CLEAN-ROOM AND CO\textsubscript{2}-LASER PROCESSING OF ULTRA HIGH-PURITY AL\textsubscript{2}O\textsubscript{3}

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ABSTRACT

Clean-room powder processing, furnace firing, and CO\textsubscript{2}-laser heating techniques to produce high-purity Al\textsubscript{2}O\textsubscript{3} ceramics were applied to a new source of high-purity Al\textsubscript{2}O\textsubscript{3} (<13 ppm total and <8 ppm cation detected impurities). The chemical analyses of the material after each stage of processing and firing indicate that the procedures used in this work give no detectable contamination of the material. The microstructure of a CO\textsubscript{2}-laser ultra high-purity Al\textsubscript{2}O\textsubscript{3} is illustrated. Densification is incomplete for this material. Calcination and deagglomeration were not optimized. Procedures, such as these are required to control the trace impurity contents in a fired ceramic material.

INTRODUCTION

There is increasing awareness of the importance of purity in the fabrication and use of ceramic materials. For example, impurities segregated at grain boundaries may form second phases and affect sintering and high temperature properties of ceramics. Traces of iron (\sim{} 10 parts per million, ppm) in alumina used for sodium vapor arc lamp tubes absorb a significant portion of the light produced. Small amounts of uranium (25 parts per billion, ppb) or thorium (80 ppb) in alumina substrates for random access memory devices emit a sufficient flux of \alpha-particles to cause soft memory errors.[1] Therefore work is underway to develop high-purity, or well-defined materials, for many optical, electronic and structural applications.[2]

The goal of this work has been to develop clean-room processing procedures and laser heating techniques for producing ceramics with virtually no contamination. As our processing procedures have improved, we have become interested in the acquisition and study of aluminas of higher purity than normally available. In this paper we demonstrate the processing of a high purity alumina under clean-room conditions, and its conversion, with retention of purity, to a partially densified, fired alumina ceramic by heating with a CO\textsubscript{2}-laser. The microstructure of the laser fired ultra high purity Al\textsubscript{2}O\textsubscript{3} is discussed. Chemical analyses at each stage of processing are presented.

ULTRA HIGH-PURITY

Chemical Analysis

Considerable care is required in the selection of sources for reliable analytical information on impurities in Al\textsubscript{2}O\textsubscript{3} at the ppm level. We have performed extensive studies of chemical analysis techniques and analysts, using multiple samples and analyses by many different techniques and by various labs using the same technique.[3] Spark Source Mass Spectrography (SSMS) is particularly suitable for analyzing abrasive and relatively insoluble ceramic powders, and both cations and anions are detected at relatively low detection limits. The accuracy and precision of this technique are...

* Presently at E. I. du Pont de Nemours and Co., Wilmington DE
Table 1. Chemical Analyses# (PPM WEIGHT)\textsuperscript{\textcircled{5}}

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<th></th>
<th>1 AL(OH)\textsubscript{3} POWDER</th>
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<th>3 DIE+ISO-PRESSED</th>
<th>4 FURNACE CALCINED*</th>
<th>5 FURNACE CALCINED\textsuperscript{6}</th>
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# (SSMS) Northern Analytical Laboratory, Amherst, New Hampshire.
\textsuperscript{5} All analyses given on an Al\textsubscript{2}O\textsubscript{3} weight basis.
\* Furnace calcined without being surrounded in powder.
\textsuperscript{6} Sample pellet enclosed in powder.

The following elements were found to be below detection limits of 0.01 ppm (atomic, uncorrected for isotopic abundance): Be, F, Sc, Ti, Ge, Se, Br, Rb, Sr, Y, Zr, Nb, Mo, Ru, Rh, Pd, Ag, Cd, In, Sn, Sb, Te, I, Cs, Ba, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Hf, Ta, W, Re, Os, Ir, Pt, Au, Tl, Pb, Bi, Th, U.
about a factor of 2 to 3. SSMS analyses were performed by Northern Analytical Laboratories, who did not analyze for hydrogen, carbon, oxygen or nitrogen. Analyses for uranium and thorium at the ppb level were performed by General Activation Analysis Inc. For further information on chemical analysis see references.[1,3-6]

