EFFECT OF ADDITIVES ON SOLID STATE SINTERING OF ALUMINA

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ABSTRACT

Effect of several additives on solid state sintering of alumina is described. Zirconia which hardly reacts upon alumina, delays the densification and the grain growth of alumina, but addition of it produces a relatively uniform, dense microstructure at high temperatures. Titania makes the solid solution with alumina to form Al^{3+} vacancies and to increase the diffusion coefficient. Consequently, adddition of titania accelerates the densification at relatively low temperatures. In the case of magnesia addition, various mechanisms have been proposed to explain the effect in producing pore free, full dense alumina. Microstructure of such fully dense alumina was analyzed and recent results of many researchers on the solid solution effects are summarized. Additionally other mechanisms of sintering of alumina, accompanied by reaction with rare earth oxides and in the case of corundum powder seeding to boehmite gel, are also described.

1. INTRODUCTION

In many sort of ceramics, several additives, being 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. One is solid solution effects and the other is effect of liquid formation (liquid phase sintering). The solid solution effect includes increase of a vacancy concentration (due to the difference of valence) and then diffusion coefficient, introduction of strain energy(due to the difference of ionic radius) to enhance the activity, and segregation of solute on grain boundaries to be expected to change the grain boundary mobility. Alumina ceramics fabricated in such

manners are important as translucent materials and also as engineering materials. Liquid formation introduces a capillary force by the wetting character, and the formed liquid acts as a lubricant to reduce an interparticle friction, and it is expected to promote the diffusion of materials. Alumina ceramics through liquid phase sintering are important for electric and electronical utilizations, such as substrates and insulators.

In this report we focus the effect of additives on solid state sintering of alumina. Therefore the solid solution effect of additives are mainly described. They are titania as an oxide having higher valence ion than alumina, Cr^{3+} as an equivalent ion, and Mg^{2+} as a lower valence ion. The effect of zirconia which hardly reacts upon alumina, and the effect of rare earth oxides, which have large cationic radii and then are not expected to dissolve in alumina, and also the sintering in the case of corundum particle seeding to boehmite gel are also presented.

2. EFFECT OF ZIRCONIA ADDITIVE

The system of $Al_2O_3-ZrO_2$ has been investigated mainly in relation to toughened ceramics. For example, Claussen et al.[1] showed that alumina ceramic containing 15 wt% monoclinic zirconia hot-pressed at 1500°C has high fracture toughness value of about 10 MPam$^{\frac{1}{2}}$ through microcracking-toughening mechanism. Zirconium ion inclines to take eightfold coordination, so that it is difficult for it to dissolve in alumina, and zirconia has no compounds with alumina. Alumina is also slightly soluble (< 2 mol%) in zirconia [2]. Therefore, nothing is known concerning the possible interaction in this binary system. What is the role of small amounts of additive for sintering in such a system? Below is the result by Lange et al.[3].

