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Microstructure, Mechanical and Wear Properties of Hot-pressed Si_3N_4-TiB_2 Composite

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Si_3N_4-TiB_2 with 2 wt% Al_2O_3 and 4 wt% Y_2O_3 additives was hot pressed in a flowing N_2 environment with varying TiB_2 content from 10 to 50 vol%. Variations of mechanical (hardness, fracture toughness, and flexual strength), and tribological properties as a function of TiB_2 content were investigated. As the content of TiB_2 increased, relative density decreased due to the chemical reaction of TiB_2 in N_2 environment. The reduction of density causes mechanical properties to be degraded with an increase of TiB_2 in Si_3N_4. Tribological properties were dependent of microstructure as well as mechanical properties, however, they were degraded strongly by the chemical reaction of Si_3N_4-TiB_2 during hot pressing in N_2 environment. SEM and TEM observations, and X-ray diffraction analysis indicate that the chemical reaction products at the interface are TiCN, Si, and SiO_2. Also, the comparison of XRD patterns of the Si_3N_4- 40 vol% TiB_2 composites hot pressed at 1,750°C for 1 hour between in N_2 and in Ar gas was made. The XRD peaks of Si and SiO_2 were not found in Ar, but still a weak peak of TiCN was presented.

Key words: Silicon nitride, Titanium diboride (TiB_2), Composites, Hot press, Tribology, Interface

I. Introduction

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

TiB_2 powder has been added to enhance the fracture toughness of the ceramic materials such as alumina (Al_2O_3)[2-3], zirconia (ZrO_2)[4], silicon carbide (SiC)[5-6], and silicon nitride (Si_3N_4)[7-9]. It has been reported that principal mechanism for toughening in Al_2O_3-TiB_2[2] and SiC-TiB_2[5] was described as crack deflection around TiB_2 particles, and the thermal expansion difference between TiB_2 and Al_2O_3 was very small and thermal residual stress facilitating crack deflection as SiC-TiB_2 composites were not expected. There are a few reports on Si_3N_4-TiB_2 composites, which were applied to enhance the electrical discharge machinability (EDM) of the electrically insulating silicon nitride.[8] In this study, TiB_2 particles were incorporated into Si_3N_4 to enhance the mechanical and tribological properties. In the brittle materials, tribological behaviors were dependent of microstructure as well as hardness and fracture toughness.[10] Various hot pressing conditions in N_2 environment were employed to find out their effect on the mechanical and tribological properties of Si_3N_4-TiB_2 composite ceramics. The goal of this study was to investigate the optimum hot

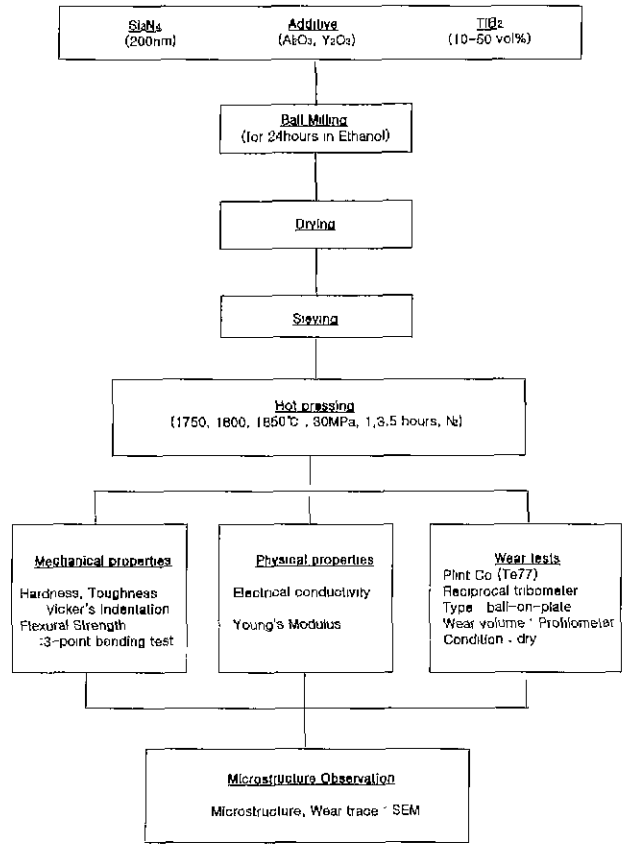


Fig. 1. Flow diagram of the experimental procedure.

