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Influence of Diaspore Seeding and Chloride Concentration on the Transformation of "Diasporic" Precursors to Corundum

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"Diasporic" precursors derived from sols formed by the controlled hydrolysis of aluminum sec-butoxide in the presence of HCl yielded mixtures of corundum and amorphous alumina when calcined between 500° and 800°C. The fraction of corundum in the calcined products depended on the HCl/alkoxide ratio used during hydrolysis and was maximized at 64 wt% when the molar ratio was 1. Precursors formed from sols hydrolyzed in the presence of HNO_3 rather than HCl yielded only amorphous products or transition aluminas when treated below 900°C. The corundum yield of the precursors was enhanced when they were seeded with diaspore (α-AlOOH) crystals. Precursors synthesized with an HCl/alkoxide ratio of 1 and seeded with 7.6×10^{16} diaspore seeds/(mol of Al_2O_3) were transformed to phase-pure corundum within 12 h at 700°C. Based on studies of the phase evolution of the precursors during calcining, it was concluded that the diaspore seeds promoted conversion by acting as corundum nuclei once they decomposed at ~450°C.

I. Introduction

Although corundum (α-Al_2O_3) is recognized as the thermodynamically stable polymorph of alumina at ambient pressure, the phase is not readily synthesized at temperatures <1100°C.[1–3] All the hydroxide precursors (gibbsite, bayerite, and boehmite) derivable directly from the Bayer process decompose to nanocrystalline transition aluminas on dehydration between 300° and 600°C. With increasing temperature, the metastable decomposition products progress through additional, well-documented series of transition phases until corundum is finally formed above 1100°C.[1–4] Alternative routes to aluminum hydroxides, such as basic precipitation from salt solutions and the hydrolysis of aluminum metal and aluminum alkoxides, almost invariably lead to the same hydroxides as those derivable from the Bayer process and, as a result, transition aluminas.[1–3] Similarly, transition phases are also generally formed during the direct decomposition or oxidation of aluminum salts, alkoxides, and metal organics.[1–3]

One well-known alumina precursor with exceptional dehydration behavior is diaspore, α-AlOOH. This hydroxide decomposes quantitatively to nanocrystalline corundum at temperatures as low as 450°C.[1–7] This unique behavior has been attributed to the structural similarities between diaspore and corundum.[1–3,8,9] In particular, both structures are based on hexagonal close-packed anion (O and OH) sublattices, and, therefore, the transformation is thought to require only small rearrangements of the oxygen and aluminum positions.[1–3,8] Diaspore is not generally recognized as a feasible precursor to corundum, however, because few natural sources of significant purity exist, and the phase is itself difficult to synthesize. Direct formation through the conversion of boehmite (γ-AlOOH) requires hydrothermal conditions with pressures >300 atm (>30 MPa) at 300°C, although the necessary pressure and temperature are decreased somewhat by the presence of diaspore or goethite (α-FeOOH) seed crystals during the reaction.[10,11]

Although hydrothermal conditions are required to synthesize diaspore, diaspore-like precursors that yield corundum at temperatures as low as 450°C recently have been synthesized at ambient pressure in the Al-O-H-Cl system.[12–16] Brand and co-workers[12–15] reported two different precursors that they synthesized using $AlCl_3{\cdot}6H_2O$. The first precursor, which was described as a basic aluminum chloride gel, was prepared by dehydrating viscous sols formed by dissolving partially decomposed $AlCl_3{\cdot}6H_2O$ in H_2O. The second precursor, a crystalline salt designated $AlCl_3{\cdot}2Al(OH)_3{\cdot}6H_2O$, was formed by reacting $AlCl_3{\cdot}6H_2O$ and gibbsite (γ-$Al(OH)_3$) in a closed vessel at 170°C. Both precursors yielded a mixture of corundum and amorphous alumina when they were calcined between 500° and 800°C, with corundum comprising up to 40 wt% of the products. However, corundum formation was observed only when the precursors were calcined in a fast (~500 L/h) stream of flowing gas (air or nitrogen) that facilitated removal of the precursor's decomposition products from the vicinity of the solid.[12–15] Otherwise, transition aluminas were formed at ~600°C and corundum was not observed until 1000°C.

Kamiya *et al.*[16] used an alkoxide-based approach to synthesize precursors that decomposed to corundum at or below 500°C. The basis of this process was the formation of a clear alumina sol through the controlled hydrolysis of aluminum sec-butoxide at 0°C in the presence of 0.8 mol HCl/(mol of alkoxide). After the sols were aged at low-temperature, they were transformed to solid, amorphous precursors by dehydration at 80°C. Similar to the precursors prepared by Brand *et al.*,[12–15] only a fraction (<35 wt%) of the product alumina was converted to corundum during

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calcination at or below 800°C. The balance of the solid was amorphous up to 800°C, at which point transition aluminas crystallized. Corundum formation, however, was not observed to rely on calcining in a fast stream of flowing gas, because these precursors yielded up to 35 wt% corundum during calcining in static air at ambient humidity.[16]

One of the consequences of the high temperatures required to convert the transition aluminas to corundum is that the transformation is frequently accompanied by unwanted microstructural changes. These changes include agglomeration and order of magnitude reductions in the surface areas of powder samples and the development of large-grained vermicular microstructures in monoliths.[17–20] Previous studies have explored the feasibility of lowering the transformation temperatures and controlling the microstructures of the product corundum.[20–29] These studies have shown that transformation and microstructure control can be exercised to various degrees through the use of seed crystals,[20–23] second-phase additions,[18,24–26] and appropriate choice of calcining atmosphere.[20,25,27–29] The addition of isostructural seed crystals, such as hematite (α-Fe_2O_3) and corundum, has proved to be one of the most effective routes.[20–23] For example, with α-Al_2O_3 seed additions, Bagwell and Messing[20] have quantitatively transformed γ-Al_2O_3 derived from boehmite gels to corundum in 1 h at 1050°C in dry air and at 925°C in steam. In contrast, unseeded samples require at least 7 h and 1.6 h at 1100°C in dry air and steam, respectively.

