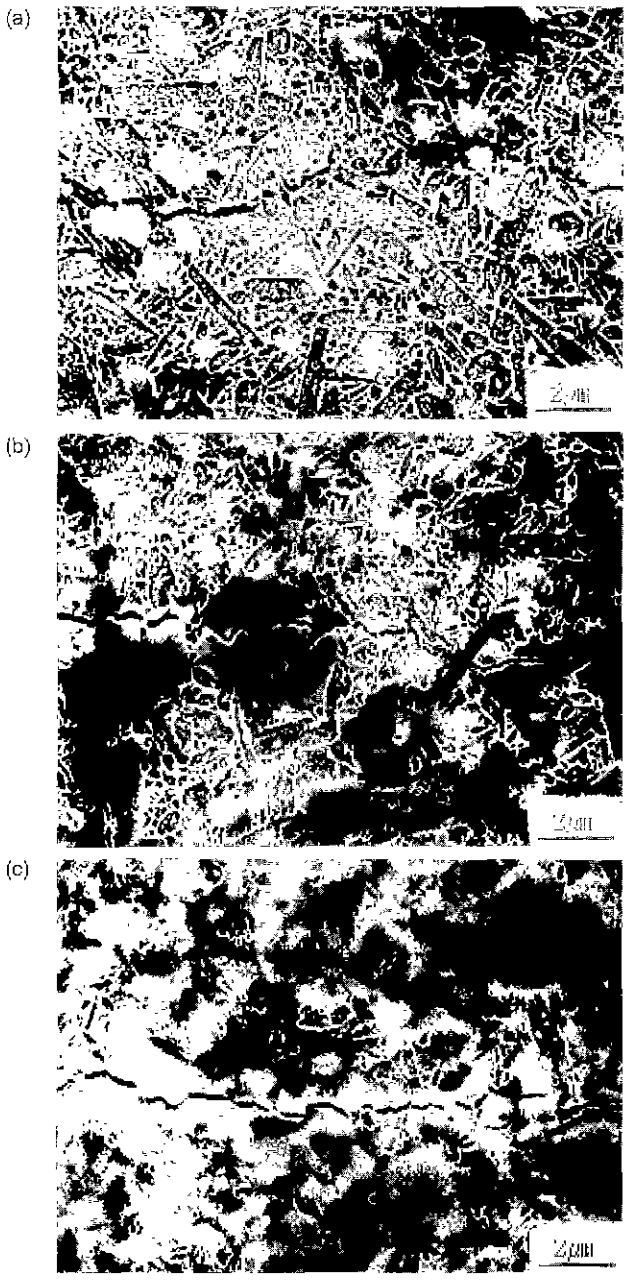

Fig. 3. SEM microstructure of the etched surface with different TiC content; (a) 10 vol%, (b) 30 vol% and (c) 50 vol%.

etched surfaces of the composites were observed by scanning electron microscopy to examine the worn surface and crack propagation.

2.2. Wear test

Friction and wear tests were performed on a reciprocating ball-on-plate tester (TE 77, Cameron Plint, Oaklands Park, U.K.). The wear sample was polishing and finished by 0.3 μm alumina paste. Specimens were cleaned by acetone and ethanol. The upper ball was silicon nitride ball. The test conditions were fixed at 10 N at sliding speed of 0.07 m/s and testing time of 1 hour, at room temperature in air. The wear volume was obtained by a profilometer (Form Talysurf Plus, Rank Talyer Hobson Co., London, U.K.). A planemeter was used to calculate wear area. Each test was repeated three times and average value of the measurements was expressed in the results.

