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Keiichiro Isomura, Toshihiko Funahashi, Ryoji Uchimura

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Advanced composite ceramics of the Si3N4-BN system have been developed. The Si3N4-BN composite ceramics (SNB) have been produced using slipcasting technique, which utilizes homogeneous mixing of ultra-fine constituent ceramic powders, and N2 gas pressure sintering. An essential feature of SNB is that it is possible to change widely their various properties by controlling the proportion of BN to Si3N4. The advantageous features of SNB are high thermal shock resistance, high corrosion resistance to molten metal, and excellent machinablity while retaining relatively high strength, i.e., the bending strength of SNB with 20 wt.% BN is 200 MPa or over. The thermal shock resistance temperature is improved by 250 to 300℃ compared with Si3N4 monolithic ceramics by incorporating 20 wt.% BN. These features indicate that SNB are well suited to machine parts for various molten metal casting facilities and jigs for heat treatment.

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Keiichiro Isomura
Senior Researcher,
New Materials
Research Center,
High-Technology
Res. Labs.

Toshihiko Funahashi
Senior Researcher,
New Materials
Research Center,
High-Technology
Res. Labs.

Ryoji Uchimura
Staff Assistant
General Manager,
Planning & Develop-
ment Sec., Research
Planning Dept. Tech-
nical Research Div.

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Advanced composite ceramics of the Si$_3$N$_4$-BN system have been developed. The Si$_3$N$_4$-BN composite ceramics (SNB) have been produced using slipcasting technique, which utilizes homogeneous mixing of ultra-fine constituent ceramic powders, and N$_2$ gas pressure sintering. An essential feature of SNB is that it is possible to change widely their various properties by controlling the proportion of BN to Si$_3$N$_4$. The advantageous features of SNB are high thermal shock resistance, high corrosion resistance to molten metal, and excellent machinability while retaining relatively high strength, i.e., the bending strength of SNB with 20 wt.% BN is 200 MPa or over. The thermal shock resistance temperature is improved by 250 to 300°C compared with Si$_3$N$_4$ monolithic ceramics by incorporating 20 wt.% BN. These features indicate that SNB are well suited to machine parts for various molten metal casting facilities and jigs for heat treatment.

1 Introduction

Active research and development are underway for practical application of fine ceramics such as ZrO$_2$, Si$_3$N$_4$ and SiC. Also known as structural ceramics for next generation, they are found attractive for their features: excellent heat resistance, bending strength, and abrasion resistance. In recent years, some successful attempts have been made to practically apply these fine ceramics to automotive engine parts, machine parts, and parts for molten metals.[1]

Structural ceramics are used in various processes of the iron- and steelmaking processes. In particular, there is a strong demand for ceramics for molten metal application, such as brake rings for horizontal continuous casting, crucibles for melting metals, and nozzles for atomizing. All of these parts, however, are employed under severe operating conditions and they require excellent thermal shock resistance, abrasion resistance, and resistance to corrosion from the molten metal. Furthermore, to incorporate them into actual equipment, it is desirable that these parts have excellent machinability. The conventional refractories cannot meet these requirements. Besides, the thermal shock resistance, machinability, etc. of ZrO$_2$, Si$_3$N$_4$, and SiC are insufficient for the above-mentioned applications.

In view of this, the authors attempted to develop composite ceramics for molten metal application, which is in great demand by the steel industry. As a result,

they succeeded in developing new Si$_3$N$_4$-BN composite ceramics that combine the excellent mechanical properties of Si$_3$N$_4$ and the superior thermal shock resistance and machinability of BN. Conventionally, a compact of Si powder and BN powder is sintered in N$_2$ by using the reaction-sintering method to produce Si$_3$N$_4$-BN composite ceramics. This method, however, tends to cause silicon to remain and the resultant product is nonuniform and inferior in machinability. In view of the freedom in shape, and simplicity in equipment construction, the slip casting technique and N$_2$ gas pressure sintering method were adopted for the present Si$_3$N$_4$-BN composite ceramics so that parts of not only simple shape but also of complex shape could be produced by near-net-shape molding.

Fiber-reinforced ceramics with improved toughness using whiskers, and the recent nano-composite ceramics are well known composite ceramics. However, the newly developed composite ceramics are composite ceramics of micron size, obtained using a homogeneous dispersion technique of ultrafine powder. Creating new functions by combining multiple ceramic components of micron size seems to be the future direction for the development of fine ceramics.