Because of the enhancing effect that isostructural seed additions have on the transformation of transition aluminas to corundum, the objective of this study was to investigate the influence of diaspore seed additions on the formation and transformation of the amorphous diaspore-like, referred to hereafter as "diasporic," precursors described by Kamiya *et al*.[16] The motivation behind the choice of diaspore seeds, rather than corundum or hematite, was the potential dual role that the seeds might serve. The first potential role was based on the hypothesis that the component of the precursor that decomposes to corundum had a structure similar to that of diaspore, as has been proposed previously.[16] If sufficiently similar, the seeds could enhance the formation of this component during precursor formation and, as a result, enhance the corundum yield of the precursor. The second potential role was based on the knowledge that the diaspore seeds would decompose to corundum *in situ* at ~450°C and, presumably, provide nuclei to promote the growth of corundum during calcination. To establish a baseline for comparison to previous work, we also examined the effect of diaspore seeding on the transformation of transition aluminas derived from a common boehmite precursor.[20–23,30,31] Although our results indicated that diaspore seeds did not significantly alter the decomposition behavior of the diasporic precursors, they did demonstrate that these precursors were significantly more susceptible to seed-assisted transformation than boehmite precursors during calcination at or below 800°C. Finally, in an attempt to enhance the yield of the precursors and gain insight into the mechanism behind corundum formation, the effect of sol/precursor chemistry on corundum yield was examined. These results indicated that chlorine was a necessary ingredient in the process and that the corundum yield could be manipulated by controlling the HCl concentration in the diasporic sol.

II. Experimental Procedure

(1) Diasporic Sol Synthesis

The diasporic sol used for the seeding experiments was prepared using a procedure adapted from that first reported by Kamiya *et al*.[16] 34.61 g (0.1405 mol) of aluminum sec-butoxide (97%, Acros Organics, Pittsburgh, PA) and a Teflon®-coated magnetic stir bar were loaded into a 500 mL wide-mouth Pyrex® flask under a flow of nitrogen-gas (UHP grade, Matheson Gas Products, Secaucus, NJ) within a glove bag (Atmosbag, Aldrich Chemical Co., Milwaukee, WI). 165 mL of absolute ethanol (200-proof, McKormick Distillery) were then gently poured on top of the alkoxide. The loaded flask was then sealed with Parafilm (American Can Co., Greenwich, CT) and immediately transferred to a constant-temperature bath ($T = 0° \pm 2°C$), where it was allowed to cool for 30 min without agitation. The container was then opened to the atmosphere and the mixture was stirred for 5 min before beginning the drop-wise addition of 129 mL of a 0.89*M* solution of HCl (p.a., Acros Organics) in deionized H_2O. Thus, the resulting sol had an HCl/alkoxide ratio of 0.82 mol HCl/(mol of alkoxide) and an H_2O/alkoxide ratio of 50 mol H_2O/(mol of alkoxide). The HCl solution was added over a period of 2 h under constant and vigorous stirring while the bath temperature was maintained at 0°C. At the conclusion of the addition, the sol was translucent and comprised of white flocks with diameters <0.25 mm. The sol was then transferred to a refrigerator, where it was peptized to clearness by stirring continuously for 8 d at 7°C. The sol was then allowed to age for another 5 d at 7°C without agitation. During the peptizing and aging steps, the flask was sealed from the atmosphere with Parafilm. The final solids concentration of the sol was determined gravimetrically by dehydrating 30 mL of the sol and then calcining the solid product at 1100°C for 12 h. The determined concentration was 0.215 mol Al_2O_3/(L of sol).

To explore the effect of diasporic sol/precursor chemistry on corundum formation, series of sols were synthesized with various HCl concentrations and with HNO_3 used in place of HCl. The procedure was identical to that described above, except smaller sol samples were prepared. Typically, these samples were one-fourth to one-fifth of the volume of the sol described above, and these preparations were conducted in 100 mL Pyrex bottles. Although the sol used for the seeding experiments and those described by Kamiya *et al*.[16] had HCl/alkoxide ratios of ~0.8 mol HCl/(mol of alkoxide), the HCl/alkoxide ratios in these sols were varied between 0.4 and 2.0. Throughout, however, the H_2O/alkoxide ratio was maintained at 50 ± 0.5 mol H_2O/(mol of alkoxide). Over the course of two months, four separate series of experiments were performed. In each of the four trials, HCl/alkoxide ratios of 0.8, 1.0, 1.2, and 1.5 were examined, and, in select trials, ratios of 0.4, 0.6, 1.8, and 2.0 were also investigated. Finally, additional series were prepared using HNO_3 (ACS reagent, Acros Organics) in place of HCl at HNO_3/alkoxide ratios of 0.6, 0.8, 1.0, and 1.2.

