Improved Ceramics through New Measurements, Processing, and Standards

Edited by

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Ceramic Transactions
Volume 133

Improved Ceramics through New Measurements, Processing, and Standards

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Ceramic Transactions
Volume 133

Improved Ceramics through New Measurements, Processing, and Standards

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Published by

The American Ceramic Society
735 Ceramic Place
Westerville, Ohio 43081
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Proceedings of the Improved Ceramics through New Measurements, Processing, and Standards Symposium held at PAC RIM 4 November 4–8 2001, in Maui, Hawaii.

COVER PHOTO: "Scanning Electron Micrographs of $Ce_2O(CO_3)_2$ doped with 10% Nd prepared by hot plate heating" is courtesy of Michiyo Kamiya, Ken-ichiro Ogata, Eriko Shimada, and Ysuro Ikuma, and appears as figure 2 in their paper "Effect of Microwaves on the Formation of $Ce_2O(CO_3)_2$ Doped With Nd by Homogeneous Precipitation," which begins on page 217.

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Printed in the United States of America.

4 3 2 1–05 04 03 02

ISSN 1042-1122
ISBN 1-57498-147-1

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Preface

The improvement of quality is one of the most important tasks in ceramic research today. Ceramics often fail to meet the conditions imposed in advanced applications in severe environments. New measurements with advanced measurement techniques are one of the key factors for improvements. The lack of measurements and data has been one of the major obstacles that has limited the progress of ceramic applications.

This symposium on Improved Ceramics through New Measurements, Processing, and Standards addressed the state-of-the-art characterization techniques and their applications for the production of ceramics. The smart application of new measurements will contribute significantly for solving many problems present in current processing. The symposium also addressed the state of international standardization, which is essential not only to the production of reliable ceramics worldwide, but also to the removal of trade barriers between countries.

Researchers from universities, government institutes, and industry have made presentations on quality improvements through new measurements and processing, new applications of ceramics, new and existing databases, and reference materials for calibration of measuring devices. Papers collected in this proceeding were peer reviewed and represent the high quality of the symposium. They will have a significant influence on the initiation of a new stage of ceramic processing.

We are grateful to The American Ceramic Society and New Energy and Industrial Technology Development Organization, Japan, for the NEDO grant and for the substantial support in organizing this symposium.

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Characterization Methods

MATERIALS DEVELOPMENT AND WEAR APPLICATIONS OF SI_3N_4 CERAMICS

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ABSTRACT

Silicon nitride (Si_3N_4) is one of the most attractive materials for wear applications because it has excellent wear resistance and advantages such as light weight, higher strength and toughness, good corrosion resistance, and a low thermal expansion coefficient. I have been involved in the creation and development of this material for a long time as a pioneer researcher. Developed high-strength silicon nitride has successfully been applied for anti-friction bearings, cutting tools and many kinds of wear components. In particular, bearing applications are quite successful and are recently expanding in production scale. This paper presents the history and present status of the material development and wear applications.

A standard high-quality Si_3N_4 ceramic for use as wear components has been fabricated from the system Si_3N_4-Y_2O_3-Al_2O_3-TiO_2-AlN, but the sintering behavior was not clear. Therefore, we have recently begun to investigate the effect of adding TiO_2 and AlN on the densification and microstructure development in the above system. As a result, we found the TiO_2 promoted the densification changing into TiN, which was precipitated between the grain boundary as isotropical grains.

Contact damage testing confirmed that the dispersion of TiN grains contributed strengthening the grain boundary, and consequently gave Si_3N_4 ceramics excellent wear resistance and especially long life in wear components.

SILICON NITRIDE CERAMICS

More than 40 years have passed since nitride ceramics were first introduced. During that period, sialons[1)2)] and effective sintering aids,[3)4)] such as Y_2O_3 and Al_2O_3, were discovered, subsequently Si_3N_4 powder[5)] and fabrication processes

Table 1 Applications of various Si_3N_4 ceramic bearings

Application	Type of bearing	Advantage
Machine tool spindle	Hybrid	Long life, high speed, high rigidity, low temperature rise
Semi-conductor production facility (ex. joints of robot)	All ceramic	Long life, non-magnetic, low vibration
Steel plant and electric train	Hybrid	Long life, Electrical insulation,
HDD (Hard Disk Drive) spindle in computer	Hybrid	Long life, High speed, quietness
Turbocharger rotor	Hybrid	Long life, low rotating torque, low acceleration resistance
Automotive front shaft	Hybrid	Long life, low friction, high corrosion resistance
Fuel injection:		
· Ceramic roller	Hybrid	Long life, low friction
· Ceramic ball	Hybrid	
· Ceramic ball with flat area	Hybrid	
Chemical and steel plant	All ceramic Hybrid	Long life, High corrosion resistance

