

Conversion of Diaspore to Corundum: A New α -Alumina Transformation Sequence

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A new two-step transformation sequence has been identified for the conversion of diaspore (α -AlOOH) to corundum (α -Al₂O₃). The powder X-ray diffraction pattern of the intermediate phase, designated α' -Al₂O₃, has been indexed to a monoclinic (P2) cell, with $a = 9.566(5)$ Å, $b = 5.124(2)$ Å, $c = 9.156(4)$ Å, and $\beta = 91.76(3)^\circ$. Nuclear magnetic resonance of α' -Al₂O₃ indicates that 15–20% of the aluminum is on tetrahedral sites, with the remainder in octahedral coordination. Controlled-atmosphere high-temperature X-ray diffraction shows that water accelerates the second transformation step, α' -Al₂O₃ \rightarrow α -Al₂O₃, acting as a mineralizer for the conversion process.

I. Introduction

THE transformations of boehmite (γ -AlOOH), gibbsite (γ -Al(OH)₃), and bayerite (α -Al(OH)₃) to alumina with the corundum structure (α -Al₂O₃) occur via an extensively studied series of transition aluminas.^{1,2} By contrast, the mechanism by which diaspore (α -AlOOH) transforms to corundum is not well understood. It is commonly stated that the nearly close-packed-hexagonal oxygen sublattices in both diaspore and corundum permit a topotactic transformation with little atomic rearrangement.^{1–3} The actual process, however, requires that one quarter of the oxygen atoms be removed and that the hexagonal sublattice then be restored. Earlier studies have noted that dehydrated diaspore sometimes shows diffraction events that are not consistent with either the diaspore or corundum cell.^{4–6} Based on the experiments reported here, we propose that under appropriate processing conditions, a two-step transformation occurs. The first step consists of H₂O removal and progressive shear, resulting in a new observed transition alumina designated α' -Al₂O₃. The second step involves diffusion of aluminum atoms to produce the corundum structure. Processing under vacuum allows the evolution of the structure to be observed, and produces α' -Al₂O₃ and α -Al₂O₃ materials with unusually high surface areas that may be valuable in catalytic applications.

II. Experimental Procedure

The availability of natural diaspore is limited, and thus the starting material utilized in this work is a synthetic, pure dia-

spore fabricated hydrothermally at 300°C and 3.45×10^7 Pa (5000 psi) over a 72 h period. Subsequent processing⁷ led to the observation of the new transitional alumina described in this report. In order to obtain nanocrystalline alumina as an end product, the softer diaspore crystals, which exhibit (010) cleavage, were ground prior to annealing. The conversion was carried out under vacuum (10^{-5} torr) or in air at temperatures ranging from 300° to 1000°C. Initial phase identification was carried out by X-ray diffractometry (XRD). One difficulty in obtaining reliable data for the α' phase is that the nanocrystalline grain size results in broad peaks which include significant overlap. In addition, it is difficult to obtain single-phase material, and most samples contain a mixture of diaspore and α' -, α' - and α -alumina, or all three (diaspore, α' , and α). Furthermore, because of the structural similarities, many interplanar spacings of α' are nearly the same as those of corundum.

Specimens were prepared for transmission electron microscopy (TEM) evaluation by depositing drops of a solution of a powder consisting of α' - α mixtures on thin carbon films supported by copper grids. The samples were examined in a Philips 420T operating at an accelerating voltage of 120 kV. Diffraction information on the transition phase was obtained by generating a selected-area diffraction pattern from an area including many particles or fragments, using a small objective aperture to isolate an individual reflection that did not arise from corundum, performing dark-field imaging with that reflection to locate the corresponding α' grain, and then obtaining a microdiffraction pattern from that specific grain.

The site occupancy of Al during the transformation was assessed by nuclear magnetic resonance (NMR). The intensity and shape of NMR spectra of quadrupolar nuclei (such as Al) depend critically on the static magnetic field strength, rf pulse width, and relaxation delay employed. The resulting difficulty of Al quantitation is well-recognized.^{8,9} For this reason, comparative measurements were performed at several field strengths (7.05 and 14.1 T), pulse widths, and relaxation delays to ensure that the NMR data were quantitative. In every case, the calculated percentages of T_d and O_h aluminum sites obtained were within 1.5% (absolute) of each other, essentially matching the expected inherent error of the NMR measurements.