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% TiB_2	SNTB10~SNTB50	1,850°C , 30 MPa, 1 hour
SNTB 20	20 vol% TiB_2	SNTB 40	Variation of temperature (1,750, 1,800, 1,850°C)
SNTB 30	30 vol% TiB_2		
SNTB 40	40 vol% TiB_2		Variation of holding time (1, 3, 5 hours)
SNTB 50	50 vol% TiB_2		

pressing condition for the mechanical and tribological properties of Si_3N_4-TiB_2 composite ceramics.

II. Experimental Procedure

2.1. Specimens

Specimens were prepared by the procedure as shown in Fig. 1. Average particle size of silicon nitride powder (UBE E-10, Ube Industries, Ltd, Tokyo, Japan) was 0.2 μm. Sintering additives were 2 wt% Al_2O_3 powder (HP-DBN grade, Leynold Co, Philadelphia, U.S.A.) and 4 wt% Y_2O_3 powder (fine grade, Hermann. C. Starck Co, Berlin, Germany). TiB_2 particle size is 0.5 μm (grade F, Hermann C. Starck Co., Berlin, Germany). Compositions and sintering condition of the specimens are shown in Table 1. Powders were weighed, mixed, and ball-milled in a polyethylene bottle with high purity silicon nitride balls in ethanol for 24 hours. The slurry was dried in a rotary evaporator. After drying, mixed powders were passed through a 45-mesh screen. Mixed powders of SNTB10-SNTB50 (in Table 1) were hot pressed at 1,850°C for 1 hour under 30 MPa in a flowing nitrogen atmosphere. SNTN40 was hot pressed at 1,750°C, 1,800°C, and 1,850°C for 1, 3, and 5 hours. Fig. 2 shows a typical hot pressing schedule.

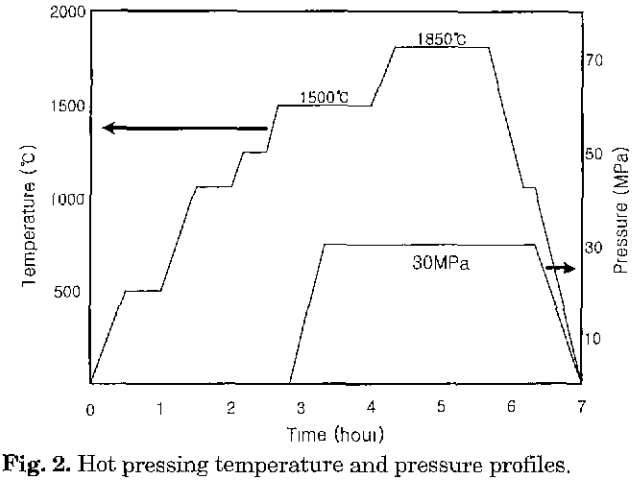


Fig. 2. Hot pressing temperature and pressure profiles.

Densities of samples were measured by Archimedes method. Zwick 3212 vickers hardness tester was employed to obtain hardness and fracture toughness of sintered samples. Indentation load was 200N and the duration time was 15 seconds. The value of fracture toughness was calculated by Evans and Charles' equation.[11] The average values of hardness and fracture toughness were obtained from 10 measurements.

For the flexural strength measurements, samples were ground and cut into 3 mm×4 mm×35 mm dimensions. The edges of the tensile side of the bend bars were chamfered at 45° by using a diamond wheel. Span was 20 mm and crosshead speed was 0.5 mm/min. All data points are the average of at least 10 measurements. Plasma-etching technique was used to reveal the grain boundary of the composites. Etched samples were coated with gold prior to SEM observation.