such as gas-pressure sintering (GPS), [6] and microstructure-controlling techniques have been developed. Consequently, high-strength Si_3N_4 ceramics were successfully fabricated and used in practical applications as new ceramic components. From the early 1980s, the developed silicon nitride ceramics were applied for structural parts[7)-11)] such as glow plugs, hot-chambers, turbocharger rotors, injector links, cutting tools and bearings. I have been involved in creating, developing and applicating in Si_3N_4 ceramics for a long time, during which wear materials development and their applications have been the most successful issue and are even now expanding in area and volume. Table 1 and Fig.1 show the applications of ceramic bearings, and an example of bearing application for a machine tool spindle.[12)13)] Small size bearings for hard disk drive (HDD) in computer become very good applications with a large production scale. Diesel engine test data on a Si_3N_4 injector link shown in Fig. 2[10)] has confirmed that the reduction in wear was significant

However, important problems such as reliability and cost compatibility remain. It is urgently necessary to resolve both problems in monolithic ceramics in the near future. To expand the application fields of monolithic Si_3N_4 ceramics, it will be necessary to develop simple and cost effective process. We have recognized in recent works that small amount of elements such as titanium (Ti)

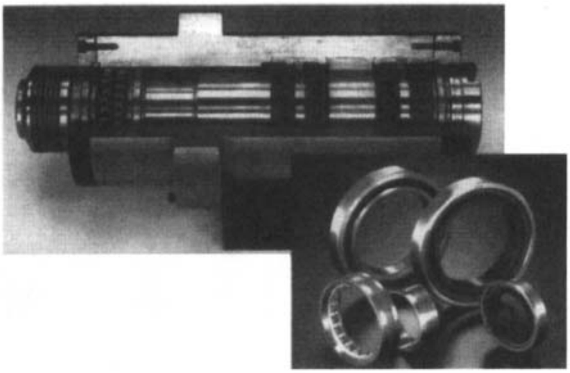


Fig. 1 An example of Si_3N_4 bearing applied for machine tool spindle.

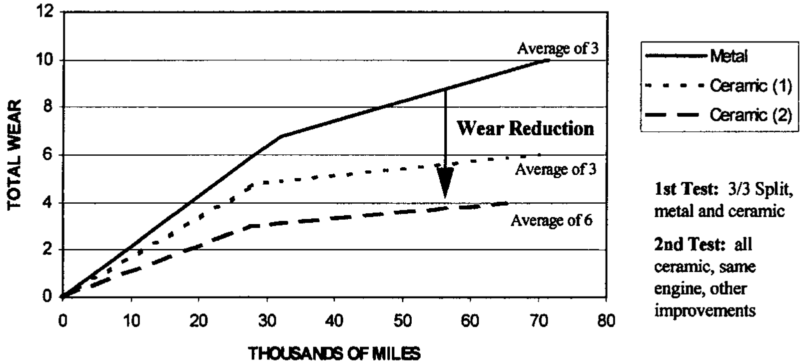
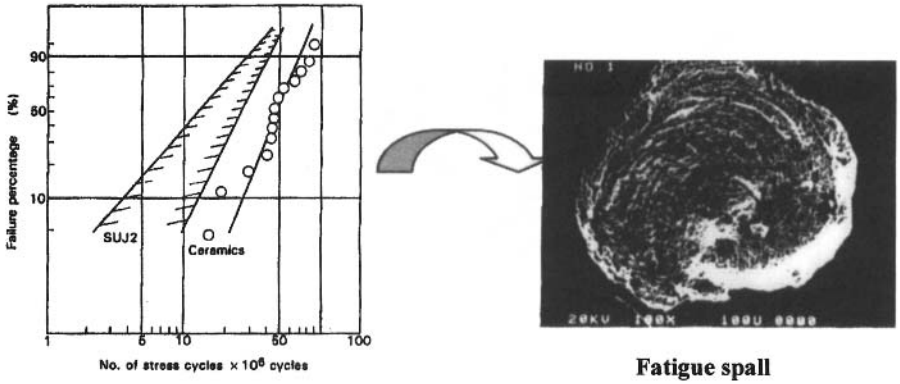


Fig. 2 Diesel engine test data on Si_3N_4 injector link.

and hafnium (Hf) in the nitride systems are effective for overcoming these problems.[14)]