They compared the sinterability of Al_2O_3/ZrO_2 composite powder compacts with that of their single-phase constituents through constant heating-rate experiments. Original Al_2O_3 particles were mainly 0.4-0.8 μm and zirconia particles were small, <0.1 μm. The addition of ZrO_2 to alumina delayed the initiation of bulk shrinkage and the temperature of maximum shrinkage rate (Fig.1). All specimens except c-ZrO_2, which were heated to 1600°C, had nearly full density (99% of the theoretical). SEM of poorly mixed Al_2O_3/ZrO_2 composite sintered at 1550°C for 3h showed that large alumina grains about 10 μm occupied in the poorly mixed regions and that small, relatively uniform alumina grains of 1 to 2 μm were present in the well mixed region, illustrating the effect of ZrO_2 inclusion phase on limiting the grain growth of Al_2O_3. From these results, they suppose that inhibition of grain growth may also inhibit densification.
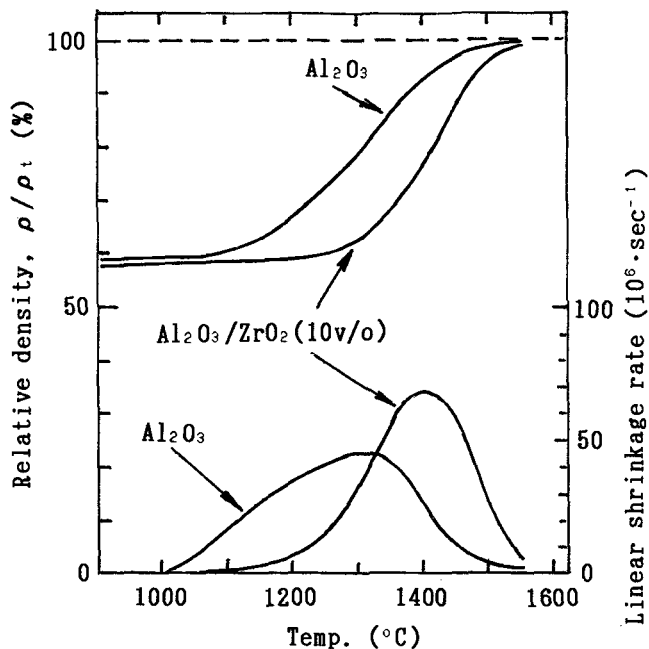
Fig.1 Relative density of linear shrinkage rate for
the Al₂O₃ and Al₂O₃/ZrO₂ composites [3].

3. EFFECT OF CHROMIUM OXIDE ADDITIVE

Chromium oxide (Cr_2O_3) has a corundum structure and forms a perfect solid solution with α-Al_2O_3 at high temperature. Ionic radius of Cr^{3+} is larger than that of Al^{3+}, so that the substitutional solid solution of Cr_2O_3 can be expected to make alumina active because of the introduction of strain energy. The role of chromium oxide on sintering of alumina is, however, negative. Papers describing positive effects of chromia addition on sintering of alumina are very few [4,5]. This reason would be based on the variability of chromium valence and the high volatility of chromium oxides. Such sintering process is complicated and the precise analysis would be difficult.

4. EFFECT OF TITANIA ADDITIVE

Rutile is stable phase of titania in air and in this structure Ti^{4+} takes sixfold coordination which is the same value as Al^{3+} in corundum. On the other hand, Si^{4+} has a small ionic radius and takes fourfold coordination in silica. Comparison of their coordination numbers suggests that TiO_2 is more soluble in alumina than SiO_2. This is considred to be true, since the solubility of TiO_2 in alumina in air is nearly constant of about 0.3 wt% with temperature above 1300°C [6,7,8], while the solubil-
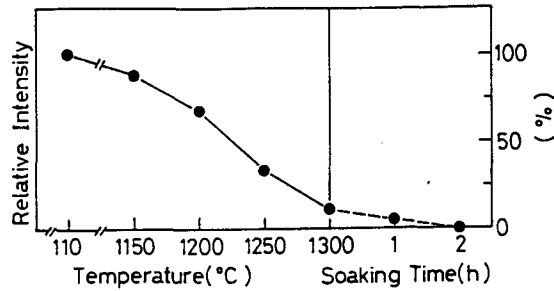
Fig.2 Ratio of X-ray diffraction intensity of rutile 110
       peak to Al₂O₃ 012 peak.

ity of silica in alumina is hardly detected.

The substitutional solid solution of TiO_2 in alumina en-
hances the aluminum vacancy concentration, as shown in the fol-
lowing equation.

$$3/2 \ TiO_2 \xrightarrow{\quad Al_2O_3 \quad} 3/2 \ Ti_{Al}{}^{\cdot} + 1/2 \ V_{Al}{}''' + 3 \ O_O{}^{x}$$

An increase of aluminum vacancy concentration should promote the
diffusion of Al^{3+} and subsequently sintering of alumina.