III. Results and Discussion

3-1. Microstructure and mechanical properties

Microstructures of Si_3N_4-TiC composites were shown in Fig. 3. Grain growth of the elongated β-Si_3N_4 phase was suppressed as the TiC content increased. The number of the elongated β-Si_3N_4 grains was reduced when the TiC content increased. But the TiC particles were connected each other and grown when the TiC content increased. The indentation crack for the Si_3N_4-10vol% TiC specimen was deflected along the β-Si_3N_4 grain as well as relatively small TiC particles. While the size of TiC particles was relatively smaller, the indentation cracks were more deflected. For the Si_3N_4-30 vol% TiC specimen the indentation crack passed through the large TiC particles. For the Si_3N_4-50 vol% TiC specimen the indentation crack was propagated almost linearly. Degree of crack deflection was reduced with increasing the TiC content into Si_3N_4. Microstructures of the Si_3N_4-40 vol% TiC composite hot pressed in the temperature range from 1,750°C to 1,850°C were similar. It was showed that the size of TiC particles became bigger and the indentation crack cut through the TiC particles. In the hot press temperature range from 1,750°C to 1,850°C the growth of TiC particles was significantly influenced rather than the formation of β-Si_3N_4 phase.

Comparison of microstructures of the Si_3N_4-40 vol% TiC composites, which were hot pressed at 1,850°C for various holding times such as 1, 3, 5 hours, indicated that a number of the elongated β-Si_3N_4 phase appeared instead of the enlargement of TiC particles. The holding time at 1850°C affected the formation of β-Si_3N_4 phase, but not the growth of TiC particles. Therefore, the higher hot press temperature and the longer holding times for the electrically conductive composites may be required to the mechanical properties.

The relative densities of Si_3N_4-TiC composites were shown in Fig. 4-6. The average value of relative density was around 99.5%, which was not changed when the TiC content increased from 10 to 50 vol%. The variation of relative density of Si_3N_4-40 vol% TiC composites was shown as a function of hot press temperature was shown in Fig. 5. It was showed that the density decreased from 1,750°C, but at 1.800°C it increased again. It may be speculated that the formation of pores between the TiC particles occurred at 1,800°C. At 1,850°C the formation of the elongated β-Si_3N_4 phase may reduce the micropores. The density increased with increasing the holding time at 1,850°C, where the holding time enhanced the sinterbility, hereby the β-Si_3N_4 phase grows stably.

Variation of microhardness as a function of the TiC contents was shown in Fig. 4. It was shown that the microhardness decreased with increasing the TiC contents because the hardness of TiC is lower than that of Si_3N_4. The linked particle size of TiC is increasing with increasing the TiC content. These results made that the Hall-Petch equation can be applied to explain the deterioration in microhardness for the composites of the higher TiC content. When increasing the sintering temperature, the size of TiC particles increased and microhardness decreased as shown in Fig. 5. The longer the sintering time, the more elongated β-Si_3N_4 phase. In the case of hot pressing at 1,850°C, the holding time enhanced the formation of β-Si_3N_4 phase rather than the grain growth of TiC particles. Therefore, the microhardness increased with increasing the holding time as shown in

