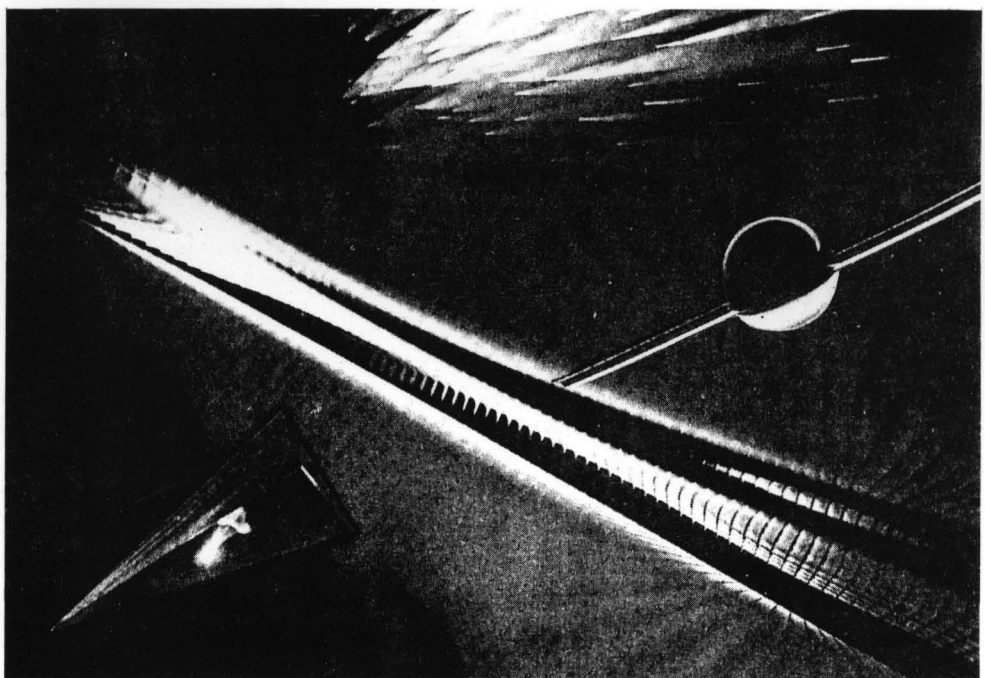


MRS-J
The Materials Research Society of Japan

日本MRS学術シンポジウム

講演要旨集



1991.7.11 川崎市KSP

The Materials Research Society of Japan

日本MRS学術シンポジウム

日 時 1991年 7月11日 (木) 10:00~19:00

場 所 KSPホール (川崎市高津区坂戸100-1 別図参照)

テーマ 第1セッション: 光生物材料研究の新展開

責任者: 松永 是 (東京農工大)

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梶原一人 (")

共催: 電気化学協会生物工学研究会

協賛: 日本化学会

第2セッション: アルミナ・アルミニウム化合物

責任者: 佐藤太一 (静岡大学)

宗宮重行 (西東京科学大学)

中川善兵衛 (東京工業大学)

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日本 M R S
学術シンポジウム・プログラム

第1セッション
光生物材料研究の新展開

7月11日(木)

9:00 受付開始
9:55 開会の辞
宗宮 重行(西東京科学大教授、日本MRS会長)

10:00 1 光バイオ素材の研究展開
松永 是(東京農工大工学部)

10:30 2 光応答性生物素子
矢戸 昌彦(東工大資源研)

11:20 3 二分子膜を利用した光材料の分子設計
下村 政嗣(東京農工大工学部)

昼 休

13:30 4 光合成反応中心のバイオエレクトロニクス材料への応用
三宅 淳、原 正之(微工研)

コーヒープレイク

14:50 5 Biotechnology on Applications of Photo-Synthetic Bacteria.
G. Bugess, (Univ. of London)

15:40 6 微細藻類の炭酸ガスの濃縮機構
都築 幹夫(東大応微研)

16:30 7 地球と光合成
藤田 善彦(基生研)

17:20 8 閉会の辞
宗宮 重行(西東京科学大)

Photoresponsive Biodevices

Masahiko Sisido
Research Laboratory of Resources Utilization
Tokyo Institute of Technology

1. Introduction

Light is a clean signal that can control chemical and biological reactions without disturbing total system significantly. Besides the photosynthetic system that utilizes photons as energy source, a variety of biological systems have been known to show photoresponsiveness. In addition, many chemists and biochemists have been attempting to modify biological systems that are not photosensitive in nature to acquire photoresponsiveness. The purpose of the additional photoresponsiveness is very broad, i.e., for fundamental research on the mechanism of biological reactions, for biomedical applications, such as phototargetting in drug delivery, and for the development of biodevices that may find applications in future. In these possible applications, the advantages of light signal are fully exploited. Light is advantageous over other signals (chemical, heat, electric, radiation, etc) in the following respects. (1) Photon may be transported through space without direct contact with the object. (2) Photon energy may be selected by the wavelength. (3) Photon signal may be compressed as a short pulse of a few ten femtosecond. (4) Photon signal may be concentrated in a small spot of $1 \times 1 (\mu\text{m}^2)$ or less. Although the application of the photoresponsive biological systems to the field of biomedical chemistry and biodevices is still very limited, the potentiality of the photoresponsive systems seems promising, because of the above characteristics. In this article, the author will try to review works that have been made in the past two decades together with recent advances in this field. Among the works in the past, pioneering attempts by Suzuki and coworkers and those of Erlanger are especially noteworthy.

2. Direct Photomodulation of Enzyme Activity

Photomodulation of enzyme activity provides an approach to switch biological processes, because the change of activity of one enzyme molecule may induce changes in a large number of product molecules. Suzuki and Karube used membranes carrying spiropyran derivatives to immobilize enzymes and found that the enzyme activity can be controlled by photoinduced change in the hydrophilic character of the medium. Enzymes has been directly modified by covalently linking photochromic groups by Aizawa and coworkers. They attached spiropyran derivatives to enzymes and showed that a reversible photoregulation of enzyme activity can be achieved due to the alteration in hydrophilicity-hydrophobicity of the protein microenvironments. Very recently, Willner, et al. reported a photoregulation of papain activity through anchoring azobenzene groups to the enzyme backbone.

3. Modulation by Photochromic Effectors

A group of low molecular weight compounds are known to regulate enzyme activity. For example, inhibitors may bind

active site of enzyme competitively with substrates and suppress the catalytic activity. Erlanger et al. synthesized artificial inhibitors that carry azobenzene groups. They showed that the activities of serine esterases (chymotrypsin, trypsin, and acetylcholinesterase) may be photoregulated by the photochromic inhibitors. They also synthesized an activator mimic carrying an azobenzene group and found that the agonist works as an open channel blockers of acetylcholine receptors on the membrane of Electrophorus electricus. They showed that the potential difference across the membrane can be regulated by exposure to light of appropriate wavelengths.

4. Photocontrol of Antigen-Antibody Reactions

The authors prepared monoclonal antibodies for oligopeptide carrying azobenzene unit. Mice was immunized with the peptide carrying trans-azobenzene unit. The antibody bound the trans peptide effectively, but not for the cis peptide. The photocontrol was reversible. Therefore, the monoclonal antibody will be used as a photoreversible carrier, that may be applicable as phototargetting of drugs. Monoclonal antibodies against molecules that are capable of trans-cis isomerization and those against quinone unit has been prepared in Schultz's group. They showed that the uptake and release of the antigen-antibody reaction can be controlled by electric signal. Harada, et. al prepared monoclonal antibodies for porphyrin unit.

5. Microphotopatterning of Biomolecules and Cells

As described above, one of the advantages of light signal is its spatial selectivity. Therefore if some photoresponsive biomolecules are placed on a 2-dimensional space and the surface is illuminated through a mask, a pattern of the biomolecules will result. Fodor, et al. performed solid-phase peptide synthesis using photolabile protecting groups on a glass surface. They succeeded to link particular pentapeptide molecules in a particular site of the glass surface by using photomasks repeatedly. They showed the formation of the pattern by attaching monoclonal antibodies against the pentapeptide.

Matsuda and coworkers. demonstrated that animal cells can be patterned on a polymer surface by linking photoreactive hydrophilic polymers.

6. Concluding Remarks

Development of photoresponsive biodevices and their arrangement or organization on 2-dimensional surface are interesting from a viewpoint of basic research. However, the utilization of these biodevices in microsensors and other bioelectronic systems will require further advances, especially, in the method for transporting biosignals between the biodevices. In this respect, studies on electron transfers inside a protein molecules or between different biomolecules as well as other signal transports will become important in the next decade.

二分子膜を利用した光材料の分子設計

Molecular Design of Artificial Photosynthesis Based on Synthetic Bilayer Membranes

Davydov Splitting and Exciton Migration in Stilbene-Containing Bilayer Membrane.

Masatsugu SHIMOMURA

下村政嗣

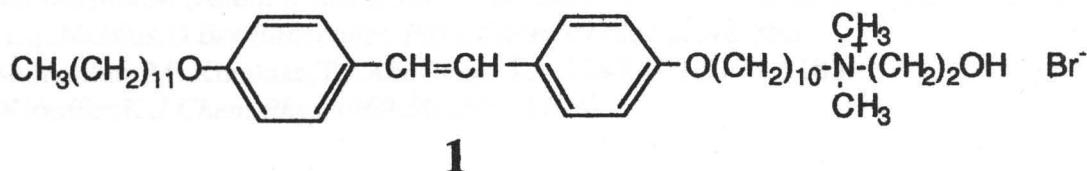
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東京農工大学工学部物質生物工学科

Construction of "artificial photosynthetic system" is an attractive subject not only from a practical standpoint of photo-energy conversion but also from biomimetic interests of molecular organizates. Effective photo-energy collection is indispensable in designing an antenna system in the artificial photosynthesis. Extremely efficient energy migration have been observed in organic molecular crystals where the excitation energy is delocalized in the crystal as "exciton". In spite of this fact, organic molecular crystals are generally considered to have little potentials for the antenna system, because of its difficulty to couple with the reaction center.

