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A STUDY OF
THE ROLE OF IMPURITIES AND ADDITIVES
ON CERAMIC DENSIFICATION

By

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Abstract:

Densification of ceramic materials has been thought to be controlled by interfacial effects, whether particle-particle, pore-particle, or grain boundary interfaces. Minor amounts of certain elements have been found empirically to aid in densification of sintered Al_2O_3 and hot pressed MgO . This study applies Auger Electron Spectroscopy to densification of Al_2O_3 with MgO , NiO , and Y_2O_3 additives and MgO with LiF and NaF additives to determine the interfacial chemistries involved and thereby understand the roles of the additives. Finally, the observed segregation is studied quantitatively in terms of Gibbsian segregation and models for densification enhancement proposed and supported with experimental evidence.

This dissertation, "A Study of the Role of Impurities and Additives on Ceramic Densification", is hereby approved in partial fulfillment of the requirements for the degree of DOCTOR OF PHILOSOPHY in the field of Metallurgical Engineering.

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I. Introduction

A. Objective

The purpose of this investigation was to study the roles of additives and impurities on the densification of sintered Al_2O_3 and hot pressed MgO . The study was undertaken because of the possibility of obtaining for the first time, definitive data on grain boundary chemistry through the use of Auger electron spectroscopy.

B. Problem Definition

In general, ceramic materials are not easy to fabricate. The raw materials are in powder form and compaction techniques must be used to shape the desired body. The compact must then be sintered or hot pressed to obtain a dense material. Relatively high temperatures are necessary for both of these processes and the finished products often contain residual porosity. Incomplete densification is often the result of a phenomenon known as discontinuous grain growth, a topic which will be examined later. Due to the rapid growth of discontinuous grains, porosity is trapped well within them. If the distance from these trapped pores to the paths of fast material transport or vacancy sinks (grain boundaries) is long, over finite times the rate of material transport necessary to close off the pores will be kinetically limited. The material will exhibit residual porosity and a duplexed microstructure with the associated poor mechanical properties.

Methods have been developed to promote the densification of ceramic materials through the use of additives. These additives, when added to the ceramic in powder form were found

to aid fabrication by either allowing densification to occur at lower temperatures in shorter times or by inhibiting discontinuous grain growth and allowing pore elimination to proceed to completion.

Use of these additives was for the most part empirical and experimental verification of their role impossible, due to the limited region over which they acted (usually assumed to be the grain boundaries or inter-particle interfaces). At least four theories were advanced to explain the effect of these additives. 1) Liquid phase assistance - In this mechanism, an additive with a lower melting point is used to aid densification. By melting and coating the ceramic particles, the rapid dissolution and transfer of the base material to fill the inter-particle spaces leads to enhanced densification. The additive has to be fairly soluble in the base ceramic and several weight percent of the additive is necessary to provide sufficient liquid phase to coat all of the powder particles. 2) Solid solution effect - This mechanism predicts enhanced bulk material transport due to the introduction of vacancies into the ceramic when a solute with a different valence is added. These vacancies render the diffusion coefficient extrinsic by making the thermal vacancy concentration insignificant up to a certain temperature and if added in sufficient quantity, can significantly alter the rate of material transport through the solid phase. The additive must be soluble in the base material and must induce vacancies which alter the rate controlling diffusivity. 3) Grain boundary pinning by a second phase - This mechanism involves the formation of second phase particles at grain boundaries in a material susceptible to discontinuous grain growth. These second phase particles act

to pin the grain boundaries, preventing discontinuous grain growth from occurring. Inclusions can increase the energy necessary for grain growth and inhibit motion of grain boundaries by lowering their energy. The energy of the moving boundary is decreased when it encounters an inclusion, since an area of boundary roughly the size of the second phase cross section has been eliminated. For the boundary to continue moving, this boundary area must be created again, a process requiring energy. Hence a boundary pinned by inclusions represents a cusp situation energetically and unless the driving force for continued growth exceeds this barrier, growth will stop. It has been found that when the grain diameter D is greater than the ratio of the average inclusion diameter, d , divided by the volume fraction of inclusions, f , growth can proceed.¹

$$D > \frac{d}{f} \quad (1)$$

4) Solute segregation to grain boundaries inhibiting discontinuous grain growth - Similar to the second phase pinning hypothesis, this involves the drag on grain boundary motion due to the presence at the boundaries of an adsorbed solute. Theoretical treatments of this problem have indicated that the controlling effect for movement of a boundary containing adsorbed solute is the ability of the solute to diffuse through the base material.²⁻⁴ Since the solute has segregated to the boundaries from the bulk to lower the free energy of the system, this energy will increase if the boundary moves on and leaves the solute behind. Hence the solute will maintain a minimum energy condition by occupying sites in the region of high energy/disorder (i.e. grain boundary).^{3,4} Conditions of high boundary velocity (high driving force for motion) and low binding energy of the solute to the boundary can

lead to "breakaway" and normal growth after the solute has been left behind. Conversely, low velocity and/or high binding energy will lead to "solute drag" as the segregant must be dragged with the moving interface. Highly dependent on the amount of solute as well as the previously mentioned factors, this latter condition will lead to a slower rate of growth since the segregant must be carried with the boundary by a diffusive mechanism, which will be slower than the atomic rearrangement responsible for normal grain growth.

All of these mechanisms are presumed to operate in certain systems. The particular one or combination operative in a given material depends on the properties and relationships between the base material and additive.

C. Use of Additives in Sintered Al_2O_3

The use of small amount (about 0.05^w/o) MgO to aid sintering of Al_2O_3 was described first by Coble in the late 1950's.⁵⁻⁷ The resulting material, marketed commercially by the General Electric Company under the trade name Lucalox, is theoretically dense with uniform equiaxed grains.⁷ The amount of MgO necessary to obtain theoretical density is not sufficient to form a continuous liquid film between particles (as was mentioned earlier, in general several weight percent additive is necessary). Further, Jorgensen and Westbrook found that the amount of MgO necessary is within the solubility limit for MgO in Al_2O_3 , thereby eliminating the second phase mechanism.⁸

Other mechanisms have received notice in recent years.

Coble⁵ and Bruch⁹ have both supported a solid solution theory involving enhancement of the sintering rate. This was presumed due to increased diffusivities because of oxygen vacancies created by Mg^{+2} ions substituted for Al^{+3} ions. Jorgensen on the other hand, favored a solute segregation theory supported in part by micro-hardness data.^{8,10}

This study was begun to test the solute segregation theory by directly measuring impurity and solute levels at grain boundaries and correlating this chemistry with densification. Since it was felt that the solid solution theory could be operative as well, previous studies of grain growth rate, densification versus time, and diffusivities in Al_2O_3 and Al_2O_3 doped with MgO were examined to determine the feasibility of this mechanism.

D. Use of Additives in Hot Pressed MgO

The use of LiF additions to obtain transparent hot pressed MgO was first described by Rice in 1962.¹¹ The addition of 2% LiF to the MgO powder allowed a theoretically dense MgO to be obtained at relatively low ($700^\circ\text{C} - 1000^\circ\text{C}$) temperatures. The mechanical and optical properties of the as-hot pressed material could be improved markedly by subsequent annealing at temperatures higher than the hot pressing temperature, until a material almost as transparent as single crystal MgO resulted.¹²⁻¹⁵ Use of NaF can also lead to a dense material, but higher hot-pressing temperatures are required. The mechanism for densification was felt to be a pressure enhanced liquid phase sintering phenomenon,^{16,17} although enhanced diffusion through vacancy alteration was also suggested.¹² The improved properties after annealing were presumed due to alteration of the grain boundary

chemistry, although it was difficult to determine what had actually changed due to the previously mentioned problems in obtaining grain boundary chemistry. The current study was begun to directly determine grain boundary chemistry, use this information to investigate mechanisms of densification, and correlate changes in mechanical and optical properties with changes in this chemistry. Spinel (MgAl_2O_4) material and Al_2O_3 , both hot pressed to theoretical density with LiF were also examined to provide additional data concerning hot pressing with LiF additives.

II. Experimental and Equipment

A. Auger Electron Spectroscopy (AES)

Auger electron spectroscopy, a technique used extensively throughout this study to obtain grain boundary chemistries, has been developed in recent years to fill a gap in the tools available for materials research.¹⁸⁻²⁰

Basically AES differs from other analysis techniques such as electron microprobe in that it is sensitive to the first few surface layers (4-20 $\text{\AA}$). In AES, an electron beam of moderate energy (1000-3000 eV) strikes the specimen and causes the ionization of an inner electron level. When an electron from an outer level fills the vacancy, a photon or an Auger electron is emitted, depending on the relaxation time for photon emission. This relaxation time is found to increase rapidly as the energy of the transition decreases. The relaxation time for Auger electron emission, however, is approximately independent of the transition energies and therefore for light elements (i.e., for transitions below about 2000 eV) Auger emission is the major relaxation mechanism.²⁰ For an individual atom with well-defined energy levels, the characteristic energy of a particular transition can be calculated from energy conservation. For example, the electron energy levels in a silver atom should give rise to an Auger emission with energy, $E_{MIV} - E_{NV} - E_{NV} = 366 \text{ eV}$ (Figure 1). E_{MIV} is the energy of the originally ionized level and E_{NV} is the energy of the doubly ionized level from which the Auger emission originates.²¹

An Auger emission is detected at 356 eV which differs from the 366 eV calculated due to the work function of the analyzer and the non-validity of the simple single atom model used for the

$$E_{AUGER} = E_{MIV} - E_{NI} - E_{NI} = 366.2 \text{ eV}$$

Figure 1 Selected Electron Energy Levels in an Isolated Ag Atom

calculation. However, it can be seen that the energy from a given transition is characteristic of the levels and therefore the element involved in that emission.

Lander first demonstrated the possibility of using the Auger emission for qualitative investigation by interpreting the small, fixed energy peaks in the energy distribution of secondary electrons as resulting from Auger transitions.²² The technique lacked sensitivity because of the high background of other secondary electrons. Later, Harris found that sensitivity could be improved by measuring the derivative of the energy distribution.²³

Then in 1967, Weber and Peria demonstrated the use of standard hemispherical low energy electron diffraction (LEED) optics to detect Auger electrons using a retarding potential technique.²⁴

The second generation of Auger electron detection equipment utilizing a cylindrical electrostatic energy analyzer, was described by Palmberg, Bohn, and Tracy in 1969.²⁵ In this technique either a coaxial (normal incidence) or grazing incidence electron gun is used and the electrons from the specimen are collected by a velocity selector (Figure 2). The outer cylinder is biased negative and is swept over the voltage range of interest. Electrons of the correct energy are focused through the exit slit and collected by an electron multiplier. Since in this case the collected signal is proportional to the energy distribution, $N(E)$, it is necessary to take only one derivative. This is obtained by applying a modulated voltage to the outer cylinder and measuring the component of collected current with that frequency. The energy of the electrons collected is proportional to the potential applied to the outer cylinder, with the propor-

Figure 2 Schematic of a Cylindrical Analyzer for AES

tionality factor dependent on the cylinder geometry.