The bending strength, thermal shock resistance and machinability of the above Si$_3$N$_4$-BN composite ceramics (hereafter referred to as the SNB ceramics) were

evaluated. The results of the evaluation were examined in consideration of the microstructure of sintered bodies. This report presents the results thus obtained.

2 Method of Experiment

2.1 Raw Materials

The properties of the raw material powders of Si_3N_4 and BN used to develop SNB are given in **Table 1**. Two kinds of Si_3N_4 powder, i.e. $Si_3N_4(A)$ powder and $Si_3N_4(B)$ powder were used: the former is a very pure and ultrafine powder and the latter is a less pure and coarse standard-grade powder. These two different powders were used to investigate the effect of the sinterability of Si_3N_4 caused by the differences of the raw material powders on the characteristics of the SNB ceramics. The BN powder is a high-purity ultrafine powder.

2.2 Manufacturing Process

The manufacturing process for the SNB ceramics is shown in **Fig. 1**. Si_3N_4 powder, BN powder, and the sintering aids for Si_3N_4 of Al_2O_3 and Y_2O_3 powders were uniformly blended and were homogeneously mixed with water in a ball mill. After slurry control, the mixture was used as a slurry for slip casting. This slurry was poured into a plaster mold, and green bodies of 50 mm × 50 mm × 10 mm were obtained with 0 to 40 wt.% BN in each 10 wt.% increment. The green bodies were dried and the binder was removed. They were then sintered in an N_2 gas of 9×10^5 Pa at 1 800°C and sintered bodies were obtained. Pieces of 4 mm × 3 mm × 40 mm were cut from these sintered bodies and their surfaces were cut in preparation for observing the microstructures and evaluating the characteristics of the test pieces.

2.3 Evaluation of Characteristics

The microstructure of SNB fracture surfaces was observed under a scanning electron microscope (SEM), and porosity and pore size distribution were investigated. The porosity was determined from the difference between the apparent bulk density measured and the theoretical density calculated from compositions. The pore size distribution was measured using a mercury penetration type porosi-meter.

Bending strength, thermal shock resistance temperature, and machinability were also evaluated. The three-point bending strength was evaluated according to the JIS method (average of 20 test pieces). For thermal shock resistance temperature evaluation, the test pieces were left in normal atmospheres at different temperatures for 1 h, and were then subject to thermal shock by rapid cooling in water at 0°C. After that, the three-point bending strength was measured according to the JIS method, and the maximum temperature that did not

Table 1 Properties of Si_3N_4 and BN powder

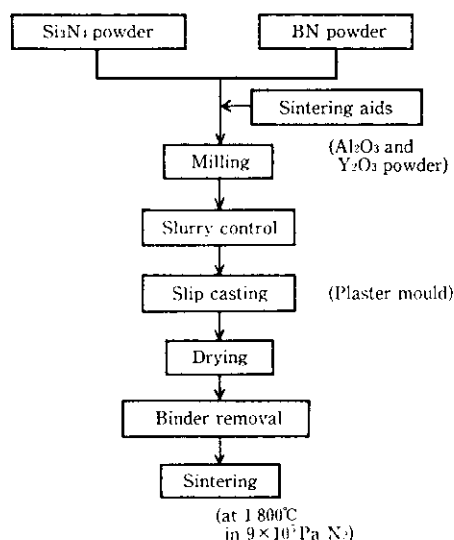|		Si_3N_4 (A)	Si_3N_4 (B)	BN
$\alpha/(\alpha+\beta) \times 100(\%)$		>97	93	
Impurities	Fe (ppm)	<50	1 800	60
	Al (ppm)	<10	1 500	<10
	Ca (ppm)	<10	1 800	<10
	Mg(ppm)	<10	<100	<10
Specific surface area (m^2/g)		10~11	7	50~60
Particle size D_{50} (μm)		0.7	1.2	0.1

Fig. 1 Manufacturing process

result in a strength decrease was regarded as the thermal shock resistance temperature ΔT (average of 10 test pieces). The three-point bending strength was measured at a span of cross head speed 30 mm and a crosshead speed of 0.5 mm/min. Machinability was evaluated by conducting lathing using WC cutting tools.