WEAR APPLICATIONS DEVELOPMENT

Joint research between Toshiba Corp. and Koyo Seiko Co., Ltd., began in the early 1980s. Prior to that Koyo completed a feasibility study for various kinds of ceramics such as Si_3N_4, SiC and Al_2O_3. As a result, a typical high-strength Si_3N_4 with a sintering aids of 5wt%Y_2O_3 -2wt%Al_2O_3, which was hot-pressed at 1700 to 1800°C under 30MPa in 0.1Mpa N_2, was selected as a candidate material.[11)] Thus, the first practical application was achieved in bearing for machine tool spindle, since the material had a very attractive advantage of wear resistance in spite of its



Rolling fatigue life

Fatigue spall

Fig. 3 Rolling fatigue life and fatigue spall of hot-pressed Si_3N_4-5wt%Y_2O_3-2wt%Al_2O_3 specimen, by thrust type test method.

high cost. Figure 3[11)] shows the very important evidence published in 1986, which is the first announcement of a real application as a ceramic bearing. Thrust type tests for evaluating the fatigue life of rolling bearings were also performed. In these tests, the silicon nitride retained a rolling life equivalent to or better than that of steel (SUJ2) bearings. Significantly, no defect such as voids or impurities were observed in the damage starting points. Damaged parts had the same as the fatigue spalls observed with conventional steel bearings, which encouraged mechanical engineers to pioneer practical applications.

During the long history of ceramic bearing development, we learned the properties required as wear materials, especially as bearing materials. These included not only strength and toughness, but also light weight, greater heat resistance, high thermal shock resistance, high thermal conductivity, excellent electrical insulation, high corrosion resistance and low friction. Applicability will be determined by the balance of advantage and difficulty in production for factors in the operating conditions such as temperature, stress and environment, and component requirements such as reliability, shape and size, dimension accuracy, guarantee level and cost. Figure 4 depicts the advantages of Si_3N_4 bearings. Long life, which results from reduced wear, leads to low emission, preventing temperature increases in bearings and thus preventing temperature rises in the system. This means Si_3N_4 components can save resources, reduce energy consumption and protect the environment, which are very desirable in the 21st century.

Thus, Si_3N_4 has been confirmed as a candidate with many advantages in wear

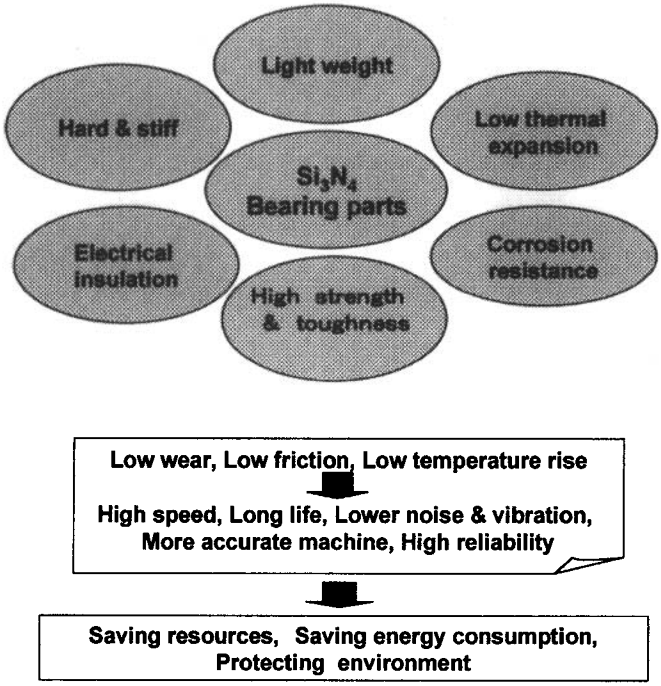


Fig. 4 Advantages of Si_3N_4 ceramics as wear resistant materials

reduction. Furthermore, it has been successfully applied for bearings, cutting tools, and parts in automotive engines from the 1980s. One standard Si_3N_4 ceramic as wear resistant material has been produced from the system Si_3N_4-Y_2O_3-Al_2O_3-AlN-TiO_2.[15)]

DEVELOPMENT OF TiN IN-SITU PRECIPITATED Si_3N_4 CERAMICS [16)17)]

The effect of TiO_2 and AlN on sintering of the Si_3N_4-Y_2O_3-Al_2O_3 system was investigated. As raw materials, Si_3N_4 (UBE Co., Ltd., E-10, 0.6 μm), Y_2O_3 (Shinetsu Industrial Co., Ltd., RU, 1.1 μm), Al_2O_3 (Sumitomo Chemical Co., Ltd., AKP-30, 0.08 μm), AlN (Tokuyama Co., Ltd., F-grade, 0.6 μm), and TiO_2 (Sakai Chemical Co., Ltd., Rutile-type, R-11・P, 0.17 μm) were used. Compositions of 0-5wt%TiO_2 and 0-5wt%AlN were prepared for addition to 92wt%Si_3N_4-5wt%Y_2O_3- 3wt%Al_2O_3 were prepared. After wet ball milling using ethanol solvent with 2wt% dispersant and binder, powder mixtures were molded into 15 ϕ × 7mm pellets with uniaxial molding followed by CIPping with