The cylindrical analyzer is superior to the LEED optics for AES for several reasons.

(1) The signal-to-noise ratio (S/N) is higher. Since the analyzer is a band pass device as contrasted to the high pass characteristics of retarding barrier techniques, the background current is as little as 10^{-4} that of a LEED device and shot noise is reduced by a factor of 100.

(2) Only the first derivative of the signal is needed; this gives an increase of four in the signal.

(3) Due to the high S/N ratio, low beam currents can be used; this is useful for experiments where high current densities can be damaging.

(4) Due to the fast response of the analyzer (10,000 eV sec^{-1}) the spectrum can be displayed on an oscilloscope.

Special problems arise in the use of AES on insulators or poorly conducting materials such as ceramics. The emission of electrons depends strongly on the ability of a material to carry away excess charge. The secondary yield of a surface (defined as the number of secondary electrons created per incident primary) is very dependent on primary energy. The primary energy dependence is not important for good conductors since the charge due to excess primaries or secondaries is easily neutralized. On insulators, however, it is important to work with primary energies which produce a secondary yield greater than 1; then, the only effect of surface charging is to shift the entire spectrum by a few eV.²⁰

Intuitively, it might be suspected that the relationship between the number of atoms contributing to Auger emissions and

the observed signal strength would be linear, but the problem is complicated by electron escape and energy loss mechanisms. What is important for quantitative work is the volume of the solid contributing Auger emissions with the characteristic energy, not the total number of emissions. To first approximation, this volume is defined by the beam diameter, surface of the solid, and effective depth from which electron escape at Auger energies (viz., 50-2000 eV) is relatively unimpeded by the atom layers above. It is found, not surprisingly, that the major portion of the signal originates in the first few surface layers and the signal drops off rapidly with increasing depth.²⁶ Therefore, a signal calibration curve of coverage should be linear up to one monolayer coverage beyond which the curve should approach an asymptote corresponding to a "saturation" coverage of the calibrated element (Figure 3). At this coverage, the volume contributing to the Auger signal lies entirely in the overlayer and the signal observed should correspond to that observed from a bulk sample of the element. Calibration curves have been obtained for two element systems which correspond to this model. For example, Weber and Johnson have shown AES to be quantitative for the system K on clean Ge (111) and linear for less than one monolayer coverage.²⁷ Yet meticulously clean surfaces are difficult to obtain for surface characterization and calibration work, and impossible to obtain in conventional surface or grain boundary investigations.

In an effort to examine the effects of multiple elements on calibration of AES, a study was done by Johnson on the effect of additional elements on the calibration curve for low Ag coverages on Au.²⁸ The results indicate that the same general curve

Figure 3 Saturation Coverage Curve

is obtained, but all of the signals are attenuated by the impurities present. The same volume of material contains less of the overlayer species since the element of interest is "diluted" by impurities. Size and electron escape differences lead to different amounts of attenuation depending upon the contaminant element concentration. Results are consistent within a given system of contaminant species at fixed concentrations, but altering the ratio of contaminants or introducing a new species invalidates the previous calibration. Although detailed quantitative statements about real samples are difficult to make, semi-quantitative results can be obtained by comparing a spectrum of a pure specimen of a given species to the signal from a contaminated surface.

To aid in calculations of coverages in this fashion, a book containing spectra of all elements obtainable in pure or combined form, all taken at the same sensitivities, is available from a commercial source.²⁹ In practice the spectrum of the unknown sample is taken and a spectrum from a clean piece of Ag taken at the same sensitivities. The unknown spectrum is then calibrated by comparing the height of the Auger peaks present with the peak to peak height in the standard book, using Ag as a reference. The results must be interpreted carefully due to the obvious errors possible from the above mentioned interference effects.

An additional difficulty when ionic materials are examined is the definition of percent coverage on the surface. In a completely rigorous definition, $\frac{a}{o}$ X would refer to the percentage of available sites for X to occupy and this can vary depending on whether X is an anion or a cation (e.g. Al_2O_3 has 2 cation sites

for every 3 anion sites). However, since in general regions of disorder (grain boundaries or surfaces) are examined rather than stoichiometric cleavage planes, and further since the presence of other ions of different valance (Ca^{+2} ions of Al_2O_3 or F^{-1} ions in MgO) can lead to ambiguities in the above definition, the following definition will be adhered to throughout this study. The a/o X refers to the percentage of total ionic sites on the given surface occupied by element X. For purposes of calculating inert ion sputter removal rates, this density of sites will be defined as 10^{15} sites/ cm^2 . From a calculation of the actual numbers of sites for different planes in MgO and Al_2O_3 it is observed that 10^{15} sites/ cm^2 is a very reasonable figure.

B. Inert Ion Sputtering

A tool used to great advantage in conjunction with AES in this study, was inert-ion sputtering. In this technique an inert gas ion beam is used to etch a surface (analogous to a microscopic sand blasting), which allows controlled removal of angstrom thick layers of substrate. Alternate use of sputtering and AES yields a profile of chemical composition perpendicular to the original surface. Unlike chemical etchants or microtome methods, there is essentially no contamination and sub-monolayer quantities can be removed.

A schematic of an apparatus used for inert-ion sputtering is presented in Fig. 4. A tungsten filament is heated to produce electrons, which are accelerated toward an anode placed in front of the filament and biased positive with respect to the filament. By backfilling the vacuum system to a low pressure of an inert gas, a cloud of ionized gas is formed near the anode from collisions between electrons and gas atoms. The target is placed

Figure 4 Schematic of an Inert Ion Sputtering Device

in front of the anode and biased negative with respect to the anode. By surrounding the filament and anode with a tantalum container maintained at anode potential and placing a hole in the container between the target and anode, a beam of ions is produced. By placing an auxiliary filament near the target, the surface is bathed in electrons, which allows proper charge neutralization on non-conducting targets. Typically, the voltage difference between the anode and the target is 200-900V and the 200-900eV ions striking the substrate material sputter etch the surface. The process is quantified by measuring anode-to-target current (i.e., total charge arriving at the surface, hence total number of ion collisions per second) and assuming a given number of substrate atoms removed per incident ion collision (dependent on collision cross sections and hence ion energy). Measurement of current is complicated due to the release of γ electrons from the surface undergoing ion bombardment. This is particularly serious for low atomic weight sputtering gases. Observed currents can be off by as much as 30% for He, 25% for Ne, 10% for Ar, 7% for Kr, and 2% for Xe.^{30,31} Hence Xe is a good choice for sputtering work.

The energy dependent removal rate is controlled by a variable known as sputter yield which is defined as the number of substrate atoms removed per incident ion collision. Extensive yield data has been tabulated by Wehner for several gases on most metals as a function of sputtering energy, but yield data for ceramics are generally not available.³⁰⁻³³ The range of sputter yields is from near zero to over 3 for most metals in the energy range 200 to 900eV. Although yield data for ceramics has not been published, data for Al_2O_3 and MgO for a particular sputtering energy were

available from contemporary studies of sputtering phenomena.³⁴ Using this yield data, removal rates were calculated for the Al_2O_3 and MgO studied (Appendix A). The rate of removal was about 1 atomic layer per minute for the conditions used and was sufficiently low to allow the experimental error to be independent of time and depend on the admittedly uncertain yield data. The final results were assumed to be accurate to within a factor of two in terms of distance sputtered into the material. This was felt to be sufficient to indicate long versus short range effects and the shape of the profile is also independent of the removal rate.

When the problem of preferential sputtering (preferential removal from a surface of an easily removed species) is recognized and it is realized that the process is an averaging technique, inert ion sputtering can be of great value when used in conjunction with AFS to obtain segregant profiles away from interfaces.

C. Scanning Electron Microscopy

Use of the scanning electron microscope for characterizing fracture surfaces is a standard technique. However, when used on insulating materials, charging of the surface can present problems. Use of a vacuum evaporated metal film over the fracture surface can eliminate this charging. In this particular study, 50-100Å of a Au-Pd alloy was vacuum evaporated on the fresh fracture surfaces.³⁵ The scanning electron microscope could then be used to characterize fracture and residual porosity.

D. Ceramic Fabrication

Some of the ceramic materials used were prepared in-house, some were obtained commercially, and the remainder were

fabricated on a service basis by an outside agency. The in-house materials were isostatically pressed in a press manufactured at Mich. Tech. and similar to a press described by McCreight (Figure 5).³⁶

Materials sintered in O_2 were fabricated in an in-house built gas torch furnace utilizing a propane-oxygen burner (Figure 6). Vacuum sintered materials were fabricated in an R-F induction furnace, which utilized a Mo susceptor tube and two Mo heat shields (Figure 7). The quenching experiments were carried out in the R-F furnace using dry He gas as the quenching medium.

The hot pressing and heat treating of the MgO and hot pressed $MgAl_2O_4$ and Al_2O_3 was carried out at Naval Research Laboratories, Washington, D.C.

In addition, optical microscopy, x-ray diffraction, and standard CCl_4 displacement techniques to measure porosity (Appendix B), were utilized when necessary.

Figure 5 Isostatic Press.

Figure 6 Gas Torch Furnace

Figure 7 R-F Induction Furnace

III. Densification in Doped Al_2O_3

A. Use of MgO to Densify Al_2O_3

In an effort to examine the role of segregants on the densification of Al_2O_3 , several commercial aluminas sintered with MgO were examined using AES. In general the samples were cut with a diamond wheel on a wafering machine into a size and shape compatible with the Auger analysis equipment utilized. This usually meant a sample of square or round cross section (with the largest cross-sectional dimensions less than 0.145") 1" long. The specimens were then placed in an UHV system and intergranular fractures obtained under vacuum. AES and inert-ion sputtering were then used on the exposed grain boundaries to determine the composition of the first few atomic layers of the boundary and to obtain a profile of species away from that boundary. Figure 8 presents a top view of the vacuum system used in this study.

The commercial aluminas doped with MgO examined this way included an alumina manufactured by AFC, a Westinghouse alumina, and a high density General Electric alumina. All three of these materials were theoretically dense and translucent. SEM fractographs from these materials (Figures 9-11) indicated intergranular fracture and the absence of pores. The Auger spectra from these fractures are presented in Figures 12-14. In addition to the Al and O peaks, a Ca peak was present on the spectra from all three alumina grain boundary fractures. Mg if present, would have a series of peaks from 1100-1200eV. There does not appear to be any Mg present. Figure 15 presents a sputter profile of Ca in the General Electric material. The AFC and Westinghouse materials

Figure 8 Top View of UHV System

Figure 9 SEM Fractograph of AFC Al₂O₃

Figure 26 SEM Fractograph of Westinghouse Al₂O₃

Figure 11 SEM Fractograph of General Electric Al₂O₃

Figure 12 AES Spectrum of AFC Al_2O_3

Figure 13 AES Spectrum of Westinghouse Al_2O_3

Figure 14 AES Spectrum of General Electric Al_2O_3

Figure 15 Sputter Profile of Ca in General Electric Al_2O_3

had similar profiles of Ca away from the grain boundaries.