The solid solution behavior of TiO_2 in alumina is shown in
Fig.2, illustrating the ratio of X-ray diffraction intensity of
rutile 110 peak to corundum 012 peak for the heated specimens
containing 0.2 wt% TiO_2 within the solid solution limit.   The
specimen was prepared by adding tetraisopropyl titanate into α-
Al_2O_3 powders of about 0.5 μm and hydrolyzing it.   The intensity
of rutile started to decrease when the temperature reached to
1150°C, and became zero when the specimen was fired at 1300°C for
2h.   The decreasing and vanishing of rutile indicate the forma-
tion of solid solution of TiO_2 in Alumina. Thermal shrinkage of
alumina compact containing TiO_2 starts at about 1050°C and the
temperatures look somewhat to be higher than that of pure alumi-
na, as shown in Fig.3.   The shrinkage rate becomes large above
1150°C and consequently the total shrinkage at 1500°C increases
with the content of TiO_2.   The increase of shrinkage rate of
compacts containing TiO_2 is well corresponding to the fact that
the progress of solid solution of TiO_2 on the densification is
effective at lower temperatures (Fig.4).   At high temperature
above 1600°C, the addition of TiO_2 does not elevate the fired
density, but accelerates markedly grain growth of alumina.   This
grain growth is also due to the enhanced aluminum vacancy concen-
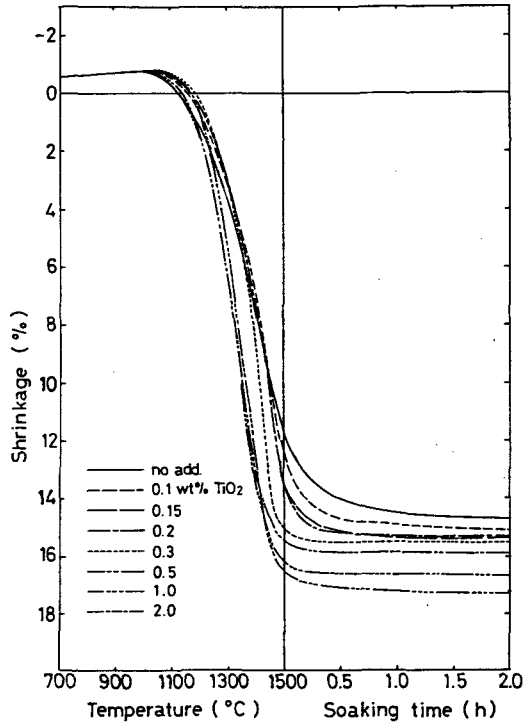tration by the substitutional solid solution of TiO_2.

Fig.3 Thermal shrinkage curves of alumina specimens
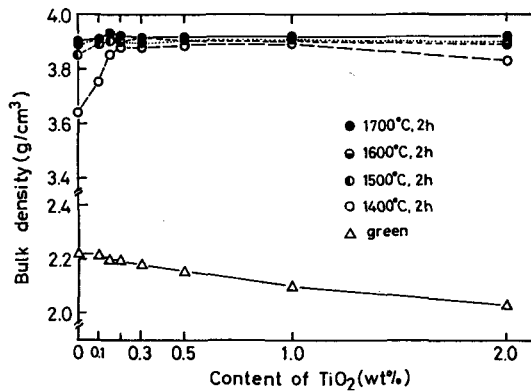containing various amounts of TiO₂.

Fig.4 Green density and fired bulk density of specimens
containing various amounts of TiO₂.

5. EFFECT OF MAGNESIA ADDITIVE

Magnesia is the most important one among additives on sin-
tering of alumina. Coble [9] first reported that small amounts
of MgO additives produce pore free, full dense alumina by sup-
pressing discontinuous grain growth. In this firing, hydrogen
or vacuum atmosphere was found to be necessary. Since then many
workers have been tried to explain the role of MgO on sintering
of alumina. CaO has similar chemical properties to MgO as the

same alkaline earth metal oxide.   As the ionic radius of Ca^{2+} is much larger than that of Al^{3+}, CaO hardly dissolve in alumina and exists at the grain boundaries and/or surface of alumina ceramics.   On the other hand, Mg^{2+} inclines to take sixfold coordination in oxides and has relatively similar ionic radius to Al^{3+}, so that small amounts of MgO can dissolve in corundum.   Firstly, microstructure of a translucent alumina ceramic is described and then our attention is focused on the role of MgO on sintering of alumina.