III. Results and Discussion

Very little decomposition of diaspore occurred upon heating under vacuum at 350°C for periods of up to 130 h, as is evident from the XRD data in Fig. 1(a). Upon further treatment at 400°C, however, the transformation proceeded (Fig. 1(b)) and the powder was composed of a mixture of the α' transition

T. E. Wood—contributing editor

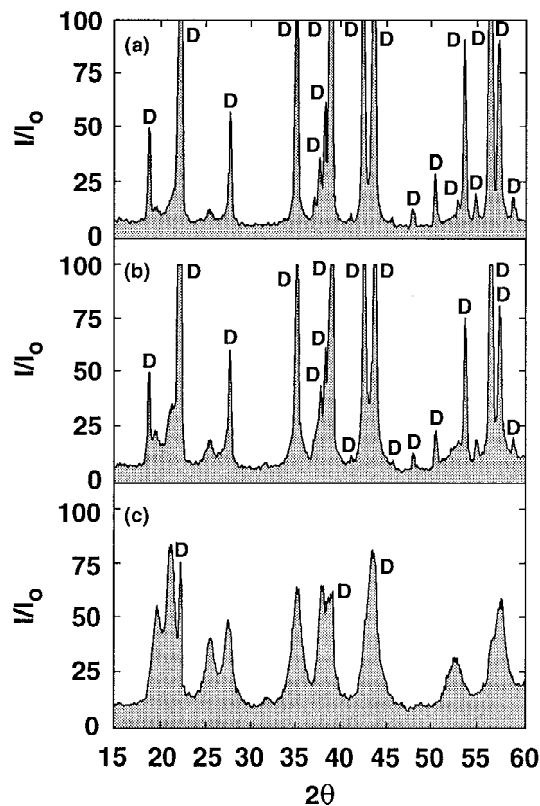


Fig. 1. X-ray diffraction patterns of diaspore transformation under vacuum to α' - Al_2O_3 ; D = diaspore, remaining peaks are from α' - Al_2O_3 : (a) Diaspore, essentially unchanged after 130 h at 350°C; (b) diaspore treated at 400°C for 17 h, showing the initial formation of α' - Al_2O_3 ; (c) diaspore of (b) further treated at 400°C for a total time of 89 h, showing a large amount of α' - Al_2O_3 (for this sample, ^{27}Al -NMR shows 16.5% tetrahedral aluminum).

phase with residual diaspore after 89 h (Fig. 1(c)). Diaspore annealed for a total of 138 h under vacuum at 400°C had been converted to a substantial amount of α' and some corundum (Fig. 2(a)). Higher-temperature exposure of the latter material completed the conversion to pure corundum (Figs. 2(b) and (c)). Annealing in air rather than under vacuum causes a direct and more rapid transformation from diaspore to corundum in which the intermediate α' -alumina is not detected by XRD. Samples consisting primarily of α' created by vacuum annealing can also be converted to corundum by a relatively brief anneal in air (~4 h at 500°C). Additionally, the α' - Al_2O_3 is observed when diaspore is dehydrated at the same temperature with dry air being circulated through the furnace, although the observed X-ray intensities of the α' - Al_2O_3 peaks were not as high as those obtained upon vacuum dehydration of diaspore.

It was thus suspected that the isolation of α' - Al_2O_3 in air was prevented by the presence of water vapor which catalyzes the transformation to corundum. This transition step, α' - $\text{Al}_2\text{O}_3 \rightarrow \alpha$ - Al_2O_3 , was studied with high-temperature X-ray diffraction in four different environments: vacuum, dry air, air (rh = 40–50%), and water-saturated air. The transformation kinetics (Fig. 3) were determined by using sample material produced by vacuum dehydration of diaspore at 400°C for 138 h, and monitoring its further conversion. The initial material was thus primarily α' - Al_2O_3 (the actual amount of this phase versus α - Al_2O_3 could not be specified because the atomic locations in α' - Al_2O_3 , and thus the structure factors, were unknown and because peaks for corundum also contain contributions from the transition phase). The percent of α' - Al_2O_3 converted upon further treatment at 475°C was then calculated by measuring the reduction in intensity of the peak at $2\theta = 21.25^\circ$, which appears only for α' - Al_2O_3 . Generation of α' - Al_2O_3 and