(2) Boehmite Sol Synthesis

The boehmite sol was prepared using a procedure similar to that previously reported by Yoldas.[30,31] 58.1 g (0.235 mol) of aluminum sec-butoxide (97%, Acros Organics) was poured directly into 400 mL of a 0.023*M* solution of HNO_3 (ACS reagent, Acros Organics) in deionized H_2O under vigorous stirring at 80°C. The flocculated suspension was then stirred uncovered for 10 min without the addition of heat. Subsequently, the sol was peptized by refluxing for 4 d at 87°C under constant stirring. The sol was then stored at room temperature for 5 d in a sealed high-density polyethylene bottle before use. The final solids concentration of the sol, determined gravimetrically, was 0.254 mol Al_2O_3/(L of sol).

(3) Diaspore Seed Sol Preparation and Characterization

The diaspore sol used for the seeding experiments was prepared by alternate cycles of ultrasonication followed by sedimentation. Coarse diaspore powder was synthesized hydrothermally and then dry-milled to a surface area of 45 m^2/g, as determined by nitrogen-gas adsorption at 77 K using the BET method.[10] 0.9502 g of the resulting powder was suspended in 100 mL of deionized H_2O and sonicated for 15 min with a horn-type ultrasonic homogenizer (Model VibraCell VC500, Sonic Materials, Inc., Danbury, CT). After the suspension was allowed to settle for 48 h at room temperature, the top most 20 mL of sol was pipetted off and transferred to a bottle for storage. The volume of the initial sol was then restored by the addition of 20 mL H_2O, and the sonication/sedimentation cycle was repeated. The entire cycle was repeated five times. The diaspore concentration in the final seed sol (comprised of the fractions pipetted off following sedimentation) was determined gravimetrically and found to be 3.30 g diaspore/(L of sol) (0.055 mol/L). This corresponded to a volume concentration, $[V]$, of 9.6×10^{-7} m^3/(L of sol), based on a diaspore density of 3.44 g/cm^3.[2]

Transmission electron microscopy (TEM; Model JEM-120 CX, JEOL, Inc., Tokyo, Japan) and atomic force microscopy (AFM; Model Autoprobe CP, Park Scientific Instruments) were used to characterize the particle-size distribution of the diaspore seed sol. This information was then used to estimate the volume-weighted number concentration of diaspore seeds in the sol, N (diaspore seeds/(L of sol)). AFM and TEM specimens were prepared by drop-depositing diluted sol on to glass substrates and holey carbon films supported on copper grids, respectively. The samples were then dried overnight at 80°C before examination. Both techniques revealed the expected platy nature of the particles with the largest faces of the plates being the characteristic {010} cleavage surfaces. To simplify characterization of the seed dimensions, the somewhat irregularly shaped {010} faces of the particles were approximated as regular rectangles. Thus, each plate (i) was approximated as a rectangular cylinder whose volume (V_i) was the product of the lateral dimensions of its {010} face, length (l_i) and width (w_i), and its thickness (t_i): $V_i = l_i w_i t_i$. Based on TEM observations of 310 seed particles, the lengths (l_i) of the particles ranged from 4 to 200 nm, with 98% <100 nm and 80% between 6 and 43 nm. The plate widths (w_i) ranged from 4 to 140 nm, with 80% between 5 and 38 nm.

Although the lateral dimensions of the plates, l_i and w_i, were easily characterized using TEM, very little information on the thickness, t_i, of the individual plates was gained because of the tendency of the plates to lay flat on the carbon support film. However, the thicknesses could be characterized to some extent using AFM. Although the majority of the particles were too small to be imaged reliably, particles with lateral dimensions >100 nm could be imaged accurately. In particular, the top surfaces of these large plates appeared flat, rather than the hemispherical shape of the end of the conical AFM tip, and individual steps were resolved on the surfaces of these particles. AFM analysis of 105 of these largest particles revealed that the thickness of each plate was approximately one-third of its longest lateral dimension: $t_i \approx l_i/3$. Assuming this relationship also held for the smaller particles, the volume of a single particle, V_i, was taken to be $V_i = w_i l_i^2/3$. The volume-weighted seed number concentration, N, of the sol was, therefore,

$$N = \frac{s[V]}{\sum_i^s V_i} = \frac{s[V]}{\sum_i^s \frac{1}{3} w_i l_i^2}$$

$$= 5.12 \times 10^{16} \text{ (α-AlOOH seeds/(L of sol))}$$

where $s = 310$ is the total number of seeds characterized using TEM and $[V] = 9.6 \times 10^{-7}$ m^3/L the volumetric concentration of diaspore in the sol.

(4) Precursor Formation and Decomposition

Solid precursors were formed from the diasporic and boehmite sols by thermal dehydration at 80°C in a gravity-circulated oven. Diaspore-seeded precursors were prepared by dehydrating composite sols formed by adding known volumes of the diaspore seed sol to the diasporic and boehmite sols just before dehydration. Seeded diasporic sols were formed by combining from 0.1 ± 0.01 to 10 ± 0.1 mL of the seed sol with 30 ± 0.1 mL aliquots of diasporic sol (HCl/alkoxide ratio of 0.82) in 100 mL Pyrex beakers. The total volume of the composite sols was then adjusted to 40 mL by the addition of deionized H_2O. Unseeded control sols were formed by combining 30 mL samples of the diasporic sol with 10 mL of deionized H_2O. Seeded boehmite sols were formed by combining from 0.1 to 20 mL of the diaspore seed sol with 25 mL samples of the boehmite sol in 100 mL beakers. Before dehydration for 15 h at 80°C, all the sols were agitated in an ultrasonic cleaning bath for 15 min to ensure dispersion of the seeds. Although Kamiya *et al.*[16] described their diasporic precursors as gels, the precursors in this study were best described as precipitates, because, during the latter stages of drying, distinct solid and liquid phases coexisted. After 15 h at 80°C, however, only a solid product remained. The boehmite precursors, on the other hand, gelled during dehydration.