2.2. Wear test

The Cameron Plint Tribometer (TE 77, Oaklands Park, U.K.) was used to carry the wear test. Friction and wear tests were performed by using a reciprocating ball-on-plate tester. The composite surface was finished with 0.3 μm alumina paste. The cleaning of the specimens was accomplished by using acetone and ethanol. The ball was a silicon nitride ball. The test conditions were fixed at 10 N, and 5 Hz (sliding speed was about 0.07 m/s) for 1 hour at room temperature in air. Wear volume of each specimen was obtained by a profilometer (Form Talysurf Plus, Rank Talyer Hobson Co., London, England). The profilometer was utilized to measure the wear depth, and a planemeter was used to obtain wear volume. Each experiment was repeated three times and

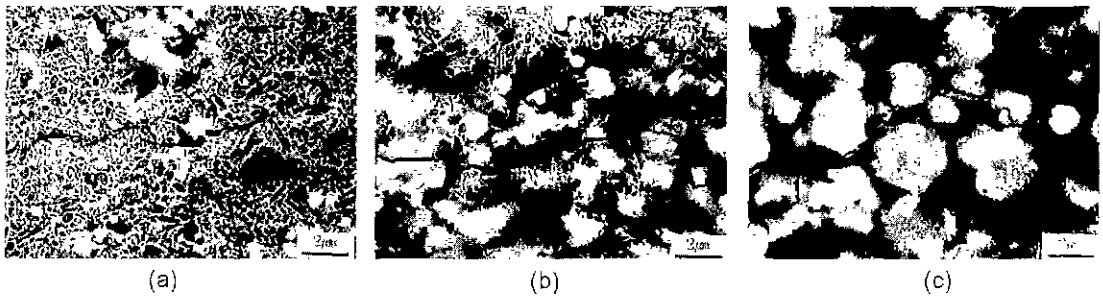
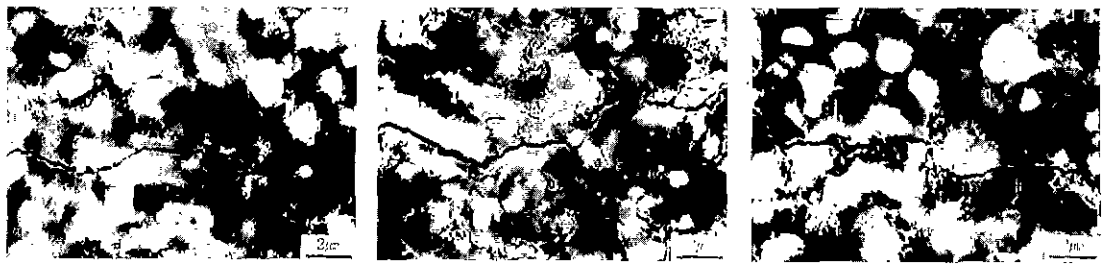
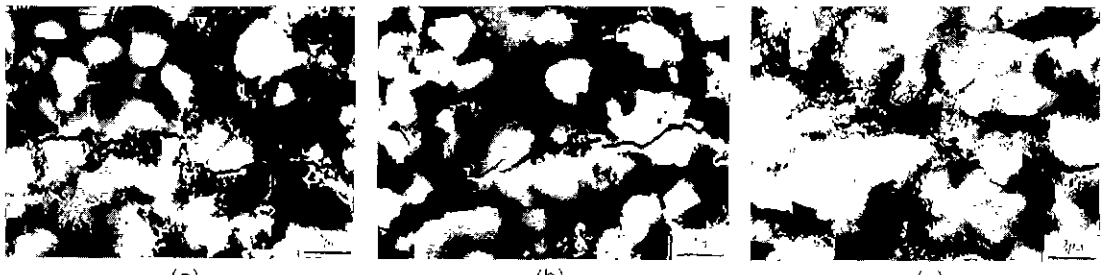


Fig. 3. SEM micrographs of the etched surface with different TiB_2 content; (a) 10 vol%, (b) 30 vol% and (c) 50 vol%.



