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MICROSTRUCTURE AND PROPERTIES OF CERAMICS

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16. Abstract

The history of research into the microstructure and properties of ceramic ware is discussed; methods of producing ceramics with particular characteristics are investigated.

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MICROSTRUCTURE AND PROPERTIES OF CERAMICS

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1. Introduction

The origin of ceramics is earthenware, which used to /582* be used for storing harvested or hunted food and for cooking it. As long as earthenware had no cracks or holes and could hold water, it served the purpose. As earthenware began to be used for religious celebrations, the whiter and better shaped became more in demand, which consequently developed the techniques for selecting, purifiying and forming the clay. As earthenware with better appearance became available, it began to be used as garment or room accessories. Its value was determined by its color, form, and engraved pattern, which belongs to the design aspect, as well as by its endurance. Thus, because the quality of earthenware was determined by its appearance, the focus was put on the selection of the raw material, its processing, technique for shaping, design and technique for fusion by sintering it tokeep itfrom deforming. These techniques have been passed on from generation to generation secretly, by which excellent earthenware has been produced.

Because this type of attitude toward earthenware and its production techniques was developed over many years, they still remain as part of our customs when we manufacture various other

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*Numbers in the margin indicate pagination in the foreign text.

types of earthenware even now. We relied on the conventional
techniques, adding many different raw materials in a consistent
order, varying the sintering temperature and time, whenever we
had to improve the quality of the earthenware or when we were trying
to develop a new product. Whenever we needed to manufacture the
product for a specific use, we knew the techniques for doing so: we
either added feldspar or bone ash to fuse the product by sintering,
or increased the amount of kaolin to improve the refractoriness,
or added talc to decrease the swelling, but we did not know why
these techniques worked. Therefore, we did not know exactly what
needed to be done when more improvement needed to be made or when
other types of ceramics with new qualities were required to be made.
Most of the time, we had to resume studying the mixing ratio of
the materials since we did not know otherwise. This meant that it
was going to be a very difficult task to develop what are called
fine ceramics of high quality because they are not found commonly.

What we need to do here, in the above example, is to study by
X-ray diffraction the product that is supplemented with talc in
the base to lower the swelling rate. In such a case, it is
necessary to clarify the fact first that the swelling was
supressed because of the formation of indialite. When raw
materials were added in the base to improve the quality, the
improvement is not a direct effect caused by the additive but
the additive affected the components of the base, such as the
type, shape, size, and distribution of crystals, the state of air

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bubbles (these comprise what is called the microstructure) and the quality of the ceramic improved as a result. That means, consequently, that the ceramic quality is directly ruled by its own microstructure. Naturally, the microstructure is formed as the reactions among the grains of the raw material occur and as it passes through the sintering process. It is an absolute /583 necessity to clarify the questions involving the manufacturing process starting with the selection of the raw material and the mutual relationship between the microstructure and properties of ceramics if we are to develop fine ceramics further in the future.

2. History of Microstructure Research

It is said that the typical human eye is capable of seeing objects 0.2 mm large. Some efforts were made to see in more detail after the end of 16th century, when a microscope was invented. The first reference to the observation of ceramics is found in the description of needle shaped crystals in hard ceramics written by Ehrenberg in 1836 [1]. Then, in 1845, Sorby made a polarization microscope. This started the optical observation. In 1847, Oschatz and others observed [2] needle shaped crystals contained in the glass matrix of a thin ceramic piece. As we entered this century, there has been an increasing number of reports written on the observation of structure using a polarization microscope. For example, Klein and others [3] observed ceramic bases of various mixing ratios sintered in various conditions. They reported the result, calling what they made a "microstructure." As implied by this, it seems that the needle-shaped crystals, illustrated in Figure 1,

became the center of attention, and consequently started active microscopic observations on ceramic base.

Figure 1: An example of a photograph of a ceramic base taken by a polarization microscope

This needle-shaped crystal was reported in 1889 by Hussak [4], to resemble sillimanite. In 1890, Vernadsky [5] measured its optical nature, and Mellor also did some studies [5] with various techniques in 1906 and he speculated that it was sillimanite. This was found to be mullite, very similar to sillimanite optically, by Bowen and others [7] only after research on $Al_2O_3-SiO_2$ started.