We have reported that a large Davydov splitting in absorption spectrum suggesting "exciton" formation was found in an aqueous bilayer membranes containing azobenzene chromophores.¹ In this article, we wish to report the first definitive evidence for "exciton" migration in a stilbene bilayer membrane, where we found a remarkable Davydov splitting and a satisfactory fitting of energy transfer to the "exciton" hopping kinetics proposed for organic molecular crystals. The finding that the "exciton" migration can be realized even in aqueous solution is quite significant not only for construction of an efficient antenna apparatus but also for creative novel aspects of molecular organizates in general.

Artificial photosynthetic systems require photoreaction centers where efficient charge separation occurs and antenna systems for effective collection of photoenergy. The reaction center has been modeled by various molecular assemblies — micelles, monolayers and multilayers, and vesicles. The photoenergy collection is based on efficient energy migration in the form of exciton. The excitonic antenna system in designed molecular assemblies was pioneered by Kuhn and Möbius using cyanine dyes embedded in the Langmuir-Blodgett film.² We are interested in construction of photoenergy-conversion systems on the basis of self-assembling synthetic bilayers.³



Absorption spectrum of **1** in ethanol shows a typical pattern of trans stilbene, whereas a large

hypsochromic shift is observed for a transparent aqueous bilayer solution. This shift is apparently attributed to the H aggregation (card-packed orientation) of the stilbene unit, as found in stilbene LB films. Red-shifted, structured fluorescence (around at 400nm) of the bilayer solution is ascribable to the "free exciton" emission from the lowest level of exciton band. Broad emission from "excimer" or "self trapped exciton" is not detected.

There is observed efficient migration of the exciton, as evidenced by energy transfer to acceptors (e.g. anionic fluorescence dyes) incorporated in the bilayer membrane. If the excitation energy is transferred via exciton hopping mechanism, quenching kinetics should follow that of the exciton diffusion model proposed by Klöpffer for organic molecular crystals.⁴ In this mechanism, quenching factor Q is defined as

$$Q = (I_0 - I) / I \quad (1)$$

where I_0 and I are fluorescence intensities of the donor membrane in the absence and presence of an acceptor molecule, respectively. Q is proportional to the trapping probability, which is given by a product of three terms; jumping probability within the exciton lifetime, absolute probability of exciton capturing by an acceptor molecule, and molar ratio of the acceptor molecule (mol/mol).

If the capturing probability is unity and only the acceptor molecule acts as energy trap (i.e., there is no excimer emission), then

$$Q = nc(1 - F) = n'c \quad (2)$$

where c is acceptor concentration (mol/mol), n is the hopping number of exciton, F is the probability that the exciton returns to its starting point in the random walk process, and n' is equal to $n(1 - F)$.

The fluorescence emission of the cationic stilbene bilayer is quenched efficiently by anionic fluorescein molecule, and fluorescence of the energy acceptor appears at 530 nm. The quenching experiment was conducted for sixty-three combinations of the donor and acceptor concentrations.

Double-logarithmic plots of the data according to eq. 2 give a straight line with slope of 1.0 as given implying that the exciton hopping model is applicable to the present system. Semi-logarithmic dependence on the quencher concentration as expected for a "static quenching sphere" model of Perrin was not observed. The value of the intercept ($\log n' = 3.0$) indicates that the singlet exciton hops around more than 1000 times within its lifetime. Although the hopping number is smaller by about one order of magnitude than those of the molecular crystal or the Langmuir-Blodgett film, it is close to the average aggregate number of the bilayer membranes, and the exciton migrates very effectively in a bilayer aggregate.

In conclusion, the stilbene bilayer produces molecular systems for efficient exciton migration. Our findings will play an important role in the design of artificial photosynthetic apparatus, especially because of the self-assembling nature of synthetic bilayer membranes.

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Application of Photosynthetic Reaction Centers for Bioelectronic Materials

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Summary

Photosynthetic reaction centers in photosynthetic membranes were found to maintain their structures and functions (charge-separation) even they were dried to a thin film. Oriented immobilization of the membrane was examined to enhance the efficiency of the photo-electric conversion.

Chromatophores of photosynthetic bacteria were prepared from Rhodospseudomonas viridis and Rhodobacter sphaeroides. Chromatophores were dried to a thin film on metal electrodes (NESA or ITO) in vacuo. Spectrum of the chromatophore film was identical to that in aqueous suspension indicating that the chromophores in protein molecules kept their spatial arrangements ^{1,2}. The dried film of R. viridis showed high stability against heating.

Thin film of chromatophore ca. 10^{-2} mm thickness was made on a transparent electrode (NESA or ITO). The film was sandwiched with a metal electrodes (Au or Hg). Pulsed excitation light by a xenon flash lamp through a light cut-off filter at 720 nm induced a transient photo-current with a peak of 10-100 pA ^{1,2}. The electric response was given by the charge separation process of photosynthesis in the reaction centers (RC) of the membrane.

Oriented immobilization of the chromatophore membrane on solid surfaces was achieved by the selective immobilization using avidin-biotin interaction ³. Rps. viridis chromatophore was used. H- And C-subunit of the RC project opposite sides of the chromatophore membrane. H-Subunit was more effectively reacted than the C subunit with sulfosuccinimidyl-6-(biotinamido)hexanoate. Biotin-bound H-subunit side of the membrane was selectively attached to the avidin-coated surface (4-fold as much as C-subunit side). Photo-electric response was much improved by the oriented immobilization ³.

A wet-type photocell was also made with two sheets of SnO₂ electrodes placed with a narrow gap ⁴. Highly concentrated chromatophore suspension was filled in the gap to make a sharp gradient of the light intensity for the generation of electron flow. Stable current response was observed under illumination.

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BIOTECHNOLOGICAL APPLICATIONS OF PHOTOSYNTHETIC BACTERIA

J. GRANT BURGESS

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Abstract

The objective of this research is to establish technologies which can be applied to microorganisms for the production of novel biological substances. In particular, the marine biotechnological use of photosynthetic procaryotes is attractive since these organisms utilize solar energy and seawater to fix carbon into utilizable biomass. In addition, the high degree of biodiversity which exists among marine organisms should allow isolation of new species or strains capable of producing novel materials. A program of genetic manipulation of marine photosynthetic bacteria has been initiated to allow improvement of desirable functions in selected marine species. Genetic and conjugative gene transformation systems have been established for non sulfur and sulfur bacteria. Expression vectors have been constructed from *Rhodobacter* specific replicons in addition to the use of broad host range plasmids. These results are discussed in view of parallel studies which have been carried out for marine cyanobacteria. The present potential of marine biotechnology for the production of new materials is very high. In addition, other biological systems such as macroalgae are also attractive bioresources. Establishing advanced recombinant DNA technologies for marine photosynthetic organisms is an essential future requirement for improving the efficiency of bioprocess industries which utilize such organisms.

Introduction

The aim of biotechnology in general is to supply products and services which are based on the materials produced by cultured microorganisms or cells. In recent years, the use of organisms from marine habitats has received much attention and the new field of 'Marine Biotechnology' has developed. The products and services which marine biotechnology can provide may be divided into six main categories: (1) Waste recycling and pollution control (Environmental Biotechnology), (2) Energy production (3) Biomaterials and their modification, (4) Heavy chemicals including animal feedstocks and solvents, (5) Fine chemicals including pharmaceuticals and agrochemicals, and (6) Extraction of minerals (metals or oil recovery). In this work I will discuss the use of Marine Biotechnology in the production of New Biomaterials with emphasis on photosynthetic microorganisms as a source of such materials. The use of solar power as an energy source is increasing in importance due to environmental considerations and to the political and economic factors associated with using conventional fossil fuels. Conventional agriculture and forestry, essentially the only technologies to use photosynthesis, are very inefficient, storing only 0.2 % of the total incident radiation¹. However, by using photosynthetic microorganisms combined with the use of photobioreactors up to 18% of incident energy can be stored². The use of photobioreactors for the primary production of biomass can readily overcome the limitations of conventional agriculture. Recently, highly efficient photobioreactors which employ light diffusing optical fibers have been developed for the production of glutamate from marine cyanobacteria^{3,4}. Such reactors are ideal candidates for scale up to the manufacture of a more diverse array of new products.

The Potential Use of Photosynthetic Microorganisms in Biotechnology.

I PHOTOSYNTHETIC BACTERIA.

Although an extremely well studied group of microbes, the biotechnological applications of photosynthetic bacteria have remained relatively limited to such processes as hydrogen production and waste water treatment. In addition, until recently the majority of studies on marine photosynthetic bacteria in particular have been confined to characterization of new marine species. It is surprising that despite the powerful molecular genetic tools which exist for the manipulation of freshwater nonsulfur bacteria such as *Rhodobacter capsulatus* and *Rb.sphaeroides*⁵ very few reports of biotechnological applications involving recombinant strains have appeared⁶. A gene transfer system for marine photosynthetic bacteria was first reported for a hydrogen producing marine *Rhodobacter*⁷. However, compared to the freshwater photosynthetic bacteria, recombinant DNA techniques for marine species are not as advanced despite recent improvements⁸. No gene transfer systems have previously been reported for purple sulfur bacteria despite their common occurrence in marine ecosystems. We have recently observed the production of antimicrobial compounds from a marine sulfur photosynthetic bacterium *Chromatium* sp.. These substances have a broad antimicrobial spectrum being antagonistic towards both Gram negative and Gram positive bacteria as well as mold and yeasts. These findings are significant in that they represent the first example of the purification of pharmaceutically important compounds from a photosynthetic bacterium. High density culture of this species has also been obtained in a photobioreactor and the structure of the active compounds determined. A gene transfer system for marine *Chromatium* sp. has also recently been established.

Recent environmental concern has prompted a renewed interest in the photoproduction of molecular hydrogen by autotrophic bacteria as a clean energy source. In addition, the production of polyhydroxyl alkananoates (PHAs)

has become increasingly important for the production of biodegradable plastics. The photosynthetic bacterium *Rhodospirillum rubrum* has recently been reported to be a potential source of

PHA based biodegradable polyesters⁹. It would appear probable that marine photosynthetic bacteria may also be used for the production of such polymers.