3 Results of Experiment

3.1 Analysis of Microstructures

SEM photographs of the SNB(A) ceramics produced using $Si_3N_4(A)$ powder are shown in **Photo 1**. The BN contents of these microstructures are 0, 10, 20, 30, and 40 wt.%. There was a noticeable growth of β-Si_3N_4 in the Si_3N_4 ceramics without BN. The degree of growth of rod-like crystals decreased with an increase in BN content, and at 30 wt.% BN rod-like crystals were not observed at all and a granular structure was formed. When the BN content increased, aggregates of fish-scale particles, which did not exist in the Si_3N_4 ceramics
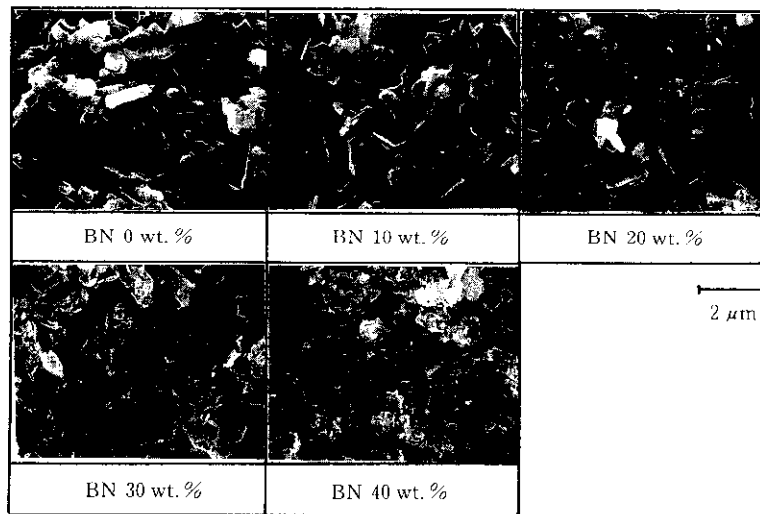
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Photo 1   SEM photographs of SNB (A) ceramics

without BN, also increased. The aggregates of fish-scale particles, which were probably BN, were distributed uniformly in the grains of the Si_3N_4 matrix. The structural change of the SNB(B) ceramics produced using Si_3N_4(B) powder showed almost the same tendency as the SNB(A) ceramics. In the SNB(B) ceramics, however, rod-like β-Si_3N_4 crystals were not observed at 20 wt.% BN and over and the range of BN content in which rod-like crystals grew was narrower than in the SNB(A) ceramics.

3.2 Porosity and Pore Size Distribution

Figure 2 shows the relationship between SNB(A) and SNB(B) ceramics in terms of their BN content, porosity, and average pore size. In both ceramics, the average pore size was constant although porosity increased with an increase in BN content, and very fine pores of 0.1 to 0.2 μm were observed. In the SNB(A) ceramics, where the average pore size is smaller than for SNB(B) ceramics, an increase in the porosity due to an increase in the BN content was small compared to the SNB(B)
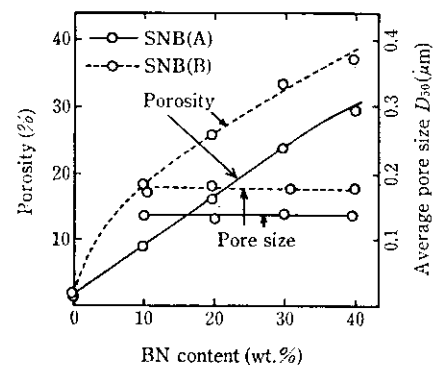

Fig. 2   Porosity and average pore size of SNB ceramics

ceramics.

Figure 3 shows the pore size distribution of the SNB(B) ceramics at 10 and 30 wt.% BN. A very sharp pore size distribution can be seen regardless of the BN content; this shows that the SNB(B) ceramics are uni-
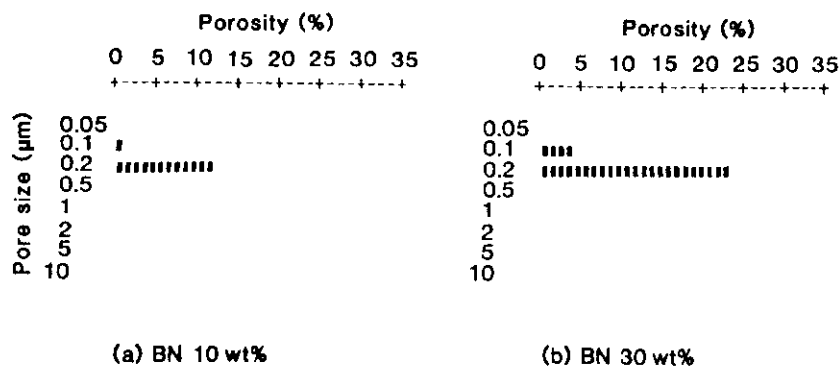

(a) BN 10 wt%   (b) BN 30 wt%

Fig. 3   Pore size distribution of SNB (B) ceramics

form ultrafine porous bodies. Similar results were obtained for the SNB(A) ceramics.