The first report of microscopic observation on ceramics appearing in the Yogyo Kyokaishi (J. of Ceramic Industry) concerns the insulator of Rihachi Shibata in 1911 [8]. Ikutaro Asai's [9] report appeared in 1911, and Ryoichi Shigemune's reports in 1927 [10].

Rieke and others [11] said that the nature of ceramics will be better understood when the testing technique of crystal optics, using a polarization microscope, is developed. There was a strong

wish to observe in greater detail at that time. The maximum

magnification of an optical microscope was 1000x-1200x at 0.2 μm

resolution. Toward the end of the 1940's, the electronic

microscope of transmission type began to be used for research.

At the beginning, the raw material powder was used as the

observation object because the specimen was made from the powder

by suspension or by throwing it. Even so, the size and shape or

thickness of the fine granules were able to be observed. Later,

as replicas became available, the structure of the sintered body

was able to be magnified more than several thousand times. The

thickness of the granule was obtained by the darkness of the

Figure 2: A photograph of a replica of a polished insulator
base etching taken by an electronic microscope
(by Lundin)

image when the powder granules were observed by transmission, but the height and depth of the protruding and hollow areas needed to be known with the replica. But, in many cases it was difficult /584 to determine whether the area protruded or was hollow. This problem was resolved to some extent when the shadowing of the material thickness became available using heavy metals such as Pt-Pd. Figure 2 shows an electronic microsope photograph of a replica of the polished base surface of an insulator, taken by Lundin [12].

However, there was a problem with this replica method: microscopic protrusions and concaves were not able to be reproduced. This problem was resolved when the scanning type electron microscope was developed. The electron beam scans through the surface of a specimen and emits a secondary electron beam for an observation. The scanning type electron microscope came to be used widely because of its ability to reproduce the surface of a specimen in three-dimensional image and because of its simple process requirement for the specimen preparation since the broken surface can be observed directly. As this type of microscope became available, the structure of granules, their size, shape, and distribution, were able to be magnified by the reproduction factor from several thousand to several million, and this became the dawn of the popular use of micros- tructure. Figure 3 shows true examples of photographs taken by electron microscope of ceramic pieces. From these photographs, it is clear that preparatory processes, such as etching, are still required before being able to observe the microstructure,

