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Design of Pores in Alumina

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Various procedures are suggested for obtaining alumina foils containing parallel cylindrical pores of uniform diameter over the size range of 1.5–20 nm. Pores larger than 6 nm are obtained by anodizing aluminum foils in solutions of sulfuric acid at low temperatures and subsequently etching them in a phosphoric acid solution. Smaller pores are obtained by anodizing 30–60-nm-thick aluminum films at low temperatures in a dilute sulfuric acid bath or in a bath containing a mixture of sulfuric and tartaric acids.

Porous aluminas can be prepared by chemical precipitation of aluminum hydroxide followed by dehydration at high temperatures. This method of preparation leads to pores with radii ranging from less than 2 to 20 nm (*1*). The size distribution of the pores cannot be controlled in this preparation. Aluminas can also be obtained by anodizing aluminum sheets in different electrolytes. They will be porous or nonporous, depending on the anodization conditions (*2*). For example, when prepared in the presence of aggressive electrolytes (sulfuric acid, phosphoric acid, oxalic acid, etc.), the aluminas are porous (*3*), while preparation in the presence of tartaric acid produces aluminas which are nonporous (*2*). The size and the density of the pores depends upon the nature of the electrolyte, the temperature, and the applied voltage (*4, 5*). The pores produced so far have been parallel to each other and closed at one end by a nonporous film (*3–5*). They generally have had distorted cylindrical shapes and average radii larger than 6 nm. Rai and Ruckenstein (*6*) have used the anodization procedure to prepare aluminas from aluminum foils containing essentially cylindrical parallel pores which penetrate the entire foil.

This paper is concerned primarily with the control of the size of the pores. If the size, shape, and density of the pores can be controlled, the aluminas can be very useful not only in the characterization of the effect of transport phenomena in porous catalysts upon the kinetics but also in the control of size-sensitive reactions (dependent, for instance, upon the size of the metal crystallites in the supported metal catalysts) or perhaps even for shape-selective catalysis. These techniques can also provide materials useful for calibrating pore size distribution methods.

As indicated above, the size of the pores can be affected by the nature of the electrolyte and the temperature of the bath. For instance, a solution of 4 wt% phosphoric acid at 24°C leads to pores of 16.5 nm, while a solution of 15 wt% sulfuric acid at 10°C leads to pores of about 6 nm (*3*). The pore density can be influenced by the applied voltage; higher pore density is obtained by lowering the

voltage. Consequently, the control of the size of the pores can be carried out by selecting an electrolyte (or a mixture of electrolytes, perhaps even a mixture composed of an electrolyte which leads to porous aluminas with one which leads to nonporous aluminas), the temperature and, as will be shown, the thickness of the foil. The pores obtained from thick foils after anodization have distorted cylindrical shapes which can be improved by etching. The etching makes the shape more cylindrical but increases the radius.

EXPERIMENTAL

Preparation of the aluminas. The alumina was obtained by anodizing aluminum sheets of 30-nm–2.5-μm thickness in different electrolyte solutions. Before each experiment the solutions were cooled in a refrigerator and maintained at 0°C during the anodization process. The aluminum sheets of 2.5-μm thickness were purchased from Ventron Corporation and precleaned with acetone before anodization. The very thin aluminum films of 30–60-nm thickness were prepared by vapor deposition of 99.999% pure aluminum in an Edwards high vacuum coater unit at 10^{-6} Torr. Before the aluminum was deposited, Victawet (purchased from Ernest F. Fullam, Inc.), was deposited as a first layer on a microscope slide in order that after anodization the alumina film could easily be removed by dipping the slide in distilled water.

In the electrolytic cell, the aluminum sheet forms the anode and stainless steel the cathode. The distance between the electrodes was 5 cm. The voltage was controlled between 20 and 45 V using a dc power supply (Model 6200B from the Hewlett–Packard Company). The current density varied for different operating conditions. For instance, for the aluminum sheets of 2.5-μm thickness anodized in 5 wt% sulfuric acid at 20V, the initial current density was 0.8 mA/cm². This dropped off continuously, but slowly, to zero when the aluminum was completely anodized. For very thin aluminum films, less than about 100 nm, the current density dropped instantaneously to zero when the circuit was connected. The time of anodization varied from 2 to 35 min. The porous aluminas obtained were closed at one end by a layer of nonporous alumina.