5.1. Microstructure of Translucent Alumina Ceramic

A translucent alumina ceramic, so-called "Lucalox", fabricated commercially as tube by adding small amounts of MgO, was analyzed microstructually by the repeated stepscanning method of X-ray powder diffraction, the observation using various microscopes, and EPMA [10].   The specimen included a small amount of spinel phase, about 300ppm, of which lattice parameter was $a_O = 0.804_9$ nm. Microstructure of the transverse section was analyzed in the area of 800 µm width (sample thickness) and 600 µm perpendicular width in which no pores were observed.   This area was polishing-etched with corundum abrasive powders of 0.3 µm. Spinel particles less than 10 µm existed at triple junctions of grain boundaries in inner part of the specimen and not in the surface sides (Fig.5).   Chemical composition of spinel phases by EPMA was about Al_2O_3 77 wt% and MgO 22 wt%, corresponding to alumina rich spinel which is saturated with alumina at 1400°C and has lattice parameter of $a_O = 0.805$ nm [11].   Mg concentration by EPMA was high in the inner part and low in the surface sides (Fig.6), and this distribution may be based on the existence of spinel particles.   Corundum grain was large in the surface sides and small in the inner part (Fig.7).   Large corundum grains would have grown after the specimen sintered to full density and
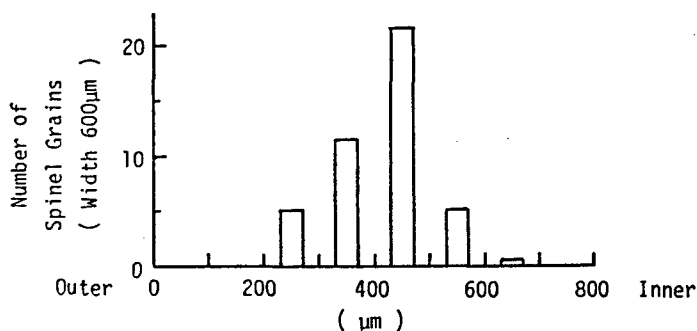

Fig.5 Distribution of spinel grains on transverse section
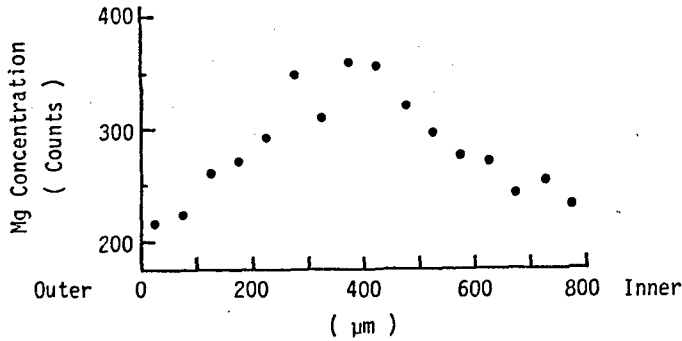of translucent alumina ceramic.

Fig.6 Mg concentration on the tranverse section of
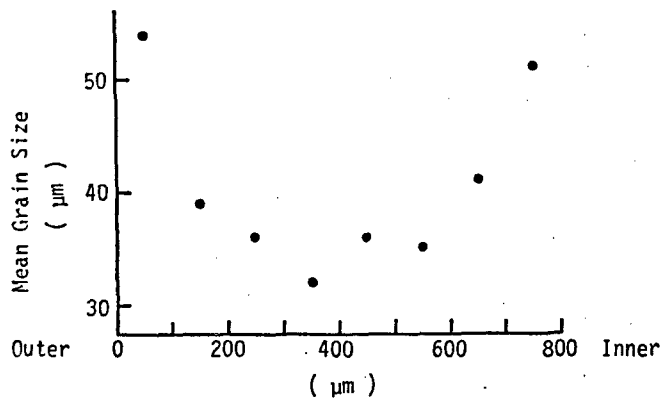   translucent alumina ceramic.