(a) (b) (c)

Fig. 4. SEM micrographs of the etched surface for SNTB40 composite with different hot press temperature; (a) 1,750°C, (b) 1,800°C and (c) 1,850°C.



(a) (b) (c)

Fig. 5. SEM microstructure of the etched surface for SNTB40 composite (1,850°C) with different hot press time; (a) 1 hour, (b) 3 hours and (c) 5 hours.

average value of the three measurements was reported.

III. Results and Discussion

3.1. Microstructure

The etched microstructures of Si_3N_4-TiB_2 composites are shown in Figs. 3, 4, and 5. The growth of elongated β- Si_3N_1 grain was suppressed when the TiB_2 content increased as shown in Fig. 3. For the SNTB50 composite the elongated β-Si_3N_4 grains are hard to be identified form the etched SEM micrograph. However, the size of TiB_2 particles was enlarged with an increase in TiB_2 content. The TiB_2 particles are linked each other. It looks like that there are pores inside the TiB_2 particles for the SNTB50 sample. These pores may forms due to following reasons. One is the chemical reaction inside TiB_2 particle. The other reason is that the TiB_2 particles are agglomerated during mixing powders of the high content of TiB_2 or linked during the sintering. The surface of the linked TiB_2 particles reacts easily and generates pores in the vicinity of the linked area. In the SNTB10 composite the indentation cracks propagate in the silicon nitride matrix, and cracks are deflected around the TiB_2 particle. But in the SNTB30 composite the indentation cracks cut into TiB_2 particles. In the SNTB50 composite the indentation cracks are deflected around the enlarged TiB_2 particles. Also some pores are observed inside the TiB_2 particles. For the SNTB40 sample the hot press temperature were varied in the range of 1,750°C, 1,800°C, and 1,850°C. We can observe many small particles around the enlarged TiB_2 particles and many tiny pores inside the TiB_2 particles. Kim *et al.*[12] showed the existence of a core/rim structure in the TiB_2 grains of SiC- TiB_2 composite. They did microanalysis using an electron probe on the rim area and suggested that the observed core/rim structure might have been developed by the dissolution of nonequilibrium phases in the liquid and a subsequent reprecipitation of equilibrium phases onto undissolve nonequilbrium particles, which constitute cores. It indicates that the grain growth of TiB_2 grains was achieved by solution and reprecipitation mechanism suggested by Rudiger and Exner.[13] However, in these experimental results the chemical reaction products are surrounding the unreacted TiB_2 grains. Fig. 5 shows how the hot press sintering time at 1,850°C changed the microstructure of the SNTB40 composite. The size of TiB_2 particles was increased with increasing the hot press sintering time from 1 hour to 5 hours. The TiB_2 particles of the SNTB40 composite hot pressed for 3 hours are linked. The size of TiB_2 particle in the SNTB40 composite hot pressed for 1, 3, and 5 hours are 2 μm, 4 μm, and 8 μm respectively.

The interface layers around TiB_2 particles were further analyzed using a TEM. Fig. 6 shows TEM micrographs of the SNTB40 composites which were hot pressed at 1,850°C for 1 hour in N_2 environment and at 1,750°C for 1 hour in Ar environment. Fig. 6(b) shows a bright field micrograph of clean Si_3N_1- TiB_2 interface hot pressed in Ar environment. However, Fig. 6(a) shows the chemically reacted products such as TiCN of the Si_3N_4- TiB_2 interface hot pressed in N_2 environment. These chemical products were determined by electron diffraction patterns, but Shew and Hunag[9] showed radial, columnar epitextures and suggested as the columnar epitexures of TiN. Also glassy phases at the triple junctions and Si_3N_4- TiB_2 interfaces were found even though small