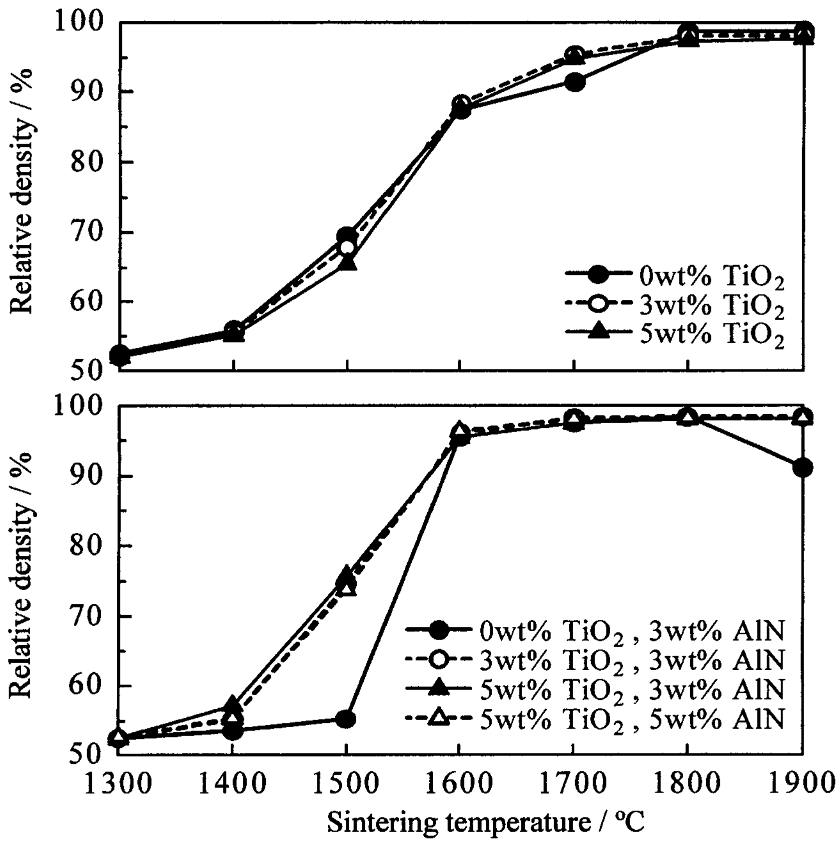


Fig. 5 Densification behavior of Si_3N_4-Y_2O_3-Al_2O_3 system with various compositions of TiO_2 and AlN, which was fired at various temperatures for 1h in 0.9MPa N_2.

200MPa. After dewaxing, each pellet was fired at 1300 to 1900°C for 1h in 0.9Mpa N_2. Sintered bodies were evaluated by density measurement, XRD (Rigaku, RAD-2R) analysis and microstructural analysis using SEM (Jeol JSM-5200), TEM (Hitachi, H-9000) and EDS (Jeol, Link, QX2000J).

Figure 5 shows the relations between relative density and firing temperature for 1h soaking. TiO_2.ddition promoted densification with an increase of TiO_2, but the effect was small. In contrast, the simultaneous addition of TiO_2 and AlN extremely enhanced the densification, and almost full density was achieved at 1600°C.

Fig. 6 TEM photographs of the 5wt%TiO_2/5wt%AlN specimens fired at various temperatures for 1h in 0.9MPa N_2. Arrow: TiN.

Phase transformation from α to β-Si_3N_4 was discussed based on XRD profiles of sintered bodies with compositions of 0/0, 3/3 and 5wt%TiO_2/5wt%AlN fired at 1300 to 1900°C. It was found that the transformation was restrained by TiO_2 addition and promoted by AlN addition. It was also found that TiO_2 changed into TiN in each composition, which means TiN was achieved at below 1300°C.

Figure 6 shows TEM photographs of the 5wt%TiO_2/5wt%AlN specimens fired at 1600 to 1900°C. At all firing temperatures, darkened small spherical grains (~ 200nm) were observed. EDS profiles in Fig. 7[18] indicate the darker grains are composed of Ti and N, and were confirmed to be TiN by XRD profiles.