Specimen preparation for electron microscopy. After anodization, the aluminas of 2.5-μm thickness had to be thinned in a 48 wt% phosphoric acid solution at 60°C for several minutes to decrease their thickness below 100 nm to make them suitable for examination by transmission electron microscope. The etching process enlarged the size of the pores and dissolved the nonporous film which closed one of the ends of the pores. The thinned aluminas were picked up on grids and washed in distilled water for several minutes. Following the washing the film was picked up once again on the grid. Specimens prepared by the vapor deposition method were cut into several small parts and dipped in distilled water. The alumina films floated off the slide were picked up on the grids. All the specimens were held at 300°C and 10^{-6} Torr for several minutes in the Edwards vacuum coater and then stored under vacuum at room temperature to avoid contamination.

RESULTS

Figure 1 is a micrograph of an alumina obtained from a 2.5-μm-thick aluminum sheet anodized at 20 V in a bath of 10 wt% sulfuric acid. The whole sheet was anodized completely in 35 min, after which it was removed from the bath and etched chemically for 3 min at 60°C in a 48 wt% phosphoric acid solution. The micrograph shows that all the pores are parallel cylinders which are rather uniformly distributed. The average radius of the pores

is 20 nm, which is larger than the size reported previously (*3*). The enlargement of the pores is caused by the chemical etching. The pores shown in the micrograph in Fig. 2 were produced by anodizing a 2.5-μm-thick aluminum foil at 20 V in a bath of 5 wt% sulfuric acid for 25 min. The unanodized aluminum was removed by dissolution in a concentrated $HgCl_2$ solution. The average radius of the pores before etching was 6.6 nm and after etching for 3 min in a 48 wt% phosphoric acid solution 11.4 nm (see Fig. 3). The etching also dissolved the nonporous layer of alumina located at one end of the pores. Thus, after etching, the pores extend across the whole thickness of the alumina; they also posses a more cylindrical shape. The pores are arranged in some order, each pore having six close neighbors. The density of the pores in the two micrographs shown in Figs. 2 and 3 is the same (112×10^9 pores/cm^2), which indicates that the chemical etching does not create new pores. Figure 4 is another micrograph showing the microstructure of a porous alumina produced in the same way as the one in the micrograph shown in Fig. 3 but with an anodizing voltage increased to 25 V and a 2-min chemical etching in a 48 wt% phosphoric acid solution. The average radius of the pores in this film is 8.4 nm and the pore density (89.9×10^9 pores/cm^2) is 20% less than that of the alumina shown in the micrographs in Figs. 2 and 3. Pores with radii smaller than 6 nm were obtained by anodizing very thin (30–60 nm) aluminum films prepared by the vapor deposition method. When aluminum films of about 60-nm thickness were anodized for 2 min at 20 V in a bath of 5 wt% sulfuric acid, pores with 3.4-nm radii were obtained (see Fig. 5). The pores are distributed rather uniformly and have well-defined cylindrical shapes. The small black particles observed

FIG. 1. Transmission electron micrograph of an alumina obtained from a 2.5-μm-thick aluminum foil anodized for 35 min at 20 V in a 10 wt% sulfuric acid bath followed by etching for 3 min in a 48 wt% phosphoric acid solution.

FIG. 2. Transmission electron micrograph of an alumina obtained from a 2.5-μm-thick aluminum foil anodized for 25 min at 20 V in a 5 wt% sulfuric acid bath followed by dissolution by amalgamation of the remaining aluminum.

FIG. 3. Transmission electron micrograph of the alumina shown in Fig. 2 etched supplementarily for 3 min in a 48 wt% phosphoric acid solution.

FIG. 4. Transmission electron micrograph of an alumina obtained from a 2.5-μm-thick aluminum foil anodized for 25 min at 25 V in a 5 wt% sulfuric acid bath followed by etching for 2 min in a 48 wt% phosphoric acid solution.