The results of this portion of the study are summarized in Table 1, which presents the amount in atomic percent of segregants detected at the boundaries, the density of the materials, and the bulk concentration of detected segregants. The dopant levels presented represent residual levels after sintering, not nominal additions. Densities were determined using standard CCl_4 displacement techniques (see Appendix II) and are reported as percentage of theoretical density (taken to be 3.987g/cc).³⁷

TABLE 1: G. B. Chemistry of Three Commercial Aluminas

<u>Material</u>	<u>Dopant</u>	<u>Density</u>	<u>G. B. Chem</u>	<u>Bulk Levels</u>
AFC	.02 ^w /o MgO	99.8%	7 ^a /o Ca ⁺²	90ppmCa ⁺²
	.05 ^a /o Mg ⁺²			
Westing-house	.01 ^w /o MgO	100%	5 ^a /o Ca ⁺²	50ppmCa ⁺²
	.025 ^a /o Mg ⁺²			
G. E.	.075 ^w /o MgO	100%	6 ^a /o Ca ⁺²	40ppmCa ⁺²
	.2 ^a /o Mg ⁺²			

Since no Mg was detected at the grain boundaries in any of these materials, as would be expected from previous studies,^{8,10} an examination was made of two points. 1) Was the previous work invalid? 2) Is Mg detectable on Al_2O_3 ?

B. Previous Evidence For Segregation

The most direct evidence from the work of Jorgensen et al for Mg segregation was obtained using microhardness techniques.

This technique involves taking microhardness measurements on a polished specimen and plotting the microhardness values as a function of distance as a grain boundary is traversed. It has been used by Westbrook and Wood³⁷ and Westbrook and Aust³⁸ to study grain boundary migration in metallic systems, along with the work of Jorgensen et al on ceramics.^{8,39}

However, basic problems have arisen in the interpretation of observed microhardness profiles. An example of a microhardness profile obtained by Jorgensen and Westbrook from MgO doped Al_2O_3 is presented in figure 16. Detectable hardening is observed as far as 10μ from the grain boundaries, and this was interpreted as due to segregation of Mg to the interface.⁸ When this profile is compared to the segregation profile of Ca observed directly in a similar specimen using AES and inert-ion sputtering (Figure 15), a discrepancy of 4 orders of magnitude in profile spread is observed.

If the hardening involved a solid solution effect, the two profiles should be of similar spread.⁴⁰ Another possible explanation for the hardening can be modeled by the image force produced on a dislocation as it approaches an interface representing a discontinuity in elastic modulus. The image force can be calculated as a function of distance from the interface.⁴¹ If a thin strip of pure MgO $20\text{\AA}$ thick is inserted between two regions of pure Al_2O_3 , the resulting force profile (calculated in Appendix C and presented in Figure 43) indicates softening beginning about $75\text{\AA}$ from the interface. Unfortunately modulus data for CaO is not available, but even if the modulus for CaO were larger than that of Al_2O_3 (which would produce a hardening effect), the spread in the profile would be comparable to that of Figure 43. Hence

Figure 6 Micro 2

Figure 16 Microhardness Profile in $\text{Al}_2\text{O}_3 + .1\% \text{MgO}$

even this upper limit value (the region of modulus change is not pure CaO) falls far short of predicting hardening 10μ from this interface.

Finally, if the observed shear at the boundary is modeled with a dislocation pile-up mechanism,⁴⁰ a calculation of the distance from an interface at which significant hardening is observed, yields only $600\text{\AA}$, still far from 10μ (Appendix C).

Therefore it appears that interpretation of observed microhardness profiles in light of direct experimental evidence does not imply adsorption of solute at the interface.

Another factor which leads to questions concerning the validity of the solute segregation model is the comparison of continuous grain growth data for pure Al_2O_3 and $\text{Al}_2\text{O}_3 + \text{MgO}$. Several sets of this data are plotted in Figure 17. Although obtained from two different investigators and involving different temperatures, this data clearly indicates that up to the point at which discontinuous grain growth begins, there is no detectable difference in rate of grain growth between the material with MgO and that without.^{5,10} If segregants were inhibiting discontinuous grain growth, they should also inhibit continuous grain growth. There appears to be no grain growth inhibition relative to pure Al_2O_3 which undergoes discontinuous grain growth.

C. Detectability of Mg on Al_2O_3

In an effort to examine the second point raised earlier concerning detectability of Mg on Al_2O_3 , two experiments were run. First, a fresh fracture surface of Al_2O_3 was covered with a thin layer of vacuum evaporated Mg. Figure 18 presents the results of an AES examination of the chemistry of this surface. The

Figure 17 Grain Growth Data for Al_2O_3

Figure 18 AES Spectrum of Vacuum Evaporated MgO

top spectrum is of the Al_2O_3 substrate with the freshly evaporated MgO. Both Mg and Al peaks are present and the concentration of Mg in the first few atomic layers is roughly $15^{\text{a}}/\text{o}$. The middle spectrum shows the same spot after the electron beam had been on the sample for 30 minutes. The Mg concentration is stable under electron bombardment and hence should be stable on the fresh fracture surfaces. The bottom spectrum represents the surface chemistry after 5 atomic layers have been removed with inert-ion sputtering. This reduced Mg concentration is also stable.

The second part of the stability question was answered by examining a sample of General Electric Al_2O_3 doped with $.1^{\text{w}}/\text{o}$ MgO and detecting the background Mg level. As indicated in Table 1, this corresponds to $.2^{\text{a}}/\text{o}$ Mg which is still detectable with AES and Figure 19 presents the high energy spectrum from this sample. The small peak labeled Mg is the only detectable Mg signal and to compare the scale of the peaks, the main Al peak should be multiplied by two. The Mg level detected appeared to be slightly greater than $.2^{\text{a}}/\text{o}$, perhaps $.4^{\text{a}}/\text{o}$, but at such low levels it is difficult to quantify the observed peaks.

The conclusion, however, is that if there was a massive segregation of Mg to the grain boundaries in these aluminas, it would be detected.

D. Use of NiO to Densify Al_2O_3

Jorgensen notes that NiO additions can lead to a theoretically dense alumina, although the material remains opaque due to the Ni ion color centers.⁸ Further, Ni was thought to be a good additive to study since it is similar in size to Mg, has the same valence, and was reported to segregate in Al_2O_3 .⁸

Figure 19

Figure 19 High Energy Region of AES Spectrum of General Electric Al₂O₃

The samples examined were mixed from Linde A alumina, .1^w/o Baker Reagent grade NiO and .5^w/o Carbowax (a ceramic powder binder) by Battelle Columbus Laboratories. The pellets were isostatically pressed at 30,000 psi, and fired in an O₂ atmosphere in a gas torch furnace for two hours at 1900°C. Coble notes that O₂, vacuum, or H₂ is necessary as an atmosphere to achieve theoretical density.⁴² The resulting ceramics were theoretically dense materials and an Auger spectrum from a typical fracture is presented in Figure 20. On the order of 1^a/o Ca was detected (bulk level ~ 12ppm Ca). Inert-ion sputtering indicated that the Ca was located within 5 atomic layers of the grain boundaries in this material. However, very little (~ .4^a/o) Ni was detected at the grain boundaries. Hence it appears that there is no massive segregation of Ni in NiO doped alumina. This result apparently conflicts with an autoradiograph obtained by Jorgensen and Westbrook indicating a high level of Ni isotope at grain boundaries in a NiO doped Al₂O₃ sample.⁸ However, since only one sample from many examined yielded this result and since it could not be reproduced, the reliability of the result is in question.⁴³ Perhaps a nucleation phenomenon produced a Ni rich second phase near the boundaries or diffusion along the boundaries caused a local build-up of Ni at the polished surface. Since the sample was unavailable for AES analysis, it was impossible to determine what was unique about this particular sample.

E. Grain Boundary Chemistry in Non-Dense Aluminas

Since it appears obvious that segregated Ni or Mg do not cause the enhanced densification experienced when these ions are used as additives, the next question to be asked concerned the importance of segregated Ca in densification.

Figure 20 AES Spectrum of $\text{Al}_2\text{O}_3 + .1\% \text{NiO}$

A sample of pure Al_2O_3 sintered at 1900°C for 2 hrs. in O_2 was examined to determine grain boundary chemistry when discontinuous grain growth has occurred. This material was 95% dense and a fractograph (Figure 21) indicates discontinuous grains and trapped pores. The Auger spectrum (Figure 22) showed about 1^a/o Ca at the grain boundaries.

A material doped with .1^W/o CaO similarly failed to achieve theoretical density (96%) and the Auger spectrum (Figure 23) showed about 2^a/o Ca at the grain boundaries.

Hence Ca appears at grain boundaries of dense and non-dense materials and does not appear to affect final density.

F. Use of Y_2O_3 to Achieve Dense Alumina

Y_2O_3 has also been used to achieve a high density Al_2O_3 . Commercial Sylvania and Coors aluminas contain Y additives and a sample of each of these was examined. The SEM fractographs (Figures 24 and 25) show intergranular failure and both materials were near theoretical density. (Coors - 99.8% and Sylvania 99.9%). The Auger spectra (Figures 26 and 27) showed some segregated Y and Ca. Table 2 summarizes the results of AES analysis of these two materials.

TABLE 2: G. B. Chemistry of Two Commercial Aluminas

Material	Dopant	Density	G. B. Chemistry	Bulk Levels
Sylvania	.02 ^W /o Y_2O_3	99.9%	3 ^a /o Y	.025 ^W /o MgO
	.02 ^a /o Y		1 ^a /o Ca	91ppm Ca^{+2}
Coors	.015 ^W /o Y_2O_3	99.8%	1.5 ^a /o Y	.03 ^W /o MgO
	.015 ^a /o Y		1 ^a /o Ca	58ppm Ca^{+2}

Figure 21 SEM Fractograph of Pure Al₂O₃

Figure 22 AES Spectrum of Pure Al_2O_3

Figure 23 AES Spectrum of $\text{Al}_2\text{O}_3 + .1\% \text{CaO}$

Figure 24 SEM Fractograph of Sylvania Al₂O₃

Figure 25 SEM Fractograph of Coors Al₂O₃

F1 : 26 AES Spectrum of Sylvania Al₂O₃

Figure 27. AES Spectrum of Coors Al_2O_3

Although it was not possible to obtain non-dense material with Y at the boundaries and therefore eliminate consideration of Y_2O_3 as a densification aid, it is interesting to note that these materials had at least as much MgO as the dense materials in Table 1. The other important point is that the Y does segregate and inert-ion sputtering indicated that all segregated species were localized within 5 atomic layers of the grain boundaries.