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although it is much simpler.
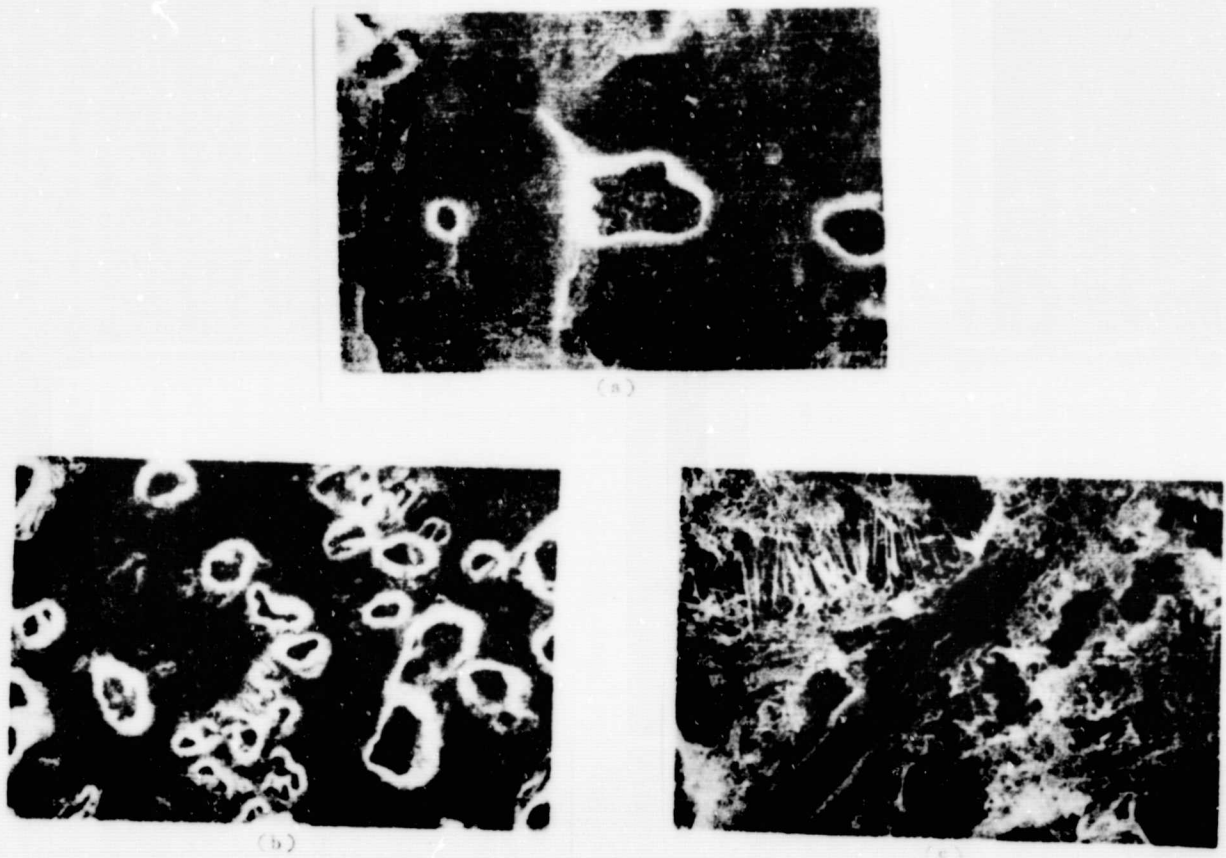
Figures 3:   Photographs of a ceramic base taken by
             scanning type electron microscope
             (a) Broken surface (b) Polished surface
             (c) Etching surface done by fluoric acid

    As the scanning type electron microscope became available,
it became easy to take pictures and easily determine what the
specimen material is only by looking at the appearance and to write
descriptions of it: this increased the danger of drawing a
completely opposite conclusion once a judgement on the photograph
is mistakenly made. In order to avoid such mistakes, specimen
crystals needed to be fixed at one position. One of the means to
achieve this was to also use electron beam diffraction, which

is to find the composing elements of the crystals. This method
became available when the technique was developed with the analysis
of the X-ray properties emitted from the specimen when an elec-
tron beam was cast on it, and they became commercially available
as EPMA, an X-ray microanalyzer. Figure 4 shows the examples of
EPMA photographs. Then, one more step was made, and what is
called an analysis electronic microscope became commercially
available, which combines the analysis technique with computers and
quantifies the composing elements of the crystals.
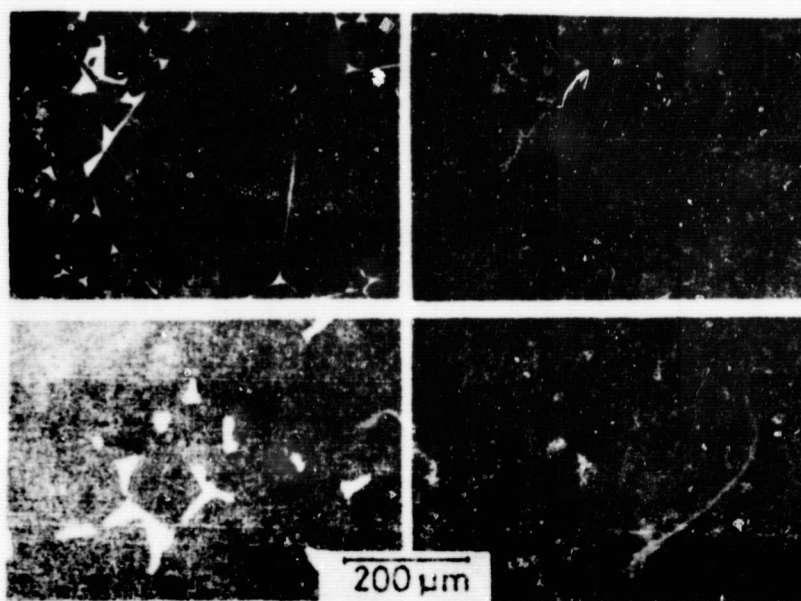
Figures 4:   Examples of EPMA photographs of an alumina sintered
             compact containing Er_2O_3, Sm_2O_3 (Hamano, Oota)