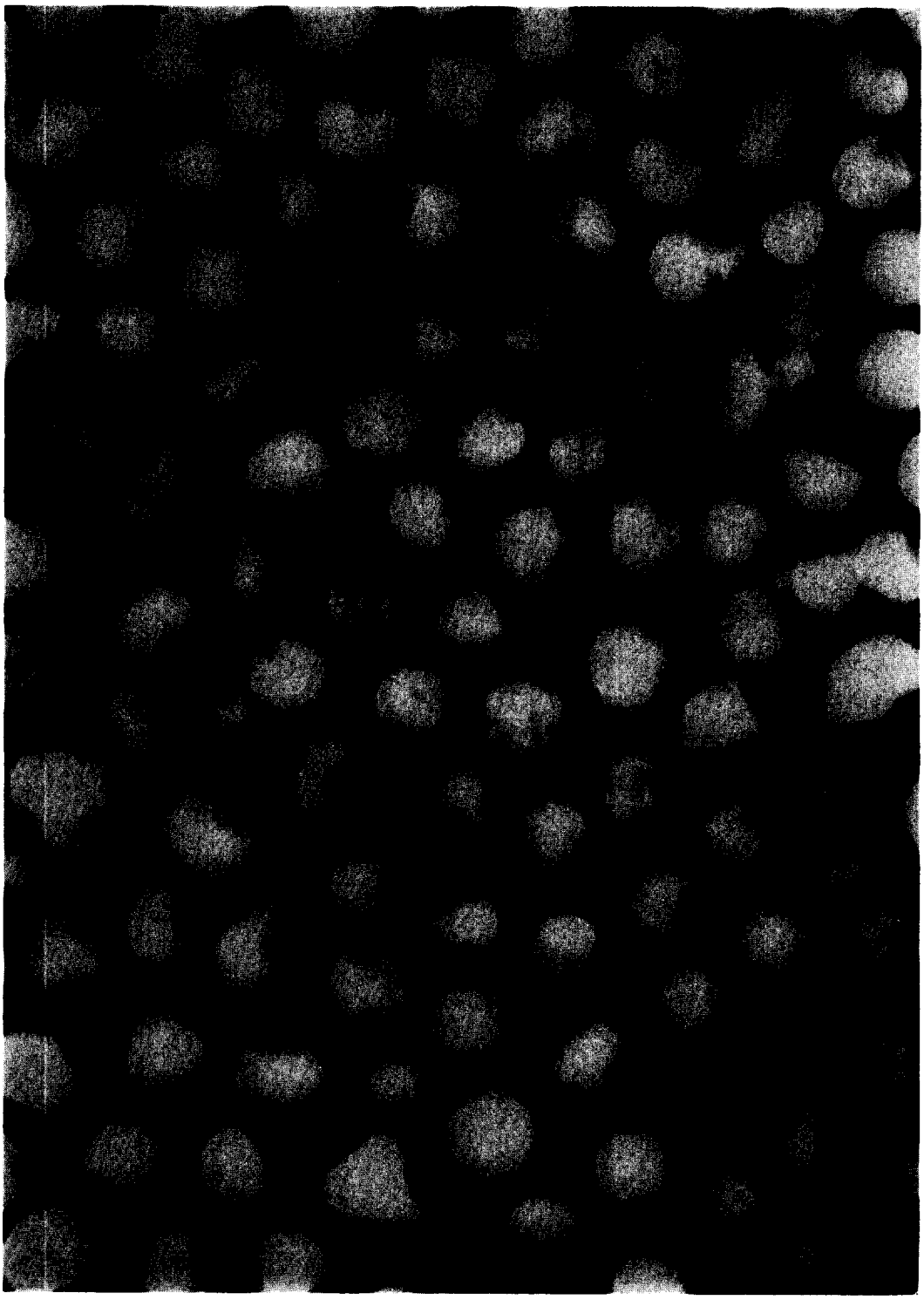
FIG. 5. Transmission electron micrograph of an alumina film obtained from a 60-nm-thick aluminum film anodized for 2 min at 20 V in a 5 wt% sulfuric acid bath.