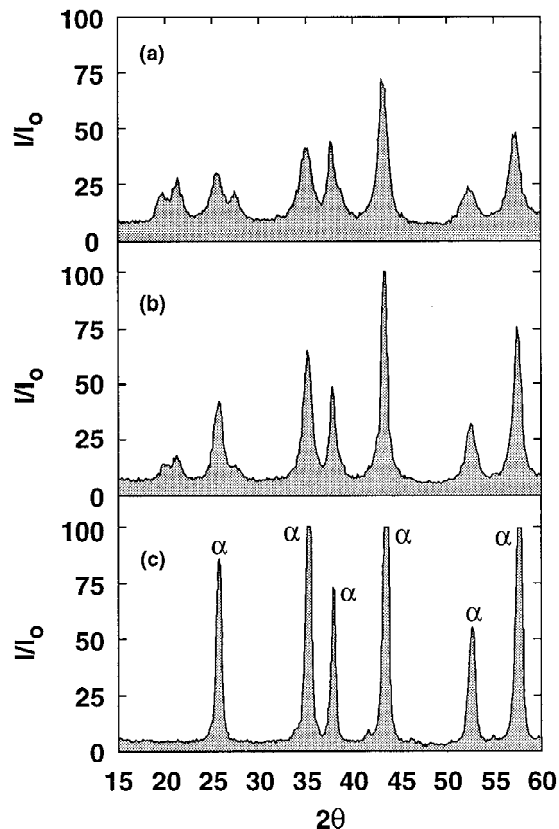


Fig. 2. X-ray diffraction patterns of the α' - Al_2O_3 to α - Al_2O_3 transformation under vacuum; $\alpha = \alpha$ - Al_2O_3 , while α' - Al_2O_3 contains the extra reflections observed in addition to ones which overlap with those of α - Al_2O_3 : (a) XRD after annealing of diaspore at 400°C for 138 h; (b) additional treatment of the same sample at 600°C for 24 h; (c) further treatment of the same sample at 800°C for 25 h.

α - Al_2O_3 by low-temperature annealing under vacuum results in nanocrystalline grain size with surface areas in excess of 100 m^2/g .

Both the diaspore and corundum structures, which are the end members of this transition series, contain only octahedrally coordinated aluminum. In contrast, nuclear magnetic resonance data defining the aluminum position in α' - Al_2O_3 show two resonances for the aluminum ions in the structure: an octahedral position (chemical shift ~0 ppm), as expected, and also a tetrahedral site (chemical shift ~60 ppm). Interestingly, the increases in the percent of tetrahedral aluminum observed in the NMR spectra correlate with the increases in the intensities of the additional X-ray reflections associated with the α' structure (Fig. 4). The relationship between these quantities (% Al_{tet} vs $I_{\alpha'}/I_{\alpha}$) exhibited a linear correlation ($r = 0.98$) for seven samples over the range 0–20% Al_{tet} . This indicates that after dehydration of diaspore in the absence of water catalysis, the intermediate structure contains 15–20% tetrahedral aluminum which is subsequently eliminated by diffusion of aluminum to the octahedral sites of corundum. This last transition step can be activated thermally at higher temperature or catalyzed by water vapor.

Transmission electron microscopy (TEM) was also used to confirm the presence of the intermediate α' - Al_2O_3 material. As an example, the single-crystal microdiffraction pattern shown in Fig. 5 provides a clear demonstration that a distinct transitional phase, structurally similar to corundum, was present. The six outer reflections correspond closely to the positions of the $\{11\bar{2}0\}_c$ reflections that would be present for corundum viewed along the $[0001]_c$ direction, but two additional reflections are present indicating a set of lattice planes parallel to $(11\bar{2}0)_c$ but with approximately double their interplanar spacing. Since cor-