G. Equilibrium Segregation of Impurities

The segregation of impurities in the materials examined in this study can be explained by Gibbsian or equilibrium segregation.⁴⁴⁻⁴⁷ The driving force for this segregation involves the reduction in free energy accompanying segregation of a poorly fitting solute species (size misfit or electronic misfit) from a matrix site to a region of high energy such as a disordered grain boundary. As the temperature of the system is lowered, more solute is expected to segregate until the boundary becomes saturated or kinetic factors begin to limit material transport to the boundaries.

A calculation of the amount of a solute expected at the grain boundaries with a given bulk concentration and change in free energy as a function of temperature, is presented in Appendix D.

$$C_{gb} = \frac{C_e^{Q/RT}}{1 + C_e^{Q/RT}} \quad (37)$$

where C_{gb} = grain boundary concentration of the solute,
 C = bulk concentration of the solute, and
 Q = interaction energy (change in free energy)

This form of the equation does not include the vibrational entropy term. An evaluation of the effect of changes in this term is included in Appendix D; from this point on, its effect

will be ignored and the equation utilized without it. c₂

An alternate way to consider the problem of grain boundary segregation has been developed by Cahn and Hilliard.⁴⁶ Beginning with Gibbs' equation for variation in boundary tension with chemical potential, they arrived at the following equation for an upper limit on the amount of excess solute located at the grain boundary at equilibrium:

$$\Gamma_{2(1)}^0 < \frac{\sigma_1}{kT[1 + \ln(x_e/x_o)]} \quad (2)$$

where $\Gamma_{2(1)}^0 = (\Gamma_2 - (x_o/(1 - x_o))\Gamma_1)$, where Γ_2 and Γ_1 are the excess quantities of component 2 and 1 respectively (defined as the differences between the actual amount and that which would be present if the phases were homogeneous up to the grain boundary);

x_e = solubility of component 2; and

x_o = bulk concentration of component 2.

This particular upper limit can be calculated and compared to the experimentally measured excess, defined as:

$$\Gamma_{2(1)}^0 = \frac{1}{A} (N_2 - \frac{x_o}{(1-x_o)} N_1) \quad (3)$$

where N_1 = number of 1 atoms removed from an area A,

and N_2 = number of 2 atoms removed from A.

By calculating the upper limit of the excess solute from equation (2) and comparing this value to the observed excess calculated from equation (3) and sputter data, a particular case can be classified as equilibrium or non-equilibrium segregation.

As mentioned earlier, the factors contributing to the driving force in equilibrium segregation can be broadly described as size misfit or electronic misfit. The size misfit factor can be treated in at least a semi-quantitative fashion; the electronic misfit

includes such considerations as electro-negativity and valence differences. These are not easy to consider quantitatively. However in these ionic materials, the valence is often the same (Mg^{+2} , Ca^{+2} , Ni^{+2} , etc.) and the electro-negativity has no real meaning. Hence to ignore them to the first approximation and deal with size misfit is appropriate.

McLean has described the elastic strain energy induced in a lattice when a larger solute is introduced onto a substitutional site.⁴⁷

$$W = \frac{24\pi KGr^3\epsilon^2}{3K + 4G} \quad (4)$$

where K = bulk modulus of the solute species,
 G = shear modulus of the matrix,
 r = radius of the solute in situ, and
 $\epsilon = (r_1 - r_0)/r_0$ is the strain induced in the lattice (r_1 = radius of the isolated solute and r_0 = radius of the unoccupied site)

Since this model was derived using a finite sphere of the solute material inserted into an infinite continuum of the base material and uses bulk moduli and shear moduli for individual ions its rigorous validity is subject to question. However, the important point and a valid one, is that the misfit strain energy is proportional to the square of the strain, i.e.

$$W \propto \epsilon^2 = \left(\frac{r_1 - r_0}{r_0}\right)^2 \quad (5)$$

From this, an estimate can be made of the interaction energy, Q , for a solute for which there is not enough data to calculate Q , by simply using a ratio of ϵ^2 and a Q for a known system.

H. Experimental Verification of Segregation Models on Al_2O_3

In an attempt to explore the points set out in the previous section, experiments were devised utilizing the Ca segregation

noted in the General Electric high density Al_2O_3 . Samples were machined from a rod of high density G.E. Al_2O_3 doped with .1^{w/o} MgO to obtain theoretical density.

The samples were heated to a given temperature, held for 5 hours to ensure equilibrium, and quenched with a blast of He gas. Although it was impossible to obtain the actual cooling rates, the samples were optical for only a few seconds, far too short a period of time for any significant material transport to occur. Three temperatures were used, 1700°C, 1800°C, and 1900°C. After the quench, the samples were fractured and the grain boundary chemistry obtained with AES. Inert ion sputtering was used to obtain depth profiles of the observed segregants and indicated that the Ca was localized to within 5 atomic layers of the fracture surface (grain boundaries).

Figure 28 presents Auger spectra from these three quenches. The only variation detected was that of the Ca peak. The Ca percentages at the grain boundaries were: 1700°C - 5.6^{a/o}, 1800°C - 4.2^{a/o}, and 1900°C - 2.8^{a/o}. The bulk concentration of Ca was 40 ppm and the solubility is assumed to be close to that value. Appendix E contains a calculation of the upper limit for equilibrium segregation of Ca in Al_2O_3 and shows that the observed amounts are within the limit. It also presents a calculation of a Q value for each of the quenched specimens. These values are all close to 28,500 cal/mole. Figure 29 is a plot of equation (37) using $Q = 28,500$ cal/mole, and $C = 0.0040$. Superimposed on this curve are plotted the three experimentally determined points. The fit is very good.

To determine if Mg, Ni, or Y should segregate, a calculation is presented in Appendix E to estimate Q values for these species.

Figure 28 AES Spectrum of Quenched Al_2O_3

Figure 29 C_{gb} of Ca in Al_2O_3

To do this, the Q value for Ca is multiplied by $(\epsilon_x^2/\epsilon_{Ca}^2)$ where ϵ_x is the misfit due to the desired species and ϵ_{Ca} is the Ca misfit. The Q values determined are listed in Table 3.

TABLE 3: Misfit Energies for Various Solutes in Al_2O_3

Species	Ionic Radius	ϵ	$Q(\text{cal/mole})$
Ca^{+2}	.99 $\text{\AA}$	1.0	28,500 (experimentally determined)
Mg^{+2}	.65 $\text{\AA}$	.32	2,550 (ratio value)
Ni^{+2}	.72 $\text{\AA}$	.44	5,470 (ratio value)
Y^{+3}	.93 $\text{\AA}$	.86	21,800 (ratio value)

Hence Ca would be expected to segregate before any other species, Y next, followed by Ni and finally Mg. Appendix E also contains a set of calculations which indicate how much Mg, Ni, or Y should segregate at 1700°C, given the Q values above. Table 4 summarizes these results:

TABLE 4: Expected Segregation of Impurities at 1700°C in Al_2O_3

Species	Bulk Level	G. B. Concentration Expected
Mg^{+2}	.2 ^a /o Mg^{+2}	.4 ^a /o Mg^{+2}
Ni^{+2}	.15 ^a /o Ni^{+2}	.6 ^a /o Ni^{+2}
Y^{+3}	.02 ^a /o Y^{+3}	4.3 ^a /o Y^{+3}

The expected grain boundary concentration of Y will be modified due to the co-segregation of Ca to that boundary, but it is important to note that the Y will segregate heavily and there will be no massive segregation of either Mg or Ni (all of

which is as observed in the previous results). Hence all of the observed segregation is consistent with the equilibrium segregation models presented.

I. Proposed Model for Densification of $\text{Al}_2\text{O}_3 + \text{MgO}$

Although the observed segregation has been accounted for, the question of how MgO aids Al_2O_3 densification remains. The obvious possibility that Ca segregates to the grain boundaries and inhibits discontinuous grain growth must be discarded, since Ca was also observed on the grain boundaries of both CaO doped and pure Al_2O_3 . Neither material was close to theoretical density and both had Ca levels close to the levels observed in the NiO doped material and another in-house prepared $\text{Al}_2\text{O}_3 + .1^{\text{W}}/\text{o MgO}$. All of these material had Ca levels at the boundaries near $1\text{-}2^{\text{a}}/\text{o}$ and the only difference was theoretical density in the samples doped with MgO or NiO, while the others were not fully dense. The conclusion reached is that Ca at the grain boundaries is not sufficient for achieving theoretical density in sintered Al_2O_3 . This result is consistent with the grain growth data presented earlier indicating that there were no substantial differences between rates of grain growth in pure Al_2O_3 and MgO doped Al_2O_3 until discontinuous grain growth began. (Figure 17).

The model involving second phase pinning by spinel particles must also be rejected. Although certain materials doped with MgO and sintered to theoretical density can show second phase particles distributed throughout the ceramic,⁴⁸ other materials and in fact the outer .015 inches of these samples are also theoretically dense and free of second phase particles. Hence second phase particles are not necessary.

As mentioned earlier there does not appear to be enough MgO added to form a liquid phase and if present during sintering, it should also be present after annealing and quenching.

This leaves the solid solution theory for enhanced sintering as another alternative. This theory was first proposed by Coble⁵ and later supported by Bruch⁹. Their contributions will be used in this treatment and enlarged upon.

J. Modification of Solvent Defect Structure

When a solute ion of different valence is introduced into an ionic material modification of the defect structure can occur.^{49,50} If for example, a divalent impurity such as Mg^{+2} is substituted for a trivalent cation such as Al^{+3} , one oxygen vacancy will be created for every 2 Mg^{+2} ions substituted into Al_2O_3 . In a material doped with .2^a/o Mg^{+2} ions, .1^a/o or 10^{-3} atom fraction oxygen vacancies are introduced. An expression for the anion diffusivity of Al_2O_3 indicates the importance of the vacancy concentration (assuming diffusion occurs by a vacancy mechanism).⁴⁹

$$D = D_o N_{Va} W_T \quad (5)$$

where D_o = pre-exponential constant,

N_{Va} = concentration of vacant anion sites, and

W_T = jump frequency.

For intrinsic behavior (i.e., for pure materials with only thermally induced vacancies), the temperature dependence of N_{Va} and W_T can be expressed in terms of enthalpies of vacancy formation, ΔH_s , and movement from a site to a vacancy, ΔH_m :

$$(\text{intrinsic}) D = D_o e^{-\Delta H_s/RT} e^{-\Delta H_m/RT} \quad (6)$$

If on the other hand, a contribution is made to N_{Va} through another mechanism, the total N_{Va} will be the sum of the thermally

induced vacancies and the other vacancies:

$$(\text{extrinsic}) \quad D = D_0 (N_{V_{a_0}} + e^{-\Delta H_s/RT}) e^{-\Delta H_m/RT} \quad (7)$$

When $N_{V_{a_0}}$ is much larger than the thermally induced vacancy concentration in a given temperature range, the only temperature dependence of D is the jump frequency and the material is said to exhibit extrinsic diffusion. To illustrate the effect of 10^{-3} vacancies on the diffusion coefficient, it is necessary to obtain a value of ΔH_s for Al_2O_3 . This value is not readily obtainable, but order of magnitude estimates can be made. Cutler notes that this value is near 5eV/atom for MgO .⁵⁰ Shewmon notes that the value for NaCl is near 2eV.⁴⁹ Further, an estimate of ΔH can be made using the approximation:⁴⁹

$$\frac{\Delta H}{T_m} \approx \frac{36 \text{ cal}}{^\circ\text{K}} \quad (8)$$

This is a standard rule for vacancy creation in metals, and a value of 3.4 eV/atom is obtained for Al_2O_3 . Table 5 contains values of the thermally induced vacancy concentration using ΔH values from 2eV up to 6eV at 1900°C for Al_2O_3 .

