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High-Resolution TEM Observations of γ-Al_2O_3 in Transition Alumina Films

Transition aluminas are widely used as catalyst supports, adsorbents, catalysts, and co-catalysts. Much of their special surface chemistry is attributed to defect acid sites which apparently occur during dehydration of the aqueous gels from which they are usually formed and dehydroxylation of the oxyhydroxides which are their precursors.

Little is known in detail about the crystal structure of these materials. For example, γ-alumina is known to be an "imperfect" or "defect" spinel, but the specific atomic arrangement has not yet been determined. Two primary reasons for this structural uncertainty are that: (1) no large single crystal specimens are available for a complete diffraction study and (2) the material of interest to catalysis is poorly crystallized by virtue of its high intrinsic surface area.

This note reports on high-resolution transmission electron microscope (TEM) studies of γ-alumina films grown on cold-rolled, polycrystalline aluminum sheet by thermal oxidation. The alumina films were prepared by baking the aluminum at 863 K for 3 h, cooling in air, chemically removing the oxide using a mercuric chloride solution, and picking up pieces of the oxide on TEM grids.

This preparation produced dense oxide films which were often highly twinned. The film was identified as γ-alumina using a large selected area diffraction (SAD) aperture; there were no extra strong rings in the powder-like diffraction pattern. Figure 1 shows a bright field image and SAD pattern from a small area of the oxide film. The large dark grains in this micrograph have a $\{110\}$ plane parallel to the surface of the TEM foil. The arrow indicates an area containing twin planes aligned parallel to a $\{111\}$ plane of the oxide. The twins are a prominent defect in crystalline oxide films that have been grown on a variety of aluminum substrates.

The high-resolution electron microscope (HREM) image shown in Fig. 2 was obtained from the dark area at the bottom of Fig. 1. This micrograph is formed by allowing only the transmitted beam, the $\{111\}$, and the (kinematically forbidden) $\{200\}$ beams to contribute to the image. Although the relationship of the high-resolution image to the actual atomic positions in the lattice can only be determined by dynamical electron scattering simulations (*1*, *2*), certain features of the oxide lattice are evident, by inspection. For example, the rows of white dots are 4.6 Å apart which corresponds to twice the interplanar spacing of the $\{111\}$ planes of oxygen ions in the γ-alumina lattice. In the $\{110\}$ projection, two sets of $\{111\}$ planes are parallel to the electron beam. Such a lattice image does not directly give any information concerning the actual surface configuration of the species exposed at the $\{110\}$ surface of the thin film. It does, however, give information about the order along directions nearly perpendicular to the axis of the electron beam. For example, the arrow in the HREM image indicates a narrow planar defect which resembles a diffuse stacking fault; broader planar defects are evident in other parts of the image. The particular area shown in Fig. 2 has been selected because it depicts a major defect structure that occurs in these γ-alumina films. Even within the macroscopically well-ordered grains, there are

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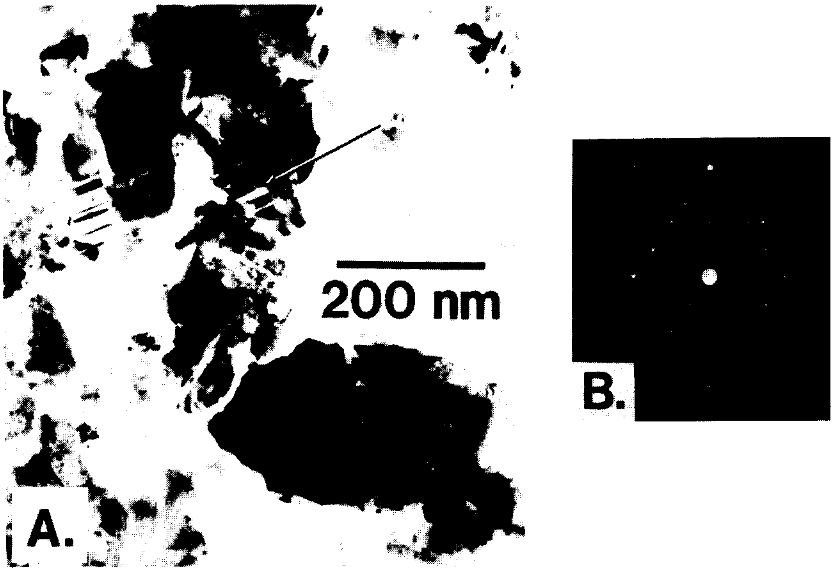

FIG. 1. (A) Bright-field image of γ-Al_2O_3 grown on cold-rolled, polycrystalline aluminum sheet by thermal oxidation. (B) Selected area diffraction pattern, γ-Al_2O_3 in {110} orientation.

only limited areas that approach perfect crystallinity at the atomic level. These nearly perfect crystalline regions are only 40–60 Å in size and comprise only 50–60% of the total area of the film. The results of the present study can be compared with the earlier work of Wilson (*3*) who presented lattice images of γ-alumina formed from aqueous gels. In that study, the areas displaying lattice fringes were only a few (15–20) percent of the field and well-crystallized regions were at most 10–15 Å in diameter.