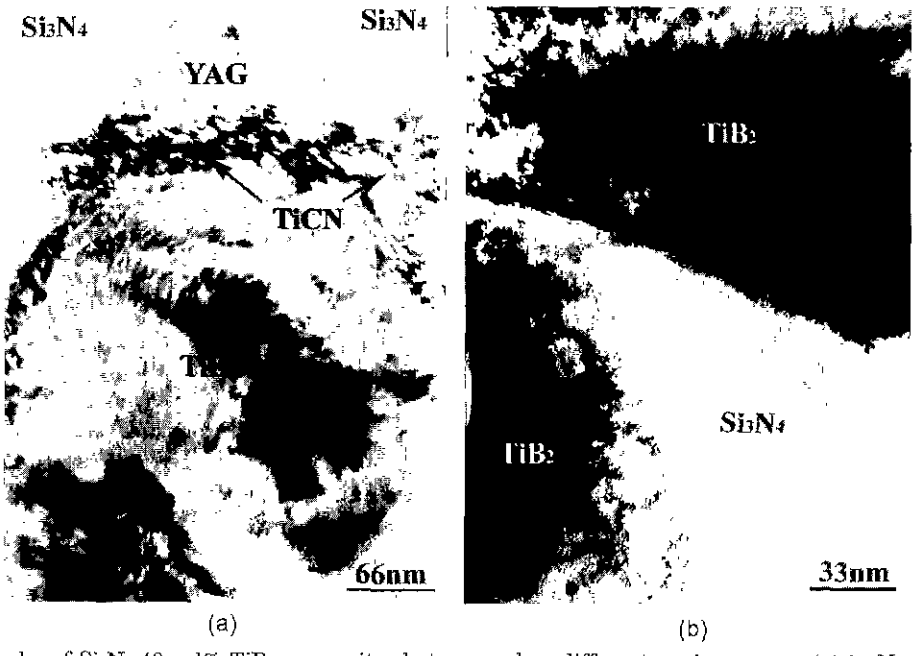


Fig. 6. TEM micrographs of Si_3N_4-40 vol% TiB_2 composites hot pressed in different environments; (a) in N_2 and (b) in Air.

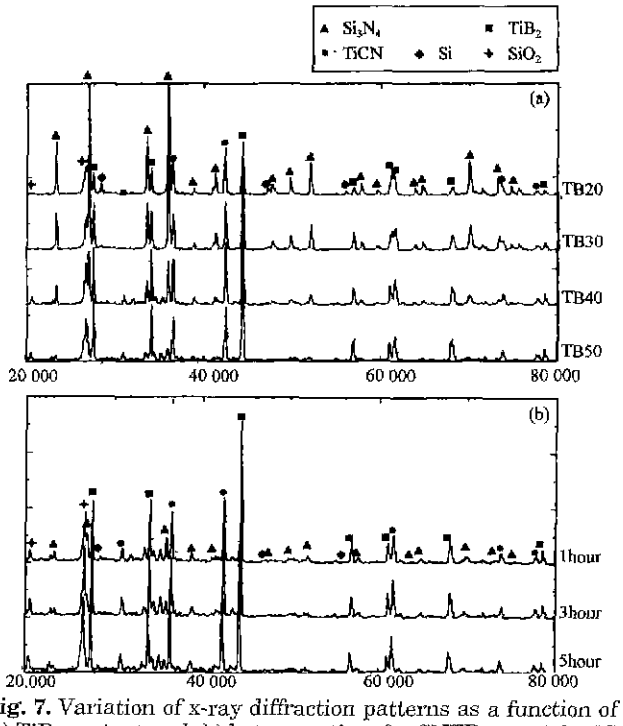


Fig. 7. Variation of x-ray diffraction patterns as a function of (a) TiB_2 content and (b) hot press time for SNTB40 at 1,850°C in N_2 environment.