The effect of diaspore seed concentration on corundum formation was explored over 3 orders of magnitude for both the diasporic and boehmite precursors. In the Results section, the seed concentrations of the precursors are reported in terms of the number of diaspore seeds per mole of Al_2O_3 in the precursor. In determining these concentrations, the Al_2O_3 contributed to the calcined products by the precursor sol and the diaspore seed additions were taken into account. The seed concentrations are also reported in terms of the weight percent of the Al_2O_3 in the calcined products attributable to the diaspore seeds.

Following dehydration, the precursors were crushed gently in an alumina mortar to produce coarse granules with dimensions of ~0.25–1 mm. The precursors were then calcined in the ambient atmosphere in a muffle furnace. The samples were held in ZrO_2–10% Y_2O_3 boats and covered with an Al_2O_3 flat during the heat treatment. The samples were ramped to the desired soak temperature at a rate of 5°C/min, held for the desired period of time (20 min to 12 h), and then cooled to room temperature at 5°C/min. Series of control samples were also calcined in Al_2O_3 boats, but there was no detectable difference in the degree of conversion between the two containers.

The decomposition of select diasporic precursors was examined using thermogravimetric analysis (TGA) and evolved-gas analysis (EGA). TGA (Model SDT 2960, TA Instruments, Inc., New Castle, DE) was performed using a heating rate of 10°C/min in an atmosphere of dry air. EGA was performed under identical heating and atmospheric conditions, but in a separate apparatus, using a mass spectrometer (Model Dycor QuadLink Q200MS, Ametek, Inc., Newark, DE).

(5) Quantitative Phase Analysis of the Product Aluminas

Quantitative powder X-ray diffractometry (XRD) was used to determine the fraction (by weight) of the solid products converted to corundum during calcination. X-ray data were collected using a diffractometer (θ-θ type, Rigaku, Tokyo, Japan) operating at 35 kV and 25 mA using a 0.05° step size in 2θ and a count time of 2 s. The NaCl standard (ACS reagent grade, Fisher Scientific Co., Pittsburgh, PA) was intimately mixed with the calcined alumina samples by grinding in an alumina mortar. The X-ray samples were then side-loaded to minimize the potential for preferred orientation in the X-ray volume. The integrated intensities of the (104) and (113) reflections of corundum (space group of $R3c$) and the (200) reflection of NaCl were determined, and their ratios were then compared with a calibration curve to determine the weight percent of corundum in each sample. The calibration curve was constructed using a sample of high-purity α-Al_2O_3 (AKP-50, Sumitomo Chemicals, Tokyo, Japan) that had been calcined at 1300°C for 6 h and then reground in an alumina mortar. The weight fractions determined using the (104) and (113) corundum peaks were always within 5% of each other, and the values presented here represent the average of the two.

The X-ray data were also used to estimate the average corundum particle size in the product aluminas, based on the broadening of the (104) corundum reflection. The crystallite size, t, was estimated using the Scherrer equation:

$$t = \frac{0.90\lambda}{B \cos \theta}$$

where λ is the wavelength of the CuK_α radiation, B the broadening of the diffraction peak measured at half its maximum intensity (in radians), and θ the peak position (in degrees θ).[32,33] B was corrected for instrumental line broadening using the following relationship:

$$B^2 = B_M^2 - B_S^2$$

where B_M is the measured breadth of the (104) reflection of the corundum and B_S the measured breadth of the (200) reflection of the NaCl standard.[32,33]

III. Results

(1) Effect of Diaspore Seeding on Precursor Decomposition

Unseeded diasporic precursors decomposed to yield corundum at temperatures as low as 450°C. Precursors synthesized from the sol with an HCl/alkoxide ratio of 0.82 yielded aluminas that contained ~28 wt% corundum after calcining for 12 h between 600° and 800°C. The balances of the solids were amorphous or very poorly crystallized aluminas. The amount of corundum formed when precursors derived from a particular sol were calcined did not vary substantially with the calcining temperature or time between 600° and 800°C and 2 and 12 h. The corundum yield was, however, dependent on the HCl/alkoxide ratio of the sol, and this dependence is addressed in Section III(3). At higher calcining temperatures, more corundum was formed, and the fraction of corundum in the samples increased with calcining temperature and time. Aluminas with up to 60 and 91 wt% corundum were formed after 12 h at 900° and 1000°C, respectively. At these higher temperatures, the balances of the solid products contained at least one transition alumina, δ-Al_2O_3. Corundum was not formed when unseeded boehmite precursors were calcined at or below 900°C. Instead, the products were poorly crystallized transition aluminas, either γ-Al_2O_3 or δ-Al_2O_3, depending on the calcining temperature.

The presence of diaspore seed crystals enhanced the formation of corundum when the precursors were calcined above 600°C. In Fig. 1, quantitative powder XRD results for a series of seeded precursors calcined for 12 h at 700° and 800°C are summarized graphically. With a diaspore seed concentration of 7.9×10^{14} seeds/(mol of Al_2O_3), a twofold increase in the corundum yield over unseeded precursors was observed. At this concentration, the seeds accounted for only 0.04 wt% of the total Al_2O_3 in the calcined sample. As was the case for the unseeded precursors, the balances of the solid products were amorphous after calcining at or below 800°C. As the seed concentration in the precursors was increased, the corundum yield increased, more rapidly at the higher temperature (800°C), and phase-pure corundum was produced within 12 h at 800°C with 7.6×10^{16} seeds/(mol of Al_2O_3). At lower calcining temperatures, the enhancing effect of the seeds was diminished. For example, after calcining for 12 h at 600°C, samples with 7.6×10^{16} seeds/(mol of Al_2O_3) contained only 38 wt% corundum, just 10 wt% more than the unseeded precursors. At 550°C, seeded and unseeded samples were essentially indistinguishable.