Table 5: Thermally Induced Vacancy Concentration

ΔH_s	$T(^{\circ}\text{K})$	$\exp(-H_s/RT)$
2eV/atom	2173	1.6×10^{-5}
4eV/atom	2173	2.4×10^{-10}
6eV/atom	2173	3.8×10^{-15}

It is obvious that even if ΔH_s is 2eV/atom, 10^{-3} vacancies introduced by MgO doping will render the diffusion coefficient extrinsic well past 1900°C where the Al_2O_3 is sintered. Hence if ΔH_s is 2 eV/atom and the introduced vacancy concentration is 10^{-3} ,

the diffusivity of oxygen in Al_2O_3 will jump 2 orders of magnitude at 1900°C . If ΔH_s is higher (which is likely), the diffusivity could jump 7 orders of magnitude or more.

The conclusion is that extrinsic behavior of Al_2O_3 due to "artificial" vacancies can alter the diffusivity of the anion species in a very marked manner. This would be expected to alter sintering behavior as well, if the anion species has the rate controlling diffusivity.^{50,51} Since the effective rate of material transport through the bulk involves the effective diffusivity,

$$D_{\text{eff}} = \frac{D_o D_A}{D_o + D_A} \quad (9)$$

this rate of transport would be expected to increase if the rate controlling self diffusivity was increased substantially.

And indeed the O^{-2} diffusivity is rate controlling for volume diffusion in Al_2O_3 .^{52*} Hence if the O^{-2} diffusivity is increased, the rate of material transport would increase, and the material should sinter faster. This is also observed in the results of density versus time determinations by Coble⁵ and Bruch⁹, both of which are presented in Figure 30. The plots compare density versus time for samples of pure Al_2O_3 and samples doped with MgO. It is obvious from the plots, that at all times, the material with MgO exhibits greater density (less porosity). Hence it is concluded that the presence of Mg^{+2} (or Ni^{+2}) in solid solution in Al_2O_3 can enhance final stage sintering through a vacancy modification mechanism.

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*Palladino and Coble report that the Al^{+3} diffusivity is rate controlling in polycrystalline Al_2O_3 and O^{-2} in single crystal due to high grain boundary mobility³ of O^{-2} . Here, however, since the bulk diffusivity implies movement through the matrix, the single crystal result is appropriate and O^{-2} is rate controlling during final stages of sintering, since bulk diffusion is the observed mode of material transport.⁵²

Figure 30 Density of Al_2O_3 Versus Time at Temperature

K. Effect of Mg^{+2} or Ni^{+2} on Discontinuous Grain Growth

The reason for the lack of discontinuous grain growth in Al_2O_3 sintered with MgO is related to the enhanced sintering effect of the additive and the nature of discontinuous grain growth. By its nature, discontinuous grain growth (secondary recrystallization) can only occur in a material in which continuous grain growth is inhibited.⁵³⁻⁵⁶ In Al_2O_3 , this restraint is supplied by the pore phase. If for example, an alumina exhibits the sort of grain structure presented in Figure 31a, normal grain growth is stopped by the pores. If due to random fluctuations, however, a region is deficient in pores, a few grains can grow at the expense of the surrounding grains until they become several times the size of the "normal" grains. These abnormal grains (Figure 31b) can now grow in a more rapid manner, since the restraint to normal grain growth (i.e. pore phase) is no longer a restraint to growth for grains with so many sides and such favorable curvature (i.e. energetics of growth favor multi-sided grains with relatively flat or concave boundaries). Once a critical size is reached, the Zener drag produced by the pores can no longer inhibit the growth of this grain and it rapidly consumes the "normal" grains surrounding it, all of which are still restrained by the pore phase.^{53,54}

This critical size can be called a "nucleus" and in some aspects the problem is analogous to nucleation of a second phase, although mathematically more difficult to model. Unlike precipitation, it is a completely heterogeneous phenomenon (i.e. dependent on inhomogeneities for occurrence) and the random fluctuations that produce it can only carry the embryo to critical size; they cannot redissolve it.⁵⁶

a. Normal Growth Inhibited by Pores

b. Discontinuous Growth Nucleating

Figure 31 Discontinuous Grain Growth

In general, if the inhibition to continuous grain growth (i.e. pore phase) is removed slowly enough as to allow the growth of a few grains at a rate comparable to this rate of removal, it has been found in metallic systems that these few large grains can gain an enormous advantage energetically over normal grains still inhibited by the pore phase. If on the other hand, the rate of inhibition removal is high compared to the rate of grain growth, the result will be uniform sized small grains with a growth rate similar to that of grains with no inhibition. All of the above is dependent on temperature, type, size, and distribution of inhibition.⁵⁴ Ultimately, the decision whether discontinuous grain growth will occur or not and the time necessary for its appearance depends on the above mentioned factors.

The "incubation" time for discontinuous grain growth, describes the period of time during which fluctuations of temperature and/or obstruction combine to create a critical grain which is no longer slowed by the Zener drag inhibiting normal grain growth. Measurements of this incubation time are easy to make, but extremely difficult to interpret. It was found that in high purity silver inhibited by second phase inclusions, the growth of secondary grains proceeded at a slower rate than normal grain growth in uninhibited material until the grain was 13 times the size of a normal grain. At that point the rate of growth was independent of size.⁵⁴ Other studies established that there is a strong dependence on normal grain size in the incubation time for discontinuous grain growth.⁵⁵

Therefore, since the evidence indicates that:

- 1) Al_2O_3 densifies faster with MgO than without (i.e. the "inhibition" - pore phase - is removed more quickly) due

to enhanced rate of material transport.

- 2) A finite time is necessary for nucleation of a discontinuous grain (incubation time).
- 3) Discontinuous grain growth does not occur in Mg doped Al_2O_3 .
- 4) Grain boundary segregants if present do not alter normal grain growth appreciably and are present in doped, theoretically dense materials, as well as samples in which porosity remains trapped in discontinuous grains.
- and 5) Second phase particles do not have to be present to obtain theoretical density.

It is concluded that discontinuous grain growth is not inhibited in doped alumina, but rather the material achieves theoretical density (i.e. all inhibition - pore phase - is removed) before discontinuous grains can nucleate. Because of the extrinsic behavior of the rate controlling diffusivity due to the MgO introduced vacancies, doped Al_2O_3 sinters faster than pure Al_2O_3 . Further, figure 30 indicates that discontinuous grain growth occurs in pure material over an order of magnitude in time after the doped material is fully dense (and all tendency for abnormal growth is removed). Since the nucleation time for discontinuous grain growth would not be expected to change much in doped material, it can be concluded that the doped alumina is already theoretically dense long before discontinuous grains can achieve critical size.

L. Conclusions of Doped Al_2O_3 Study

1. Ca^{+2} and Y^{+3} segregate heavily to grain boundaries in Al_2O_3 when present.

2. Mg^{+2} and Ni^{+2} if present at all at grain boundaries are relatively weak segregants.
3. All of the observed segregation can be understood and explained in a quantitative manner from equilibrium segregation theory.
4. Segregants are neither necessary, nor sufficient to obtain theoretical density in high purity Al_2O_3 .
5. Sintering is enhanced in final stages by the presence of vacancy creating divalent ions in solution in Al_2O_3 (Mg^{+2} , Ni^{+2}).
6. Discontinuous grain growth is avoided, not inhibited by MgO and NiO through an increase in the rate of removal of the inhibition (pore phase) responsible for the abnormal growth.
7. The effect of Y^{+3} on density is questionable, but both Y_2O_3 doped materials examined had sufficient MgO to achieve theoretical density in spite of other additives.

IV. Role of Additives in Hot Pressing MgO

In order to establish the role of additives and impurities in the densification of hot pressed MgO, a study was begun on the relationship between grain boundary chemistry and density of MgO. As mentioned earlier, use of a few weight percent LiF or NaF additive markedly improve hot press ability of MgO. Typically hot-pressed at 1300°C when pure, MgO can be hot pressed with additives at 1000°C (LiF) or 1100°C (NaF).^{12,13,15,57} Further, although room temperature fracture strength is not good, it can be markedly improved by annealing at a temperature higher than the hot pressing temperature.

A. Hot Pressed MgO With No Additives

Two samples of MgO hot pressed without additives were examined. The first represented the as-hot pressed state and the second represented a similar material that had been given a subsequent 1150°C anneal. Both samples gave totally intergranular fracture (Figs. 32a and 32b) and the grain boundary chemistries were similar, although with different amounts of segregants (Fig. 33). The as-hot pressed materials exhibited about 9^a/o Ca and 2^a/o Ti at the boundaries while the annealed sample showed 5^a/o Ca and 2^a/o Ti. In both cases the species were segregated to within 3 atomic layers of the grain boundaries.

In general it is expected that if one material is annealed at a lower temperature than another, the driving forces for equilibrium segregation would increase, causing a build up of the segregant at the boundary. However, both the kinetic limitations of diffusion at low temperature, as well as the bulk concentration dependence of the relationship for the expected segregation, indicate that there can be exceptions. In this particular case,

the two samples were from different lots of material, hence had different levels of bulk Ca impurities and the amount necessary to attain equilibrium in the 1150°C sample was less than the amount that was needed to attain it in the 1300°C (as hot pressed) sample. Hence the observed segregation is still consistent with the equilibrium segregation model presented earlier.

B. MgO Hot Pressed With LiF

Two lots of MgO hot pressed with 2^w/o LiF were examined to determine the location of the residual additives. Bulk chemical analysis indicated that around .9^w/o fluorine remained in the bodies after hot pressing, but only trace amounts of Li.⁵⁷ SEM fractographs of the first lot of MgO are presented in Figure 34. Figure 34a is the as-hot pressed fracture surface, 34b is of the same material given a subsequent 1315°C anneal and 34c is after a 1540°C anneal. The corresponding AES spectra from these fracture surfaces are presented in Figure 35. In the as-hot pressed state the MgO grain boundaries contain a significant amount of fluorine. The F peak was unstable with time under electron bombardment and decayed rapidly. However, an estimate for the original concentration of between 30-40^a/o F in the first few layers is within reason. No lithium was detected, which is consistent with the above mentioned lack of Li in bulk chemical analysis. A calculation of the amount of F accounted for by the observed grain boundary concentration is contained in Appendix F. The results indicate that all of the residual F in the MgO is accounted for at the grain boundaries. This coupled with the fact that these materials are cooled relatively quickly from hot pressing temperatures (in contrast to the slow cooling of the sintered Al_2O_3 discussed earlier) indicates

a. As Hot Pressed

b. Annealed At 1315°C

c. Annealed At 1540°C

pressing, although the Li apparently is lost due to volatilization during the process. The apparent contradiction in residual Li levels noted when these results are compared to those of Carnall is attributed to the fact that his specimens were at least 10 times as thick as the ones used in this study.¹⁴ The limiting step in the volatilization process would be expected to be the transport of the Li from the interior of the sample to the surface. Samples with dimensions large compared to diffusion distances would be expected to retain more Li than those with dimensions comparable to these diffusion distances.