    Thus the requirement for studying the phase, composition,
shape, size and distribution of the specimen crystals could
be satisfied by the development of microscopes, from the
optical to the electronic one. Since more than ten thousand

magnification became available with the electron microscope, requests to see the crystal lattice configuration began to emerge. The resolution of the electron microscope can be increased by raising the acceleration voltage, which shortens the wavelength of the electron beam, since its resolution is approximately 1/2 of the used electromagnetic wavelength. Thus, the acceleration voltage of the microscope is increased from the initial voltage, approximately 50 or 60 kV, and sometimes raised to several thousand kilovolts, which also consequently increased the degree of vacuum in the cylinder. From this, a high resolution /585 electron microscope of angstrom order was made. This microscope made it possible to directly observe the atomic configuration and the crystal lattice disorder. Some of the examples of photographs taken by this type of microscope are shown in this paper.

Besides the super-high voltage electronic microscope used for observing the atomic configuration directly, there have been another method for studying the crystal configuration indirectly, using X-ray diffraction through crystals, which was discovered by Laue in 1912. The X-ray diffraction apparatus was difficult to operate at the initial stage and it took a long time to do the operation; therefore, it was mainly used for analyzing the structure of crystals. The study on celite by Shukichi Yamauchi [13] and the analysis on the structure of aluminum titanate by Goro Yamaguchi [14] are examples of research conducted in those days. This method was also used for studies on the ceramic base: an example is the report on the crystal configuration of commercial ceramic bases made by Toshio Nakai in 1939 [15]. After an

X-ray diffractometer, composed of Geiger tubes, became
commercially available, X-ray diffraction began to be
used widely as the easiest and simplest method of identifying
crystals. Meanwhile, the analysis of crystal microstructure
was remarkably improved in terms of its accuracy and efficiency,
because the accuracy of instruments was improved, new instruments
were developed, and a new four-axle single crystal diffraction
apparatus was made. In addition to X-ray diffraction, various
physical techniques were developed for measuring crystals, such as
the electron beam, neutron beam diffraction, or the technique of
measuring the absorbed spectrum. These techniques made it possi-
ble to gain a great deal of knowledge.

Thus, the method for studying the factors affecting the ceramic
nature has been developed to the point where the optical microscope
electronic microscope are used and to the details of atomic order,
after starting off examining the defects with the human eye.

3. The Meaning of Microstructure

When small size structures were able to be observed by using
a microscope, instead of just being observed with the human eye,
this structure was called either fine structure or microstructure.
As the electron microscope became available, the word micro-
structure began to be used more often. Some people differen-
tiated the construction such as crystals, observed by X-ray diffrac-
tion, from the microstructure, but recently the word microstructure
has been used to signify both the fine structure and construction,

because instruments were improved and became capable of handling both the observation and the analysis of the structure and the observation was improved to the atomic order level, and because both the construction and structure can affect the nature of ceramics.

The word equivalent to "microstructure" in Japanese is "bikozo." When I used the word "bikozo" in 1948 to 1952, not much interest arose about bikozo (microstructure) then [16]: there were a few cases where microstructure was dealt with, such as the studies done by Kiyoji Kondo [17] in 1931 and others [18]. Occasionally, the expression "bisai kozo soshiki" is used as the word equivalent to "microstructure," meaning the micro-structure-construction, but it seems that the word "bikozo" has become established as the Japanese equivalent word meaning microstructure.

According to the Yogyo Dictionary [19], the definition of micro-structure is described as "the constitution of the microstructure that can be studied by using a microscope or by applying X-ray measurement technique. Concretely, this means the type, constitution, construction (including defects and disorders) of glass and crystals; the intergranular field among the crystals, the consti-tuent distribution, the distribution of the interior stress; the shape, size, ratio and distribution of air bubbles and voids.