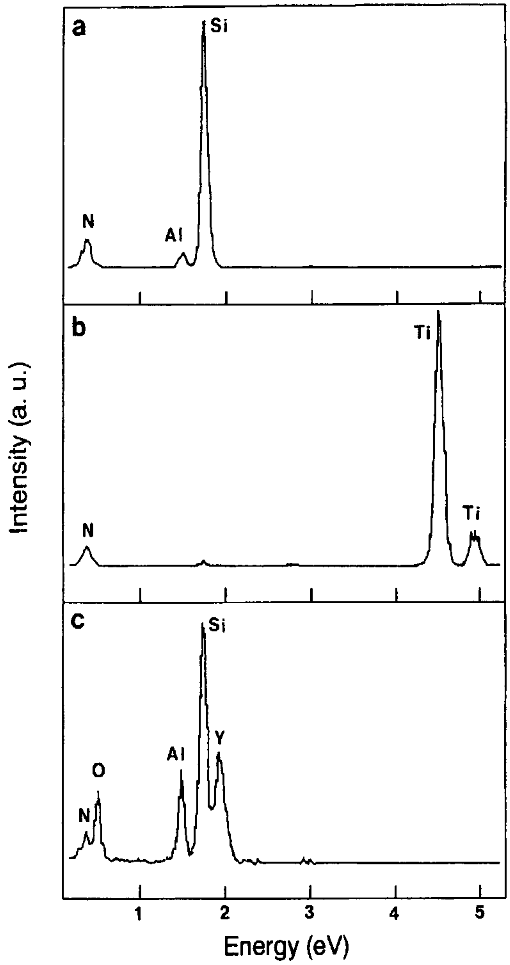


Fig. 7 EDS profiles of 5wt%TiO_2/5wt%AlN specimens fired at 1800C for 1h in 0.9MPa N_2: a ; elongated grain, b; darker spherical grain, c; grain boundary phase.

Since the particle size of raw TiO_2 powder is about 0.17μ m, the size of TiN seems to be reflected by that of the raw TiO_2 powder. A high resolution micrograph of higher contrast TiN grain in the 5wt%TiO_2/5wt%AlN specimens fired at 1800°C is shown in Fig. 8.[18] Many edge dislocations are observed, suggesting the grain was subjected to high stress during firing. Furthermore, the fact that Ti does not exist in grains and grain boundary phases seems to suggest all

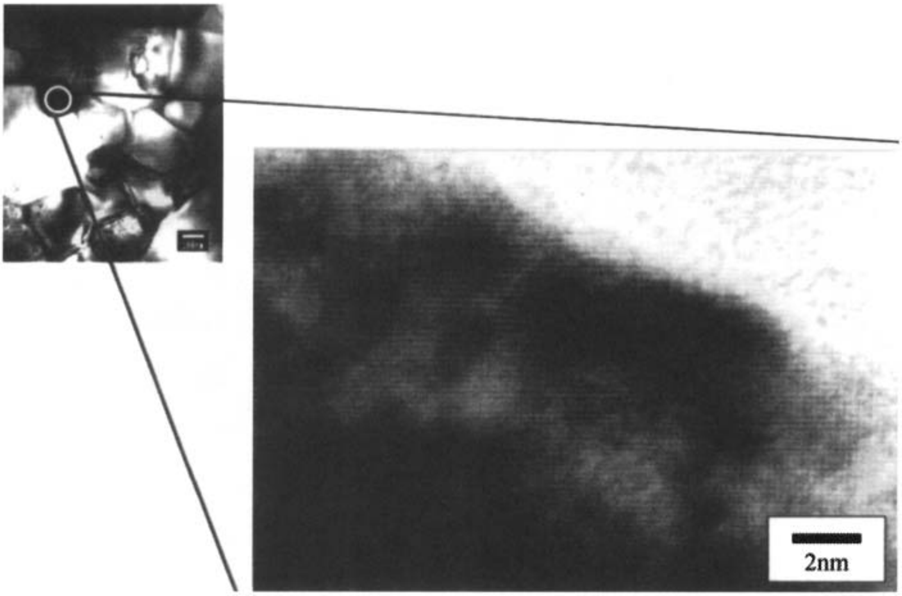


Fig. 8 High resolution micrograph of a TiN grain existed in the grain boundary of the 5wt%TiO_2/5wt%AlN specimens fired at 1800C for 1h in 0.9MPa N_2.

of the TiO_2 is changed into TiN (see Fig.7). Thermodynamically, TiO_2 is considered to react with Si_3N_4 and AlN to produce TiN, SiO_2 and Al_2O_3. Formed SiO_2 and Al_2O_3 probably change the compositions and the amounts of liquid phase at higher temperatures, consequently accelerating the densification. In the sintering promotion, oxide layers on the surface of nitride grains seem to very homogeneous, enabling more effective densification. However, since the above information does not adequately explain the densification mechanism, especially the role of AlN addition as shown in Fig. 4, further experiments should be done in more detail.