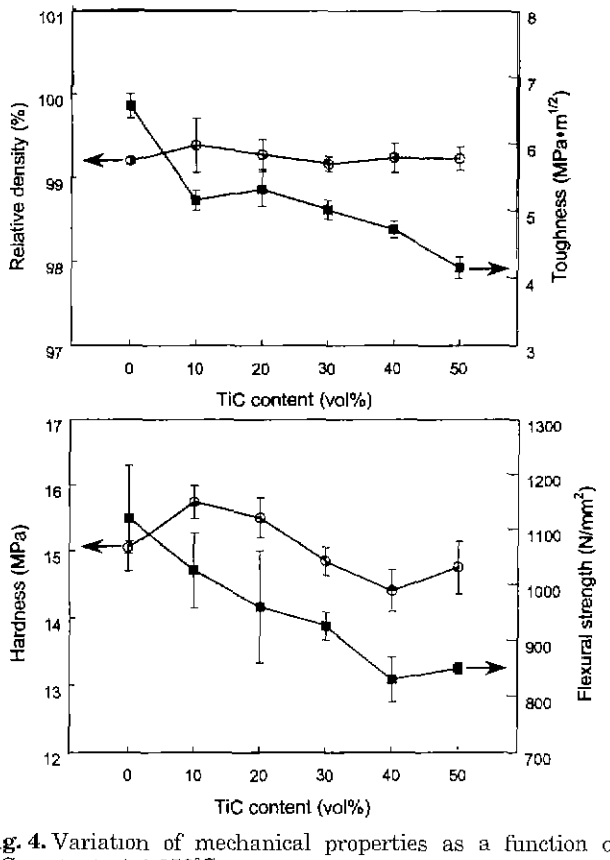

Fig. 4. Variation of mechanical properties as a function of TiC content at 1,850°C

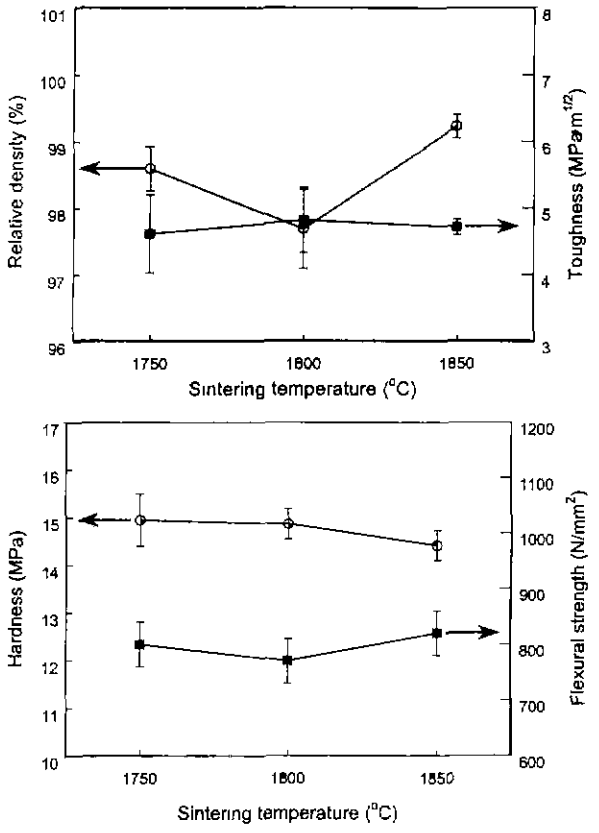

Fig. 5. Variation of mechanical properties as a function of hot press temperature for SNTC40.

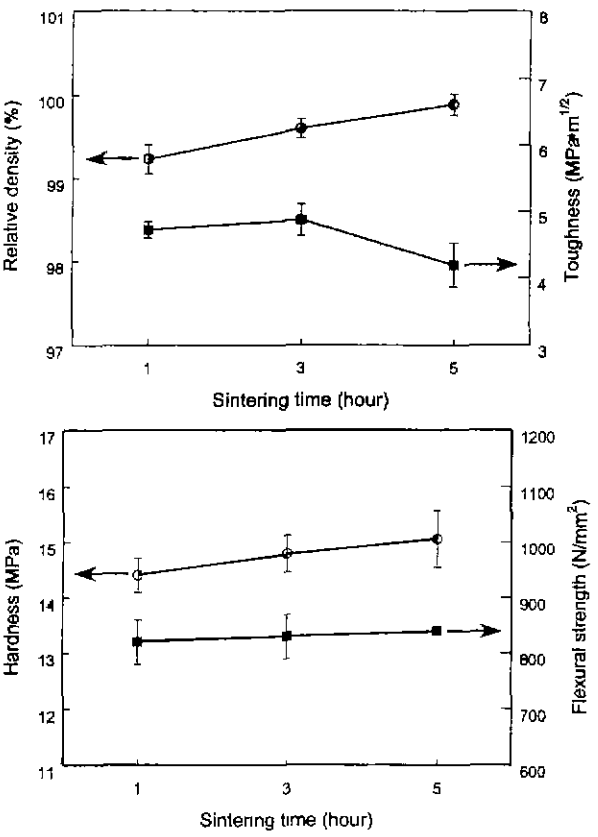

Fig. 6. Variation of mechanical properties as a function of hot press time for SNTC40 at 1,850°C.