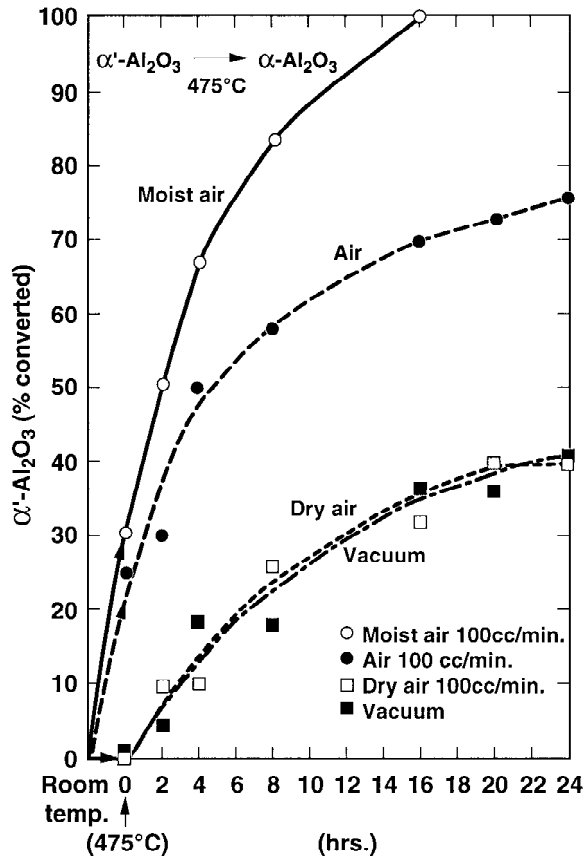


Fig. 3. Conversion of α' - $\text{Al}_2\text{O}_3 \rightarrow \alpha\text{-Al}_2\text{O}_3$ using high-temperature X-ray diffraction and an α' - Al_2O_3 sample preformed by vacuum dehydration. Conversions are performed at 475°C ; the four environments are moist air, room air ($\text{rh} = 40\text{--}50\%$), dry air, and vacuum. Heating rates are $5^\circ\text{C}/\text{min}$. The arrow tips at $t = 0$ indicate the extent of conversion upon heating of the X-ray furnace from room temperature to 475°C .

responding half-order diffraction maxima are not seen for the other $\{1120\}_c$ -type reflections, the sixfold symmetry of the pattern is destroyed. An orthorhombic (or lower symmetry monoclinic) structure is thus indicated for the unit cell of the transition alumina. (Note that the asymmetric intensity of the diffraction spots is primarily due to a slight tilt from the exact zone axis direction; the small size of the individual crystals ($\sim 10\text{--}20\text{ nm}$) makes it difficult to precisely align the beam along a crystallographic axis.) Further TEM diffraction results showed reflections at d_{hkl} values of 5.1, 4.75, and 4.17 Å in addition to those expected for corundum. The cell dimensions and X-ray diffraction pattern indexing are given in Table I. In this (conventional) setting for the monoclinic unit cell (slightly off orthorhombic, with $\beta = 91.76^\circ$), $a_{\alpha'}$ is parallel to a_d and the c -axis of corundum.

Intermediate states have been observed in prior work⁵ on dehydration of diaspor, although subsequent workers have suggested that the diffraction phenomena seen arose from periodic porosity.⁶ The available data indicate that the α' - Al_2O_3 phase described in this report is distinct from the transition structures reported earlier. The presence of α' - Al_2O_3 is most readily apparent in our work by the development of well-defined Bragg peaks in powder X-ray diffraction. These specific diffraction events were not reported by Lima-de-Faria⁵ or Watari *et al.*,⁶ despite their detection of satellites and diffuse halos in single-crystal X-ray rotation photographs and TEM diffraction patterns. In the case of Lima-de-Faria, the satellites in the X-ray photographs indicate a periodicity of about 39 Å in the direction parallel to the c -axis of the final corundum structure, which is not consistent with the unit cell that we have