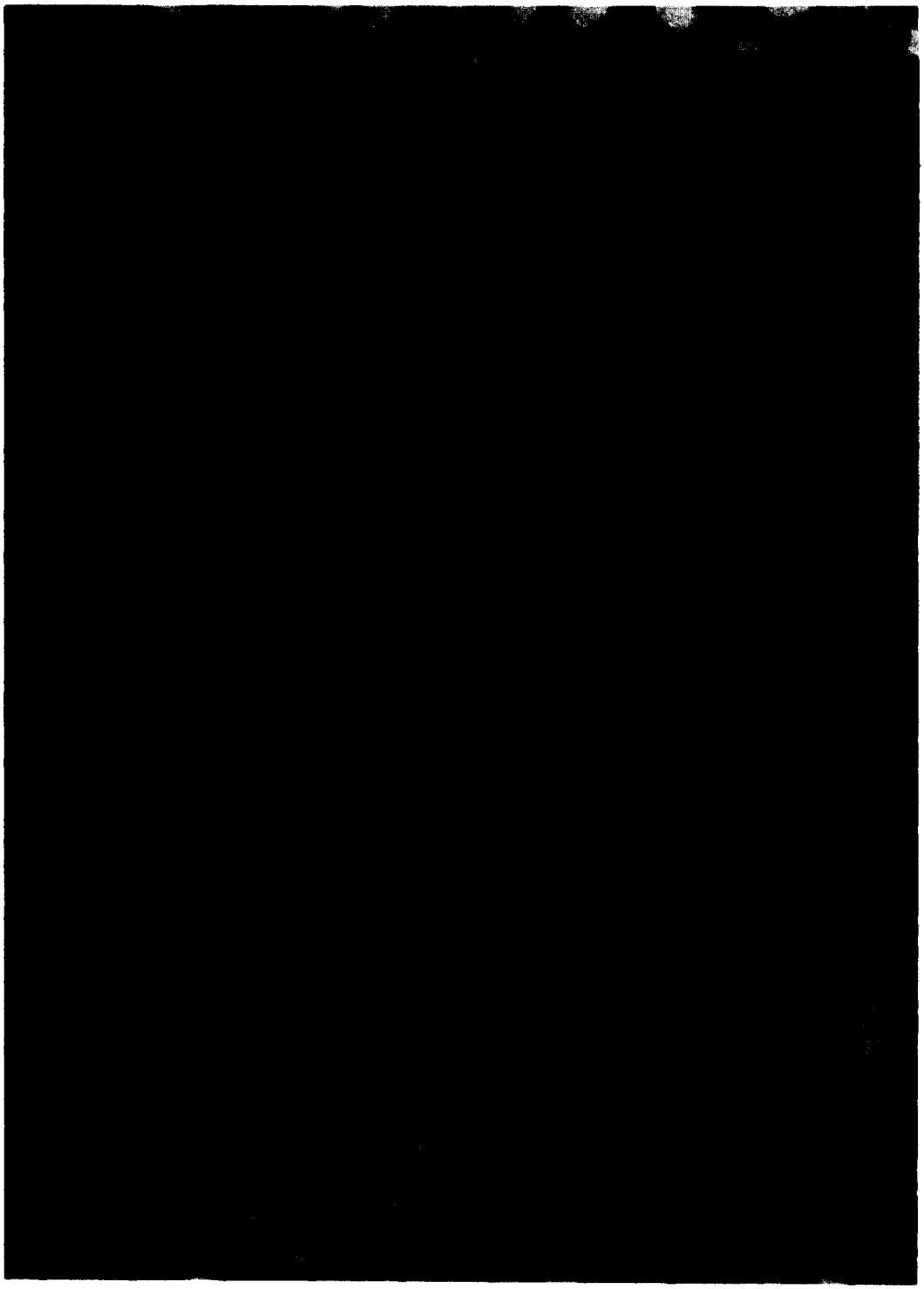
FIG. 6. Transmission electron micrograph of an alumina film obtained from a 60-nm-thick aluminum film anodized for 2 min at 30 V in a 5 wt% sulfuric acid bath.