3.3 Bending Strength

The relationship between the BN content and three-point bending strength of the SNB(A) and SNB(B) ceramics is shown in **Fig. 4**. In both ceramics, the strength decreases with an increase in BN content. At the same BN content, however, the strength of the SNB(A) ceramics is higher than that of the SNB(A) ceramics. For 20 wt.% BN or less, the bending strength of SNB(A) ceramics is higher than 30 kgf/mm^2, while that of SNB(B) is limited to around 20 kgf/mm^2. As shown in Fig. 4, these strength values are two to four times those of Si$_3$N$_4$-BN composite ceramics produced according to the reaction sintering method.[2,3]
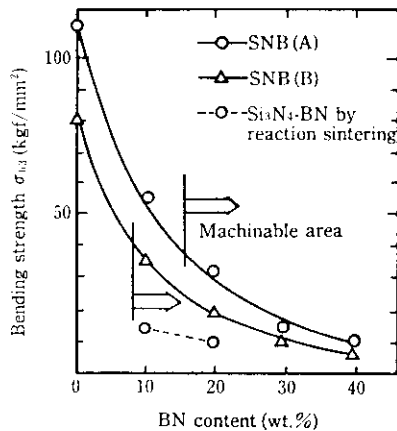

Fig. 4 Bending strength and machinability of SNB ceramics

3.4 Thermal Shock Resistance Temperature

The relationship between the BN content and thermal shock resistance temperature (ΔT) of the SNB(A) and SNB(B) ceramics is shown in **Fig. 5**. In both ceram-
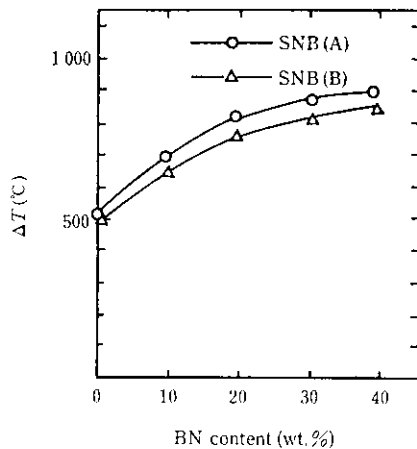

Fig. 5 Thermal shock resistance of SNB ceramics

ics, ΔT increases with on increase in BN content. The values of the SNB(A) ceramics are a little higher than those of the SNB(B) ceramics. The thermal shock resistance of Si$_3$N$_4$ ceramics have to date been considered relatively good. However, it is now apparent that the SNB ceramics have an excellent thermal shock resistance because the thermal shock resistance of the SNB(A) ceramics is 1.4 times that of Si$_3$N$_4$ in terms of ΔT at 10 wt.% BN and 1.7 times at 30 wt.% BN.

3.5 Machinability

Figure 4 shows the BN content of the SNB(A) and SNB(B) ceramics and the machinability with WC cutting tools. Good machinability is ensured at 15 wt.% BN or higher for the SNB(B) ceramics and at 10 wt.% or higher for the SNB(A) ceramics. Machinability increases with an increase in BN content.