An additional advantage of using marine bacteria for biotechnological applications is the high degree of biodiversity which exists in marine environments. Recently two completely new phylogenetic groups of bacteria were discovered after PCR amplification of 16S RNA genes from natural populations of marine picoplankton¹³. One group was related to the oxygenic phototrophs while the other was phylogenetically related to the α -purple bacteria. We have also found during the course of our studies that the physiological diversity of marine anoxygenic photosynthetic bacteria isolated from coastal and open waters from the Pacific and the Sea of Japan is greater than previously reported. One marine *Rhodobacter* strain NKP0021 was found to be sensitive to oxygen, being unable to grow aerobically in the dark. In addition, strain 0021 was found to be sensitive to sulfide since growth was not possible at concentrations of over 7mM sulfide.

" NEW MATERIALS " FROM PHOTOSYNTHETIC BACTERIA

ENZYMES	RESTRICTION ENZYMES EG <i>RSAI</i> AND <i>RSR II</i> FROM <i>RHODOBACTER SPHAEROIDES</i> PROTEASES POLYNUCLEOTIDE PHOSPHORYLASE (USED IN INTERFERON PRODUCTION) 6 APA ASES (PRODUCTION OF PENICILLIN DERIVATIVES)
PIGMENTS	PORPHYRINS (ANTI TUMOUR THERAPY)
ANTIBIOTIC	BROAD SPECTRUM ANTIBIOTICS FROM MARINE <i>CHROMATIUM SP.</i>

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" NEW MATERIALS " FROM PHOTOSYNTHETIC BACTERIA

ENZYMES

RESTRICTION ENZYMES EG *RSAI* AND *RSR II*
FROM *RHODOBACTER SPHAEROIDES*
PROTEASES
POLYNUCLEOTIDE PHOSPHORYLASE
(USED IN INTERFERON PRODUCTION)
6 APA ASES
(PRODUCTION OF PENICILLIN DERIVATIVES)

PIGMENTS

PORPHYRINS (ANTI TUMOUR THERAPY)

ANTIBIOTIC

BROAD SPECTRUM ANTIBIOTICS FROM MARINE
CHROMATIUM SP.

1-5-6

LIPO POLYSACCHARIDES

PRODUCTION OF DIPHOSPHORYL A FROM
LIPOPOLYSACCHARIDES

(PREVENTION OF ENDOTOXIN SHOCK
DURING GRAM NEGATIVE INFECTION.)

PHA

RB. SPHAEROIDES 60 - 70 % DRY WEIGHT

RPS. RUBRUM 45 % DRY WEIGHT

" NEW MATERIALS " FROM PHOTOSYNTHETIC BACTERIA

APPLICATIONS OF MOLECULAR BIOLOGY

EXPRESSION OF FOREIGN GENES IN PHOTOSYNTHETIC BACTERIA

CELLULASE

TUNA GROWTH HORMONE

LIGHT HARVESTING COMPLEX

RUBISCO

SECRETION OF FOREIGN PROTEINS

NEW VECTORS,

COPY NUMBER MUTANTS

PROTEIN ENGINEERING

REACTION CENTERS

LIGHT HARVESTING COMPLEXES

ENERGY STORAGE DEVICES

ATRAZINE BIOSENSORS

" OPERON ENGINEERING "

NOVELPHOTOSYNTHETIC

COMPLEXES

IMPRIVED PIGMENT PRODUCTION

(CAROTENOID BIOSYNTHESIS)

METABOLISM CONTROL

II CYANOBACTERIA

The development of recombinant DNA methods for marine cyanobacteria has also occurred less rapidly than for freshwater species. Genetic transformation procedures are now available for marine *Synechococcus* sp.¹⁰ using shuttle vectors constructed from endogenous cryptic plasmids. The strain for which these techniques were developed, *Synechococcus* sp. NKBG 042902, has been found to contain compounds which stimulate somatic embryogenesis of carrot¹¹. In addition, extracts of this cyanobacteria greatly enhance germination frequency when added to artificial seeds encapsulating carrot somatic embryos. Marine cyanobacteria have also been used for the production of glutamate and γ -linoleic acid¹².

BIOTECHNOLOGY OF MARINE CYANOBACTERIA

" TRADITIONAL "

HYDROGEN PRODUCTION

SPIRULINA

HEALTH FOOD

PHYCOCYANIN (IMMUNODIAGNOSTICS)

SCP FOR ANIMAL AND FISH FOOD

Γ LINOLENIC ACID

" NEW BIO MATERIALS "

BIOACTIVE METABOLITES

LYNGBYA SP. O-METHYL ACID A GRAM POSITIVE ANTIBIOTIC

RIVULARIA SP ANTI INFLAMMATORY DRUGS

HAPLOSIPHON SP POTENT ANTIBIOTIC

ANTICANCER AGENTS (TUMOUR PROMOTERS)

TOXINS (NEUROBIOLOGICAL RESEARCH)

PLANT GROWTH REGULATORS

PROMOTION OF SOMATIC EMBRYOGENESIS AND PLANTLET FORMATION USING EXTRACTS FOM MARINE BACTERIA.

PHOTOPRODUCTION OF NIROGENOUS COMPOUNDS

AMMONIA, AMINO ACIDS EG. GLUTAMATE
SECRETION

U.V. ABSORBING COMPOUNDS USED IN COSMETICS / SKIN CARE

In addition to the production of useful substances photosynthetic biomass production by cyanobacteria also results in fixation of carbon dioxide. This CO₂ recycling process may be used to absorb excess CO₂ released by other industrial processes thus reducing the quantity of CO₂ released into the atmosphere. The manufacture of new materials by marine photobiotechnology may therefore be beneficial to the environment.

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現在、大気中の CO_2 濃度は約 350 ppm で、1年間に約 1 ppm の割合で上昇し続けている。これが続くと地球の温暖化を引き起こすことから、今や早急な対策が求められている。そのため、それぞれの産業界で生産工程の効率化が計られているが、その一方で、物理的、化学的、さらには生物学的手段によって、工場から出る排ガスや大気から CO_2 を固定し、その濃度を減らすことも必要である。光合成の利用は、その中で重要な生物学的手段である。光合成のメカニズムをより深く理解し、それをどのように利用するか、その時どんな問題点があるのか、明らかにする必要がある。ここでは、藻類の光合成 CO_2 固定の特徴の一つである CO_2 濃縮について紹介する。

1. 微細藻類の光合成に及ぼす生育時の CO_2 濃度の影響

クロレラやスピルリナなどの微細藻類は、大気中の CO_2 濃度条件下で生育すると、その光合成活性は、 CO_2 に対し高い親和性を示す。その特性は、2~5% の高い CO_2 濃度条件下で生育すると、失われることから生育中の CO_2 濃度に依存した現象と考えられている。その原因として、1. 微細藻類では、無機炭素(Ciと略す。 CO_2 、 HCO_3^- 、 CO_3^{2-} などの総称)を細胞内に濃縮蓄積すること、2. カーボニックアンヒドラーゼ(CAと略す)が CO_2 と HCO_3^- の間の水和脱水反応を触媒し、リブローズ 1, 5-ビスリン酸カルボキシラーゼ(RuBisCO)への CO_2 供給を促進することがあげられる。しかし、そのCi輸送のメカニズムは、種によって多様化しており、まだ不明な点が多い。これまで、らん藻と緑藻を中心に研究が行われてきた。両者では現象としても、また、研究のストラテジーとしても対照的である。

2. らん藻における CO_2 濃縮

らん藻では、光合成の時、Ciを1000倍も細胞内に濃縮する。反応速度論による解析から、 HCO_3^- を能動的に輸送する系が細胞膜に存在すると考えられ、その能動輸送に関与するタンパク質が探索されてきた。しかし、多くの研究者の努力にもかかわらず未だ見い出されていない。そこで、らん藻から高 CO_2 条件でしか生育できない変異株を得て、野生株の遺伝子による相補性を調べるという研究も合わせて行われてきた。しかし、これまで解析された変異株のほとんどは、RuBisCOの遺伝子付近に変異が見られるもので、 HCO_3^- の能動輸送に関する変異株は、小川(理研)の報告した一株だけである。その株の変異部分はNAD dehydrogenaseのサブユニットと高いホモロジーをもっていた。

3. 緑藻におけるCi輸送とクラミドモナスの細胞表層CA

緑藻では、らん藻ほどにはCiを細胞内に濃縮しない。しかし、細胞内に取り込んだCiを、らん藻より効率よく固定するため、 $K_m(\text{CO}_2)$ 値は、らん藻も緑藻も変わらない。そこで、単細胞緑藻の *Chlorella vulgaris* 11h においてCiが細胞内へ取り込まれRuBisCOによって固定される過程を解析した。その結果、細胞は CO_2 も HCO_3^- も共に取り込むが、定常的にはほとんどが CO_2 であること、葉緑体内にあるCAが CO_2 と

HCO_3^- の平衡化をはかることによって、 CO_2 の固定効率が高められていることが明らかとなった。

ところが、CAは種により細胞内のみならず細胞表層にも存在する。*Chlamydomonas reinhardtii*の細胞表層のCAは、細胞表層で HCO_3^- を CO_2 に変換すると考えられるが、可溶性で比較的安定であることから、研究が進んでいる。大小2つのサブユニットが2個ずつS-S結合で結ばれている糖タンパク質で、大サブユニットにZnが結合している。福澤らは、その遺伝子を得て解析した結果、大サブユニットの後に小サブユニットがコードされていること、その遺伝子は10個のイントロンによって分断されていること、大サブユニットのN末側に20のアミノ酸残基からなるシグナルペプチドが存在すること、そのCA遺伝子(CAH1)と非常によく似た遺伝子(CAH2)がCAH1とタンデムに並んでいることなどが明らかになった。CAH1は低 CO_2 濃度光条件下で転写するのに対し、CAH2は高 CO_2 条件下で転写されていることも明らかになった。

しかし、細胞表層にはCAを持たない藻類がいることから、細胞表層のCAは、 CO_2 への高い親和性に不可欠のものとは考えにくく、むしろ、高い親和性によって生じる、新たな律速段階を解除すると考えられる。緑藻では、 CO_2 に対する高い親和性の直接の要因として、葉緑体内のCAとピレノイドがあげられる。ピレノイドは主にRuBisCOからなり、低 CO_2 濃度条件下で発達する点では、らん藻のカーボキシゾームとよく似ているが、ともに、まだこれから研究される状態である。そのため、 CO_2 濃縮の詳細なメカニズムは、まだ殆ど仮説の段階にすぎない。とはいえ、現在、生理学レベルの研究方法やその知見がかなり充実しつつある点を考慮すると、例えばポリサッカライドを細胞外にためるポルフィリディウムなど、 CO_2 固定による環境保全だけでなく、有用物質生産もあわせて工業的に利用さうる可能性もあろう。