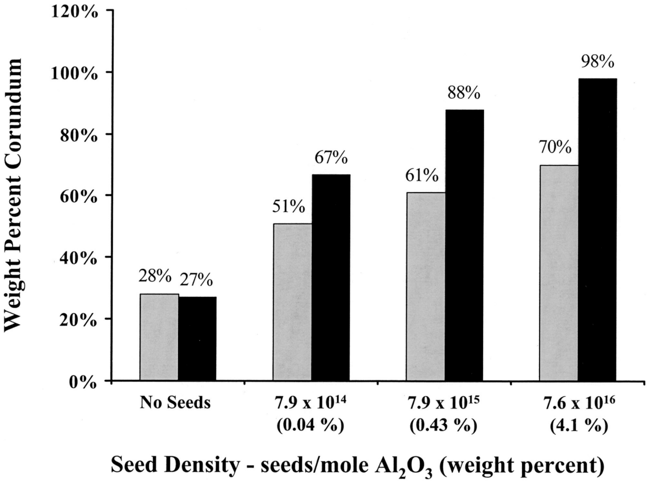

Fig. 1. Effect of diaspore seed concentration on the corundum yield of diasporic precursors calcined for 12 h at (gray bars) 700° and (black bars) 800°C. Seed concentrations are expressed in terms of diaspore seeds/(mol of Al_2O_3) and weight percent.

Diaspore seeding also influenced the size and homogeneity of the corundum particles derived from the precursors. This is illustrated in Fig. 2 with scanning electron microscopy (SEM) images of the aluminas calcined at 800°C. The corundum particles derived from the unseeded precursors (Fig. 2(a)) had dimensions ranging from 200 nm (and possibly less) to >2 μm. Although the particular area depicted in Fig. 2(a) appears to have a large fraction of corundum crystallites, these corundum-rich regions were distributed inhomogeneously through the calcined product, and other areas of the sample were free of observable crystals. As the seed concentration was increased, the particle size decreased, and the microstructures of the product aluminas took on more homogeneous appearances (see Figs. 2(b)–(d)). With 7.6×10^{16} seeds/(mol of Al_2O_3) (see Fig. 2(d)), a concentration sufficient for complete conversion, corundum particles with dimensions ranging from 30 to 120 nm were formed, as determined by direct observation using TEM. Decreased particle size with increased seed concentration was also reflected in XRD data by broadening of the corundum diffraction peaks. Based on the broadening of the (104) corundum reflection, the average particle size, t, for the various seed concentrations was 80 nm with 7.9×10^{14} seeds/(mol of Al_2O_3), 51 nm with 7.9×10^{15} seeds/(mol of Al_2O_3), and 39 nm with 7.6×10^{16} seeds/(mol of Al_2O_3).

Diaspore seeding also enhanced conversion of the boehmite precursors to corundum. However, the diasporic precursors were significantly more susceptible to seed-assisted transformation. This is shown in Fig. 3, where the degrees of conversion of diasporic and boehmite precursors with comparable seed concentrations are presented as a function of calcining time at 800°C. At seed concentrations of 7.9×10^{15} seeds/(mol of Al_2O_3), 89 wt% of the alumina derived from the diasporic precursor was corundum after 12 h at 800°C. In contrast, boehmite precursors with an equivalent seed concentration (1.5×10^{16} seeds/(mol of Al_2O_3)) yielded aluminas with only 11 wt% corundum. To achieve comparable conversions, boehmite precursors could require seed concentrations 2 orders of magnitude greater than the diasporic precursors. For example, although 7.9×10^{14} seeds/(mol of Al_2O_3) was sufficient for the formation of an alumina with 67 wt% corundum from the diasporic precursor in 12 h at 800°C (see Fig. 1), a concentration 190 times this value (1.5×10^{17} seeds/(mol of Al_2O_3)) was required to attain a comparable yield (59 wt%) with the boehmite precursor.

(2) TGA/EGA of Diasporic Precursor Decomposition

The procedures used here and by Kamiya *et al.*[16] to synthesize the diasporic precursors relied on the use of substantial quantities of HCl, i.e., HCl/alkoxide ratios of ~ 0.8. Thus, we expected some level of chlorine or HCl to be present in the precursors and, potentially, the product aluminas as well. TGA/EGA during precursor decomposition indicated that there was indeed a significant amount of chlorine in the precursors. On heating, the precursors began to lose mass and H_2O at ~100°C. This continued up to 230°C, at which point the precursors had lost ~35% of their original mass, and the evolution of water subsided. Shortly thereafter ($T \approx 250$°C), the samples began to expel HCl and continued to lose mass, although at a lesser rate. This continued up to 500°C, at which point HCl evolution and the rate of mass loss decreased, although the samples did not attain their final mass, 40.9% of the original, until they were heated above 1100°C. A conservative estimate put the fraction of precursor mass attributable to chlorine or HCl at 15 wt%. Thus, at least 70% of the chlorine introduced during sol synthesis was retained in the precursor. Seeded precursors behaved similarly, but, as the seed concentration was increased, the rate of mass loss above 300°C increased and the temperature at which the final mass was achieved decreased, indicating that chlorine was expelled at a higher rate. Precursors with the highest seed concentration investigated attained their final mass (41.0% of the original) at ~930°C.