Fig.7 Grain size distribution of corundum on transverse
       section of translucent alumina ceramic.

then spinel particles disappeared by MgO evaporation during
firing.   Total MgO content of this transparent alumina specimen
was evaluated by emission spectroanalysis to be about 300 ppm of
which value was larger than the amount of MgO estimated from the
content of spinel phase, about 70 ppm.   The difference between
two values means that MgO dissolves in corundum.   From these
results, the MgO-enhanced densification of sintered alumina was
considered to be related to the solid solution of MgO in corun-
dum.

5.2. Role of MgO

Many workers have proposed to explain the role of MgO addi-
tives in producing full dense alumina ceramic by suppressing
discontinuous grain growth.   These are mostly classified to
following groups [12].

(a) Second phase mechanism; spinel precipitates which are reac
    tion products of MgO additive with Al_2O_3 pin the grain bound-

aries during final stage sintering and prevent discontinuous grain growth [9].

(b) Solute-segregation mechanism; MgO additive segregates to the grain boundaries and inhibits discontinuous grain growth by a solute drag mechanism [13,14].

(c) Solid solution mechanism; the sintering rate is enhanced relative to the grain growth rate by the solute.

Johnson and Coble [12] conducted the following experiment to determine if MgO added within the solubility limit in Al_2O_3 is sufficient to suppress discontinuous grain growth of alumina. An undoped alumina pellet was sintered for 10h at 1950°C in a hydrogen atmosphere in a closed Mo boat next to, but not in contact with, a preequilibrated, two-phase mixture of Mg-Al spinel and alumina as a MgO source. The firing produced a sintered alumina pellet with a dense outer shell and a porous core. That is, the MgO-doped outer surface of the undoped pellet did sinter to full density. And this region was free of second phase. Grain boundaries had no Mg segregation, but Ca segregation which was approximately the same in the dense outer region and in the inner porous region. From the results they concluded the beneficial effect of magnesium is related to the solid solution, but due neither to second-phase pinning nor to Ca impurity segregation.

Berry and Harmer [15] summarized MgO functions following four schools as the solid solution mechanism . There are some discrepancies among them because of results of many workers.

(a) Magnesia acts to increase the rate of densification directly through a raising of the diffusion coefficient, $D_{lattice}$ or $D_{boundary}$. This is expected to change the grain size/density trajectory during sintering to give smaller more mobile pores at a given density (or grain size), thereby avoiding pore breakaway and abnormal grain growth.

(b) Magnesia acts to raise the pore mobility, M_p, directly through a raising of the surface diffusion coefficient, $D_{surface}$. This assumes that the pore move by a surface diffusion mechanism. This is expected to change the grain size/density trajectory to give larger grains and larger pores at a given density.

(c) Magnesia acts directly to decrease the rate of grain growth during sintering through a lowering of the surface diffusion coefficient. This assumes that grain growth is controlled by surface diffusion-controlled pore drag. This is also expected to change the grain size/density trajectory to give (hence smaller pores) at a given density.

(d) Magnesia acts directly to lower the grain-boundary mobility, M_b (i.e., the mobility of the pore-free segment of the boundary), thus enabling the pores to stay attached to the moving grain boundaries during sintering.

Harmer [16] considered the separate effects of MgO doping in the atomic mechanisms responsible for densification and grain growth during sintering of alumina, and he explained the role of MgO as a solid-solution additive on the grain size/density trajectory.