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地球と光合成—地球環境を決定し維持している光エネルギー変換系

基礎生物学研究所

藤田善彦

分子状酸素を20%も含む大気にかこまれた地球に生活する殆どすべての生物にとって酸素の存在する環境は生きる上での前提となっている。我々人間を含めた動物や菌類はもちろん、光合成を営む植物の場合でも、酸素呼吸—有機物を酸化分解しエネルギーを生産する代謝によって生命を維持するエネルギーをいっている。酸素なしの環境では今日の地球の生物界を考えることが出来ない。ではこのような地球環境は40億年を越える生物の進化の前提として存在したのであろうか。近年になり著しく進歩した進化の研究によれば今日の地球環境は長い歴史を持つ生命活動の所産であり、また今日の生物による生命活動により支えられているものと言える。微化石の研究から約35億年前には今日のバクテリアと同様な細胞が誕生していたことが判っている。そして、それから数億年後に今日の植物が営む酸素を発生する光合成が誕生し、地球環境に酸素をもたらした。太陽エネルギーを用いて炭酸を固定し酸素を発生する光合成が一方では地球環境を変え、他方ではそこに生きる生物へ有機物を供給し、今日の多様な生物界を生み出す原動力となって来た訳である。酸素を発生する光合成は我々が普通植物と呼ぶ陸上の高等植物のみが営むものではない。水の中に生活し光合成を営む藻類、そして今日でもバクテリアと同じく原核体制で生きるラン藻も同じしくみの光合成を営む。高等植物が出現したのは約4億年前と言うので酸素を発生する光合成の誕生から二十何億年と言う長い間は水の中で光合成が営まれ、その長時間をかけて光合成生物の進化の営みが進められた。今日の光合成生物の系統群の殆どが水の中に生活するものであることはその結果である。基本的には同じしくみで営まれる光合成も、その光エネルギーの集め方など藻類の系統群ごとに特徴があるのはそのためである。

酸素を発生する光合成の特徴は、水を酸化して酸素を発生する光化学反応を営む光化学反応複合体(PS II)とNADP⁺の還元をもたらす複合体(PS I)の2種の光化学反応が協調的に働くことにあり、この協調性の維持と光エネルギー捕獲効率により光エネルギー変換の効率が大きく決定される。光エネルギー捕獲からエネルギー変換固定にいたる過程は高い効率で進行している。この効率を維持する上で2段階の調節能をエネルギー変換系に持ち、光合成の光環境に対応して効率の維持をはかっている。

第一は言わば粗調節に当たるもので、光捕獲を行う光合成色素系では光強度に対して色素系のサイズが、また光質にたいしては光吸収色素の分子種を変えて対応する。光化学反応系レベルでは協調が破られると、これを回復するようにPS IとPS IIの量比が変更調節される。これらの粗調節は光合成色素系の形成、PS I、PS IIの形成とともに行われるもので、葉緑体や細胞の増殖が前提となる。

これに対して言わば微調節となっているものは、光合成色素系からPS I、PS IIへのエネルギー移動の比率の調節で、PS IとPS IIの協調が破られるとまずこの調節がおこり次に上の粗調節がおこる。このような調節能が存在することは比較的最近になって判って来たので、その詳細な機構には不明な点が多い。しかし、原核生物であるラン藻から高等植物までの光エネルギー変換系が共通に持つ能力らしく、酸素発生を行なう光合成が成立して以来持ちつづけられて来た能力のように思われる。光エネルギーを化学エネルギーに変換するという物理化学的性格を持つ系でも生物特有の調節が働いている訳で、光合成の機能分子の分子機構と共に、これらシステムとしての調節のしくみが動的に働いて光合成効率が維持されていると言えよう。

ここでは、酸素を発生する光合成と地球環境の遷移を概観すると共に、その特徴を藻類と言う水の中の光合成生物の場合について述べてみたいと思う。

日本 M R S
学術シンポジウム・プログラム

日時 第2セッション
アルミナ・アルミニウム化合物

7月11日(木)

9:00 受付開始

9:50 開会の辞

宗宮 重行(西東京科学大教授、日本MRS会長)

10:00 1 水酸化アルミニウム、アルミナの物理化学
水酸化アルミニウムの水熱反応とアルミナの水和
佐藤 太一(静岡大名誉教授)

11:00 2 アルミナの焼結及び粒界移動
浅賀 喜与志(西東京科学大学教授)

11:30 3 アルミナの焼結に対する添加剤の効果
中川 善兵衛(東工大助教授)

————— 昼 休 —————

13:00 4 アルミナセラミックスの評価法
高津 學(名工大教授)

13:50 5 電子部品用アルミナセラミックスの製法と特性
大塚 寛治(株日立製作所)

————— コーヒーブレイク —————

15:10 6 SiC whisker 強化アルミナ複合材料の製法と高靱性化
山田 恵彦(西東京科学大教授)

16:00 7 Creep Damage Mechanisms in Alumina During Tensile and Bent Testing
D. S. WILKINSON and C. H. CACBRES (McMaster University, Canada)

16:30 ポスター概要発表(現在18件、一件約3分)

17:30 ポスターと懇親会

The Materials Research Society of Japan

Symposium on Alumina and Aluminum Compounds

July 11, 1991

Kanagawa Science Park, Tel:044-819-2001, Fax:044-819-2009
100-1, Sakado, Takatsuku, Kawasakishi 213

ORAL PRESENTATION

9:50-10:00 OPENING REMARKS

Shigeyuki SOMIYA, President of MRS of Japan

10:00-11:00

Physical Chemistry of Aluminum Hydroxides and Aluminas—Hydrothermal
Reaction of Aluminum Hydroxides and Hydration of Alumina—

Taichi SATO

Faculty of Eng., Shizuoka University, and Queen's University

11:00-11:30

Sintering and Grain Boundary Migration of Al_2O_3

Kiyoshi ASAGA

Dept. Mater. Eng., the Nishi Tokyo University

11:30-12:00

Effect of Additives on Sintering of Alumina

Zenbe-e NAKAGAWA

Res. Lab. Eng. Mats., Tokyo Institute of Technology

12:00-13:00 LUNCH

13:00-13:50

Evaluation of Thermal and Mechanical Fatigue Properties of Alumina
and Feed-Back Treatment to Control its Microstructure

Manabu TAKATSU

Dept. Mats Sci. Eng., Nagoya Institute of Technology

13:50-14:40

Alumina Ceramics Preparation and its Properties for Electronics Uses

Kanji OTSUKA

Device Development Center, Hitachi Ltd.

14:40-15:10 COFFEE BREAK

15:10-16:00

SiC Whisker-Reinforced Alumina Composite

Shigehiko YAMADA

Dept. Mater. Eng., the Nishi Tokyo University

16:00-16:30

Creep Damage Mechanisms on Alumina During Tensile and Bend Testing

David S. Wilkinson

Dept. Mats. Sci. Eng., McMaster University

POSTER PRESENTATION

16:30-17:30

Oral Presentation (3 minutes for 1 paper)

17:30-19:30

Poster and Discussion

Physical Chemistry of Aluminium Hydroxides and Aluminas

— Hydrothermal Reaction of Aluminium Hydroxides and Hydration of Aluminas

Taichi Sato

(Faculty of Engineering, Shizuoka University, Hamamatsu, Japan and Queen's University, Metallurgical Engineering Department, Kingston, Ontario, Canada)

Crystalline aluminium hydroxide is composed of five kinds of hydrargillite (and/or gibbsite), bayerite and nordstrandite classified as aluminium trihydroxide and of boehmite and diaspore classified as aluminium oxyhydroxide. Gelatinous aluminium hydroxide consists of amorphous aluminium hydroxide, pseudoboehmite and intermediate boehmite. The aluminium hydroxides prepared by various procedures are thermally decomposed to a number of anhydrous aluminas in a process leading ultimately to α -alumina. In this presentation, the results for the hydrothermal reaction of crystalline and gelatinous aluminium hydroxides and the hydration of aluminas are given in relation to the properties of aluminium hydroxides and aluminas.

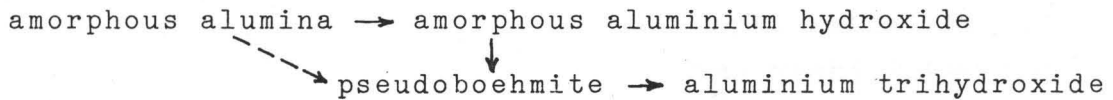
(1) Hydrothermal reaction of aluminium hydroxides

The heating treatment of crystalline and gelatinous aluminium hydroxides were made in the presence of water in an autoclave. As a result, it was found that the hydrothermal reaction of gelatinous aluminium hydroxide occurs at a lower temperature than that of crystalline aluminium hydroxide. For the hydrothermal conversion of gelatinous aluminium hydroxide into boehmite, the conversion-temperature of the aluminium hydroxide containing pseudoboehmite is lower than that of amorphous aluminium hydroxide. In the crystalline hydroxide, the rate of hydrothermal conversion into boehmite is higher for bayerite than for hydrargillite. Further the hydrothermal conversion of aluminium hydroxides into diaspore is discussed in comparison with the formation of boehmite.

(2) Hydration of aluminas

The hydration of amorphous and crystalline aluminas was investigated by suspending them in water for specified times at temperatures of 30, 50, 70 and 95°C. In the hydration of amorphous alumina at 30°C, amorphous aluminium hydroxide or pseudoboehmite is formed initially and followed by aluminium trihydroxides such as

bayerite, and hydrargillite and/or nordstrandite: the trihydroxides appear after about ten days and then increase gradually according to the period of contact with water. With raising the temperature, the rate of hydration is increased, and pseudoboehmite is formed at first and bayerite and subsequently nordstrandite. Accordingly, the hydration of amorphous alumina proceeds in the following sequence:



Furthermore the hydration of crystalline aluminas proceeds slowly when they are kept in contact with water at 30°C, but η - and γ -aluminas are hydrated to aluminium trihydroxides and pseudoboehmite, respectively, when the temperature is raised.