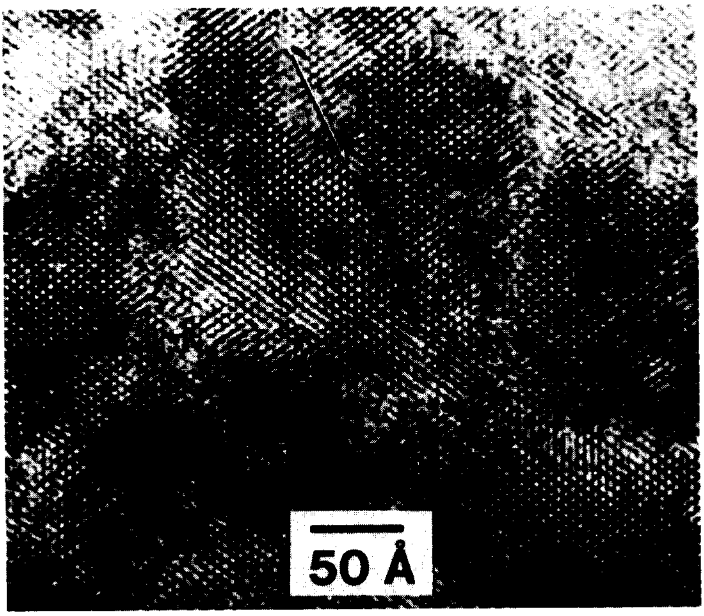

FIG. 2. High-resolution electron microscope image from a grain of planar γ-Al_2O_3 with {110} orientation.

The present observations are the first published high-resolution images of the detailed defect structure of planar γ-alumina of uniform thickness.

It is not prudent from this work to assert that the films produced by thermal oxidation on polycrystalline aluminum have a structure and surface chemistry similar to those aluminas that are synthesized from hydrous gels. Some of the defects, for example, may be caused by defects in the metal substrate. However, in this study a variety of different substrates, including those with the low index faces of well-ordered single crystals have been used, and it was found that the morphology of the oxide layers is in general independent of the mechanical history of the metal surface from which it was grown. The size of the alumina grains are always smaller by a factor of 10 or so than those of the metallic substrate. Therefore, even those layers grown on polycrystalline metals have been grown on "single crystal" substrates. Mechanical polishing of the aluminum surface before oxidation produces smaller grained oxides than those grown on surfaces of unpolished rolled stock. All of the oxide grains, however, are large on the scale of the highly ordered crystalline areas of 40–60 Å shown in the lattice image of Fig. 2. It is therefore believed that the major features shown in this lattice image are not dependent on the substrate and preparation procedures. More complete details on the effect of the substrate on the morphology of the resulting oxide can be found elsewhere (*4*).

It is only possible to speculate at this point on whether the fabled defects giving rise to acidity reside within the crystalline regions, within the disordered regions, at twin planes, or at some other less prominent lattice defect yet to be identified. Such planar samples can be studied, however, with the impressive array of spectroscopic techniques now routinely used in modern surface science. Their surface chemistry can be explored and compared to that of the more conventional aluminas, and they can be used as model substrates for supported catalyst systems. As an example of the latter, we have already reported a preliminary study of molybdenum particles on planar transition alumina and on α-Al_2O_3 produced thermally within a transition alumina matrix (*5*). The Mo crystallites were shown to be three-dimensional faceted particles in registry with the α-Al_2O_3 substrate that are two to three times larger on α-alumina than they are on the transition alumina.

Only after a considerable amount of research along these lines will it be possible to associate the structural details of these materials with those of the high surface area aluminas common to catalytic practice. A more complete review of the possible use of planar aluminas as model catalysts and catalytic supports is available (*6*).

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KAREL K. CZANDERNA
KAREN J. MORRISSEY
C. B. CARTER
ROBERT P. MERRILL*

Department of Materials Science
*and *School of Chemical Engineering*
Cornell University
Ithaca, New York

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