As has been discussed above, the techniques for measuring and observing the microstructure have developed remarkably, for both the construction and structure. However, this does not mean that our knowledge of microstructure has expanded to the same

degree.   The information on the microstructure can only be obtained
after each measurement and observation result is gathered.   It
means that a segment of information gathered by one technique does
not make up a sufficient amount of information.   Segments of infor-
mation obtained by applying each technique need to be gathered,
compared and complemented to make up the deficiencies in the segments.
I have written the outline of a description and comparison of the micro-
structure testing methods before [20]; so, I will not discuss it here.

4.   The Relation Between the Microstructure and their Properties

The basic properties of a material are determined by the types
of constituent elements, the bonding types of atoms, the
crystal configuration, and they are also affected by the defects and
disorders of the crystal lattice.   The properties of a single
crystal are frequently controlled by structural factors.
However, the fact is that more multi-crystals are used than
single crystals in reality.   The properties of multi-crystals
are affected by the size, shape, distribution of crystal
granules; and the thermal-expansion coefficient, intergranular
stress caused by anisotropic elasticity, and the nature of the
intergranular field, which are all related to the former factors
listed above.

In many cases, a multi-crystal contains air bubbles, or it
may have cracks.   Naturally, the amount or size and the shape of
such voids can affect the nature of crystals.   The multi-crystals
used in reality are most likely to have more than two types of

crystals, or the glass phase may be contained in them. Therefore,
the properties of the ceramic materials which are most often
used contain the glass phase, and air bubbles and voids are affected
by many factors arising from the structure.

The following lists examples of the very close relationship
between the properties of materials and the factors arising
from their microstructure. The examples of the structural
factors are semiconductivity, the crystal configuration
regularity of silicon, and the relation observed when a small
amount of B or P of different valence, is added to silicon.
Electric and magnetic characteristics are most often ruled
by the construction factors of crystals. An example of
the nature ruled by the structural factor is that the mechanical
strength of the material is decreased, naturally, as more air
bubbles are contained because this decreases the part of the

Keys:
1. Binding intensity
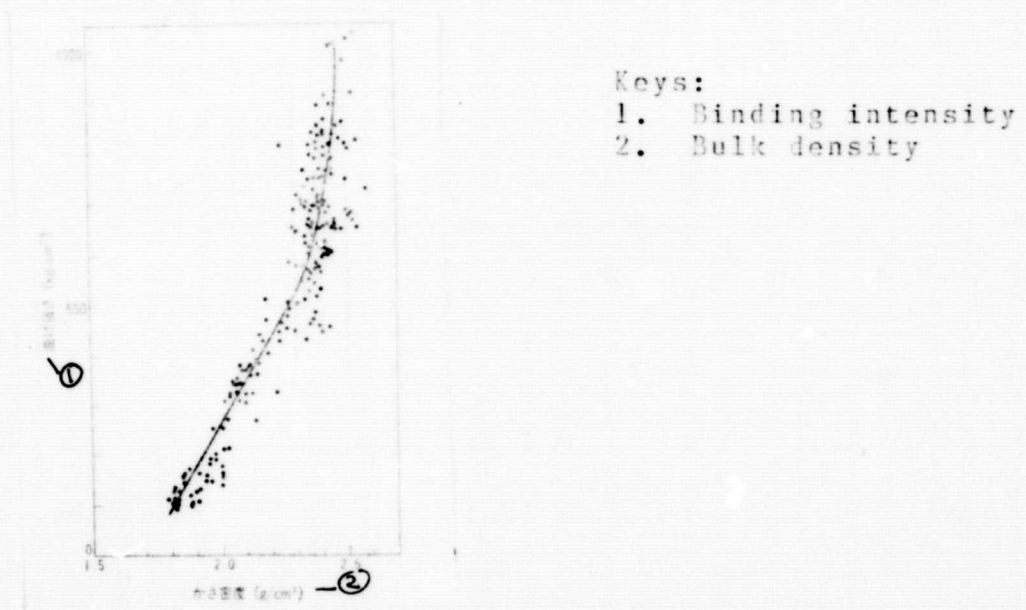2. Bulk density

Figure 5: The bulk density and bending strength of ceramic base
           (From Hamano and Lee [21])

material that is able to support the weight when a weight load is added to the material externally. Figure 5 shows the relationship between the bulk density and bending strength: the strength /587 increases as the base has a higher bulk density. On the other hand, if you look at a high bulk denisty range, for example from 2.3 to 2.5 g/cm^2, the bending strength is distributed quite wide although the bulk density range is not so large. The speculation from this is that there are some other factors affecting it.