4 Discussions

4.1 Microstructures

According to a lot of reports on liquid phase sintering using sintering aids for Si$_3$N$_4$[4,5,6], the growth of rod-like β-Si$_3$N$_4$ crystals is markedly found with sintering aids for Si$_3$N$_4$. Excellent mechanical properties of Si$_3$N$_4$ ceramics, such as high toughness and high strength, are attributed to this growth of rod-like crystals. It is known that the rod-like β-Si$_3$N$_4$ crystals grow while Si$_3$N$_4$ grains dissolve and precipitate in the liquid phase of sintering aids and grow.[7,8]

In the SNB ceramics, BN may impede the dissolution and precipitation of Si$_3$N$_4$ grains in the liquid phase because the growth of rod-like β-Si$_3$N$_4$ crystals decreases when the BN content increases as shown in Photo 1. From the results of this sintering (in N$_2$ of 9×10^5 Pa at 1 800°C), it is judged that BN itself is unlikely to be sintered. Therefore, the condition of the existences of BN hardly changes from the as-molded condition. This suggests that BN impedes the sintering of Si$_3$N$_4$ grains by preventing them from becoming densely packed and contracting. When the BN content increases, therefore, the sintering of Si$_3$N$_4$ is impeded and the growth of rod-like β-Si$_3$N$_4$ crystals is suppressed. The difference in the degree of growth of rod-like crystals between the SNB(A) and SNB(B) ceramics seems to be due to the difference in the sinterability of Si$_3$N$_4$ resulting from the difference in the raw material powders.

As shown in Fig. 2, the increase in porosity associated with the increase in the BN content is due to an increase in the volume ratio of the BN component that impedes the close packing and contraction of Si$_3$N$_4$. Further, it seems that the smaller increase in porosity in the SNB(A) ceramics than in the SNB(B) ceramics is, as with the difference in the degree of growth of rod-like β-Si$_3$N$_4$ crystals, due to the difference in sinterability resulting from the difference in the raw material Si$_3$N$_4$

Table 2 Various physical properties of SNB (B) ceramics

BN content (wt.%)	Young's modulus (N/m²)	Poisson's ratio	Thermal expansion coefficient (RT~1 000°C) (1/°C)	Thermal shock resistance parameter R (°C)
10	1.50×10^{11}	0.21	3.4×10^{-6}	550
20	5.89×10^{10}	0.18	3.2×10^{-6}	850
30	3.41×10^{10}	0.13	3.1×10^{-6}	1 120
40	1.71×10^{10}	0.13	2.7×10^{-6}	1 280

powders. These results are in agreement with the fact that the higher the purity, the smaller the grain size and the higher the α-phase content, the better the sinterability of the raw materials will be, as reported by Kansaki et al.[9] concerning the relationship between the properties of the raw material Si_3N_4 powders and sinterability. Furthermore, the fact that pore sizes are very small and their distribution is very sharp irrespective of BN content shown in Fig. 3, is considered due to the uniform dispersion of ultrafine BN particles in the Si_3N_4 matrix. This is greatly contributed to the fact that Si_3N_4 and BN are uniformly dispersed in the slurry used during the slip casting molding (shown in Fig. 1), which is one of the features of the present method.

4.2 Mechanical Properties

It has long been reported that the bending strength of ceramics is governed greatly by porosity.[9,10] The higher the porosity, the more the bending strength will decrease, because the bending strength is proportional to the effective area which faces vertical direction to the supporting load of the material itself.

An increase in porosity in the SNB ceramics is regarded as a great factor for the decrease of the three-point bending strength occurred with the increasing BN content, as shown in Fig. 4. However, the combined effect of Si_3N_4 and BN on the bending strength cannot be clarified. The fact that strength of the SNB(A) ceramics is higher than that of the SNB(B) ceramics is mainly caused by the lower porosity of the SNB(A) ceramics resulting from the difference in the sinterability of the raw material powders.

4.3 Thermal Shock Resistance

For the thermal shock resistance of ceramics, the parameters of thermal shock resistance induced from thermal stresses by thermal shock and material characteristics are well known and various equations are used depending on thermal shock conditions and crack propagation conditions.[11] Since the initiation of cracks by water quenching is a problem in the thermal shock test conducted in the experiment, the thermal shock resistance was analyzed using the parameter of thermal shock resistance R given by Eq. (1):

$$R = \frac{S(1 - v)}{E\alpha} \quad \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots (1)$$

where S: Rupture strength
v: Poisson's ratio
E: Young's modulus
α: Thermal expansion coefficient

Young's modulus, Poisson's ratio and thermal expansion coefficient were measured using the SNB(B) ceramics with BN contents of 10, 20, 30 and 40 wt.%. The results are given in **Table 2**. The ultrasonic pulse method was employed to measure Young's modulus and Poisson's ratio. Young's modulus, Poisson's ratio and thermal expansion coefficient decrease with increasing BN content. The decrease in Young's modulus is especially noticeable, and the value obtained at 40 wt.% BN is lower by one order of magnitude than that at 10 wt.% BN. This decrease in Young's modulus with an increase in the BN content is considered attributable mainly to the increase in porosity.