(3) Thermal transformation of aluminium hydroxides to aluminas

The thermal transformation of crystalline and gelatinous aluminium hydroxides to various aluminas are discussed on the basis of the results obtained by the present author.

Sintering and Grain Boundary Migration of Al_2O_3

Kiyoshi ASAGA

Dept. Mater. Eng..

The Nishi Tokyo Univ.

Sintering process of Al_2O_3 was studied by means of isothermal shrinkage and observation of microstructure, using various type of Al_2O_3 powders. Topics are classified as follows.

- (1) Sintering mechanism of Al_2O_3
Isothermal shrinkage of spherical powder compacts
Effect of particle size
- (2) Microstructure changes in the initial stage
Change in surface area
(Kr adsorption method)
Changes in the pore size distribution
(mercury penetrating porosimeter)
- (3) Microstructure changes in the final stage
Changes in the grain size distribution
(measuring the pore size in the polished surface)
Changes in the pore size distribution
(measuring the pore size in the polished surface)
- (4) Effects of process
Powder preparation
Packing
Firing

Effect of Additives on Sintering of Alumina

Zenbe-e NAKAGAWA

Research Laboratory of Engineering Materials

Tokyo Institute of Technology

In many ceramics, some additives, which are limited in the range of the amount not to degrade their main properties, are usually used to obtain densified bodies. The role of additives is classified into two large groups. The one is solid solution effects and the other is effects of liquid formation (liquid phase sintering). The solid solution effects include an increase of vacancy concentration, introduction of strain, and segregation of solute on grain boundaries and surfaces. Liquid formation introduces a capillary force, acts as a lubricant, and is expected to promote the diffusion of species. Alumina ceramics through liquid phase sintering are important for electric and electronic utilizations, such as substrates and insulators.

In 1958, Coble invented a translucent alumina "Lucalox", using MgO as additive. MgO acts as an inhibitor of abnormal grain growth of alumina but the mechanism is continued to discuss up to the present.

In this report, solid solution effects of additives on sintering of alumina are mainly presented, including the role of MgO, and the effect of rare earth oxides which are not expected to dissolve in alumina are also presented.

Evaluation of thermal and mechanical fatigue properties of alumina and feed-back treatment to control its microstructure

M.Takatsu and T.Nishikawa

Dept. Materials Science and Engineering
Nagoya Institute of Technology

ABSTRACT

It is well known that ceramics generally exhibit the incompatible properties. For the alumina ceramics having the same porosity, the critical intensity factor K_{Ic} and bending strength S_r are variable in inverse proportion with the amount of impurity or particle size etc. Therefore, it is important to use these alumina ceramics considering of their properties.

Authors investigated the properties on mechanical cyclic fatigue test or on thermal fatigue test, and arranged the data with fracture mechanic. For the former test, we changed the applied stress ratio (minimum stress σ_{min} /maximum stress σ_{max}) and discussed quantitatively with using n and A values, which were derived from the crack propagation rate equation $V=AK_I^n$.

The above mechanical cyclic fatigue properties of alumina showed the following results;

- 1) The fundamental difference with fracture mechanic between alumina and mullite ceramics caused the fracture behavior, in which the inter-granular fracture was predominant for the former and trans-granular fracture was for the latter.
- 2) R-curve appeared with increasing of particle size for alumina ceramics, but acceleration to the short life time was observed on cyclic fatigue test.
- 3) The connection of cusp in grain boundary may accelerate the crack propagation on the cyclic fatigue.

While, the thermal fatigue results showed as follow;

- 1) As the stress ratio could not be varied on thermal fatigue test, one fatigue parameter n hardly changed. However, the another fatigue parameter A value changed clearly corresponding to its microstructure.
- 2) The n values on thermal fatigue test were nearly equal to those on mechanical fatigue test.

Lately, the feed-back treatment to control and obtain the most suitable microstructure applying to using condition, was investigated and discussed.

Alumina Ceramics Preparation and its Properties for Electronics Uses

Kanji Otsuka

Hitachi Ltd., Device Development Center

Abstract

Electronics circuit systems tend to density, to be smaller and even higher performance. Electrical wiring density of these systems increase depend on the requirement. It has been recognized which alumina ceramic multi-layer boards are matched to it, because of the fine line wiring.

Electrical signal transmission through the wiring in these boards takes a certain time that is signal delay. High speed signal processor needs to make the high speed transmission wiring. The delay is affected by the dielectric around the wiring as the relation of $T_{dp} = l \cdot \epsilon_r / c$. Where, T_{dp} is the delay, l is the wiring length, ϵ_r is the specific dielectric constant and c is light speed. Therefore, the reducing dielectric constant of alumina ceramics is promoting to study now.

Table 1 shows the recent new materials for the cofired multilayer board in high performance computers. Almost of these are in alumina based. The doctor-blade tape casting method still continue to use for them. Glass contained alumina bodies decrease their firing temperature, and weaken their strength. These make the difficulty of the burn-out of binders, and control void distribution. Each problems are improving to produce cofired multilayer boards with precised fine dimension.

Table 1. Recent Ceramic Multilayer Board

Material	Rough Compositon	Dielectric Constant	Thermal Expansion Coefficient (ppm)	Modulus of Rapture (Mpa)	Wiring Metal	Maker
Alumina-Glass System	Al ₂ O ₃ 18-23, SiO ₂ 55-55, MgO 18-25, P ₂ O ₅ , B ₂ O ₃	5.2	3.0	210	Cu	IBM
	Alumina, Borosilicate Glass	5.6	4.0		Cu	Fujitsu
	^h _A Potosensitive Alumina-Glass	3.5			Au	NEC
Mullite	Mullite, Glass	5.9	3.5	200 or more	W	Hitachi
Alumina	~95% Alumina	9.0 ~10.0	6.0	300 or more	W	Reference

SiC WHISKER-REINFORCED ALUMINA COMPOSITE

Shigehiko Yamada
Dept. Mater. Eng.,
The Nishi Tokyo Univ.
Eiichi Yasuda
Res. Lab. Eng. Mater.,
Tokyo Inst. Tech.

During these several years we have been engaged with the research work on the SiC whisker(w)-reinforced alumina composite, particularly on the preparation and improvement of toughening, since R & D of the whiskers themselves were carried out in industry.

The view-point of the relevant work can be classified as it follows, so that the mechanism of toughening of this type of reinforcement can be clarified.

- (1) Dependency of size, shape and volume fraction of SiC(w) on the flexural strength and fracture toughness
- (2) Dependency of alignment of SiC(w)
- (3) Influence of surface oxidation of SiC(w)
- (4) Influence of surface roughness of SiC(w)
- (5) In-situ preparation of SiC(w) from "mullite and C" to form SiC(w)-reinforced alumina composite

Several results of the other researches, mainly concerning (1) and (3) mentioned above, appeared in literatures, are also introduced to compare with each other.

As is well known, this type of composite can be regarded as the first successful industrial material of the whisker-reinforced ceramic composites. Such a scientific approach to this composite may be an effective guidepost to understand the improvement of fracture toughness of ceramics.

Creep Damage Mechanisms in Alumina During Tensile and Bend Testing

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Extensive testing on 2 commercial hot-pressed aluminas, in both tension and bending, have shown that a gradual transition occurs in the dominant damage mechanism with decreasing stress. At high stress failure is rapid and controlled by the growth of a microcrack emanating from a major flaw in the material. As the stress is lowered multiple microcracking is found, with failure resulting from crack coalescence. At even lower stress cavitation starts to dominant and flaws become unimportant. These mechanisms will be illustrated. In addition, some anomalies in damage behaviour associated with bend testing will be discussed.

ポスタープレゼンテーション

1. Effects of Specimen Size on Bending Strength and Fracture Toughness of AlN

Chang-Sam KIM, Toyohiko YANO*, and Takayoshi ISEKI

Department of Inorganic Materials, Tokyo Institute of Technology

*Research Laboratory of Nuclear Reactors, Tokyo Institute of Technology

2. Alumina/Aluminum Composites Prepared by Directed Oxidation of Aluminum Alloy

Takanori WATARI, Toshio TORIKAI, and Ohsaku MATSUDA

Department of Applied Chemistry, Saga University

3. Synthesis of Alumina from Alkoxide Modified by Organic Complexing Solvent

Kazuyuki MAEDA, Fujio MIZUKAMI, Masaharu WATANABE*, Kouji MASUDA**,

Shu-ichi NIWA, Makoto TOBA, and Tsuneji SANO

National Chemical Laboratory for Industry

*Toyo Gosei Kogyo Co. Ltd.

**Central Engineering Laboratory, Nissan Motor Co. Ltd.

4. Processing of Translucent Alumina with Submicron Grains

Koichi HAYASHI, Hiromochi TAKEBE*, and Kenji MORINAGA*

R & D Division, ToTo Ltd.

Graduate School of Engineering Science, Kyushu University

5. High Purity, Fine Alumina Powders Obtained by Thermal Decomposition of Ammonium Dawsonite

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Government Industrial Research Institute of Nagoya

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6. Reference Sintered Materials for Grinding (Al_2O_3 Sintered Material)

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Japan Fine Ceramics Center

7. Mechanical Properties at High Temperature of Alumina Ceramics

Hiroshi OHNISHI, Akira KOUCHI, and Toshio KAWANAMI

Nikkato Corp.