Most of the air bubbles contained in the ceramic base are close to a spherical shape, while the voids contained in ceramic bases in general have various shapes. As the curvature radius of the tip end of the void changes, the concentration of the load changes and the change affects the strength of the material. Figure 6 shows the relationship between the stress and curvature radius ρ of the tip end of a notch made in a sintered alumina compact,
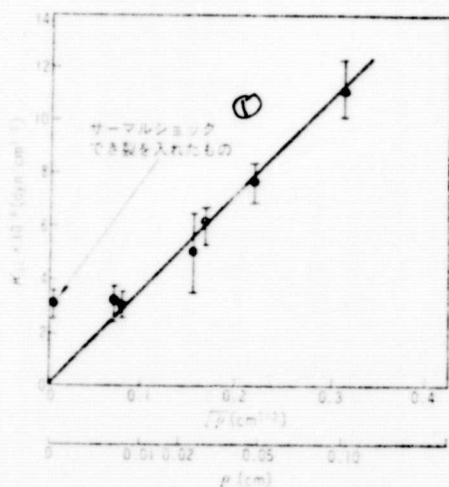
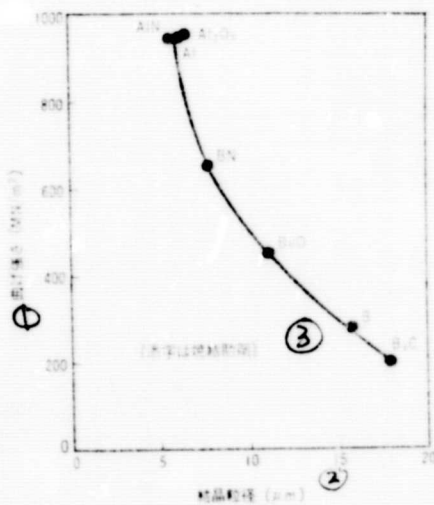Keys:
1. Specimen cracked by thermal shock

Figure 6: The relationship between the curvature radius of a notch made in a sintered alumina compact and K$_{IC}$ (From Bertolotti)

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and the expansion coefficient K_{IC} [23]. The diagram indicates that the smaller the curvature radius is and the sharper the tip end of the void is, the smaller K_{IC} turns.

The strength of ceramics varies according to the voids or cracks contained in them. According to Griffith [23], the strength δ of a brittle material has the following relationship with the legth of a crack 2C,

$$\delta = \sqrt{2 E \gamma_s / \pi c}$$

E represents the Young modulus: and γ_s, the break start surface energy. It is clear from this equation that the longer the crack length is, the smaller the material strength is. This means that the amount, shape and size of voids contained in ceramics affect their mechanical strength, and it is also affected by the granule diameter of the constituent crystals. Figure 7 shows the relation

Keys:
1. Bending intensity
2. Bulk density
3. The characters written on the line represent sintering agents.

Figure 7: The granule diameter and bending strength of SiC sintered compact
(By Nakamura et al.[24])

between the granule diameter and strength of a SiC sintered
compact which was added with various additives at 1-2 wt % and
hot pressed, and whose relative density measured higher than 98%.
The compact was made by Nakamura et al [24]. It is indicated that
the smaller the granules are, the higher the strength grows.

One of the shortcomings of ceramics is their brittleness. It
is known that the materials of a long interatomic distance, small
surface energy, and high Young modulus, generally show brittleness.
Ceramic crystals of bonds between positive and negative ions
or between negative ions, which mean ionic or homopolar
bonds, make up the primary bonding of ceramic crystals and
create a particular bonding direction. Thus atoms are not packed
well and long distances are left among atoms, which causes the
surface energy to be small because the electron density is low,
and the crystals do not deform easily because there is a parti-
cular bonding direction: this makes the Young's modulus high.
All these particularities match with the conditions that causes
the brittleness; therefore, brittleness is the basic nature of
ceramics as it arises from their construction and there is no way
to avoid this shortcoming.