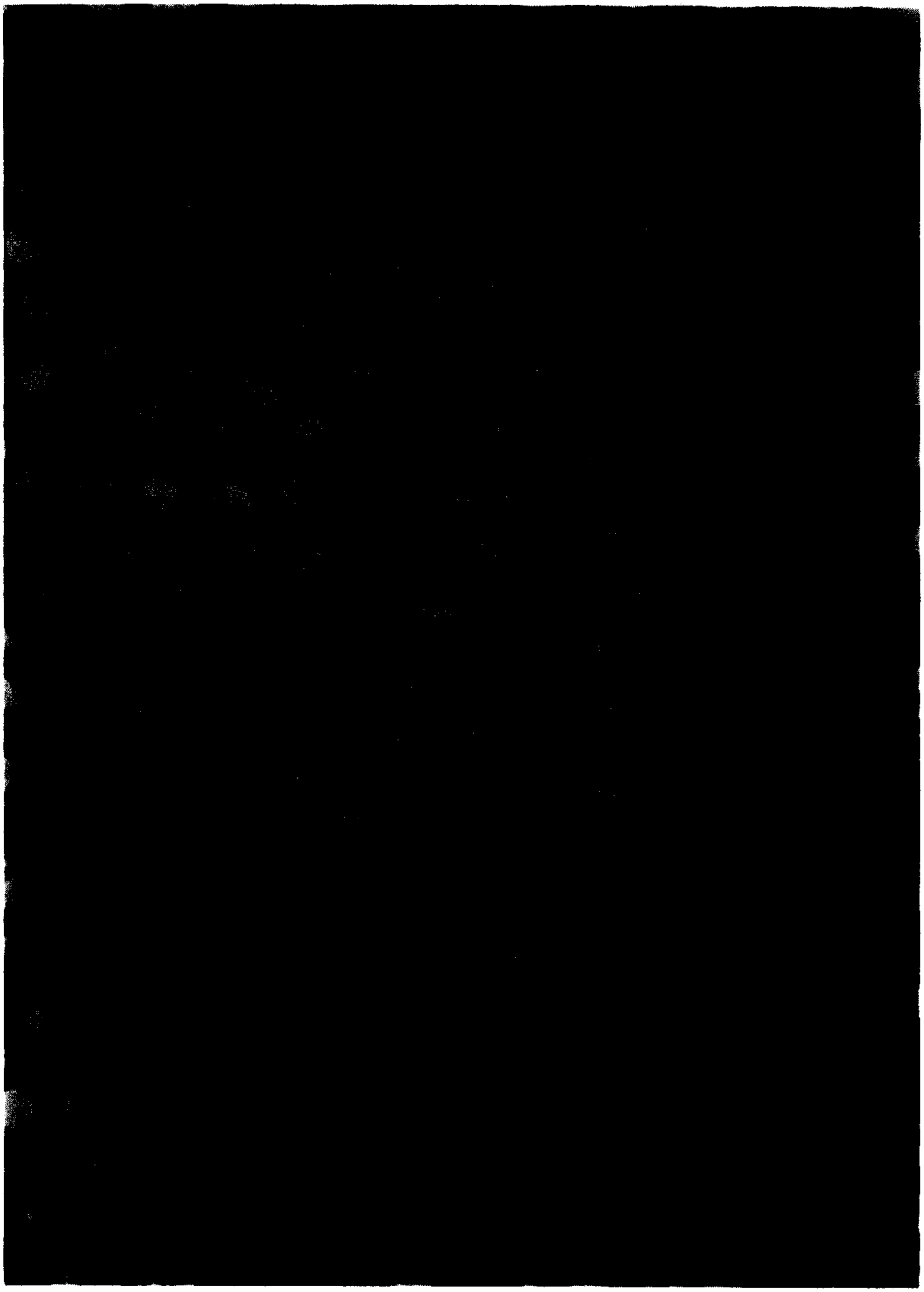
FIG. 7. Transmission electron micrograph of an alumina film obtained from a 30-nm-thick aluminum film anodized for 2 min at 20 V in a 5 wt% sulfuric acid bath.