After annealing at 1315°C, the fluorine level at the boundary has dropped by a factor of 4 and Ca and Si peaks have appeared. After a 1540°C anneal, no fluorine is detected and the Ca peak has become larger, while the Si is gone. The Ca concentration increased from about 4^a/o to 5^a/o and the Si concentration at 1340°C was about 2^a/o. Another series of MgO samples doped with LiF produced similar results. Figure 36 presents SEM fractographs and Figure 37 gives the Auger spectra. Again substantial F was detected at the grain boundary, a small amount (2^a/o) of Ca, and a trace of Ti. After annealing at 1150°C the fluorine is down and the Ca has increased to about 4^a/o.

All of the above can be explained on an equilibrium segregation basis. The F is residual additive from the hot pressing process and since it is located in the region of disorder (grain boundaries) there is no driving force for the segregation of the Ca to this interface during hot pressing. During annealing however, two competitive processes are occurring. First the fluorine is being boiled out of the sample at the higher temperatures. The boundary sites again become available for relocation of poorly

a. As Hot Pressed

b. Annealed At 1150°C

Figure 36 SEM Fractographs of Lot II MgO Hot Pressed With 2% LiF

Figure 37 AES Spectra of Lot II MgO Hot Pressed with $2\% \text{LiF}$

fitting solutes (such as Ca, Si, or Ti). The number of sites available for cations will be determined by the free energy of the interfacial region, which in turn is determined by the composition of the region. The Si appears at 1315°C and then disappears at 1540°C , because it is driven to the boundary at the lower temperature, but then is redissolved in the matrix at the higher temperature. It should indeed be possible (although the limited amount of material available in this study did not allow it) to anneal the MgO at even higher temperatures and quench the Ca back into the bulk; hence the concentration of Ca at the boundaries should decrease as was observed for the Ca in Al_2O_3 quenching experiments presented earlier.

That the observed grain boundary chemistry is indeed characteristic of an equilibrium condition is substantiated by analyzing a sample of MgO hot pressed with .3^{w/o} LiF, which had been annealed at 1000°C for 60 hours* instead of the 1/2-1 hour anneals given these samples. The results are presented in Figure 38 and indicate that the residual fluorine is apparently an equilibrium condition, as is the segregation of Ca, not just a point on the way to total elimination of F and/or Ca from the sample. The 60 hour anneal allows sufficient time for elimination of all the fluorine if it were kinetically controlled. An indication of the rate of movement of the fluorine is the rapid loss of the species in 1/2 hour at 1315°C as in the previously mentioned sample. Hence the grain boundary chemistries represent the end point of an equilibrium process.

C. Hot Pressed MgO With NaF

A series of MgO samples hot pressed at 1100°C with 2^{w/o}

Figure 38 AES Spectrum of MgO Doped with LiF Annealed for 60 Hours

NaF were examined to determine the effect of doping with this additive. The as-hot pressed material was close to theoretical density, but was not translucent. Bulk analyses indicated cation additive remained as well as residual fluorine (.22^w/o Na and .9^w/o F). Annealing at 1370°C improved the optical properties, but the material was still not as transparent as the LiF doped materials. SEM fractographs (Figure 39) indicate total intergranular fracture in both specimens and the presence of residual porosity. AES analysis (Figure 40) indicated residual F and Na in the as-hot pressed material, and loss of the additives and segregation of about 4^a/o Ca and 3^a/o Si after annealing.

The levels of Ca and Si are both consistent with the results obtained earlier at 1315°C for the LiF doped material. The retention of the Na is consistent with the bulk chemical analysis and presumably occurs due to the greater stability of Na then Li in MgO at these temperatures. In all of the materials examined, the grain boundary chemistry variation did not extend over 5 atomic layers from the boundary.

D. Hot Pressing of Al₂O₃ and MgAl₂O₄ With LiF

A sample of Al₂O₃ hot pressed at 1100°C with 2^w/o LiF and a sample of MgAl₂O₄ (Spinel)* hot pressed at 1600°C with 1.5^w/o LiF were also examined to determine location of residual additives.

The Al₂O₃ AES results (Figure 41) indicated residual F, but no cation impurities. The MgAl₂O₄ results (Figure 42) indicated much less residual F, but no cations. These results agree with the MgO results and also with bulk analyses indicating less

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* Sample Obtained From D. Sellers, Coors Porcelain Co., Golden, Colo.

a. As Hot Pressed

b. Annealed At 1370°C

Figure 39 SEM Fractographs of MgO Hot Pressed
With 2% NaF

Figure 40 AES Spectra of MgO Hot Pressed with 2% NaF

Figure 41: AES Spectra of Al_2O_3 Hot Pressed with 2% LiF

Figure 42 AES Spectrum of MgAl₂O₄ (spinel) Hot Pressed with 1.5^w% LiF

retained F. This in turn, is consistent with the higher temperatures and lower quantities of additives used for the spinel.

E. Analysis of Results in Terms of Densification

The observed residual additives offer unequivocal evidence that the additives affect the grain boundaries of the hot pressed material. These results further support the theory of liquid phase hot pressing assistance in fabrication of MgO with additives.^{16,17} Residual grain boundary additives and their loss on annealing are consistent with lower fracture strength in MgO¹⁵ as well as lower strength and greater tendency for intergranular failure in MgO and MgAl₂O₄.⁵⁸

Hence liquid phase assistance (formation of a liquid phase between particles and enhanced diffusivity through this liquid phase) is proposed as the model for densification enhancement and is supported by the findings of this study.

F. Conclusions of Hot Pressed MgO Study

1. Ca, Ti, and Si impurities segregate to the grain boundaries in MgO during hot pressing and/or annealing.
2. The presence of F and Na at the grain boundaries in MgO hot pressed with additives is unequivocally demonstrated, hence supporting proposed densification (e.g. liquid phase) mechanisms and alteration of mechanical behavior. Greater retention of F and loss of Li or Na and F are corroborated.
3. Smaller quantities of F also were shown to be present at the grain boundaries of spinel and Al₂O₃ hot pressed with LiF.

The lower quantities of F are consistent with the volatility of the additive and higher temperatures used in fabrication of these materials.

4. All additives and impurities were found to generally occupy only a few atomic layers along the boundaries.

V. Appendices

- A. A Calculation of Sputter Removal Rates
- B. Use of CCl_4 Displacement to Measure Porosity
- C. Calculation of Image Stress From a Segregant
- D. Calculation of Grain Boundary Concentration of a Segregant
- E. Calculation of Interaction Energies and Upper Limits for Segregants in Al_2O_3
- F. Calculation of Residual Fluorine Levels in MgO
- G. Further Study of Equilibrium Segregation

Appendix A: A Calculation of Sputter Removal Rates

The important parameters determining the removal rate from a surface undergoing inert-ion sputtering are:

1. I_β = The ion beam current (number of coulombs of charge striking the surface per second).
2. E_s = Sputtering energy (difference in potential between the anode and the target imparts this potential energy to an electron or singly charged ion).
3. Y_s = Sputter yield (experimentally determined ratio of substrate atoms removed per incident ion - depends on energy, type of ions, and type of substrate).
4. ρ_A = Surface atom density (Number of substrate atoms per unit area of surface in first atomic layer - the number 10^{15} atoms/cm² will be used).
5. A = Area of beam incident on surface.

The rate of removal in monolayers per second is:

$$R = I_\beta \left(\frac{\text{coulomb}}{\text{sec}} \right) \times \frac{1 \text{ electronic charge}}{1.6 \times 10^{-19} \text{ coulomb}} \times \frac{1 \text{ Xe}^+ \text{ ion}}{1 \text{ electron charge}} \times$$

$$Y \frac{(\text{number of atoms removed})}{1 \text{ Xe}^+ \text{ ion}} \times \frac{1}{\rho_A} \times \frac{1}{A} = \frac{Y I (\mu A)}{A (\text{cm}^2)} \times$$

$$10^{-6} \times \frac{10^{19}}{1.6} \times 10^{-15} = \frac{6.25 \times 10^{-3}}{A (\text{cm}^2)} \times Y \times I (\mu A) \quad (10)$$

If for example, the typical sputter conditions of $E_s = 500\text{eV}$ and $I = 1\mu A$ were used on a specimen of square cross section (.100" x .100"),

$$R = \frac{6.25 \times 10^{-3}}{(.254\text{cm} \times .254\text{cm})} \times Y \approx 10^{-2} \times 10^{-2} \times Y$$

From private communication,³⁴ it was learned that $Y_{\text{Al}_2\text{O}_3}(500\text{eV}) \approx Y_{\text{MgO}}(500\text{eV}) \approx .2$

Therefore, $R_{\text{Al}_2\text{O}_3} = R_{\text{MgO}} = 0.02 \text{ atom layers/sec}$

Appendix B: Use of CCl_4 Displacement to Measure Porosity

Use was made of a single crystal (sapphire) as a standard for theoretically dense Al_2O_3 . All samples were suspended by a thin wire and their weight measured in air and CCl_4 . The wire alone was then weighed in air and in CCl_4 .

W_{ww} = Weight of the wire wet

W_{wd} = Weight of the wire dry

W_{xw} = weight of the unknown sample wet

W_{xd} = weight of the unknown sample dry

W_{sw} = weight of the sapphire wet

W_{sd} = weight of the sapphire dry

ρ = density of CCl_4 (function of temperature)

Percentage of theoretical density = $\frac{\text{Mass of unknown}}{\text{volume of unknown}} \times 100 = \frac{\text{Mass of sapphire}}{\text{volume of sapphire}} \times 100 =$

$$\frac{1}{\rho} \frac{W_{xd} - W_{wd}}{(W_{xd} - W_{wd}) - (W_{xw} - W_{ww})} \times 100$$

$$\frac{1}{\rho} \frac{W_{sd} - W_{wd}}{(W_{sd} - W_{wd}) - (W_{sw} - W_{ww})}$$

$$\%T.D. = 100 \times \frac{(W_{xd} - W_{wd})[(W_{sd} - W_{wd}) - (W_{sw} - W_{ww})]}{(W_{sd} - W_{wd})[(W_{xd} - W_{wd}) - (W_{xw} - W_{ww})]} \quad (11)$$

Note that the final form does not depend on ρ which is troublesome to use since it is so temperature and impurity sensitive.