8. Effects of Additives on the Sintering of Alumina

Chii-Shyang HWANG, Ching-Yie LIN, and Shuenn-Ching TSAUR

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9. Preparation of Al_2O_3 /Pd Particulate Composites Using an Electroless Plating Technique

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**Advanced Technology Laboratory on Bending Strength and

- 10. Song-Bae SON
KIST, Korea
- 11. Fabrication of Highly Porous Alumina Ceramics
Y. ENAMI, M. KANO, M. HASHIBA, and Y. NURISHI
Department of Chemistry, Gifu University
- 12. Zone Sintered Large Translucent Alumina Tubes
Shunzo SHIMAI
FC Div., Toshiba Ceramics Co., Ltd.
- 13. Mullite Matrix Composites Reinforced by SiC Plus Yttrium-Stabilized ZrO₂ Particulates
X.X. HUANG, J.S. HONG, and D.S. YAN
Shanghai Institute of Ceramics, Chinese Academy of Science, China
- 14. Alumina Technology in Zhengzhou Light Metals Research Institute (ZLMRI)
Gen-You TIAN, Wan-Kun CHEN, and Quan-Cai YAN
Zhengzhou Light Metals Research Institute, Shangjie, Zhengzhou, China
- 15. Microstructure of Mullite Ceramics and Silica-Alumina Diagram
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- 17. New Alumina-Based Ceramics "LX11" — Ideal Tool Grade Cutting Hard Ferrous Metals—
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Osamu MIYAZAWA
Ceramics Laboratory, Mitsubishi Material Co., LTD.
- 19. KM Mullite
Hideo BANNO
Kyoritsu Ceramic Materials Co., LTD.

Effects of Specimen Size on Bending Strength and Fracture Toughness of AlN

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Bending strength and fracture toughness of AlN were measured at room temperature for pressureless-sintered specimens by three-point bending test and SEPB (Single Edge Precracked Beam) method, respectively. Dimensions of four different rectangular specimens were 0.8 by 2 by 12 mm, 2 by 2 by 25 mm, 2 by 4 by 25 mm and 3 by 4 by 40 mm. Bending strengths of these specimens were 342, 314, 314 and 323 MPa, respectively, each of which is the mean value for 20 test pieces. The results of the measured strengths were incompatible with the size-effect law based on the weakest-link theory. For example, bending strength of the smallest specimen was 28% lower than the strength predicted by the size-effect law with the obtained Weibull modulus of 9. This discrepancy between the measured and the predicted strength may be attributed to a difference in the proportion of the types of origins of fracture (e.g., surface flaw and internal flaw) in the specimens. The size-effect law does not consider a measured strength variation due to a difference in this proportion.

Fracture toughnesses of the 2 by 2 by 15 mm, 2 by 4 by 25 mm and 3 by 4 by 25 mm specimens were 2.5, 2.7 and 2.7 MPam^{1/2}, respectively. The standard deviation in K_{IC} of each specimen was < 0.20 MPam^{1/2}. For the same-sized specimen, K_{IC} value appeared to decrease as the precrack length shortened. The precrack length dependence of K_{IC} is due to an R-curve behavior. This is the reason of the low K_{IC} value measured for the 2 by 2 by 15 mm specimen, because the precrack length of this specimen was relatively shorter than those of the others.

Alumina/Aluminum Composites Prepared by Directed Oxidation of Aluminum Alloy

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Department of Applied Chemistry, Saga University

The brittleness of monolithic ceramics limit their widespread use in mechanical applications. Metal phase incorporated into a ceramic matrix make it possible to increase the toughness of ceramics. Among many methods to make ceramic/metal composites, the directed metal oxidation method (DIMOX¹) is a exciting process owing to the following benefits; (1) ease of making composites, (2) low cost and (3) net or near-net shape capability. This paper is intended to outline Al₂O₃/Al composites prepared by DIMOX process.

DIMOX Al₂O₃/Al composites are formed by reaction between molten Al alloy and a vapor-phase oxidant (e.g. oxygen). The composites were formed initially on the exposed surface of the molten alloy and then grew outward. The composites consisted of a three-dimensionally interconnected Al₂O₃, interconnected and isolated Al alloy. The dopant metals in Al alloy are essential. The composites grew on Al alloys such as Al-Mg-Si(Ge,Sn or Pb), Al-Si-Zn-Cu-Fe-Mg, Al-Mg-Si-Zn and Al-Si-Zn(in contact with MgAl₂O₄). The growth rate (R_g) changed with alloy components and oxygen partial pressure (P_{O₂}). For example, R_g of the composite prepared with Al-Mg-Si alloy was proportional to (P_{O₂})^{1/4}.

Following table shows one example of physical and mechanical properties of DIMOX Al₂O₃/Al composite. Young's modulus, bend strength and fracture toughness of the composite are about 0.7, 1 and 2 times those of commercial Al₂O₃, respectively.

Metal content (vol%)	Density (kg·m ⁻³)	Young's modulus (GPa)	Bend strength (MPa)	Fracture toughness (MPa·m ^{1/2})
20	3530	231	350 (300K)	9.5 (300K)
			200 (700K)	8.5 (680K)

1) DIMOX is a registered trademark of Lanxide Co., Newark, DE.

Synthesis of Alumina from Alkoxide Modified by Organic Complexing Solvent

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Abstract

The authors found that characteristics of aluminas synthesized from alkoxide were affected by organic complexing agents used as solvent. The synthesis and property of the aluminas are reported.

The aluminas were synthesized from aluminum isopropoxide dissolved in some diols, polyglycols, or glycol ethers on heating. This synthetic process is featured by modification of alumina precursor with complexing agent. The alumina obtained via hydrolysis and drying followed by stepwise calcination up to 1000°C was characterized by BET specific surface area, pore distribution, XRD, TG-DTA TEM and so on.

Branched diols, especially 2-methyl-2,4-pentanediol, gave the alumina of the high specific surface area. Effect of synthetic conditions on the characteristics of this alumina also was examined. The alumina made from polyglycol monoalkyl ethers also showed high surface area. On the contrary non-branched diols or polyethyleneglycols, especially of lower molecular weight, gave aluminas of lower specific surface area. Furthermore, the crystallization temperature to α -phase of these aluminas generally depended on the boiling point of the solvents. TEM images revealed that solvents of low complexability or of low boiling point gave alumina of needle particle, otherwise of round particle.

From above results, the authors assumed that moderately strong complexing agent like branched diol or polyglycol monoalkyl ether protected alumina hydrate precursor from development of particle and gave high surface-area alumina. Non-branched diols or polyethyleneglycol were supposed to form so stable complex as to make structure of precursor gel fragile.

Table Characterization of representative aluminas

Complexing solvent	Specific surface area (m ² /g)					$\alpha/\alpha+\gamma$ %	α -Crystallization temperature (°C)	Shape of particle
	600	800	1000	1050	1075			
Calcination Temp.(°C)	600	800	1000	1050	1075	1075		1000
(A)	316	239	169	118	100	1	1251	round
(B)	292	225	152	119	94	7	1261	needle-like
(C)	352	241	166	100	88	14	1215	round
(D)	313	226	140	60	24	81	1193	round
(E)	277	214	136	112	102	<1	1228	needle-like

(A) 2-Methyl-2,4-pentanediol, (B) Diethyleneglycol dimethyl ether,

(C) Diethyleneglycol monomethyl ether, (D) Diethyleneglycol, (E) 2-Propanol (ref, reacted at 70°C)

Processing of Translucent Alumina with Submicron Grains

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Ammonium aluminum carbonate hydroxide (AACH), a precursor of α -alumina fine powders, was synthesized from aqueous solutions of between ammonium hydrogen carbonate (AHC) and ammonium alum (AA). The effects of pH of the AHC aqueous solution and reaction temperature on the formation of AACH were discussed. In order to obtain homogeneous, spherical alumina fine particles, the transition process of AACH to α -alumina was studied precisely. Alumina green bodies with a uniform microstructure were formed by injection molding.

Packing states of the alumina particles after injection molding were compared with those after CIP. Translucent alumina ceramics with high in-line transmittance for visible beams as well as high mechanical properties were produced by applying the HIP processing to a sample which was pressureless-sintered at a low temperature of 1280 °C. Various factors affecting the in-line transmittance were evaluated, and the mechanism of light scattering was proposed.

High Purity, Fine Alumina Powders Obtained
by Thermal Decomposition of Ammonium Dawsonite

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*Government Industrial Research Institute of Nagoya

**Taimei Chemicals

A high purity (>99.99%), monodispersed α -alumina powder with a primary particle size of about 0.1 μ m, which is produced by thermal decomposition of ammonium dawsonite (ammonium aluminum hydroxy carbonate), is commercially available \S . It can be sintered to density up to 98% of theoretical at considerably low temperatures about 1250°C. Structural features of the ceramics sintered at low temperatures were of the uniform one with fine grain sizes. Such ceramics are expected to have the excellent mechanical properties. In fact, the MOR of the HIPed product of this powder reached over 1000 MPa and the wear resistance was at a level comparable to that of PSZ ceramics.

We will survey the references regarding this peculiar alumina, which are that on the powder preparation including the synthesis of ammonium dawsonite, the sintering behavior of the powders and the characteristic features of the ceramics made from it.

\S TM-D (Taimei Chemicals, Nagano)

Reference Sintered Materials for Grinding
(Al₂O₃ Sintered Material)

Isao SUGIURA and Jun-ichi TSUBAKI

Japan Fine Ceramics Center

Advanced ceramics have excellent properties, and they have been expected as new industrial materials. In order to use them as reliable standard materials, it is needed to conquer of brittle and reduce of manufacturing cost. The half of advanced ceramics cost is for grinding.

The researches are being done in many fields to reduce the grinding cost. However, test pieces of advanced ceramics are not standardized or normalized enough in their properties and the manufacturing process is not opened, then it is hard to compare the grinding test results each other.

It is strongly hoped to distribute the reference sintered bodies which can evaluate the grinding machines and tools.

JFCC has been developing the reference sintered materials. At the beginning, we have questionnaire of needs for reference sintered materials in grinding fields. From the questionnaire of needs in grinding field, JFCC decided to start from Al₂O₃ sintered body.

The features of the reference sintered materials (JFCC call them REFERCERAM).

- (1) Equivalent or superior than commercial available Al₂O₃ ceramics in properties.
- (2) To be opened manufacturing process.
- (3) The properties are controlled well.
- (4) To be stable supplied for the long terms.