Although the brittle nature of ceramic crystals is
unavoidable, they have what is called a structure because many
ceramic raw materials are composed of a large number of crystals,
in which the glass phase and air bubbles are contained. Recently,
some experiments have been conducted actively, trying to overcome
this brittleness of ceramic raw materials by utilizing structural

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factors. Some of the examples involve efforts trying to
disperse fine zirconium granules in alumina to develop and
distribute microscopic cracks homogeneously, which is to prevent
the development of larger cracks [25], or another effort is to
distribute tetragonal zirconium fine granules of the quasi-
stable phase in tetragonal zirconium homogeneously in order to
absorb the energy used for cracking the tip end by transforming
the tetragonal zirconium to monoclinic crystals [26]. Or, microscopic
secondary phase granules were precipitated and dispersed, as
shown in Figure 8, as an effort to prevent the development of
cracks [27]. These examples represent the efforts that have
been made in improving ceramic properties by utilizing factors
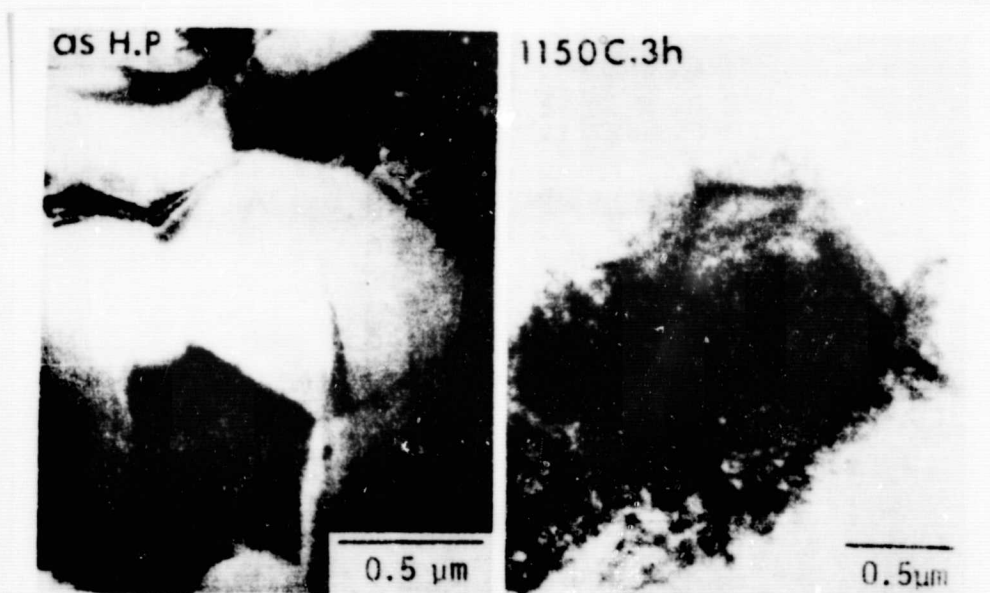arising from their microstructure.

Figure 8: A photograph of a spinel compact composed of excessive
alumina before and after reheating, taken by
transmission type electron microscope
(From Kamizaki, Hamano, Nakagawa, Saito [27])

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The above discussion described the fact that the character-
istics of ceramics are related closely to its microstructure, by
drawing examples from ceramics' mechanical characteristics. The
same can be said about other characteristics of ceramics also.