EVALUATION BY CONTACT DAMAGE METHOD[19)]

The contact damage test method developed by B.R. Lawn[19)] was adapted for tribological evaluation of the sintered specimens. In order to prepare test pieces, powder compacts of 40×40×6mm with three kinds of compositions, 0/0, 3/3 and 5wt%TiO_2/5wt%AlN were fired at 1800°C for 1h in 0.9MPa N_2, followed by Hipping at 1700°C for 1h in 100MPa N_2. The test pieces (4×3×30mm) were prepared from the sintered bodies. Figure 9 shows the apparatus and a test jig for the evaluation. A tungsten carbide ball with 1.98mm in diameter was used as the loading indentor. In the experiment, ring-like crack called cone crack, are formed

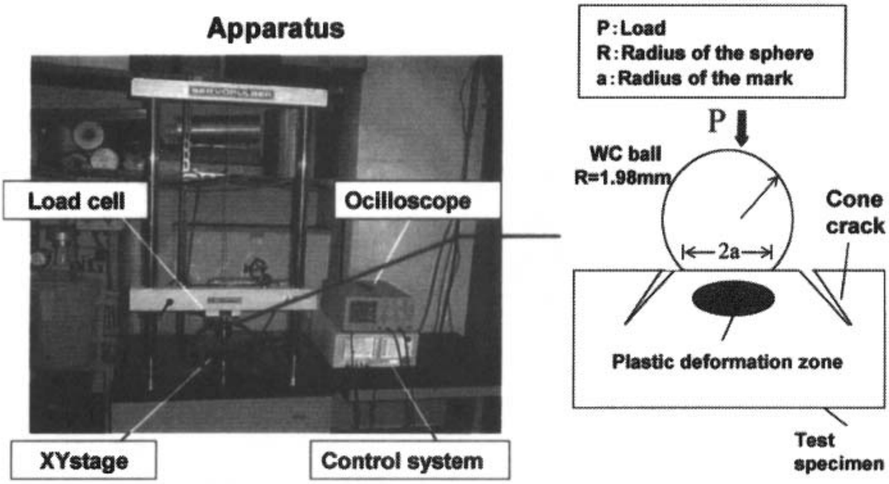


Fig. 9 Apparatus and test jig for contact damage test.

by the loading from the top of the tungsten carbide ball. The initiation of the cone crack and crack propagation behavior were discussed by observation with an optical microscope. The critical crack generation load, P_c, and critical yield load, P_y, were defined as loads at which a Hertz crack completely becomes in a ring and at which the stress ($P/\pi a^2$; P : applied load, a : contact area)-strain(a/R ; R : radius of spherical indentor) curve in the indentation test deviates from Hook's law was observed, respectively.

It was recognized by the observation of indented surfaces that any cracks did not appear in lower value of applied load, but a cone crack was getting more remarkable as increasing of applied load. Figure 10 shows P_c and P_y for compositions of TiO_2 and AlN. This picture confirms that P_c decreases and P_y increases with increase of the amount of TiO_2 and AlN addition. A cone crack also appears and grows by cyclic loading even at lower value of load. Critical cyclic number at which cone crack is completely formed was defined as critical cyclic number for crack generation, n_c. Figure 11 shows the relations between number of cycles and bending strength of the specimen after cyclic indentation under a condition of P=2500N and f(frequency)=10Hz. As seen in the figure, the bending strength of the specimens without TiN particles falls down with increasing the number of cycles. On the other hand, that of TiN particle-dispersed Si_3N_4 specimens is the same value as those before indentation. This fact means that the dispersion of TiN particles prevents the crack propagation under the cyclic indentation. The limitation of the crack propagation probably results from the