Figure 6 shows the relationship among the BN content, R calculated from Eq. (1), and thermal shock resistance temperature (ΔT) of the SNB(B) ceramics. The three-point bending strength shown in Fig. 4 was used as rupture strength S. As mentioned earlier, the thermal shock resistance expressed by ΔT improves
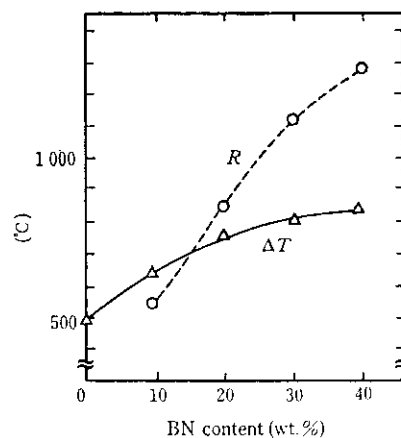

Fig. 6 Thermal shock resistance ΔT and its parameter R of SNB (B) ceramics

markedly with an increase in the BN content when compared with the Si_3N_4 ceramics without BN, showing a tendency corresponding to the R-value. From Eq. (1), it is considered that this improvement in the thermal shock resistance is mainly caused by a decrease in the thermal stress resulting from the remarkable decrease in Young's modulus.

4.4 Machinability

The mechanism of machinability of SNB ceramics has been reported by Enomoto et al.[12] who conducted experiments on SNB(B) ceramics.

According to this report, the width of flank wear land decreases (**Fig. 7**) and the surface roughness also decreases (**Fig. 8**) with an increase in BN content; this shows an improvement in machinability.

A crack initiated during cutting propagates almost straight in the Si_3N_4 matrix. When this crack reaches a BN grain, it propagates along the boundary between the BN grain and the Si_3N_4 matrix or in multiple directions by the cleaving effect of BN. In other words, it suggests that BN grains promote the propagation of cracks by changing the direction of propagation, thus enabling cutting grains to be continuously generated and ensuring good machinability. The above tendency is noticeable when the BN content increases, and it may safely be said that the machinability of SNB ceramics is determined by the dispersion condition and cleavage of BN and the existence of uniform and fine pores.

5 Application to Parts for Molten Metals

The newly developed Si_3N_4-BN composite ceramics were applied to parts for use with molten metals in Kawasaki Steel's various new processes, for example, parts for thin slab casters, brake rings for horizontal
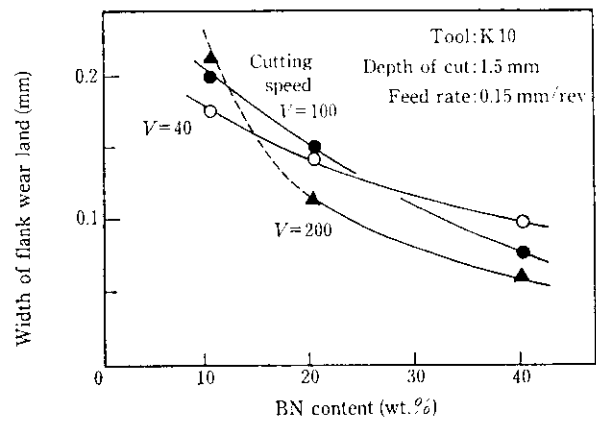

Fig. 7   Relation between BN content and width of flank wear land of SNB (B) ceramics
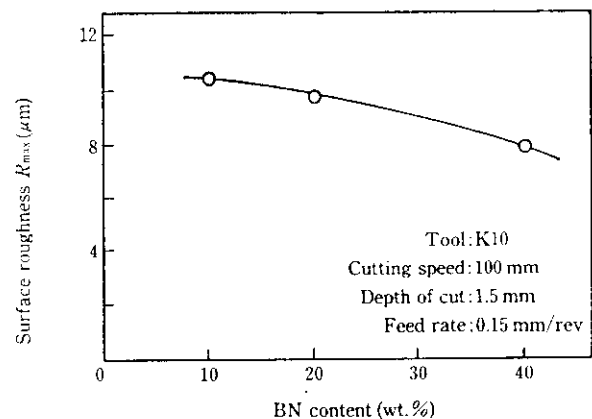