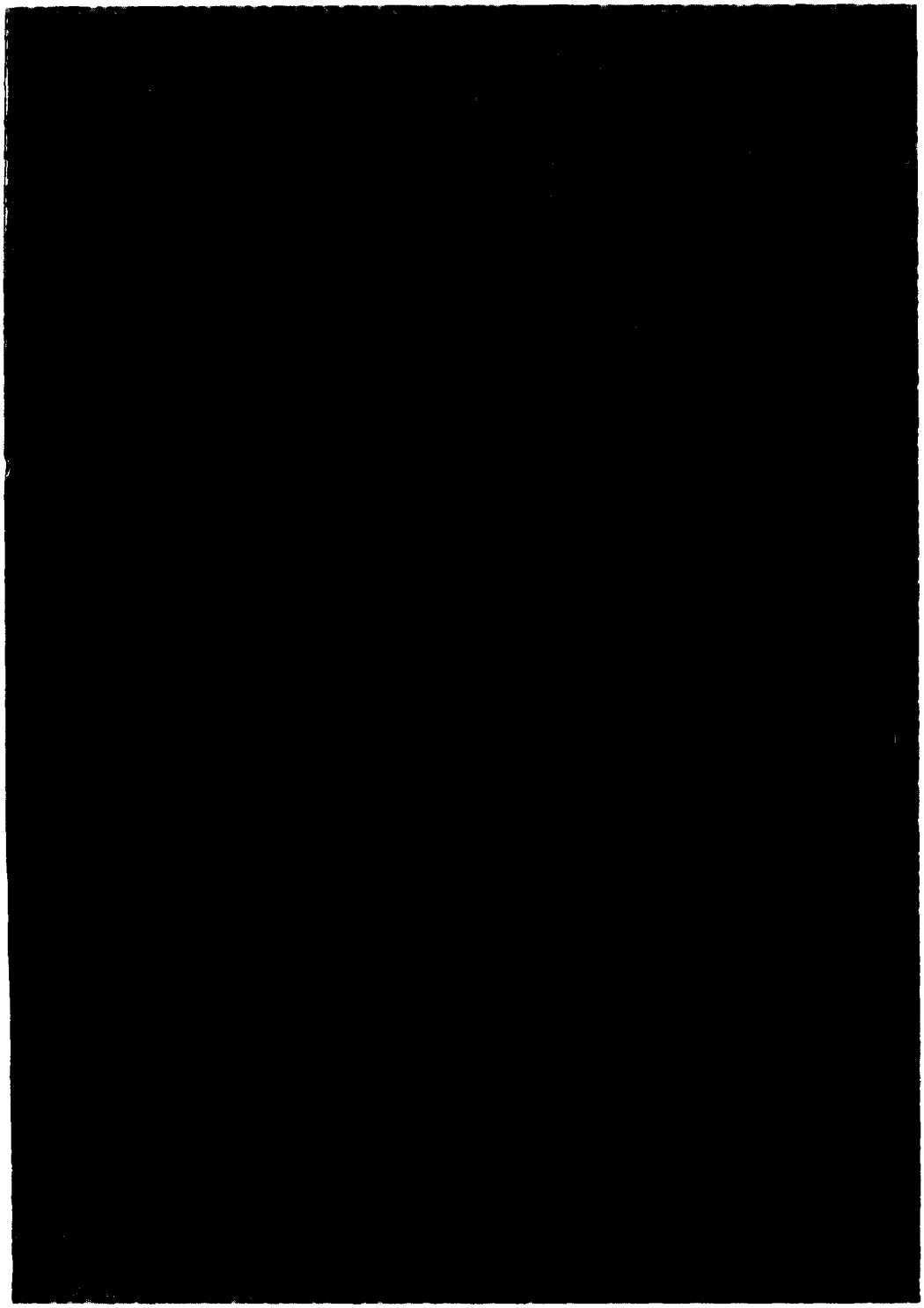
FIG. 8. Transmission electron micrograph of an alumina film obtained from a 30-nm-thick aluminum film anodized for 2 min at 45 V in a 3 wt% oxalic acid bath.