Mechanical Properties at High Temperature of
Alumina Ceramics

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ABSTRACT

The mechanical properties at high temperature of high-purity Al_2O_3 , fabricated using seven kinds of commercial Al_2O_3 powder which were prepared by the Bayer process and from aluminium compounds, have been investigated. Density, grain size and grain size distribution of each specimen were different by powder properties and its chemical composition. And a little of impurity formed the glassy phases at grain boundaries. The strength at R. T. was independent on grain size and Al_2O_3 content. But its at high temperature showed different temperature dependence. The degradation of the strength and the creep strain rate influenced by Al_2O_3 content, impurity composition and its value. But the creep mechanism of each specimen was same. The degradation of the strength was in good agreement with that of the shear modulus, and the creep strain rate was in good agreement with the internal friction peak. These differences were explained by the amount of grain boundary impurity phases.

Effects of Additives on the Sintering of Alumina

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To improve the sinterability and/or mechanical properties of alumina composites, some oxides (TiO_2 , ZrO_2 , SiO_2) were selected as additives. In the produced Al_2O_3 - ZrO_2 , Al_2O_3 - SiO_2 composites, alumina comprises the matrix and ZrO_2 , SiO_2 comprise the second phases. The starting materials were M-alkoxides ($M = \text{Ti}, \text{Zr}, \text{Si}$) and α - Al_2O_3 powder. By accurately controlling the amount of solvent and water during the hydrolysis of M-alkoxide, a mixture of Al_2O_3 and the oxide additives was obtained. The effects of additives on the sintering temperature of alumina, the microstructure and phase transformations of sintered body have been investigated.

It is shown that the sintering of Al_2O_3 has been markedly enhanced by TiO_2 , but retarded by ZrO_2 and SiO_2 . In the Al_2O_3 - ZrO_2 mixture, the Al_2O_3 particles were coated with a layer of fluffy ZrO_2 gel. After calcination, ZrO_2 gel was transformed into ultrafine crystalline particles and was distributed uniformly on Al_2O_3 surface. The sinterability of Al_2O_3 seems to be affected by the physical state of ZrO_2 . In the Al_2O_3 - SiO_2 mixture, the Al_2O_3 particles were also coated with SiO_2 . However, after calcination and even firing, SiO_2 was still coated on Al_2O_3 particles. The reaction of SiO_2 and Al_2O_3 forming mullite is found to occur at temperature >1400 C. The densification of Al_2O_3 decreases with the increase of SiO_2 content. The addition of TiO_2 also enhances the sinterability of Al_2O_3 - ZrO_2 and Al_2O_3 - SiO_2 composites.

Preparation of Al₂O₃/Pd Particulate Composites Using an Electroless Plating Technique

Hidemi Watanabe : Ashikaga Institute of Technology

Osamu Kimura : Shonan Institute of Technology

Sinroku Kawasumi : Advanced Technology Laboratory

Abstract : It is generally expected that dispersed-phase metallic inclusions in ceramics contribute to toughness via plastic deformation. In this work, ductile and chemically non-reactive Pd metal particles are dispersed in Al₂O₃ matrix. In order to avoid formation of mechanical flaw centers resulted from segregation of inclusions, it is necessary to disperse metal particulate into a matrix as uniformly as possible. For this aim, 3 to 20 vol% Pd metal layer is deposited on each surface of fine Al₂O₃ particle (0.2-0.3 μ m in diameter) by utilizing an electroless plating technique. Then, the Pd coated Al₂O₃ particles are hot-pressed into composite samples with a flowing nitrogen atmosphere at 1350 °C for 45 minutes at a pressure of 30 MPa.

Mechanical and electrical properties of the composites are evaluated. Fracture toughness increases to 5 MPam^{1/2} for the 10 vol% composite but flexural strength decreases somewhat. Low vol% composites are electrical insulators, abrupt increase in electrical conductivity, however, is observed for the 15 vol% composite, which shows almost metallic conductivity.

SEM observations and EDX analysis on the fractured surfaces of the composites reveal that uniform dispersion of fine Pd particulates into the matrix is attained by this dispersion procedure.

Fabrication of Highly Porous Alumina Ceramics

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Processing factors to fabricate a highly porous alumina body with 50 μm in open pore diameter by slip casting method, such as some organics to increase the porosity, dispersants to thicken the alumina slurries in conformity with the organics to the limit and the binders to be castable and to bind the thin skeleton of the highly porous body, were discussed.

Some organics exceeding 30vol% ; that volume was the limit attained by ordinary packing of the starting alumina particles, were necessary to obtain a higher porosity. Potato starch and a phenolic resin were successfully examined as a natural organics and as a synthetic organics with uniform particle size, respectively.

Thickening of the alumina slurries keeping high organic contents, were important to make open pores, which was attained with the aid of dispersant to fluidize the slurries. Polyacrylic dispersant or carboxylic co-polymer with a suitable chain length was useful to thicken the alumina slurries in conformity with the organics and to form the highly porous alumina body with 80 vol% of the limit porosity.

Some binders, such as PVA or urea resin which were added to the slurries in a monomer form and was bound the body by polymerization, were useful to keep thin skeleton of the highly porous body.

Zone Sintered Large Translucent Alumina Tubes

Shunzo Shimai

(Toshiba Ceramics Co., Ltd. FC Div., Tech. Dep.)

Large translucent alumina tubes are fabricated by isostatic pressing and hydrogen atmosphere vertical zone sintering. Maximum size of the tube is 120mm diameter, 3000mm length.

Zone sintering have many advantages for sintering of long ceramics as follows.

(1) Small sized sintering furnace

Batch type furnace must have inside dimension which can keep green bodies long as 3500mm.

(2) Reduction of energy for sintering

The greater part of energy is consumed for heating up furnace itself in case of large ceramics especially. It is unnecessary these energy for zone sintering.

(3) Shortening of sintering lead time

In case of batch type furnace, it is necessary long time for cooling furnace.

(4) High yield rate

It happens frequently in the batch type furnace that a failed sintering body breaks others.

(5) High quality

Zone sintering give homogeneity of microstructure to long ceramics because any part of ceramic body can pass same heating condition.

In-line transmittance of large PCA tubes were improved by chemical polishing from 20% to 40%. And total transmittance of them were over 96%.

Zone sintering processes were studied by the specimen stopped on the way of zone sintering, it had gradient feature from initial to the final sintering stage continuously. This half-zone sintered tube was characterized after cut to many small pieces. These pieces were characterized by BET specific surface area, mercury porosimetric, X-ray diffractometer, photomicrograph, and SEM. In-line transmittance of chemical polished and as-sintered samples were measured also.

γ - α transformation occurs with reduction of specific surface area at the initial sintering stage. Open pores disappear at the density 92% theoretical. In-line transmittance increasing with grain growth was depends on surface roughness.

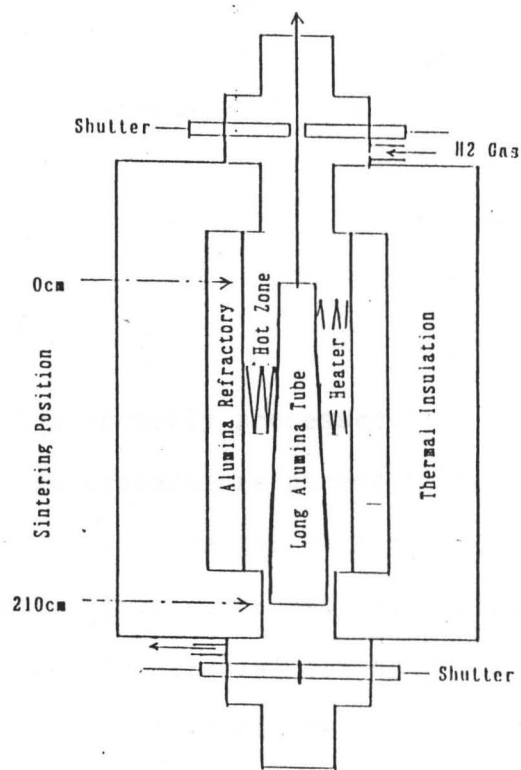


Fig. 1. Schematic diagram of a zone-sintering furnace and sintering position of alumina long tube.

Mullite Matrix Composites Reinforced by SiC Plus Yttrium-Stabilized ZrO₂
Particulates

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Mullite is a good structural material when properly processed. However, this paper will report that its high temperature strength, fracture toughness as well as its thermal shock resistance can be substantially improved by double reinforcement with SiC and yttrium-stabilized zirconia particulates. Such mullite matrix composite material can hold its flexural strength at a level of 600 MPa from room temperature to 1000 °C. Its fracture toughness has a value of 6.7 MPam^{1/2} and a thermal shock resistance of 500 °C when quenched to water. Its enhanced fracture behavior has been preliminarily analyzed. This composite material has been fabricated into piston caps for adiabatic engine and successfully tested for well over hundred hours.

ALUMINA TECHNOLOGY

IN ZHENGZHOU LIGHT METALS RESEARCH INSTITUTE(ZLMRI)

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ABSTRACT

Tree entries of alumina technique which has been developed successfully in ZLMRI are briefly described: (A) intensive digestion technique for diasporic bauxite by tube heating-autoclave digester; (B) production of sandy alumina from high concentration sodium aluminate by two-stage precipitation. (C) production of high calcined low soda alumina. In ZLMRI, the pilot tests for processing PINGGUO and HENAN diasporic bauxite have been carried out and the following results were obtained: digestion temperature: 260-275 °C, heating time: 10-12 min., heating preservation time: 25-40 min., liquor concentration Na_2O : 160-230 g/l, molar ratio ($\alpha k = \text{Na}_2\text{O}/\text{Al}_2\text{O}_3$): 1.45-1.55, alumina relative yield ηr : >92 %. It is demonstrated that the energy consumption for processing diasporic bauxite by the intensive digestion at high temperature can be reduced to 3500 kcal/t-alumina; the most effective intensive digestion device is the tube heating-autoclave digester. In ZLMRI, the pilot tests to product sandy alumina from a high concentration sodium aluminate solution (Na_2O : 155 g/l, αk 1.55) with a scale of 6.5 m³/hr also were organized. The yield of alumina was 73.7kg/m³, with its particle size of +100 mesh for 0.2 %, and +320 mesh for 7.3 %, attrition index of 24.2 % and specific surface area of 63.8m²/g. Using aluminum hydroxide which is made in ZLMRI, by adopting of special addition agents and special process treatment, ZL-series high calcined low soda alumina which is easy to crush, high sintering activity and low sintering temperature has been produced. ZL-ALUMINAS have high chemical purity (alumina: 99.7-99.8 %), low residual soda content (Na_2O : 0.14-0.06 %), high density (3.96-3.98 g/cm³), high melting point (2040 °C), good thermal conductivity and heat-shock resistance, high electrical resistivity at room and elevated temperature.