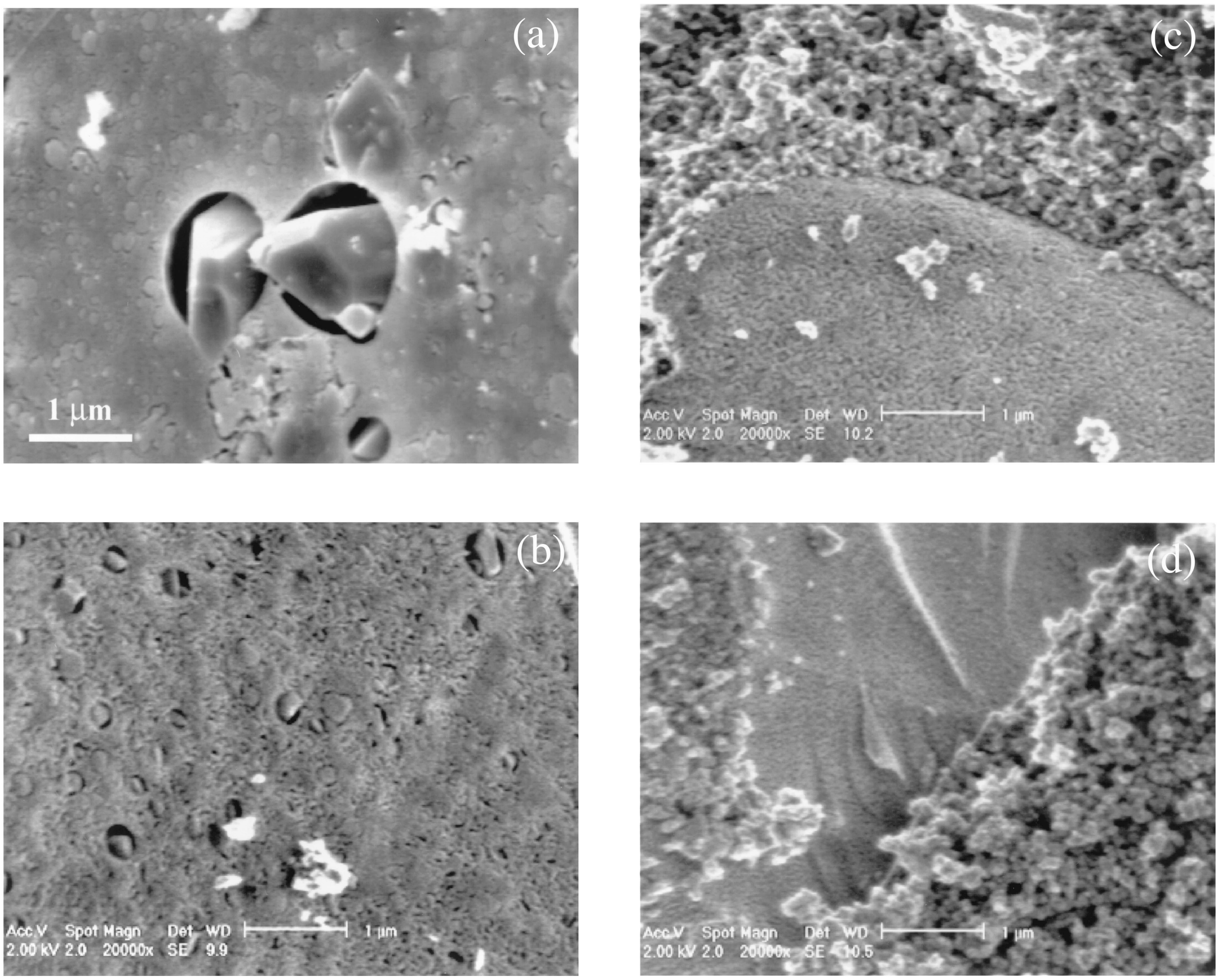

Fig. 2. SEM images illustrating the effect of diaspore seed concentration on the particle size of corundum derived from diasporic precursors calcined for 12 h at 800°C. Seed concentrations of the samples are (a) no seeds, (b) 7.9×10^{14}, (c) 7.9×10^{15}, and (d) 7.6×10^{16}. All images were acquired at the same magnification on uncoated samples using a field-emission SEM operating at an accelerating voltage of 2 kV. With increased seed concentrations, the average corundum particle size decreased (see text for a complete description). Images in (a) and (b) are of the external surfaces of calcined precursor chunks, whereas in those in (c) and (d) the smooth regions are external surfaces and the rough regions are interior portions that were exposed by fracture following the heat treatment.

Residual chlorine was detected in the energy-dispersive X-ray (EDX) spectra of some of the alumina samples that had been calcined for 12 h at 800°C. Analysis of unseeded samples indicated that 1%–2% of the anions in the alumina were chlorine, based on the assumption that oxygen and chlorine were the only anions present. With seeding and higher conversions, however, the chlorine impurity level decreased. In phase-pure corundum samples (7.6×10^{16} seeds/(mol of Al_2O_3)), chlorine levels above the background level of the SEM were not detected. Because of the large difference in the ionic radii of oxygen and chlorine, the solubility of chlorine in corundum is probably quite small, and, therefore, we anticipate that the chlorine resides in the amorphous balance of the calcined aluminas or on the surfaces of the corundum crystallites. In support of this, the refined lattice parameters of the corundum samples were unperturbed from their expected values, regardless of the chlorine impurity levels or corundum contents of the samples.