Fig. 6.

The flexural strength of the Si_3N_4-TiC composites was also shown in Fig. 4-6. While increasing the TiC content, the flexural strength decreased. The flexural strength of the Si_3N_4-TiC composites was dependent upon the size of TiC particles. Fig. 3 showed that the size of TiC particles became larger with increasing the TiC content and the indentation cracks cut into the TiC particles rather than the β-Si_3N_4 phase. The flexural strength of the SNTC40 sample also decreased when the sintering temperature was raised from 1,750°C to 1,800°C as shown in Fig. 5. In this temperature range the TiC particle size became larger, but at 1,850°C the elongated β-Si_3N_4 phase appeared. Therefore, the crack may be deflected around the elongated β-Si_3N_4 phase. The fracture toughness is mainly dependent upon the crack bridging (or grain bridging) rather than crack deflection. The elongated β-Si_3N_4 grains increases the fracture toughness, the smaller β-Si_3N_4 grains enhances the flexural strength. In this study, the formation of small β-Si_3N_4 grain and the grain growth of TiC particles are competed each other, which can be controlled by TiC content, hot press temperature, and sintering time. The formation of the elongated β-Si_3N_4 phase governed fracture toughness of the Si_3N_4-TiC composites as shown in Fig. 5. Hereby, the smaller TiC particles causes to resist the crack propagation as shown in Fig. 4. In this study fracture toughness de-creased with increasing the TiC content, but was not influenced significantly by the sintering temperature and sintering time.

3-2. X-ray diffraction analysis

The density, the microhardness, flexural strength, and fracture toughness were dependent upon the TiC content as well as the hot press temperature and holding time. These hot pressing conditions to control the mechanical properties may cause a chemical interaction. The chemical reaction during the sintering Si_3N_4-TiC powders has been reported by the previous investigators.[16] The X-ray diffraction analyses for all specimens were carried out to determine the chemical reaction as shown in Fig. 7. The X-ray diffraction spectra showed the presence of TiCN, SiC, and SiO_2 phases. Generally chemical interaction of composites was affected by three factors[17]; (1) chemical compatibility, determined by the mutual compatibility of the composite constituents; (2) internal stability involving mainly the inherent stability of the constituents themselves or the impurities introduced during processing; and (3) environmental stability, a measure of the interactions between the constituents and the atmosphere ender the processing conditions or in actual use. Yeh and Hon[18] summarized the chemical interaction of Si_3N_4-TiC composites and drawn into two classifications. Silicon nitride does not have a real melting point but inherently decomposes to silicon and nitrogen. Carbon which is