 * author to brief at the MRS-J's symposium about alumina and aluminum compounds(1991.7.11).

MICROSTRUCTURE OF MULLITE CERAMICS AND SILICA-ALUMINA DIAGRAM

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The microstructure of mullite ceramics was studied by using transmission electron microscope (TEM) with energy dispersive X-ray spectroscopy (EDS).

Highly pure mullite powder with 3:2 $\text{Al}_2\text{O}_3/\text{SiO}_2$ molar ratio is hot-pressed at temperatures from 1550° to 1700 °C for 1 hr under 10 MPa in vacuum. The relative density of the specimen hot-pressed above 1575°C reaches approximately 100%.

High resolution transmission electron micrographs and EDS analyses show that HP-1575 (specimen hot-pressed at 1575°C) consists of mullite grains with 3:2 $\text{Al}_2\text{O}_3/\text{SiO}_2$ molar ratio. No other phase except mullite is found in HP-1575. Silica-rich glassy phases containing a small amount of Ca and/or K are observed in HP-1600 and HP-1700. Impurities, such as Ca and K, concentrate in the glassy phases. These phases are observed more frequently in HP-1700 than in HP-1600. They exist at three-grain junctions, and do not exist at two-grain boundaries.

A lattice parameter a_0 of a highly pure mullite powder varies with increasing temperature, suggesting that the $\text{Al}_2\text{O}_3/\text{SiO}_2$ ratio of the mullite crystal increases in the range from 1500°C to 1700°C.

TEM observation and the variation of the lattice constant a_0 suggest that the alumina content of mullite and the amount of the glassy phase increase with increasing temperature, i.e. the boundary line between mullite and mullite plus liquid phases bends over to the alumina side at high temperatures in the region of mullite ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$). These results are consistent with a SiO_2 - Al_2O_3 phase diagram by Klug and Prochazka (1987).

Crack Propagation in Alumina Ceramics

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Research Laboratory of Engineering Materials,
Tokyo Institute of Technology

Crack deflection, crack bending and crack branching are considered as the strengthening mechanism to make ceramics tough. If pores exist on the path of propagating cracks, they may interrupt the simple propagation of cracks and have effects on the mechanism described above. However, in the propagation of cracks, it is not so clear how the cracks behave with pores and/or second phases in ceramics.

Al_2TiO_5 is not stable and decomposes to $\alpha\text{-Al}_2\text{O}_3$ and rutile below about 1300°C , accompanied with shrinkage of approximately 10 vol.%. This phenomenon can be applied to produce TiO_2 doped alumina ceramics with dispersed pores. In this study, crack propagating in high purity alumina and TiO_2 doped alumina which have various porosities was observed, in order to clear the effect of pores on crack propagation.

New Alumina-Based Ceramics " LX 1 1 "

~Ideal tool grade for cutting hard ferrous metals~

TOSHIBA TUNGALOY Co.,LTD.

Toshiyuki Takahashi

○Features

- 1) Consists of highly resistant alumina and highly tough titanium carbonitride fine crystal (see photo.).
- 2) Has a uniform, fine structure, exhibits a higher strength and toughness than conventional Al_2O_3 -TiC ceramics, and offers good thermal conductivity.
- 3) High wear resistance by special coating.
- 4) Ideal for high-precision, high-efficiency machining of hardened steel (HRC40-60).
- 5) Exhibits a high performance comparable to PCBN and offers many cutting edge corners at 1/10 the price of PCBN (per workpiece).

○Application

Continuous cutting for:

- 1) Hardened steel
- 2) Chilled cast iron
- 3) Carburized and hardened steel

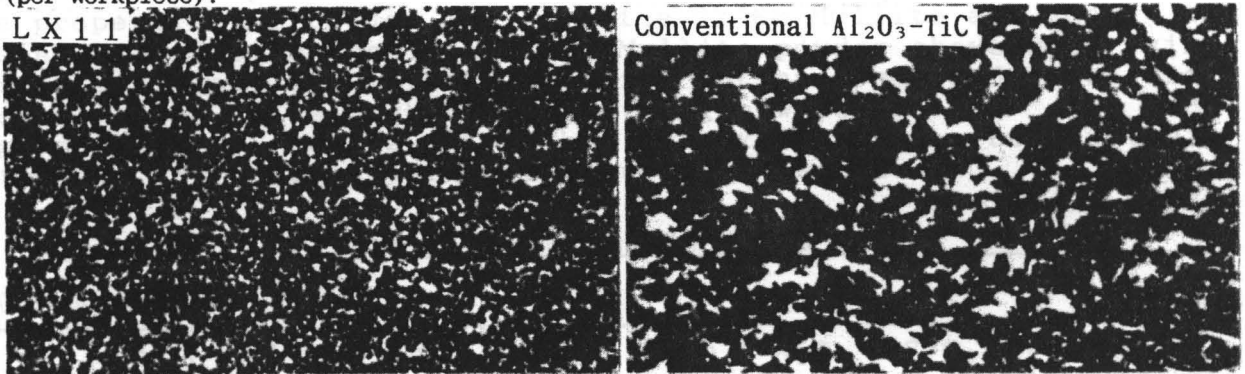


Photo.1 Microstructure of "LX11" compared with a conventional Al_2O_3 -TiC ceramics.

○Physical and mechanical properties

Grade	density g/cm ³	hardness HRA	Transverse rupture strength kgf/mm ²	Fracture toughness MN/m ^{3/2}	Compressive strength kgf/mm ²	Modulus of elasticity 10 kgf/mm ²	Thermal conductivity kcal/m.h.°C
LX11	4.30	94.0	90	5.7	390	4.1	21.9
Conventional Al_2O_3 -TiC	4.24	94.3	80	4.3	320	3.8	19.0

○Cutting performance

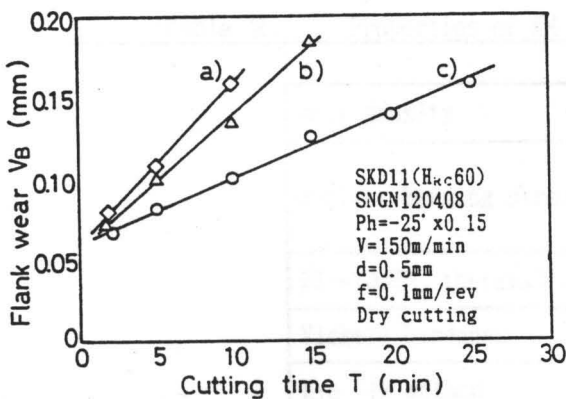


Fig.1 Flank wear of "LX11" compared with other cutting tool materials in turning test of steel.
a) Conventional Al_2O_3 -TiC tool
b) Polycrystalline CBN sintered compacts
c) LX11

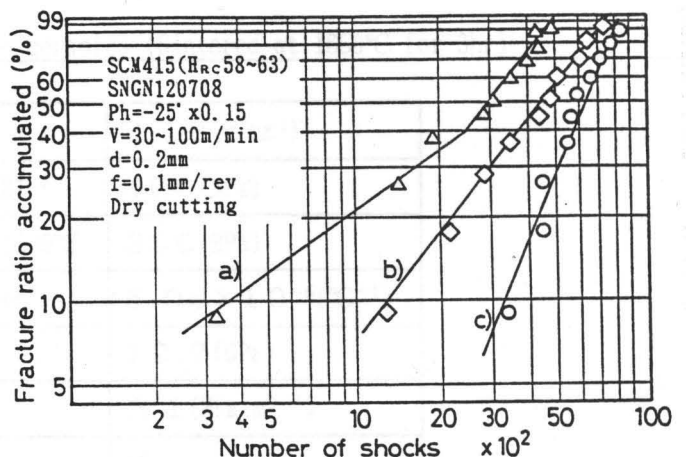


Fig.2 Fracture resistance of "LX11" compared with other conventional Al_2O_3 -TiC ceramics.
a), b) conventional Al_2O_3 -TiC ceramics
c) LX11

KM MULLITE

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Highly pure mullite powder was obtained from aluminum sulfate and fumed silica. Fumed silica was poured into aqueous solution of aluminum sulfate with vigorous stirring to realize the stoichiometric mullite composition, and slurry was stirred for 5 h. Resultant sol was spray-dried at 280°C. The granules obtained were heated at 1000°C to decompose the aluminum sulfate and subsequently to react with amorphous silica to form gamma-alumina phase precursor. The single phase of mullite was obtained by heating the precursor at 1400°C. The fine particles of highly pure mullite powder was easily obtained by attrition-milling. The properties of powder and ceramics of KM Mullite are shown in Tables 1 and 2, respectively. KM Mullite powder shows good sinterability, and the mullite ceramics hot-pressed and pressureless-sintered give high bending strength which do not show the degradation up to 1200°C. They are expected to be suitable materials for high temperature structural ceramics.

Table 1. Properties of KM Mullite powder

Chemical composition (wt%)

	SiO ₂	Al ₂ O ₃	CaO	MgO	Na ₂ O	K ₂ O	ZrO ₂	Ig.loss
101	27.8	70.8	tr.	tr.	0.01	tr.	tr.	1.00
102	27.7	70.7	tr.	tr.	0.01	tr.	0.09	1.01

B.E.T. specific surface area	27(m ² /g)
Particle size	100 to 200(nm)
Lattice constants of the powder	a ₀ 0.4571(nm)
heated at 1400°C	b ₀ 0.7690(nm)
	c ₀ 0.2884(nm)

Table 2. Properties of KM Mullite ceramics (Sintered at 1650°C for 3hr)

bulk density	3.13(g/cm ³)	
3-point bending strength	RT	400(MPa)
	1300°C	350(MPa)
RT~1000°C thermal expansion	5.06×10 ⁻⁶ (°C ⁻¹)	
Vickers hardness	12.7(GPa)	
K _{1c} IM method	2.1(MPa·m ^{0.5})	
ε(1MHz)dielectric constant	7	
insulation resistance	>10 ¹⁴ (Ω·cm)	

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