The effect of additives on microstructure development is thought to be through its influence on the various diffusivity and mobility terms: lattice diffusion, D_L, diffusion parallel to the grain boundary, D''_b, surface diffusion, D_s, and grain boundary mobility, M_b. The effect of process variables such as these on microstructure development is predicted by mapping approarches. One example is shown in Fig.8. The map is divided into regions of different simultaneous densification, coarsening mechanism pairs with the respective mechanisms indicated by a diffusion coefficient pair, $D_{densification}$: $D_{coarsening}$. The pore-boundary separation region appears as an area on the far right-hand side of the diagram. The effect of additives on diffusion coefficients and M_b was considered with the aid of this diagram. Figure 8 shows the effect of raising D_L by additives by a factor of 10. In this case, the trajectory is altered sufficiently to undercut the separation region, thereby enabling full density to be attained. From such analyses, he recommended to raise D_L and/or D''_b, to lower M_b , and narrow size distribu tion of the initial particle , and explained the complex effects
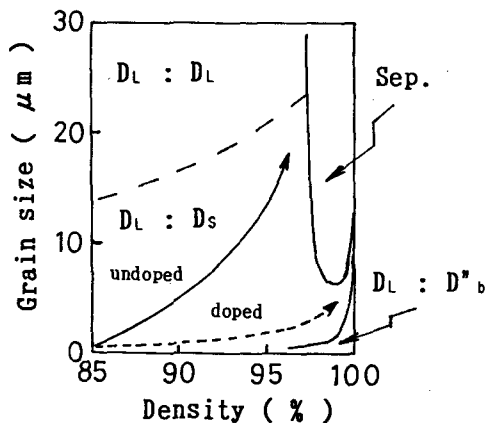

Fig.8 Microstructure development map for Al_2O_3
showing the effect of raising the lattice
diffusion coefficient by a factor of 10 [16].

of D_s with M_b and D_L. As his collected data included that MgO raises D_L, MgO lowers M_b, and MgO either leaves D_s unchanged or lowers, he mentioned that MgO affects all of the diffusivity and mobility terms in the most favorable way. It is not, however, so simple, because the addition of MgO lowers M_b in the dense alumina body by [17] but increases it during sintering [15], for one example. Recent results by Bennison and Harmer [18] reveal that MgO enhances the densification rate/coarsening rate ratio by a modest factor of 1.8, and they mentions that the primary role of MgO is the (relative) suppression of grain boundary motion.

Handwerker et al.[19] described the role of MgO additives from another point of view. Doping with MgO reduces the effects of chemical inhomogeneities, possibly by increasing the solubility of impurities, particularly Si^{4+}, thereby reducing or eliminating the liquid phase. With MgO additions, the dihedral angle distribution remains narrow throughout the microstructure, pore-boundary separation is eliminated, and discontinuous grain growth does not occur.

5.3. Solid Solubility of MgO in Alumina

The amount of solid solubility of MgO in alumina is very important to consider the role of MgO on sintering of alumina, but is too small to detect by lattice parameter shifts. Roy and Coble [20] determined the solubility by spectrochemical analysis of a small alumina powder about 2 μm, saturated with MgO. Their samples were prepared by annealing an undoped alumina powder with a preequilibrated two-phase mixture of Al_2O_3 and spinel, but separately set, in a closed Mo crucible. The results are listed in Table 1.

Table 1 Solubility of MgO in Al_2O_3

Temperature	Roy and Coble [20]		Ando and Momoda [21]	
	wt ppm	at.ppm (Mg/Al)	wt ppm	at.ppm (Mg/Al)
2073 K	890	1126	95	120
1973 K	406	513	55	70