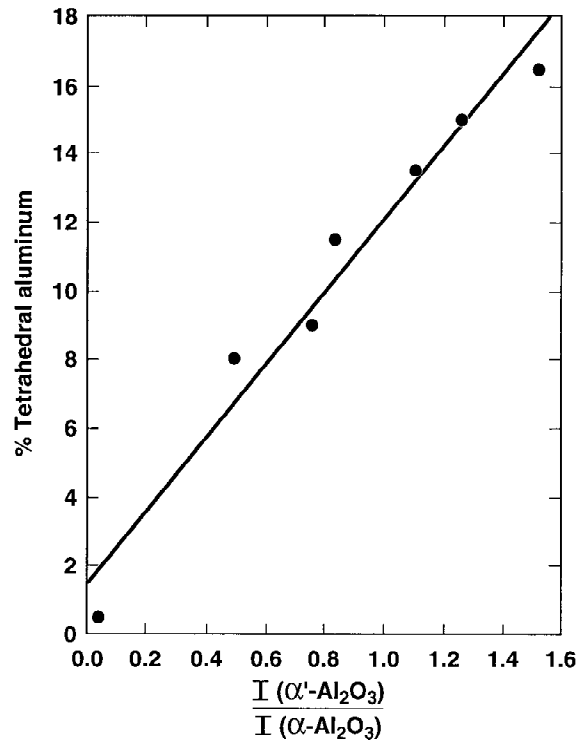


Fig. 4. Percentage of tetrahedral aluminum as determined by ^{27}Al NMR versus the ratio of the X-ray intensity of a distinct α' - Al_2O_3 peak ($2\theta = 19.6^\circ$) to an $\alpha\text{-Al}_2\text{O}_3$ peak ($2\theta = 25.5^\circ$). This indicates the correlation of the additional reflections to the aluminum occupancy of the tetrahedral sites in the hexagonal close-packed oxygen sublattice.

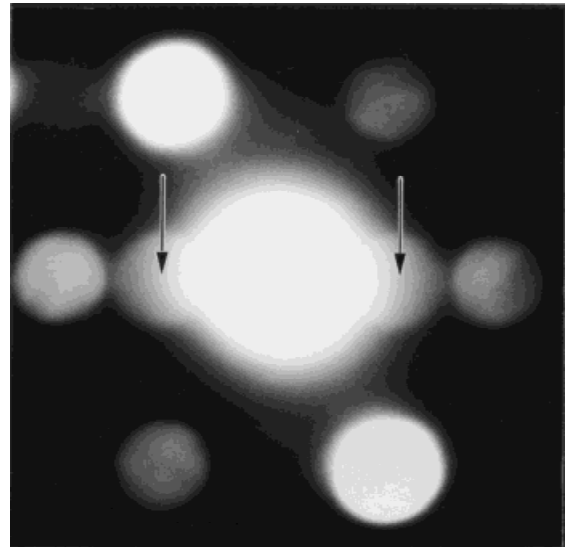


Fig. 5. Electron microdiffraction pattern of a single grain of α' - Al_2O_3 along approximately the a -axis of the unit cell (corresponding to the $[0001]_c$ axis of corundum). Additional reflections at one-half the reciprocal lattice spacing of the $(1120)_c$ planes (arrowed) break the threefold crystal symmetry and indicate a larger unit cell for the transition phase.

derived for α' - Al_2O_3 . Notably, while the first three layer lines for corundum (containing hkl reflections for $l = 1, 2, 3$) and the first layer line for diaspor ($h = 1$) are clearly observed and can be used to calibrate the vertical displacement coordinate ζ , the additional ($h = 1$) layer line at $\zeta \approx 0.202$ corresponding to the a -axis magnitude of the α' - Al_2O_3 phase is not present. Furthermore, the diffraction periodicities for α' - Al_2O_3 in our

Table I. Indexing of X-ray Powder Diffraction Data for α' -Al₂O₃[†]

h	k	l	2 θ values (deg)		I/I ₀ (%)
			Calculated	Observed	
1	1	0	19.64	19.64	54
1	0	$\bar{2}$	21.25	21.26	74
2	1	0	25.46	25.46	42
2	1	$\bar{1}$	27.50	27.49	45
2	1	$\bar{2}$	31.82	31.66 [‡]	4 [‡]
0	2	0	35.00	34.99	61
1	2	$\bar{1}$	37.70	37.72	74
2	1	$\bar{3}$	38.71	38.66	51
4	0	2	43.20	43.21	100
4	2	0	52.30	52.29	31
3	0	$\bar{5}$	57.21	57.22	58
4	2	4	66.54	66.55	36
4	2	4	68.19	68.18	45

[†]Miller indices are based on the calculated unit cell parameters of $a = 9.566(5)$ Å, $b = 5.124(2)$ Å, $c = 9.156(4)$ Å, and $\beta = 91.76(3)^\circ$, obtained with an error of fit = 2.04. [‡]Diffuse peak, not used in calculation of lattice parameters. When included, error of best fit increases to 6.11.