Fig. 8   Relation between BN content and surface roughness of SNB (B) ceramics

Table 3   Application of SNB (B) ceramics to the parts for molten casting

Customer	A	B	C	D	E	F	G	H
Metal	Al	Al	Cu-Zn	Cu-Zr	Cu-Su-Pb	Ni-Cr	Fe-Ni-Cr	Co-Cr
Temp. (°C)	700	700	1 200	1 200	1 600	1 600	1 600	1 600
Application	Protector tube for magnetic pump	Tube for dicasting	Break-ring for semi-continuous casting	Mould for up-casting	Nozzle for atomizing		Break-ring for horizontal continuous casting	
Feature	· Heat shock resistance · Erosion resistance	· Erosion resistance · Possibility of moulding	· Heat shock resistance · Erosion resistance · Insulation	· Heat shock resistance · Erosion resistance			· Heat shock resistance · Insulation · Erosion resistance	
Conventional materials	RB-Si_3N_4 Si_3N_4 Sialon	Pig iron Steel	Carbon	Carbon HP-BN	ZrO_2 NS-BN	ZrO_2 Al_2O_3 HP-BN	RB-Sialon-BN HP-BN HP-ZrO_2-BN	

HP: Hot pressing   NS: Normal sintering   RB: Reaction bonding

casting, and nozzles for amorphous metal. As a result, it was ascertained that these ceramics not only have excellent machinability, favorable for their incorporation into equipment, but also have excellent bending strength, thermal shock resistance, resistance to the corrosion from molten metal, and abrasion resistance, thus showing greater longevity than conventional ceramics.

Based on these results, attempts are being made to apply these ceramics to parts for use with various molten metals other than iron. **Table 3** lists the various applications of SNB(B) ceramics as parts for use with different various molten metals. In addition to these applications, these ceramics are also used where their thermal shock resistance and machinability can be taken full advantage of jigs for heat treatment, such as setters for sintering and muffles, and parts for glass forming.

6 Conclusions

New composite ceramics of the Si_3N_4-BN system (SNB ceramics) were developed using the slip casting technique and N_2 gas pressure sintering method. By evaluating these ceramics in terms of microstructure observations and mechanical properties, the relationship between their mechanical properties and microstructures was investigated and the following results were obtained:

(1) In both SNB(A) ceramics, produced using a fine Si_3N_4 powder, and SNB(B) ceramics, produced using a coarse Si_3N_4 powder, BN was uniformly distributed throughout the Si_3N_4 matrix, thus showing a composite structure. Rod-like β-Si_3N_4 crystals grew when the BN content was low. A granular structure in which Si_3N_4 grains and BN coexisted was formed when the BN content was high.

(2) Porosity increased with an increase in BN content. Porous ceramics with porosity of more than 25% were produced at 30 wt.% BN or higher. The average pore size is very small, with 80% of all pores within the range of 0.1 to 0.2 μm. Therefore, the newly developed ceramics were ultrafine homogeneous bodies.

(3) Three-point bending strength decreased with an increase in BN content. This was mainly due to an increase in porosity. High strength values of more than 50 and 30 kgf/mm^2 were obtained at 10 and 20 wt.% BN, respectively, for the SNB(A) ceramics, and those of more than 30 and 20 kgf/mm^2 were obtained at 10 and 20 wt.%, respectively, for the

SNB(B) ceramics.

(4) The thermal shock resistance, determined according to the water quenching method, improved as the BN content increased. Compared with Si_3N_4 ceramics without BN, the thermal shock resistance temperature (ΔT) increased by 150°C to 200°C at 10 wt.% BN and by 300° to 350°C at 30 wt.% BN. This improvement of the thermal shock resistance with an increase in the BN content may have been caused mainly by a decrease in thermal stress, which was largely due to a decrease in Young's modulus caused by an increase in porosity.

(5) It was possible to machine the SNB(A) ceramics of 15 wt.% or higher BN and the SNB(B) ceramics of 10 wt.% BN or higher with WC cutting tools. These ceramics had a high bending strength of more than 30 kgf/mm^2 as well as excellent machinability.

(6) The newly developed SNB ceramics were applied to parts for use with molten metal in Kawasaki Steel's new processes and good results were obtained. These SNB ceramics are also used in wider applications, such as parts for use with various molten metals other than iron, and in jigs for heat treatment.

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