5. Microstructure Formation

The microstructure of ceramics, which determines the ceramics'
characteristics directly, is formed, as one can suppose, during
the manufacturing process. The crystal phase of the sintered
compact, the type of glass phase, and their ratio depend on the
types and nature of the used raw materials. The mixing ratio of
the raw materials and the size of the sintered compact also affect
the microstructure that is grown as a result of sintering. Solid
phase reactions occur among granules and generate compounds and solid
solutions during a heat processing. At the same time, sintering occurs
among the coexisting granules. According to the degree of this
sintering, the rate of air bubbles changes. In some cases,
comelting occurs among the contacting granules, and some of the
granules melt, and in this melt other granules melt. When the
components of the melt change, a new crystal phase may grow. Or,
sintering or crystal granule growth may be promoted by the melt.
The shapes and sizes of the contained voids may even change
because of the existence of a liquid phase. Some crystals, depending
upon their type, may transform to another type of crystal when
they are switched to cooling after heating. This can sometimes
entail a volume change also. Crystals may be deposited from the

melt, or liquid phase or solid phase fissions may occur during cooling, and after a while the viscosity of the melt that did not crystallize will grow higher to the point where it solidifies in the glass phase keeping the crystal granules and voids. As the cooling progresses, both the glass phase and the crystal granules shrink, which can cause cracks in the case where crystals of different types and directions are sintered since different types of stress will be generated in the intergranular field. Table 1 summarizes these changes that may occur during sintering.

Table 1: Changes observed during the sintering of a ceramic base

. Water discharge among solid granules

. Adsorption water discharge

. Dihydration, decomposition, oxidation

. Solid phase sintering

. Solid phase reactions (formation of chemical compounds and solid solution)

. Comelting, melting and dissolution

. Sintering involving liquid phase

. Crystal deposition, crystallization

. Granule growth

. Phase transition (swelling, shrinkage)

. Liquid phase fission, solid phase fission

. Residue melt phase solidification into glass

. Composing phase shrinkage by heat (Swelling)

. Generation of intergranular stress (intergranular fission)

Keys:
1. Heating
2. Cooling

1   2

The ceramic microstructure is formed when going through these processes. These reactions and the sintering process are affected, for example, by the type, size and condition of the raw material granules as well as the conditions of granule dispersion and packing. The conclusion is that ceramic microstructure is strongly influenced by all the processes: raw material selection, pretreatment, mixing, forming, sintering and manufacturing.

6. Microstructure Design and Property Control

As has been discussed above, the ceramic characteristics are controlled directly by its microstructure. When a ceramic of certain particular characteristics needs to be developed, we should be able to know which crystal and glass phases have to be selected for the purpose of including the expected characteristics and at what level they need to be grown in order to obtain the kind of microstructure that is expected. It is also possible for us to speculate what kind of changes need to be made in the microstructure when certain properties need to be improved. An example was given above referring to brittleness. The word microstructure design is used when the concept of the kind of microstructure to be made is formed in order to add certain characteristics to ceramics that they do not now possess.

Once the microstructure is designed, the whole manufacturing process should be determined before the actual manufacturing. The decisions involve the selection of the raw material and its pretreatment, mixing and forming techniques, and sintering condi-

tions.   When the manufacturing process conditions and the compact

microstructure are changed for the purpose of controlling

the characteristics of the ceramics, it is called property

control.

The microstructure design and property control of ceramics

are the ideal techniques for the people involved with ceramics.

However, when these techniques are going to be actually used, a

sufficient amount of the basic materials, relating to the rela-

tionship among the factors of the ceramic properties and micro-

structure, are required.   In addition to this requirement,   one

needs to have basic knowledge of the reactions, sintering and

transition of phases that occur during the raw material treatment

and sintering, as shown in Table 1.   There have been some success-

ful experiments already conducted in microstructure design using

such materials and knowledge.   But, unfortunately, we do not have

yet such materials and knowledge developed to the full degree.

We have to admit the fact, furthermore, that we have very little

knowledge of fine ceramics that is expected to be developed in the

future.

7. Postscript

Microstructure design and property control are the kind of

matters that are easy to discuss but difficult to do.   On the

other hand, it is obvious that the capabilities expected of fine

ceramics, that cannot be satisfied by other materials, would not

be achieved by the traditional approaches, by adding various

additives or changing sintering conditions. In any case, it is absolutely necessary to add more properties to ceramics and determine them in terms of microstructure. Fortunately, the method of microstructure research has improved tremendously and the general understanding of microstructure has grown remarkably in recent years. Our hope is that many researchers will continue to develop materials, knowledge and information of the superior quality and they will be utilized actively.

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