On the other hand, Ando and Momoda [21] measured the solubility in Al_2O_3 single crystal by EPMA. Their samples were prepared by annealing a diffusion couple contructed with a tablet of fully dense, polycrystalline Al_2O_3 doped with 400 wt ppm MgO and a tablet of high purity single-crystal Al_2O_3, mounted in Al_2O_3 powder doped with 400 wt ppm MgO to suppress the evaporation of MgO from the specimen. The 400 ppm MgO-doped polycrystalline Al_2O_3 contained small amounts of spinel phase after

firing at the same temperature, showing over saturated with MgO. Measured values of the solubility of MgO were the same at the boundary side of single crystal and in the large grains in poly-crystalline Al_2O_3. Their results are also listed in Table 1. Table 1 shows fine powder of Al_2O_3 has higher solubility of MgO than that of single Al_2O_3 crystal, and also coarse Al_2O_3 grains. This means the possibility that the solid solubility of MgO in alumina changes with sintering and/or grain growth of alumina. In many papers, the role of MgO on sintering of alumina has been discussed on the base of results by Roy and Coble [20]. There-fore, some re-examinations on the role of MgO may be necessary whether the function of MgO effectively acts within the solid solubility, or out of the solid solubility, as mentioned by Ando and Momoda [21].

6. EFFECT OF RARE EARTH OXIDE ADDITIVES

The cationic radii of rare earth oxides are about twice as large as that of Al^{3+}, so that they hardly dissolve in alumina (for example, the solubility of yttrium in alumina is < 10 ppm even at temperatures approaching the melting points of alumina [22]), and they have high melting temperatures and high eutectic points above 1700°C with alumina. From these properties, solid solution effects or liquid phase sintering are not expected for the addition of rare earth oxides to alumina below 1700°C. Rare earth oxides, however, react with alumina to form compound oxides with elevating temperature. These reactions may affect the sintering of alumina body.

Hamano et al.[23,24,25] investigated sintering behavior of alumina in the case of addition of rare earth oxides. Additives selected are Y_2O_3, La_2O_3, Sm_2O_3, and Er_2O_3. Rare earth metal nitrates were wet-mixed with alumina powder of about 0.5 μm and calcined at 800°C to decompose them. Rare earth oxide in cal-cined powders was very small about 10 nm in diameter. Reaction of rare earth oxides with alumina occurred above 1000°C under solid state. The result of Er_2O_3, as one example is shown in Fig. 9. Although initial product was the compound with low alumina content, the content in reaction product increased with elevating temperature. Above 1400°C, 3:5 phase which has a garnet structure and is a stable phase in the $Al_2O_3-Er_2O_3$ phase diagram became to form.

The addition of rare earth oxides delayed initial sintering of alumina, preventing direct contact between alumina particles due to the existence of their small particles, but the shrinkage rate increased with progress of the solid state reaction. As the results, fired density above 1500°C of the specimen contain-ing rare earth oxides except La_2O_3 was higher than that of pure
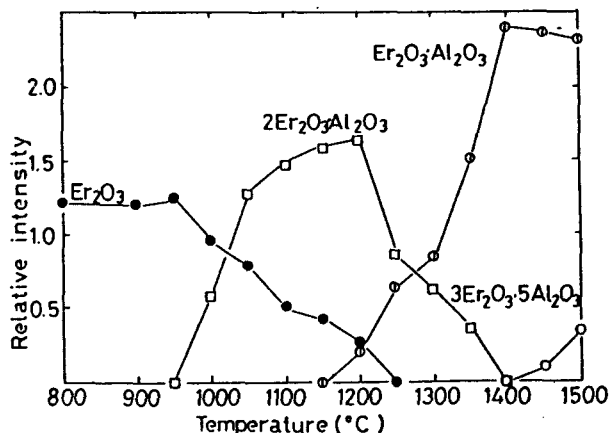
Fig.9 Relative intensity of Er_2O_3-Al_2O_3 compounds
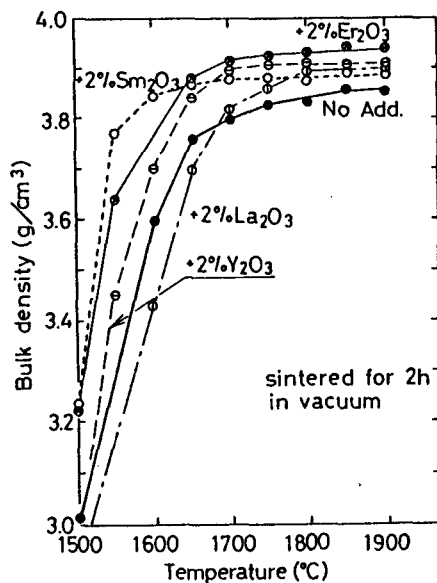as a function of temperature (heating rate: 10°C).