**Al(OH)_3 Powder**

The powder used in this study was obtained from E. I. du Pont de Nemours and Co. The details of the synthesis of this powder are to be published elsewhere. The chemical analysis by spark source mass spectrography (SSMS) is given in Table I. The results shown for the powder are the average analyses of four separate samples. The total detected impurity concentration is $< 13$ ppm and the total detected cation impurity concentration is $< 8$ ppm. The U and Th concentrations, determined by neutron activation analysis[8], are $<0.006$ ppm and $<0.018$ ppm, respectively, the lowest concentrations of U and Th of the Al_2O_3 powder sources that we have analyzed.[1] This powder is extremely pure relative to most commercial aluminas which normally contain more than 100 ppm of impurities (commonly Si, Ca, Fe, Na, Mg).

The particle size and crystalline form of the powder were determined by transmission electron microscopy with a JEOL 200 CX electron microscope at 200 kV. Figure 1 shows a dark field image of the powder. The pointer in the corresponding diffraction pattern indicates the portion of the ring used for the dark field image in Figure 1. The image indicates that the powder is at least partially crystalline with crystallite sizes of approximately 70 Å. Figure 2 is a bright field image of the powder showing that the powder also contains large spherical particles on the

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8 General Activation Analysis Inc., San Diego, CA
* JEOL Co., Tokyo, Japan
order of 1000 Å to 2000 Å in size. Figure 3 is the diffraction pattern of this area with the selected area aperture around the large particles, but also includes some smaller ones. The spots obtained were indexed with the faint rings; these correspond to the powder being at least partially composed of the triclinic crystalline form of Al(OH)$_3$, Nordstrandite.[7]

Calcination

Calcination of the powder was conducted at 1000°, 1100°, and 1200° C for 1 and 3 hours in air, in a furnace using the 'clean' techniques discussed below. X-ray powder diffraction was used to determine the time and temperature for complete transformation. The X-ray data indicate that heating the powder to 1200° C for 1 hour results in its complete transformation to α-Al$_2$O$_3$, determined by the disappearance of a peak corresponding to a d-spacing of 2.44 Å. This interplanar spacing is common to many of the transition aluminas (γ, δ, η, θ, κ, and λ).[8] Figure 4 is a TEM bright field image of the powder calcined at 1200° C for 1 hour. The average particle size is 0.2 μm.

CLEAN-ROOM PROCESSING

To process high-purity materials without contamination clean-room techniques previously developed were used.[1,5,6] All powder handling was done in class 100 laminar-flow hoods using talcless gloves, and polytetrafluoroethylene (PTFE) utensils. Pellets for calcination and sintering were hand-pressed in a PTFE die, which had been cleaned in a 3:1 mixture of HCl/HNO$_3$ then soaked in deionized water (18 MD-cm) and rinsed in high-purity acetone. This cleaning procedure was used for all PTFE utensils that came in contact with the powder. The pellets, after pressing, were approximately 0.64 cm in diameter and 0.2 cm thick (0.05 g). After calcination the pellets were isopressed in cleaned polyethylene bags inside cleaned rubber bags to 3.2 x 10$^7$ Pascals.

CALCINATION AND FIRING

Furnace Heating

As we have done previously to prevent contamination during furnace firing, pressed pellets were buried in the source powder and were contained in cleaned sapphire crucibles during furnace firing.[1,5,6] No detectable contamination was introduced; the powder acts as a getter for airborne contaminants. Initially, the Al(OH)$_3$ was calcined in cleaned sapphire crucibles, without a surrounding powder layer. The furnace was a cleaned Al$_2$O$_3$ tube furnace. The analysis in column 4 of Table I indicates that furnace firing without powder surrounding the sample can result in significant contamination. Fe, Ga, and Si contamination in furnaces have previously been reported.[9,10] Pellets were furnace calcined at 1200° C for 1 hour in air. The heating rate was an average of 6° to 7°/minute for each of the samples. The cooling rate was an average of 7° to 9°/minute. After calcining, the pellets were re-packaged, isopressed, and fired at 1500° C for one hour in air. The
average heating and cooling rates were approximately 8 °/minute and 11°/minute, respectively. The samples were heated and cooled by pushing the sapphire crucible through the horizontal furnace with a cleaned Al₂O₃ rod. The heating and cooling rates were low to prevent cracking of the sapphire crucible.