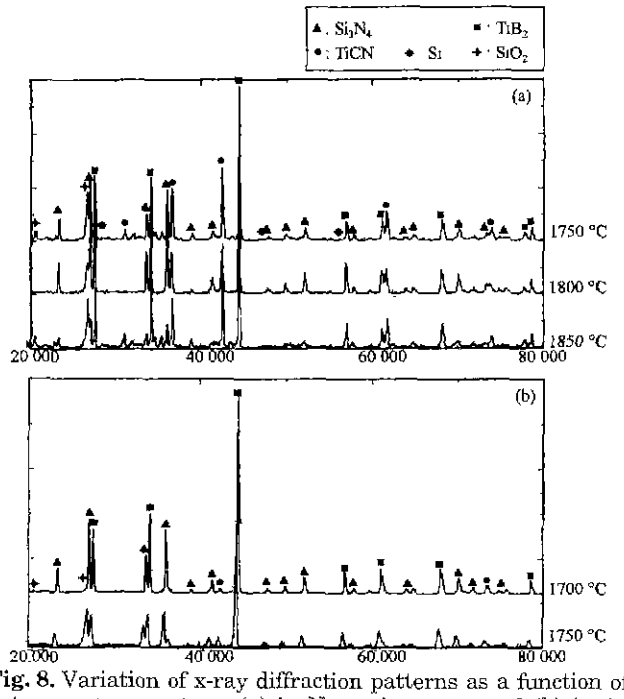


Fig. 8. Variation of x-ray diffraction patterns as a function of hot press temperature: (a) in N_2 environment and (b) in Ar environment.

amount of sintering additives were used in this study. This feature is almost identical to numerous observation found in Si_3N_4 ceramics. The TiB_2 interface area were found to be very clean when the Si_3N_4- TiB_2, composites were hot pressed in inert gas environment.

3.2. X-ray analysis

Fig. 7 shows the comparison of x-ray diffraction patters of Si_3N_4- TiB_2 composites by varying the TiB_2 contents from 20 vol% to 50 vol% (in (a)), and the hot press holding time from 1 hour to 5 hours (in (b)). The peaks of β-Si_3N_4 phase decreased and the peaks of TiB_2 phase increased with increasing the TiB_2 content. The peaks of free Si phase, SiO_2, and TiCN phases were observed. Particularly the intensity of Si phase disappeared when added the 50 vol% TiB_2 into Si_3N_4, but the intensity of SiO_2 is slightly higher.

The intensity of TiCN was not changed even though the TiB_2 content increased. These two peaks of TiCN and SiO_2 are from chemical reactions. The formation of free Si phase and SiO_2 are associated with the decomposition of Si_3N_4 during the hot press processing.. Even though the hot press holding time was changed from 1 hour to 5 hours, the intensity of most phases were not influenced as shown in Fig. 7(b). When the hot press temperature for the SNTB40 composites decreased down to 1,800°C and 1.750°C, the intensity of Si_3N_4 phase increased and the peaks of other phases were not changed as shown in Fig 8(a). This result indicates that the chemical reaction between TiB_2 and Si_3N_4 in N_2 environment was accelerated only as the hot pressing temperature, the hot press holding time did not accelerate the chemical reaction, but enlarged the size of TiB_2 particles as shown in Fig. 5.

B. Y. Shew and J.L. Huang[9] suggested that a chemical reaction between TiB_2 and Si_3N_4 occurred. TiB_2 was reported to react with Si_3N_4 to form TiN and N_2 gas.[14] But in this study, it is found that peak of TiCN is formed into the flowing nitrogen atmosphere. The formation of TiCN rather than TiN as showed in the Fig. 6-7 is due to chemical reactions between TiB_2 and Si_3N_4 in N_2. This chemical reaction was a part of reason for the formation of pores inside and outside of TiB_2 particles as shown in Fig. 3-5. The source of carbon is speculated from the hot press furnace refractory carbon wool, graphite mold, and the carbon electrodes. This chemical reaction can be accelerated with increasing hot pressing temperature.

In order to avoid the chemical reaction between TiB_2 and the flowing N_2 gas, the mixture of Si_3N_4- 40 vol% TiB_2 powders was hot pressed in Ar atmosphere for 1 hour at the different temperatures of 1,700°C and 1,750°C. The x-ray diffraction patterns of the SNTB40 composites hot pressed at different environment between Ar and N_2 are compared in Fig. 8. Fig. 8(b) shows that the peaks of free Si phase and SiO_2 phase were not detected, but still the TiCN phase was presented even in Ar environment. This result also indicates that the decomposed N from Si_3N_4 and the decomposed Ti from TiB_2 can react chemically to form TiCN.