Fig.10 Fired bulk density of alumina specimens
containing rare earth oxides.

alumina specimen (Fig.10). The effect of densification is due to the promotion of material transport based on the solid state reaction. The addition of La_2O_3 is not so effective because of the formation of β-alumina which is strongly anisotropic. The addition of rare earth oxides also formed a relatively uniform microstructure of fired bodies, suppressing the gain growth of alumina by pinning effect of small second phase particles.

7. SEEDING EFFECT OF α-ALUMINA

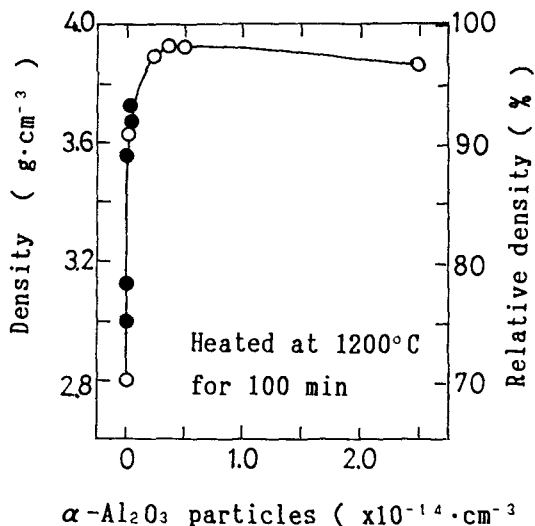It is known that reconstructive transformation of ceramic materials is usually accelerated by the addition of seeding

Fig.11 Density as afunction of number of seeding alumina
particles per volume of boehmite gel heated at 1200°C
(●; 0.4 μm seeds.   ○;0.1 μm seeds.) [26].

crystals, to circumvent the high activation energy of nucleation.
This seeding that a material with other morphology (crystal) is
added to the same component material is thought to be one kind of
additives.   Kumagai and Messing [26] reported the densification
of alumina from a boehmite sol-gel by a-Al_2O_3 seeding .   They
dispersed fine a-Al_2O_3 particles to boehmite hydrosols, stirred
them on a hot plate to make gels, and measured the rate of a-
Al_2O_3 transformation and the sintered density. a-Al_2O_3 seeding
resulted in an increase in the transformation kinetics and lower-
ing of the transformation temperature by as much as 170°C.   The
transformed a-Al_2O_3 was sintered to full density with a submi-
crometer grain size at 1200°C and the sintered density depended
on the number of a-Al_2O_3 particles added per unit volume of
boehmite (Fig.11), rather than the weight % of a-Al_2O_3 or the
particle size.   They observed an aggregate-free submicrometer
microstructure in seeding specimens, different from the vermicu-
lar-like microstructure of no seeded specimen which usually
characterizes the a-Al_2O_3 transformation from boehmite gel.
They suggested that seeding method might be used for microstruc-
tural control in the many ceramic systems which transform by
nucleation and growth and they tried to apply this method to
other systems [27,28].

8.   SUMMARY
   Additives are used, in many cases, to sinter an available
powder to a desired body (for example, dense materials), or to

control microstructure of fired bodies. Magnesia is the most important additive for sintering of alumina, and the function of MgO is not simple and being investigated even now. Recently many sinterable ceramic powders have been produced and new forming or casting methods such as sol-gel process, etc. have been developed. These factors are also important, as well as the selection of additives for an available powder.

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