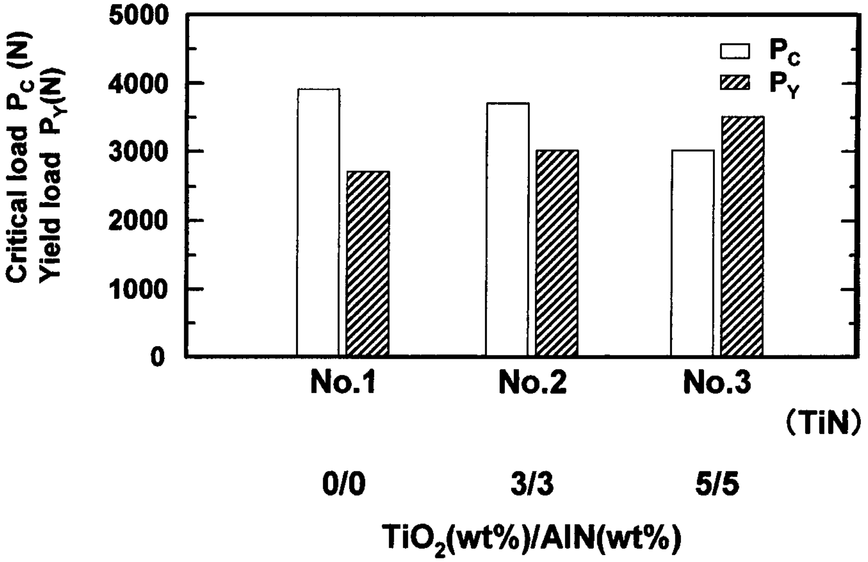


Fig. 10 Critical crack generation load, Pc, and critical yield load (Py) for three types of Si_3N_4 ceramics. No. 1, No.2 and No. 3 specimens were prepared by 0/0, 3/3, and 5wt%TiO_2/5wt%AlN addition in the Si_3N_4-Y_2O_3-Al_2O_3 system, respectively, fired at 1800C for 1h in 0.9MPa N_2. Dispersion concentration of TiN grains is the order of No. 1<NO. 2<No. 3.

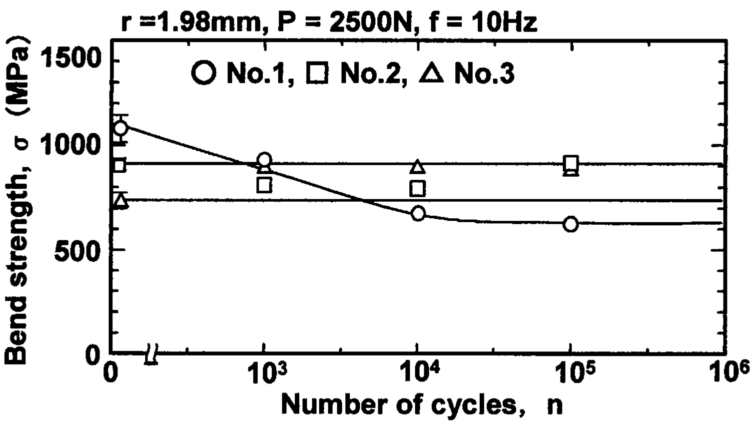


Fig. 11 Bending strength of three types of Si_3N_4 ceramics before and after cyclic indentation. No. 1, No.2 and No. 3 specimens were prepared by 0/0, 3/3, and 5wt%TiO_2/5wt%AlN addition in the Si_3N_4-Y_2O_3-Al_2O_3 system, respectively, fired at 1800C for 1h in 0.9MPa N_2. Dispersion concentration of TiN grains is the order of No. 1<NO. 2<No. 3.

compressive residual stress in grain boundary because of the difference in thermal expansion coefficient between Si_3N_4 and TiN.

It is also understood from the above results that the contact damage test by spherical indentor is much worthy not only to carry out screening of material for tribological applications, but also to evaluate the relation between fatigue behavior and microstructure for material development.

FUTURE WORK

Silicon nitride ceramics are promising candidates for wear parts in various industries. Recently, new or more severe conditions, such as higher operating temperature, more corrosive environments and electrically conductive materials, must be satisfied. To meet these requirements, innovation in creating and improving materials is strongly needed. Another important issue is the tribology of ceramics, especially the theory and evaluation method. The contact damage method is very convenient, but differs from real wear conditions. Fortunately, many articles recently appeared in this area, which is considered to contribute to the progress of Si_3N_4 ceramics as advanced wear materials.

SUMMARY

Silicon nitride ceramics has been confirmed to be an excellent material for wear applications such as bearings. A Si_3N_4-Y_2O_3-Al_2O_3 system with various amounts of TiO_2 and AlN was precisely examined in sintering behavior, microstructure, and tribological characteristics.

Sintering experiments in a firing range of 1300 to 1900°C for 1h in 0.9MPa N_2 revealed the densification was accelerated by the simultaneous addition of TiO_2 and AlN. The phase change from α to β-Si_3N_4 depended on TiO_2 and AlN (i.e., delayed by TiO_2 addition and promoted by AlN addition). Titanium existed only as TiN. From the TEM observation, TiN was located at the grain boundary as spherical grains with about 200nm in diameter, which was independent of firing temperatures. TiN grains were highly stressed, which was confirmed by TEM observation. Furthermore, contact damage test shows that the TiN paricles play an important role in prolonging the life of Si_3N_4 ceramics under cyclic loading.