Appendix C: Calculation of Image Stress from A Segregant

From Fleischer, a dislocation of Burgers vector b , a distance x from a thin region of width δ and change in modulus ΔG , will be under an image stress:⁴²

$$\tau = \frac{\Delta G}{8\pi} \left(\frac{\delta}{x+\delta} \right) \frac{b}{x} \quad (12)$$

Examine a pure MgO strip 20 Å wide at a grain boundary:

$$\tau = \frac{(13-15)}{8\pi} \times 10^{11} \frac{\text{dynes}}{\text{cm}^2} \left(\frac{20 \text{ Å}}{x + 20 \text{ Å}} \right) \frac{5 \text{ Å}}{x}$$

$$\tau = - 8 \times 10^9 \frac{\text{dynes}}{\text{cm}^2} \left(\frac{100}{x+200} \right) \frac{1}{x}$$

τ is plotted versus x in Figure 43. Obviously, τ is negligible beyond 100 Å. The answer for MgO is always negative, implying that the presence of MgO at the boundary should lead to a softening. Data is not available for the modulus of CaO, but the important variables in the above equation are the width of the segregated region, δ , and the distance from the region, x . Hence the segregated CaO could not extend the hardening out much farther than the MgO softening extends.

If a multiple dislocation model is considered (i.e. a pile up at the interface) an estimate of distance can be made based on the back stress on the last dislocation in a pile-up.⁴¹

$$\tau_o = \frac{Gbn}{\pi L} \quad (13)$$

where n = number of dislocations in the pile-up,

b = Burgers vector,

G = shear modulus of the material, and

L = distance from pinned dislocation to the last one in the pile-up.

If n is assumed to be 10^2 - 10^3 dislocations, $G = 15 \times 10^3$ psi, $b = 5 \text{ Å}$, and the ultimate tensile strength is used for τ_o .

Figure 43 Image Stress for A Dislocation

(yield stress should be used, but is unavailable for Al_2O_3), an estimate can be made of how far from the boundary a stress of yield strength proportions could be felt:

$$L = \frac{15 \times 10^3 \text{ psi}}{40 \times 10^3 \text{ psi}} \frac{(5\text{\AA})}{\pi} n = .6 n \text{\AA} \quad (14)$$

$$\text{If } n = 10^2 \quad L = 60\text{\AA}$$

$$\text{or if } n = 10^3 \quad L = 600\text{\AA}$$

Appendix D: Calculation of Grain Boundary Concentration of a Segregant

The following derivation is based on a treatment given in McLean's text on grain boundaries.⁴⁷

Assume that there are N undistorted lattice sites with P solute atoms distributed throughout and n distorted lattice sites containing p atoms. The n sites would correspond to areas of disorder such as grain boundaries and the N sites refer to normal lattice positions. If the distortion energy (both size and electronic misfit) of a misfitting solute atom on an N site is given by E and on an n site is given by e , the total free energy of the system is given by:

$$F = H - TS = pe + PE - T[S_{\text{pos.}} + S_{\text{vib.}}] \quad (15)$$

Further, the positional entropy can be expressed by using statistical thermodynamics:⁴⁷

$$S_{\text{pos.}} = k \ln n!N! - k \ln (n-p)!p!(N-P)!P! \quad (16)$$

The vibrational entropy can also be expressed utilizing a harmonic oscillator approach (Einstein statistical thermodynamics).⁵⁹

$$S_{\text{vib.}} = p k \left(\ln \frac{kT}{h\nu} + 1 \right) + P k \left(\ln \frac{kT}{h\nu'} + 1 \right) \quad (17)$$

where ν = Einstein frequency of oscillation of solutes on distorted sites and

ν' = Einstein frequency of oscillation on undistorted sites. (Assume the frequencies are independent of T at high temperatures)

Therefore:

$$F = pe + PE - T\{k \ln n!N! - k \ln (n-p)!p!(N-P)!P! + p k \left(\ln \frac{kT}{h\nu} + 1 \right) + P k \left(\ln \frac{kT}{h\nu'} + 1 \right)\} \quad (18)$$

To get the equilibrium (i.e. minimum) value, the total differential is taken and set equal to zero with p and P variables:

$$(N-P)]dP + [\ln \frac{kT}{hv} + 1] dp + [\ln \frac{kT}{hv'} + 1]dP \quad (19)$$

But since $p + P = \text{constant}$ (i.e. conservation of total solute),

$$dp = - dP \quad (20)$$

$$\text{and } dF = (e-E) + kT \left\{ \ln \frac{p}{n-p} - \ln \frac{P}{(N-P)} + \ln \frac{kT}{hv} - \ln \frac{kT}{hv'} \right\} = 0 \quad (21)$$

Solving for $(E-e)$,

$$(E-e) = kT \ln \left[\left(\frac{p}{n-p} \right) \times \left(\frac{N-P}{P} \right) \left(\frac{v'}{v} \right) \right] \quad (22)$$

Let $C_{gb} = p/n$ (concentration in the distorted region),

$C = P/N$ (concentration in the undistorted region), and

$Q = (E-e)/N_0$ where $N_0 = \text{Avogadro's number}$.

$$Q = RT \ln \left(\frac{p}{n-p} \times \frac{N-P}{P} \times \frac{v'}{v} \right) \quad (23)$$

or:

$$\exp(Q/RT) = \left(\frac{p}{n-p} \right) \left(\frac{N-P}{P} \right) \left(\frac{v'}{v} \right) = \left(\frac{C_{gb}}{1-C} \right) \times \left(\frac{1-C}{C} \right) \left(\frac{v'}{v} \right) \quad (24)$$

Solving for C_{gb} gives for the concentration at the grain boundary at equilibrium at temperature T :

$$C_{gb} = \frac{e^{Q/RT}}{\frac{v'}{v} \left(\frac{1-C}{C} \right) + e^{Q/RT}} \quad (25)$$

multiply through by C ,

$$C_{gb} = \frac{C e^{Q/RT}}{\frac{v'}{v} + e^{Q/RT}} \quad (26)$$

Since the Debye temperature, θ , is equal to $h\nu_m/k$ where ν_m is the maximum frequency, the ratio v/v' can be approximated by,

$$\frac{v'}{v} = \frac{\theta'}{\theta} \quad (27)$$

Since at temperatures above room temperature, $v \approx \nu_m$ (i.e. where $T \gg \theta$).

Hence an alternate way to write the frequency term is:

$$C_{gb} = \frac{C_e \frac{Q}{RT}}{\frac{\theta'}{\theta} + C_e \frac{Q}{RT}} \quad (28)$$

But Debye temperatures as a function of order/disorder are no more readily available than frequencies; hence an estimate must be made as to the size of the ν'/ν term.

From the Einstein theory, the energy of a group of harmonic oscillators all having the same frequency, is:^{60,61}

$$E = \frac{Nh\omega}{e^{(h\omega/kT)} - 1} = \frac{Nh\nu}{e^{(h\nu/kT)} - 1} \quad (29)$$

At high temperatures ($T \gg \theta$), most oscillators have the same frequency ν_m and the term $e^{(h\nu/kT)} \ll 1$.

Hence for $T \gg \theta$

$$E \propto \nu_m \quad (30)$$

Also, the potential energy of cohesion of an ionic material (i.e. coulombic forces) can be related to ion separation:⁶²

$$E \propto \frac{1}{r} \quad (31)$$

Hence the maximum frequency can be related to ion separation:

$$\nu_m \propto \frac{1}{r} \quad (32)$$

The assumption concerning $T \gg \theta$ is valid in this instance since although no data was available for Al_2O_3 , most ionic materials have $\theta < 300^\circ\text{K}$, while the temperature range of interest in this study is $T > 1900^\circ\text{K}$. Hence $\theta/T < \frac{1}{6}$ and $e^{1/6} \approx .002$, which is much smaller than 1.

If the assumption is now made that the Ca^{+2} ion is compressed to fit the unaltered octahedral interstice in Al_2O_3 usually occupied by Al^{+3} , the distorted size of the Ca^{+2} ion will be the size of the site.

$$r_{\text{distorted}} = .5\text{\AA} \quad (33)$$

Further if the Ca^{+2} ion at the grain boundary is assumed to be "free" (i.e. not compressed at all) and allowed to fill a site as large as its free ionic radius,

$$r_{\text{undistorted}} = .99\text{\AA} \quad (34)$$

Hence the lower limit value on the ratio between the two frequencies can be calculated.

$$\frac{\nu'}{\nu} \text{ (lower limit) } = \frac{.5\text{\AA}}{.99\text{\AA}} \approx \frac{1}{2} \quad (35)$$

The actual value will be closer to one, since the Ca^{+2} ion in the distorted site will expand the lattice somewhat and an ion at the grain boundary is not "free", but will be compressed somewhat.

Therefore, since the spread in values of $\frac{\nu'}{\nu}$ will be:

$$\frac{1}{2} < \frac{\nu'}{\nu} < 1 \quad (36)$$

It appears justifiable to use one as an approximation.

The final form for the $C_{\text{g.b.}}$ equation and the form in which it will be used, is:

$$C_{\text{g.b.}} = \frac{C_e^{Q/RT}}{1 + C_e^{Q/RT}} \quad (37)$$

Appendix E: Calculations of Interaction Energies and Upper Limits for Segregants in Al_2O_3

A. Calculation of Q for Ca in Al_2O_3

Utilizing equation (37) from Appendix D, a relation for Q as a function of C_{gb} and C can be obtained.

$$C_{gb} = \frac{C_e \frac{Q}{RT}}{1 + C_e \frac{Q}{RT}} \quad (37)$$

$$Q = RT \ln \left[\frac{C_{gb}}{(1 - C_{gb})} \times \frac{1}{C} \right] \quad (38)$$

In the quenched General Electric alumina $C = 40 \text{ ppm} = 4 \times 10^{-5}$

1700°C

$$C_{gb} = 5.6^a/o = .056$$

$$\begin{aligned} Q(1700^\circ C) &= \left(1.98 \frac{\text{cal}}{\text{mole}^\circ K} \right) (1973^\circ K) \times \ln \left[\frac{.056}{(1 - .056)} \times \frac{1}{(4 \times 10^{-5})} \right] \\ &= 28,500 \frac{\text{cal}}{\text{mole}} \end{aligned} \quad (39)$$

1800°C

$$C_{gb} = 4.2^a/o = .042$$

$$\begin{aligned} Q(1800^\circ C) &= \left(1.98 \frac{\text{cal}}{\text{mole}^\circ K} \right) (2073^\circ K) \times \ln \left[\frac{.042}{(1 - .042)} \times \frac{1}{(4 \times 10^{-5})} \right] \\ &= 28,700 \frac{\text{cal}}{\text{mole}} \end{aligned} \quad (40)$$

1900°C

$$C_{gb} = 2.8^a/o = .028$$

$$\begin{aligned} Q(1900^\circ C) &= \left(1.98 \frac{\text{cal}}{\text{mole}^\circ K} \right) (2173^\circ K) \times \ln \left[\frac{.028}{(1 - .028)} \times \frac{1}{(4 \times 10^{-5})} \right] \\ &= 28,350 \frac{\text{cal}}{\text{mole}} \end{aligned} \quad (41)$$

B. Calculation of Q for Mg, Ni, and Y in Al_2O_3

$$\text{Given : } r_{Mg} = .65 \text{\AA}$$

$$r_{Ni} = .72\text{\AA}$$

$$r_Y = .93\text{\AA}$$

$$r_{Ca} = .99\text{\AA}$$

$$r_{Al} = .50\text{\AA}$$

$$\text{and } Q_{cal} = 28,500 \text{ cal/mole}$$

$$Q_{Mg} = \frac{\epsilon_{Mg}^2}{\epsilon_{Ca}^2} \times Q_{Ca} = \frac{(.65 - .50)^2}{(.99 - .50)^2} \times (28,500 \text{ cal/mole})$$

$$= 2,550 \text{ cal/mole} \quad (42)$$

$$Q_{Ni} = \frac{\epsilon_{Ni}^2}{\epsilon_{Ca}^2} \times Q_{Ca} = \frac{(.72 - .50)^2}{(.99 - .50)^2} \times (28,500 \text{ cal/mole})$$

$$= 5,479 \text{ cal/mole} \quad (43)$$

$$Q_Y = \frac{\epsilon_Y^2}{\epsilon_{Ca}^2} \times Q_{Ca} = \frac{(.93 - .50)^2}{(.99 - .50)^2} \times (28,500 \text{ cal/mole})$$

$$= 21,800 \text{ cal/mole} \quad (44)$$

C. Calculation of Expected Grain Boundary Concentrations

In the General Electric material, there is .2^a/o Mg⁺².