(3) Effect of Diasporic Precursor Chemistry on Corundum Formation

In the initial study of Kamiya *et al.*,[16] all the diasporic sols were synthesized using an HCl/alkoxide ratio of 0.8. Our own experiments, however, demonstrated that the corundum yield of the precursors was dependent on the HCl/alkoxide ratio used during hydrolysis. In Fig. 4, the yields (after calcining for 12 h at 800°C) of precursors from two of the four series in which the HCl/alkoxide ratio was varied are summarized graphically. These two series were chosen because they exhibited the maximum and minimum yields of the four trials. Although all the samples in Fig. 4 were calcined for 12 h at 800°C, the yields of select samples calcined at lower temperatures (down to 600°C) or for shorter times (2 h) were not significantly different.

Sols with HCl/alkoxide ratios ≤ 0.6 did not peptize, but solid precursors could be formed from the suspensions by dehydration. When these precursors were calcined at or below 800°C, an amorphous or poorly crystallized product was formed. Precursors derived from sols with an HCl/alkoxide ratio of 0.8 decomposed to aluminas with between 27 and 38 wt% corundum, more or less consistent with the sol used for the seeding experiments and the results of Kamiya *et al.*[16] The corundum yield peaked at 52–64 wt% at the HCl/alkoxide ratio of 1 but then decreased markedly as the acid concentration was increased further. Above ratios of 1.8, the precursors could take several days to dry and their calcined products appeared to be amorphous.

The underlying source of the yield variation at specific HCl/alkoxide ratios from series to series is not clear. One possibility

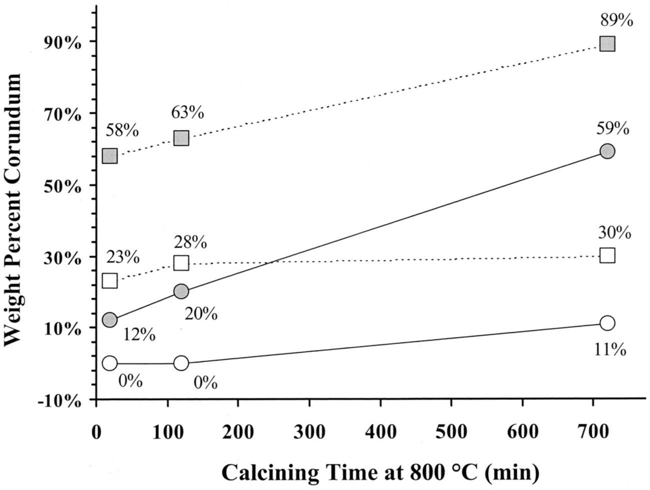

Fig. 3. Influence of seed concentration and calcining time at 800°C on the conversion of diasporic and boehmite precursors to corundum ((□) diasporic with no seeds, (■) diasporic with 7.9 × 10^{15} seeds/(mol of Al_2O_3), (○) boehmite with 1.5 × 10^{16} seeds/(mol of Al_2O_3), and (●) boehmite with 1.5 × 10^{17} seeds/(mol of Al_2O_3)). Time intervals are 20, 120, and 720 min. Lines joining the data points are intended solely to guide the eye.

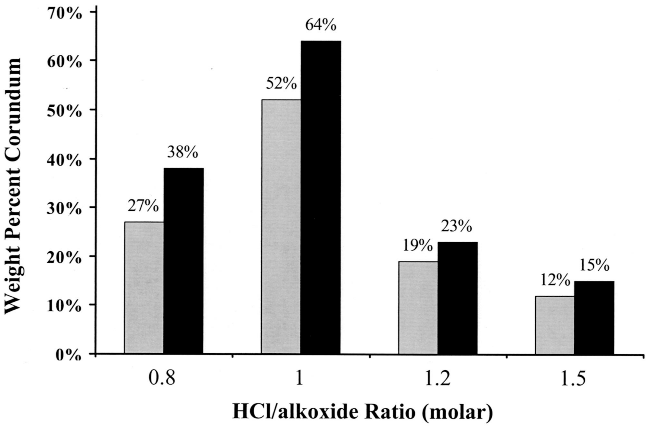

Fig. 4. Effect of sol HCl/alkoxide ratio on the corundum yield of diasporic precursors. Data presented are from two separate series in which different source alkoxides and sol-aging times were used ((gray bars) 15 d and (black bars) 5 d). All samples were calcined for 12 h at 800°C in static air at ambient humidity. These two series exhibited the maximum and minimum corundum yields observed over the course of four separate synthesis trials.

could be the purity or age of the source alkoxides. The series that yielded more corundum was synthesized using a bottle of alkoxide that was first opened just before synthesis, whereas the alkoxide used for the second series was first opened (and exposed to the atmosphere in the glove bag) a week earlier. This difference in exposure probably resulted in alkoxides that were polymerized to different extents.[31] The fact that yields of up to 38 wt% corundum (at an HCl/alkoxide ratio of 0.8) could be attained using sols that were aged for only 5 d conflicts with the observation of Kamiya *et al.*[16] that aging times in excess of 15 d were needed to realize yields greater than a few percent. This discrepancy could also reflect differences in the purity of the source alkoxides.