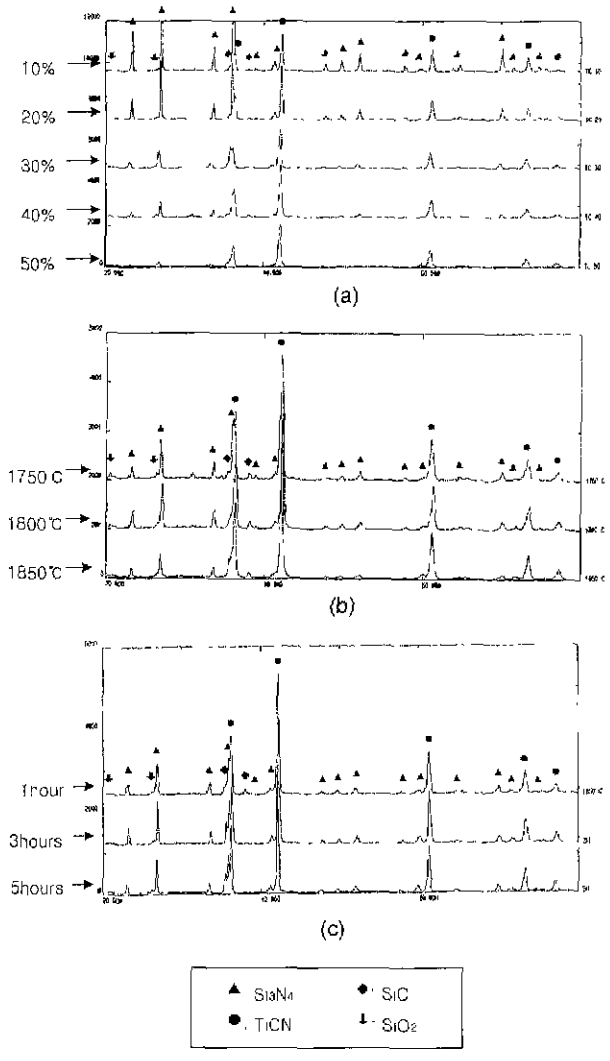

Fig. 7. X-ray diffraction patterns of Si_3N_4-TiC composities as a function of; (a) TiC content at 1,850°C, (b) hot press temperature for SNTC40 and (c) hot press time for SNTC40.

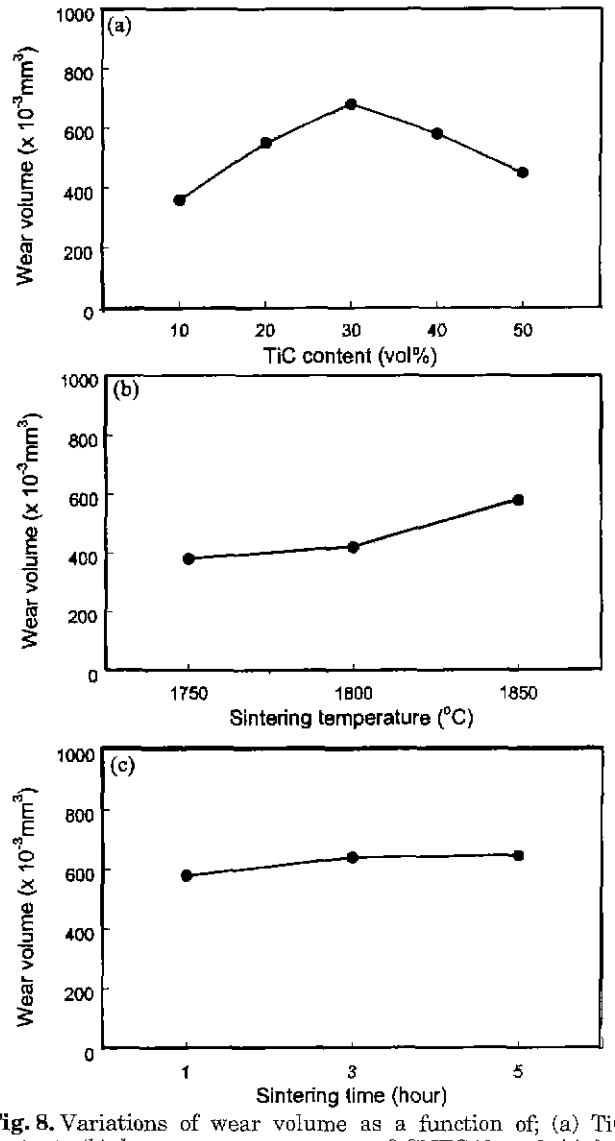

Fig. 8. Variations of wear volume as a function of; (a) TiC content, (b) hot press temperature of SNTC40 and (c) hot press time of SNTC40 at 1,850°C.

diffused from titanium carbide, which assist the decomposition of Si_3N_4 and forming the SiC.[19] Because the titanium carbide is nonstoichiometric, vacancies in its carbon sublattice can be filled by nitrogen atoms, forming a titanium carbonnitride solid solution.[20] If assuming that the titanium carbonnitride solid solution is ideal and that its lattice parameters obey Vegard's law, then the Gibbs free energy can be changed for the titanium carbonnitride formation. Therefore, the formation of SiC and TiCN as products of the chemical interaction in the Si_3N_4-TiC composites should be dependent upon the hot press temperature. The intensities of TiCN and SiC peaks in X-ray diffraction spectra increased with increasing hot press temperature as well as hot press time.