Hence, using the Q_{Mg} above and equation (37) at 1700°C,

$$Mg: C_{gb} = \frac{(.002)\exp[2550/(1973)(1.98)]}{1 + (.002)\exp[2550/(1973)(1.98)]} = .4^a/\text{o Mg} \quad (45)$$

For the NiO doped Al₂O₃ at 1700°C,

$$Ni: C_{gb} = \frac{(.0015)\exp[5470/(1973)(1.98)]}{1 + (.0015)\exp[5470/(1973)(1.98)]} = .6^a/\text{o Ni} \quad (46)$$

And finally in the Sylvania Al₂O₃, the Y⁺³ level was .02^a/o,

$$Y: C_{gb} = \frac{(.0002)\exp[21800/(1973)(1.98)]}{1 + (.0002)\exp[21800/(1973)(1.98)]} = 4.3^a/\text{o Y} \quad (47)$$

D. Calculation of Segregation Upper Limit of Ca in Al_2O_3

An upper limit value for Ca^{+2} segregation in the General Electric Al_2O_3 quenched from 1700°C can be calculated from:⁴⁶

$$r_{2(1)}^o < \frac{\sigma_1}{kT[1+\ln(x_e/x_o)]} \quad (2)$$

σ_1 = surface (grain boundary energy) of Al_2O_3 =
65 ergs/cm² (This value was determined by grain
boundary grooving techniques)⁶³

Assume $x_e = x_o = .00004$ Ca in the General Electric material

$$\therefore r_{2(1)}^o < \frac{65 \text{ erg/cm}^2}{1.38 \times 10^{-16} \frac{\text{erg}}{\text{K}} (1973^\circ\text{K})} = 2.4 \times 10^{14} \frac{\text{atoms}}{\text{cm}^2} \quad (48)$$

The excess observed experimentally can be calculated from
Figure 14:⁴⁶

$$r_{2(1)}^o = \frac{1}{A} \left[N_2 - \frac{x_o}{1-x_o} N_1 \right] \quad (3)$$

$$x_o = 4 \times 10^{-5}, \text{ so } \frac{x_o}{1-x_o} \approx 4 \times 10^{-5}. \quad (49)$$

This will make the second term in the brackets above insignificant,
hence:

$$r_{2(1)}^o \approx \frac{1}{A} N_2 \quad (50)$$

From Figure 14, the following tabulation gives the percentage
Ca in each of the atomic layers away from the grain boundary:

<u>Layers Removed</u>	<u>% Ca</u>	<u>number of ions/cm²</u>
at g.b.	5.6 ^a /o	$2(.056 \times 10^{15})$
2 layers	1.08 ^a /o	$2(.01 \times 10^{15})$

<u>Layers Removed</u>	<u>% Ca</u>	<u>number of ions/cm²</u>
3 layers	.89 ^a /o	2(.009 x 10 ¹⁵)
4 layers	.39 ^a /o	2(.004 x 10 ¹⁵)
6 layers	.1 ^a /o	2(.001 x 10 ¹⁵)
*1 layer	3.3 ^a /o	2(.033 x 10 ¹⁵)
*5 layers	.25 ^a /o	2(.0025 x 10 ¹⁵)
		<u>23.1 x 10¹³ $\frac{\text{atoms}}{\text{cm}^2}$</u>

The factor of two enters into the calculation since there are really two sides to the segregation profile, not one as the sputter profile would tend to indicate.

Hence the calculated excess is:

$$\frac{\Gamma^0}{2(1)} = 23.1 \times 10^{13} \frac{\text{atoms}}{\text{cm}^2} \quad (51)$$

and the upper limit is

$$\frac{\Gamma^0}{2(1)_{\text{U.L.}}} < 24 \times 10^{13} \frac{\text{atoms}}{\text{cm}^2} \quad (52)$$

$$\therefore \text{Since, } 23 \times 10^{13} \frac{\text{atoms}}{\text{cm}^2} < 24 \times 10^{13} \frac{\text{atoms}}{\text{cm}^2} \quad (53)$$

the segregation is within the thermodynamic limits of equilibrium segregation.

It should be noted that the value of σ_{gb} used appears to be extremely low. Kingery found that the surface energy of Al_2O_3 at 1805°C was 905 $\frac{\text{erg}}{\text{cm}^2}$.⁶⁴ The grain boundary energy should be somewhat lower, but 65 $\frac{\text{ergs}}{\text{cm}^2}$ appears excessively low. Any increase in σ_{gb} would just increase the upper limit value and give a greater difference between the calculated excess and the limit value.

*interpolated value between two experimental points.

Appendix F: Calculation of Residual Fluorine Levels in MgO

To calculate the amount of fluorine at the grain boundaries, it is necessary to obtain the ratio of the number of ions at the grain boundary to the bulk.

Starting with 1μ diameter spherical grains (Figure 34 indicates that the as-hot pressed grain size is about 1μ), the area of the grain is:

$$A = \frac{4\pi d^2}{4} = \pi \times 10^{-12} \text{ m}^2 \quad (54)$$

Further, the volume is:

$$V = \frac{4}{3} \pi \frac{d^3}{8} = \frac{\pi}{6} \times 10^{-18} \text{ m}^3 \quad (55)$$

The total number of ions on the grain boundary area is (assume $10^{15} \frac{\text{ions}}{\text{cm}^2}$):

$$N_A = \frac{10^{15}}{\text{cm}^2} \times \pi \times 10^{-12} \text{ m}^2 \times \frac{10^4 \text{ cm}^2}{1 \text{ m}^2} = \pi \times 10^7 \text{ ions} \quad (56)$$

In the grain (assume $10^{22} \frac{\text{ions}}{\text{cm}^3}$):

$$N_V = \frac{10^{22}}{\text{cm}^3} \times \frac{\pi}{6} \times 10^{-18} \text{ m}^3 \times \frac{10^6 \text{ cm}^3}{1 \text{ m}^3} = \frac{\pi}{6} \times 10^{10} \text{ ions} \quad (57)$$

Hence the atom fraction of ions in a monolayer at the grain boundary is

$$X_A = \frac{\pi \times 10^7}{\frac{\pi}{6} \times 10^{10}} = 6 \times 10^{-3} = .006 \quad (58)$$

If an assumption is now made concerning the percentage of the grain boundary sites found to be occupied by F^{-1} ions, an estimate of the atom fraction of fluorine that this represents can be made.

Assume that 40% of the sites in the first 5 layers away from the boundary are occupied by fluorine ions:

$$X_A = .006 \times .4 \times 5 = .012 \quad (59)$$

This means that there is $1.2^a/o F^{-1}$ at the grain boundaries of the MgO. Bulk analysis indicates that in similar samples, $.9^w/o$ or $1.8^a/o F^{-1}$ remains after hot pressing.

Hence the conclusion is reached that most if not all of the residual fluorine additives are at the grain boundaries in the hot pressed MgO.

Appendix G: Further Study of Equilibrium Segregation

The results of this investigation of densification in Al_2O_3 and MgO , have revealed new possibilities and opportunities to study equilibrium segregation to interfaces. The basic model utilized describes adequately the behavior observed in the Al_2O_3 - Ca^{+2} system and is consistent with the segregation or lack of segregation of other cation species (Mg^{+2} , Ni^{+2} , and Y^{+3}).

The basic equation which relates the grain boundary concentration of a segregant to the other system variables is:

$$C_{gb} = \frac{C_e^{Q/RT}}{1 + C_e^{Q/RT}} \quad (37)$$

where all of the terms are as defined previously.

Use of this equation in the current study produced consistency in the interpretation of the experimental data and the values obtained implied that the Ca^{+2} segregation in Al_2O_3 is equilibrium in nature. A further test of the nature of the segregation would involve establishing the reversibility of the observed segregation. This indeed has been done for the Ca^{+2} segregation observed in MgO hot pressed without additives. Auger samples were annealed at 1500°C for 5 hours to ensure equilibrium at temperature. One specimen was then quenched in ice brine and a second furnace cooled to allow segregation of Ca to occur. The Auger data indicated $2^a/\text{o}$ Ca at the grain boundaries of the quenched specimen and $6^a/\text{o}$ in the furnace cooled specimen. This clearly establishes that the Ca is not boiling out of the sample at high temperature, but rather is incorporated into the MgO lattice.

Further studies are planned to establish similar irrefutable

evidence of reversibility in the Al_2O_3 system as well and to study the effect of bulk composition on both Q and C_{gb} . The Q value reported in this work is an average Q for a given grain boundary. It is reasonable to expect that there are high energy (large amount of disorder) as well as low energy (small amount of disorder) sites at the grain boundary. Hence it possible that Q is concentration dependent and the driving force for segregation will change as the high energy sites are depleted by segregation. Experimentally in this study, no method of distinguishing between Q values was found; hence the Q values reported are "average" values. It would be of interest to study the concentration dependence of Q .

Finally it should be noted that it is possible to utilize the observed segregation to study solubility limits of segregants. For example by doping Al_2O_3 to various levels of Ca^{+2} , the segregation behavior could be studied and the discontinuity in the increase in segregation noted when the amount of Ca in the bulk exceeds the solubility limit. At that point, equation (37) indicates that the increase in C_{gb} occurring as the overall bulk level is increased would remain fixed at the value corresponding to C equal to the solubility limit. Further Ca additions would precipitate out and would not contribute to the segregation. The system would maintain only the soluble amount of Ca in solution.

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