3.3. Mechanical properties

Fig. 9 shows relative density, hardness, flexural strength, and fracture toughness of Si_3N_4- TiB_2 composites in terms of the TiB_2 content. Generally, the SEM observation of cracks induced by Vickers indentations has shown the crack deflection around the hard secondary particles. Meanwhile, sometimes cracks cross over and shear the particle. In this experiments, most of the indentation cracks cut into the enlarged TiB_2 particles, but the small TiB_2 particles deflected the indentation cracks as shown in Fig. 3. This mode of indentation crack propagation in the secondary hard particles dispersed into the softer matrix is strongly dependent upon the secondary particle size, and also influence fracture toughness. The degree of crack deflection was lower when TiB_2 was added to Si_3N_4.

For the monolithic Si_3N_4, the relative density is above 99.5% and it reveals a dense microstructure, which has better mechanical properties such as hardness, flexural strength, and fracture toughness than those of Si_3N_4- TiB_2 composites. The porosity of Si_3N_4- TiB_2 composite increases with increasing the TiB_2 content. All mechanical properties are decreasing with increasing the TiB_2 content. It means that TiB_2 addition does not provide a beneficial effect on the mechanical properties of Si_3N_4 hot pressed in N_2 environment. TiB_2 is harder than Si_3N_4, the higher hardness should be obtained when the TiB_2 content increases. In our case, the influence of porosity is predominant: the hardness drops when the porosity increases with the increasing TiB_2 percentage. The hardness drops for the SiC- TiB_2 composites with increasing the TiB_2 content, which was sintered even under argon. The same result as this was also reported by Blanc, *et al.*.[15] For the flexural strength, monolithic Si_3N_4 has higher values than Si_3N_4-TiB_2 composites. These results can be explained by referring the microstructure shown in Fig. 3. Also the large particles of TiB_2 act as crack-initiating flaws resulting a relative low hardness and strength. Therefore, higher hardness and strength could be expected since the size of crack-initiating flaws are decreased from the large TiB_2 particles to the lower porosity as well as small TiB_2 particles. It means that the composites have a weak bond between Si_3N_4 and TiB_2. As shown in the x-ray diffraction analysis, there were chemical reactions between Si_3N_4 and TiB_2 in N_2 environment.

A discontinuity in the bulk (porosity) may stop the crack, but the weak bonding between the Si_3N_4 and TiB_2 can not resist the crack propagation. In our experiments, the fracture toughness decreased with increasing the TiB_2 content. This is mainly due to the chemical reaction. This chemical reaction was a part of reason for the low sintering densities

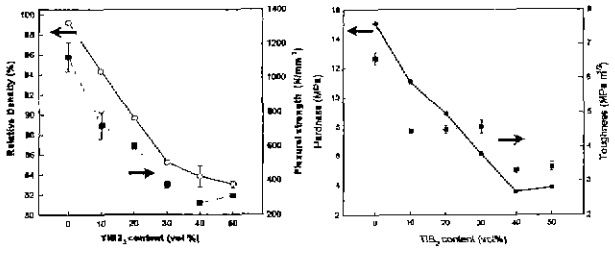


Fig. 9. Variation of mechanical properties as a function of TiB_2 content.

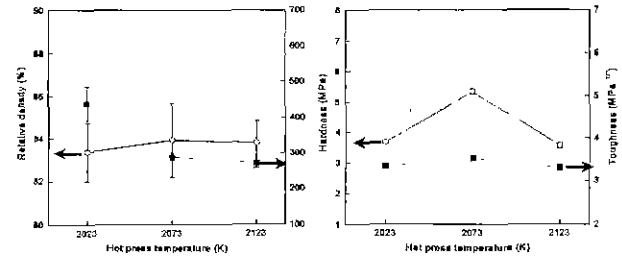


Fig. 10. Variation of mechanical properties as a function of hot press temperature for SNTB40 for 1 hour.