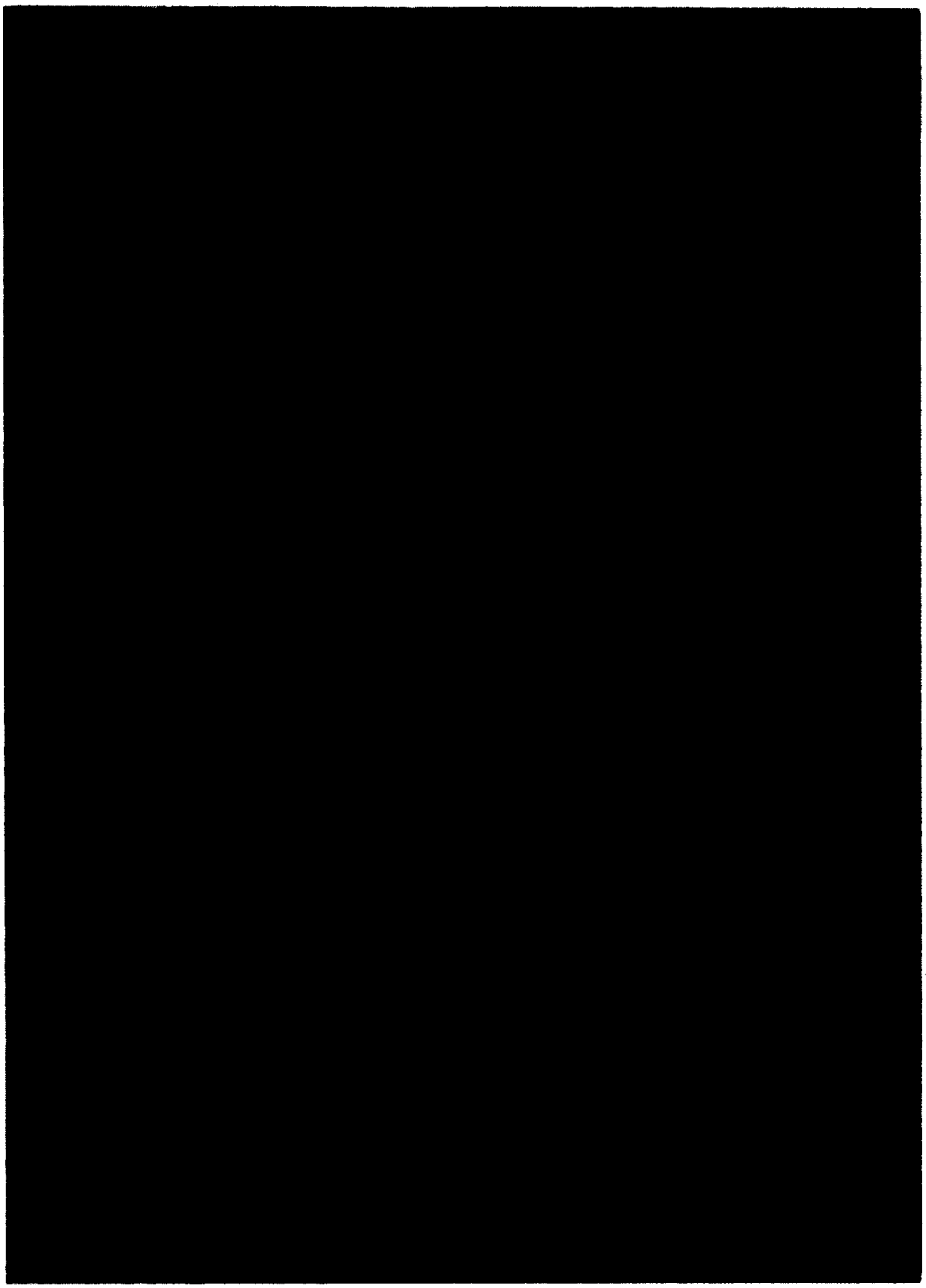
FIG. 9. Transmission electron micrograph of an alumina obtained from a 30-nm-thick aluminum film anodized for 2 min at 20 V in a mixed bath which contains 5 wt% sulfuric acid and 1 wt% d-tartaric acid with the pH maintained at 5.5 by addition of ammonium hydroxide solution.