3-3. Wear property

Variation of wear volume as a function of TiC content into Si_3N_4 was shown in Fig. 8(a). Wear volume increased up to 30 vol% of TiC into Si_3N_4. And then wear volume decreased with increasing the TiC content up to 50 vol%.

The wear of the Si_3N_4-TiC composites was abrasive in its character. Since the sliding velocity is relatively small, frictional heating is negligible. There is thin wear debris layer film in the wear surface. Maybe Si_3N_4 and TiC grains of the microstructure are only slightly covered by an oxide layer thus forming the wear reducing oxide film. This tribo film forms with increasing the TiC content. However, the chemical interaction of the Si_3N_4-TiC composites is more severe when increasing the amount of TiC. Micropores around the TiC particles and Si_3N_4 grains as well as the inside of TiC particles, enhanced both of the crack formation and the propagation during sliding under the unlubricated condition. The combination of the wear reducing tribo-oxide film and the chemical interaction of the Si_3N_4-TiC composites leads a maximum in wear volume versus the TiC con-

tent.

Fig. 8(b) shows that wear volume increased when increasing the hot press temperature. The flexural strength and fracture toughness were not changed significantly with increasing the sintering temperature, however, the chemical interaction of Si_3N_4-TiC composite was more severe when increasing the sintering temperature. Therefore, wear became more severe when increasing the sintering temperature. Fig. 8(c) shows that wear volume decreases with increasing the hot press time. When increasing the hot press times, the grain size of β-silicon nitride phase was slightly bigger, but the size of TiC particles did not change much, and then the microhardness increased. Because the small β-Si_3N_4 phase formed more, the crack formation and crack propagation, which induce materials removal, were reduced during sliding under the unlubricated condition.

IV. Conclusions

Microstructure, mechanical and tribological properties of the Si_3N_4-TiC composites, which were hot pressed in N_2 environment, were investigated by varying the TiC content, hot press temperature, and hot press time

The number of the elongated β-Si_3N_4 grains was reduced, and grain growth of the elongated β-Si_3N_4 grains was suppressed as the TiC content increased. Because of the enlargement of TiC particles with increasing the TiC content, the indentation cracks cut into the enlarged TiC particles. The X-ray diffraction analysis indicated the presence of the chemical interaction of the Si_3N_4-TiC composites. The X-ray peaks of TiCN, SiC, and SiO_2 phases as the chemical reacted products were found. The tribological behaviors of the Si_3N_4-TiC composites were characterized by microstructure and mechanical properties such as flexural strength, fracture toughness as well as hardness. However, the chemical interaction of the Si_3N_4-TiC composites degraded wear properties with increasing the TiC content.

For the Si_3N_4-40 vol% TiC composite hot pressed in the temperature range from 1,750°C to 1.850°C, it was found that the size of TiC particles became larger with increasing hot press temperature and the indentation cracks cut into the TiC particles. Mechanical properties as well as wear properties were degraded with increasing the hot press temperature in N_2 environment. The higher the hot press temperature be, the more severe the chemical interaction occurs. For the Si_3N_4-40 vol% TiC composites hot pressed at 1,850°C, the longer sintering time led to the grain growth of β-Si_3N_4 grains rather than the enlargement of TiC particles. Therefore, the mechanical properties as well as wear properties were improved slightly with increasing the hot press time.

Acknowledgment

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