**CO₂-Laser Calcining and Firing**

Since conventional furnaces are a major source of contamination, we have examined electron beam, Xe-arc lamp and CO₂-laser methods of heating. With these methods, only the sample is heated; deposition of impurities from hot furnace walls is eliminated. Of the three techniques, CO₂-laser heating is the most efficient and controllable. CO₂-laser heating has been used previously for float zone crystal growth, high temperature vacuum ultraviolet spectroscopy, synthesis of ceramics and powders, and for studying solidification microstructures of laser melted Al₂O₃ powder compacts.[5,6,13-14]

A CO₂-laser heating system was designed and built for annealing, calcining, or firing high-purity ceramic materials. A schematic of the chamber is shown in Figure 5. An Apollo® 80 watt cw CO₂-laser (10.6 μm) is used for heating. Most ceramics (except the halides) absorb strongly at this wavelength. The 1.1 cm diameter beam is split with a KCl beam splitter and directed to a power meter for continuous monitoring of the laser power. Front-surface infrared mirrors are used for directing the beam into the sample chamber. An aperture is used to produce a more uniform power density spatially.

The sample chamber is stainless steel with an anodized Al sample stand base serving as a beam dump. The sample-stand is a sapphire tripod. The chamber has a ZnSe laser window and two sapphire windows for temperature measurements. The gas system consists of PTFE tubing and filters and stainless steel regulators. Only high-purity gases were used. The system is capable of firing ceramics in a variety of atmospheres, or vacuum. The chamber was cleaned with trichlorethylene, acetone, alcohol, then high purity acetone prior to use.

Laser firing has been shown to be a clean heating method for most ceramic materials, but measuring the temperature is a problem. The temperatures were measured using a micro-focus optical pyrometer, and an emissivity of one was assumed for polycrystalline Al₂O₃. If the emissivity is <1 then the optical temperature will be lower than the actual temperature of the sample. Correlation of optical to actual temperatures requires the use of an embedded thermocouple in a test sample.[11]

Pellets of Al₂O₃ were calcined for two hours in low vacuum (flowing high-purity air at 200 μm). Pellets were used because they were more easily accommodated on the tripod sample stand. Heating the sample from the top surface led to a temperature gradient in the sample (1270°C at the top, 1030°C at the bottom). The temperature distribution across the top surface of the pellet was

Figure 5. Schematic of the CO₂-laser heating chamber.

* Apollo Lasers Inc., Chatsworth CA
relatively uniform. The beam power to obtain this temperature was approximately 25 watts. The power ramp (rate at which laser power is changed) was 0.68 watts/minute (corresponding to 34°C/minute sample temperature). Samples were cooled by closing the shutter of the laser. To maintain a stable lasing condition at low power (<8 watts) the laser was operated in a chopped mode at 100 Hz.

After calcining the pellets were re-packaged for isopressing (3.2 x 10^7 Pascals). The pellets were then fired for 1 or 2 hours at a temperature of 1620°C (top of the sample) in vacuum (flowing high-purity air at 200μm). The temperature gradient across the top of the sample was ± 40°C. The temperature gradient through the sample resulted in a bottom temperature of 1350°C. The peak laser power was 60 watts. The power ramp was 0.75 watts/minute (corresponding to ~20°C/minute sample temperature) and samples were cooled by closing the shutter of the laser. Surface melting was a problem on heating of samples through laser powers of 30 to 35 watts. The power ramp was decreased to about 0.3 watts/minute in this regime to minimize surface melting, but melting of a layer about 60 μm in thickness still occurred. Surface melting presumably results from the strong absorption of the laser power in the surface layer and could be avoided by splitting the beam and directing it simultaneously onto both sides of the sample or by using a heat shield. Both of these would also reduce the temperature gradients through the sample. The temperature gradients across the top of the sample could be reduced by using a beam integrater or a heat shield.

RESULTS AND DISCUSSION

The chemical analyses, by SSMS, of the material, as-received, and after each processing step are summarized in Table I. The total detected impurity concentration (column 1) in the starting powder is < 13 ppm and the detected cation concentration is <8 ppm, much lower levels than are found in commercial aluminas, which typically contain at least 100 ppm impurities.