Series of experiments were also performed in which HNO_3 was substituted for HCl at HNO_3/alkoxide ratios of 0.6, 0.8, 1.0, and 1.2. Although the HNO_3/alkoxide sols peptized in the same manner as those synthesized using HCl, precursors derived from the HNO_3/alkoxide sols did not yield corundum when they were calcined at or below 800°C for up to 12 h. Instead, amorphous or poorly crystallized products were formed. Finally, precursors that yielded more corundum intrinsically (i.e., those derived from sols with HCl/alkoxide ratios of ~1) were also more susceptible to the seed-assisted transformation to corundum. For example, the sol/precursor that yielded 64 wt% corundum was transformed to phase-pure corundum (97 wt%) within 12 h at 700°C with 7.6 × 10^{16} seeds/(mol of Al_2O_3).

IV. Discussion

The initial choice of diaspore seeds was motivated in part by the possibility of promoting the formation of the diasporic precursor component responsible for corundum formation. This was based on the hypothesis that the component's structure, which has yet to be definitively characterized or described, might be similar to that of diaspore.[16] Based on the conversion data presented in Figs. 1 and 3, it appears that the seeds did not significantly affect the formation of the hypothesized diaspore-like component during dehydration. Although the corundum yield of unseeded precursors did not vary significantly with calcining temperature or time between 600° and 800°C and 2 and 12 h, the yields of seeded precursors clearly increased with increased calcining temperature and time. These observations indicate that the enhancing effect of the seeds is linked to a thermally activated process. Most likely, the corundum nuclei formed when the diaspore seeds decomposed provided homoepitaxial substrates for corundum growth from the amorphous balance of the product aluminas. Thus, the temperature and time dependence of conversion reflects its dependence on mass transport in the solids. The mechanism by which the seeds enhance conversion, therefore, appears to be the same as that which operates in transition aluminas that have been seeded with corundum or hematite.[20–23]

Although our results demonstrate that the diasporic precursors are more susceptible to seed-assisted transformation than the boehmite precursors, it is not immediately clear why. The development of any explanation is certainly complicated by the fact that the formation of corundum at temperatures <500°C during decomposition of the precursors is itself not understood. Based on the relationship between anion sublattice packing and the topotactic manner in which diaspore and boehmite decompose to corundum and γ-Al_2O_3, respectively, we might expect the precursor to have some structural elements similar to those found in diaspore or corundum,[1,2,5–10] for example, local regions in which the anions assume nearly hexagonal configurations. Brand *et al.*[14] proposed such elements in precursors synthesized using $AlCl_3{\cdot}6H_2O$; however, the relationship between their precursors and those described here is not clear. Apparently, the elements in the salt-derived precursors were active only when decomposition was performed in the absence of H_2O and HCl, a condition that was not observed in the alkoxide-derived precursors.[12–16]

Based on the TGA and EGA data, a substantial portion, at least 70%, of the chlorine introduced during sol synthesis was later incorporated into the solid diasporic precursors. There are several ways in which this chlorine could, potentially, enhance or bring about corundum formation. A first possibility is that chlorine or HCl acts as a mineralizer. It is well established that halogens and halo acids can act in this capacity, and their presence generally lowers the transition alumina-to-corundum transformation temperature.[1,2,28,29] A second possibility is that chlorine is an integral constituent of the precursor that helps establish a structure or local coordination environment favorable for corundum nucleation. A third possibility is that chlorine is simply a spectator during the decomposition reaction. For example, it might be the pH of the sol that is important, although this seems unlikely when the HNO_3 experiments are considered. Most difficult to explain within a mineralization framework is the peculiarly low temperature, <500°C, at which corundum first nucleates. At the same time, it is difficult to support or refute a chlorine-stabilized precursor structure, which is prone to corundum formation, with the available data.

Several factors may have contributed to the relative magnitude with which diaspore seeds influenced conversion of the diasporic and boehmite precursors. The fact that the corundum yield of unseeded diasporic precursors did not increase appreciably with calcining time or temperature (at or below 800°C) indicates that the intrinsic concentration of corundum nuclei in the precursors was less than the lowest seed density investigated, 7.9×10^{14} seeds/(mol of Al_2O_3). Thus, if the non-corundum balance (70 wt%) of the solid were simply γ-Al_2O_3, we would expect diasporic and boehmite precursors with comparable seed concentrations to have comparable yields at concentrations $>10^{16}$ seeds/(mol of Al_2O_3). This, however, was not the case, because boehmite precursors required seed concentrations 2 orders of magnitude greater than the diasporic precursors. This may indicate that the amorphous balance of the alumina derived from the diasporic precursor is thermodynamically less stable with respect to corundum than γ-Al_2O_3. Alternatively, it may also reflect kinetic differences related to the mass transport characteristics of the solids.

V. Summary

Diaspore seeding was used to hasten conversion of diasporic alumina precursors to corundum.[16] Phase-pure corundum was formed at 800°C using a seed concentration of 7.6×10^{16} seeds/(mol of Al_2O_3). The corundum agglomerates synthesized under these conditions were composed of submicrometer crystallites with sizes ranging from 30 to 120 nm. Although diaspore seeding also accelerated the transformation of boehmite precursors to corundum, seed concentrations up to 2 orders of magnitude greater were required to attain comparable yields. The corundum yield of the diasporic precursors also could be enhanced by controlling the HCl/alkoxide ratio of the precursor sols. Aluminas containing up to 64 wt% corundum could be formed directly at 600°C from sols with an HCl/alkoxide ratio of 1. With the addition of 7.6×10^{16} diaspore seeds/(mol of Al_2O_3), these precursors could be transformed to phase-pure corundum at 700°C.

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