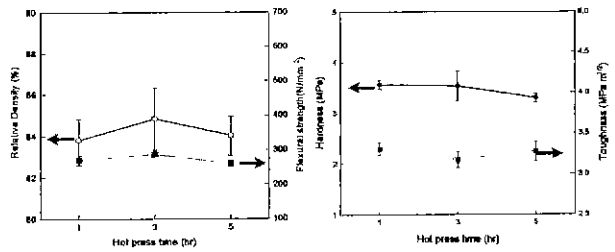


Fig. 11. Variation of mechanical properties as a function of hot press time for SNTB40 at 1,850°C.

due to the production of generating large volume of pores and chemical reacted products around the TiB_2 particles as shown in Figs. 3-5. Microstructures of TiB_2 in Si_3N_4 showed pores (in Figs. 3(c) and 5(a)). The reduction of density was also caused by voids around the TiB_2 particle generated during cooling because TiB_2 particle have a higher thermal expansion coefficient than Si_3N_4. The reduction of density causes mechanical properties to be deteriorated when adding more TiB_2 into Si_3N_4. This influence of the chemical reaction on mechanical properties was shown in terms of hot press temperature and holding time was shown in Figs. 10 and 11. The hot press time did not change much the relative density and mechanical properties, but the lower hot press temperature influence the flexural strength significantly.

3.4. Wear properties

For the abrasive wear behavior of brittle materials, the wear rate was an inverse function of their hardness and fracture toughness.[16-18] Wear resistance was enhanced by increasing the fracture toughness. The variation of the wear volume of the specimens as function of TiB_2 content, hot press temperature, and hot press holding time were shown in Fig. 12. The wear volume was found to increase as the TiB_2 content increased. Higher hot press temperature and longer hot press time reduced the wear resistance of the composites. The reason for the increase of wear volume was poor density, resulting from the chemical reaction in Si_3N_4-TiB_2 composite in N_2 environment. The frictional behaviors of these specimens were similar to the wear behaviors.

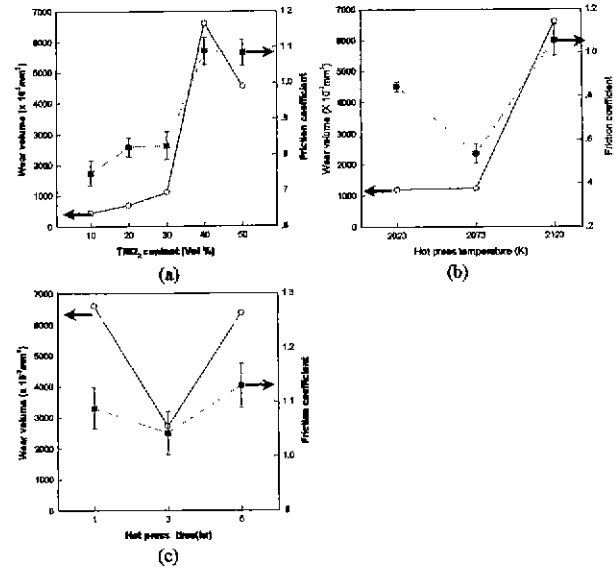


Fig. 12. Wear volume and friction coefficient as a function of; (a) TiB_2 content, (b) hot press temperature for SNTB40 at 1 hour and (c) hot press time for SNTB40.

IV. Conclusions

TiB_2 reacted with Si_3N_4 in the graphite mold and electrodes to form TiCN in N_2 and Ar environment, which is in part responsible for the decrease of sintered densities. Therefore, the reduction of density causes mechanical properties such as hardness, flexural strength, and fracture toughness to be deteriorated when adding more TiB_2 into Si_3N_4. Higher hot press temperature facilitated the chemical reaction between TiB_2 and Si_3N_4 during hot pressing in N_2 atmosphere rather than longer hot press sintering time. It was shown by x-ray diffraction analysis (Figs. 7-8). TiCN was formed by chemical reaction between TiB_2 and Si_3N_4 in a graphite mold.

Acknowledgment:

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