When our clean-room procedures outlined here are followed, the purity of the material is maintained as shown in the tabulated analyses (columns 2 and 3). When the material is heated in a cleaned sapphire crucible in a hot-tube furnace, contaminants released from the walls of the furnace are transferred to the sample (column 4). But by surrounding the pellet with a layer of the starting powder, the contaminants are 'gettered', and the pellet is protected both at 1200°C (calcination, column 5) and at 1500°C (firing, column 6). With the CO₂-laser heating technique, the walls of the 'furnace' are near ambient temperature and such protection procedures are not needed. The purity of the pellet is unchanged after laser heating at ~1200°C (column 7) or ~1500°C (column 8).

The chemical analysis results indicate that the procedures outlined in this paper give no detectable contamination of a material with impurity concentrations much lower than typical aluminas [1,5,6] By using this higher purity Al₂O₃, any contamination resulting from processing procedures can be detected at much lower levels than previously possible. High-purity materials and procedures such as these have been demonstrated to produce ceramic materials for technological applications requiring low concentrations of trace impurities.[1]

Figure 6 is a cross section of a laser calcined and fired (2 hours) pellet, heated as described above. The microstructure of the pellet is relatively uniform, although the top of the pellet was melted (see above). Figure 7 is a magnified view of the top portion of this pellet. The average grain size is ~ 20 μm and necks have formed between the particles. This material is in the intermediate stage of sintering.

Typical Al₂O₃ fired ceramics contain 1000's of ppm impurities. Other work has been done on firing high-purity aluminas. Morris and Coble fired high-purity Al₂O₃ (<93 ppm total detected impurity content) with no contamination of the material from processing or firing.[5] Blendell
sintered Al$_2$O$_3$ containing ~80 ppm detected impurities, after firing. [10] Bennison hot-pressed an Al$_2$O$_3$ containing 260 ppm C and <65 ppm other total impurities using 'clean' techniques, but did not report the impurity concentrations after processing and firing. [15] The laser fired material in this work is the highest purity Al$_2$O$_3$ fired ceramic yet reported. It seems clear from the neck growth and grain growth that higher densities could be achieved if calcination, deagglomeration, and fabrication procedures were optimized.

The temperature dependent grain growth rate constant has been shown to be reduced by a factor of 50 by the addition of MgO to Al$_2$O$_3$ with lower impurity concentrations (starting powder: 260 ppm C and <65 ppm other total impurities) while being reduced by only a factor of 5 for addition of MgO to Al$_2$O$_3$ with higher impurity concentrations (starting powder: ~100 ppm). [15,16] The analyses of the final fired materials were not reported. The starting powders and processing procedures were different for the two studies. A liquid phase and lath-like shaped grains were found in the less pure material, neither of which were observed in the more pure material. This indicates that trace impurities have large effects on grain growth occurring in Al$_2$O$_3$.

Many of the problems associated with the potential improvement and understanding of ceramic materials and processes originate from their impurity contents. Due to the high intrinsic defect energies for many ceramics (e.g. Al$_2$O$_3$ has a calculated Schottky defect energy of 25 ev [17]), ppb to ppm concentrations of impurities at temperatures between 1500$^\circ$ to 2000$^\circ$ C control the defect structure of the 'pure' material. More carefully controlled experiments need to be performed on ceramics if the effects of trace impurities on properties of and processes in ceramics are to be understood. The procedures and techniques reported here are to be used in our work to optimize the calcination, deagglomeration and fabrication of this ultra high-purity alumina to determine the effect of impurities on sintering, grain growth and properties of Al$_2$O$_3$.

**SUMMARY AND CONCLUSIONS**

The clean-room powder processing and firing techniques developed in...
this work result in no detectable increase in the concentration of impurities above the levels contained in the $\text{Al}_2\text{O}_3$ powder. ( $<13$ ppm total and $<8$ ppm cation detected). This new source of $\text{Al}_2\text{O}_3$ has lower impurity concentrations than other $\text{Al}_2\text{O}_3$ sources previously reported.

Firing in a furnace without contamination of the material from the hot furnace wall can be accomplished if the sample is protected by a layer of powder.

Ultra high-purity $\text{Al}_2\text{O}_3$ has been fired without contamination using CO$_2$-laser heating.

To understand the properties of and processes in ceramic materials, procedures such as those presented here should be used to control the trace impurity contents in the material during processing and firing.

ACKNOWLEDGEMENTS

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