XRD studies are fixed and do not vary or evolve with further time at elevated temperatures or with orientation. This is in contrast to the pore coarsening observations of Watari *et al.*,⁶ in which the periodicity of satellite spots in electron diffraction patterns changed as the porosity coarsened and the modulation period became larger, and the satellite spacing was also a function of the incident direction of the electron beam.

It is not surprising that α' -Al₂O₃ was not found in the prior studies, since in those cases diaspore was heated in a moisture-containing ambient or with little control over temperature (beam heating within a TEM). In the present experiments, α' -Al₂O₃ is only detected under carefully controlled dehydration in a dry environment. Note also that the models described in the earlier investigations are not consistent with the present observations. While a cation concentration wave or a quasi-periodic textured porosity could lead to diffraction events representing large (30–50 Å) periodicities, higher-order diffraction from such “superstructures” would not be observed as distinct diffraction events at shorter periodicities due to the irregular and/or incommensurate spacings involved.

From the present evidence, two distinct steps can be identified in the transformation of diaspore to corundum under vacuum. In the first step, the dehydration of diaspore leads to the formation of the transition phase, α' -Al₂O₃. Based on experimental weight loss data, this phase is anhydrous. The second step, which is catalyzed by the presence of water vapor, must involve a localized atomic rearrangement in which the tetrahedrally coordinated Al in the α' -Al₂O₃ structure move to octahedrally coordinated sites in the corundum structure. Considering the fact that the O atoms in the two end members of the transition series (diaspore and corundum) both have a hexagonally close-packed arrangement, the complete destruction and reformation of the sublattice should be unnecessary. In fact, considering the low temperature at which the reaction occurs, long-range diffusion seems unlikely. Thus, it is suspected that the O atoms in the transition phase, α' -Al₂O₃, also have a (nearly) hexagonal arrangement with four close-packed layers stacked along the a -axis in each unit cell. It is possible that the mechanism by which α -AlOOH is dehydrated to form

α' -Al₂O₃ is directly analogous to the mechanism by which TiO₂ is reduced to Ti₂O₃: removal of lattice O (or water in the case of the dehydration reaction for alumina), followed by crystallographic shear.¹⁰

The diffraction data for the α' -Al₂O₃ transition phase is limited (due to the metastable nature of the phase, peak overlaps with corundum, and nanocrystalline grain size), and so an absolute determination of atomic positions is problematic. A model relying on the shear mechanism is being refined to adequately map the transformation from the structure of diaspore (containing all octahedrally coordinated aluminum) through dehydration and shear resulting in α' -Al₂O₃ (containing 15–20% tetrahedrally coordinated aluminum) to the final corundum structure (again containing only octahedrally coordinated aluminum). Given the experimental difficulties with direct structural determination, this shear model approach holds the most promise for establishing accurate atomic positions in α' -Al₂O₃.

Recent quantum-mechanical calculations predict alumina phase transformations at high pressures,¹¹ but the α' -Al₂O₃ phase observed during vacuum dehydration does not correspond to any of the postulated high-pressure polymorphs. Prior work on alumina transformations has demonstrated that a wide variety of transitional aluminas are possible. In light of earlier findings on the formation of the rho phase (ρ -Al₂O₃) in vacuo from gibbsite and bayerite,² the identification of α' -Al₂O₃ suggests that further investigation of controlled vacuum dehydration of alumina precursors is warranted. Characterization of dehydration products by NMR, X-ray diffraction, and more localized techniques such as electron microscopy may help to isolate intermediate phases in the transitional alumina series.

Acknowledgments: We acknowledge helpful discussions with and comments from C. Misra, M. L. Weaver, A. Pearson, and G. L. Messing.

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