ACKNOWLEDGEMENTS

I acknowledge New Energy and Industrial Technology Development Organization (NEDO) and Japan Society for the Promotion of Science (JSPS), and Fine Ceramics Research Association (FCRA) for financial supports and continuous encouragement. I thank for Toshiba Corp., especially Mr. M. Komatsu and Mr. Y. Abe, Koyo Seiko Co., Ltd., especially Dr. H. Takebayashi, and Cummins Co., Ltd. for their kind support to present this lecture. I also thank you for my colleagues, Dr. T. Meguro, Dr. J. Tatami, and students, Yokohama National University, Japan and D. K. Kim, KAIST, Korea, for their much efforts on this item. I thank for Fine Ceramics Research Association (FCRA) for his continuous encouragement.

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MEASURING THE ISOELECTRIC POINT OF CERAMIC POWDER SUSPENSIONS: A PRE-STANDARDIZATION STUDY

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ABSTRACT

The isoelectric point (IEP) is a key material property for aqueous-based processing of advanced ceramic powders. The IEP characterizes the acid-base behavior of the powder surface, which in turn influences powder dispersion and chemical interactions at the powder surface. However, international standards for IEP determination are generally lacking. We describe the preliminary results of an international collaborative pre-standards investigation, in which we examine the influence of various material, instrument and measurement factors on IEP determination in moderately concentrated suspensions. These studies focused on electrokinetic sonic amplitude (ESA), colloid vibration potential (CVI), and particle charge determination (PCD), because of their capacity to analyze opaque suspensions.

INTRODUCTION

The isoelectric point (IEP) is defined as the suspension pH at which the electrokinetic potential is zero. The electrokinetic potential is associated with the plane of shear, displaced only a few molecular layers outward from the particle surface. When derived from measurements in which the particles are caused to move under the influence of an electric field, this potential is generally referred to as the zeta potential. The IEP should be differentiated from the point of zero charge (PZC), the latter being the pH at which the surface charge (and surface potential) is zero. IEP and PZC are equivalent only under conditions where specific adsorption of ionic species at the particle surface is absent. PZC, although accessible, is not convenient to measure since it requires at least three independent potentiometric titrations, carried out at different concentrations of supporting electrolyte. The convenience of electrokinetic measurements, coupled with the established correlation linking zeta potential with colloidal stability,[1] has led to their wide use in industrial and academic laboratories.

The "native" IEP is a material property determined by the chemical and phase composition at the powder surface. The measured IEP is sensitive to compositional changes in solution and to the adsorption or desorption of ionic species. The IEP is particularly important for advanced ceramics, where processing is typically surface-driven. That is, the high surface-to-volume ratio of ultrafine ceramic particles determines their behavior to a large extent. Most of these materials are processed in a liquid medium, where the properties of the ceramic suspension are dependent on interactions at the solid-solution interface. Failure to properly control surface reactions can lead to colloidal instability, dissolution, desorption of surfactants, particle agglomeration and, ultimately, poor property performance or high defect rates for manufactured parts.

Unfortunately, there is a lack of established standard procedures for electrokinetic measurements in ceramic systems, and for determining the IEP. As a consequence, wide variations in reported results occur, and reliability of these measurements is called into question. Principal measurement concerns include poor reproducibility, poor precision, unknown or poorly understood dependencies, undefined instrument and technique limitations, unknown and undefined material limitations, and anomalous electrokinetic behavior.

The purpose of the present study is to develop methodology and basic guidance for measuring the IEP of ceramic powders in non-dilute suspensions using commercially available instrumentation. The ultimate goal is to produce a set of standardized test procedures developed in a transparent and cooperative manner at an international level. These test procedures will be bundled and collectively proposed as an ISO standard. Pre-standards research is essential for creating a reliable and fundamentally sound method with well-defined parameters and applicability limits. The importance of collaboration in the development of international standards has also been acknowledged.[2] With this goal in mind, a joint research team was formed, which included participants from standards development organizations in Japan (JFCC), Germany (BAM) and the United States (NIST).

METHODS AND MATERIALS

Some key issues associated with measurements of zeta potential and IEP in *dilute* systems (e.g., using laser Doppler scattering), can be reduced in magnitude or eliminated by the use of more concentrated suspensions.[3] The increased buffering capacity in concentrated systems reduces the adverse effects of contamination and solubility. Efforts have therefore focused on techniques that