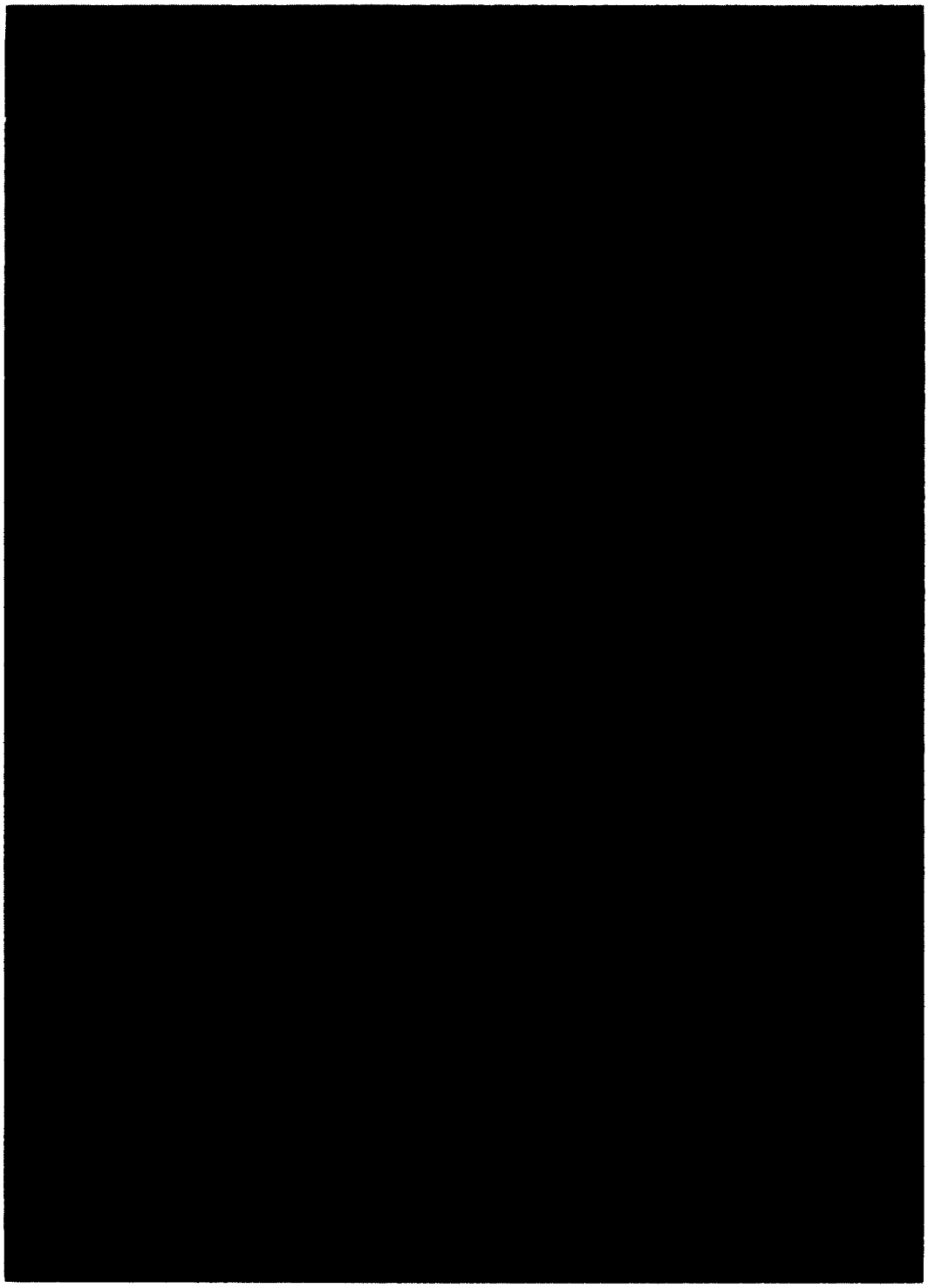


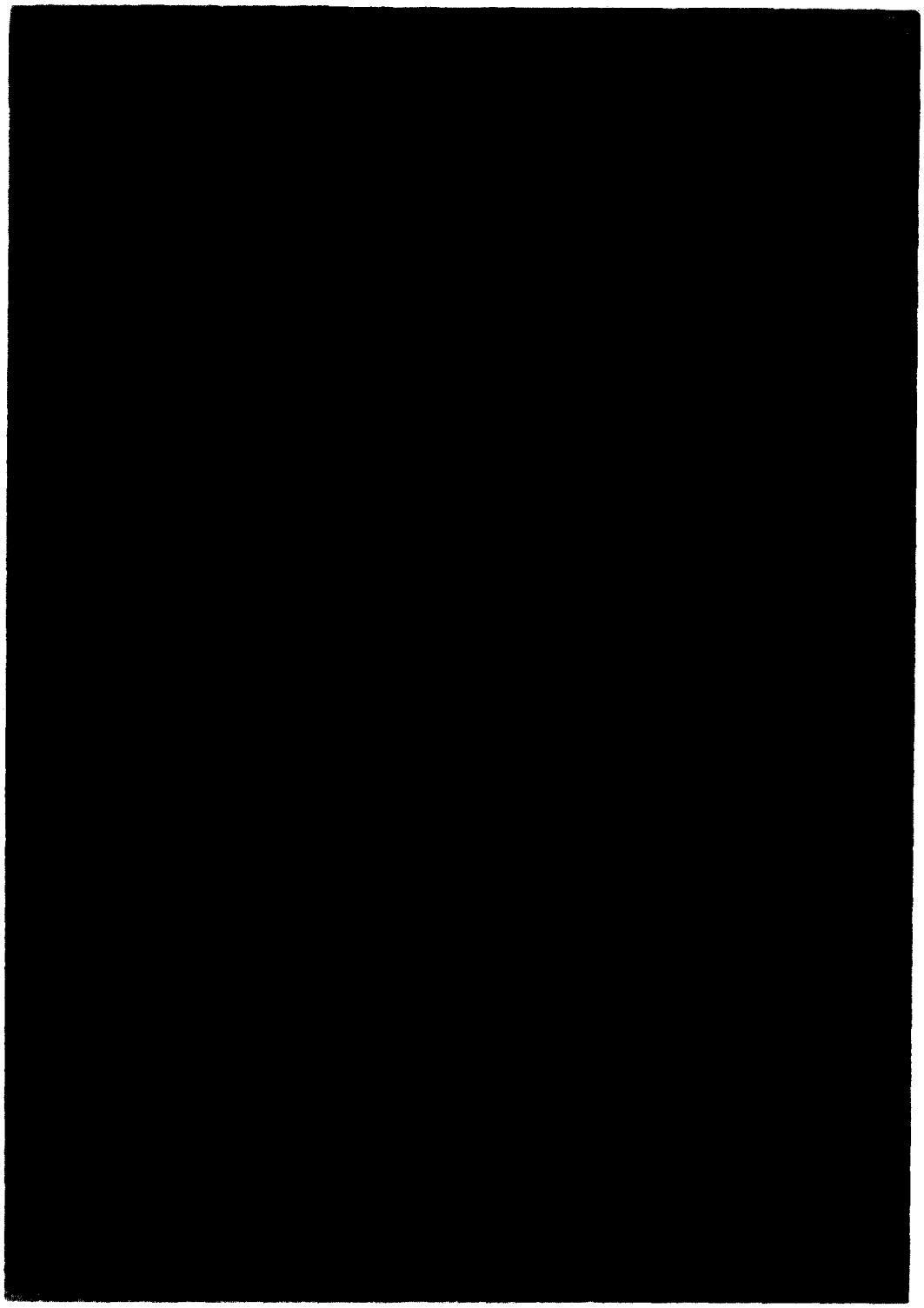


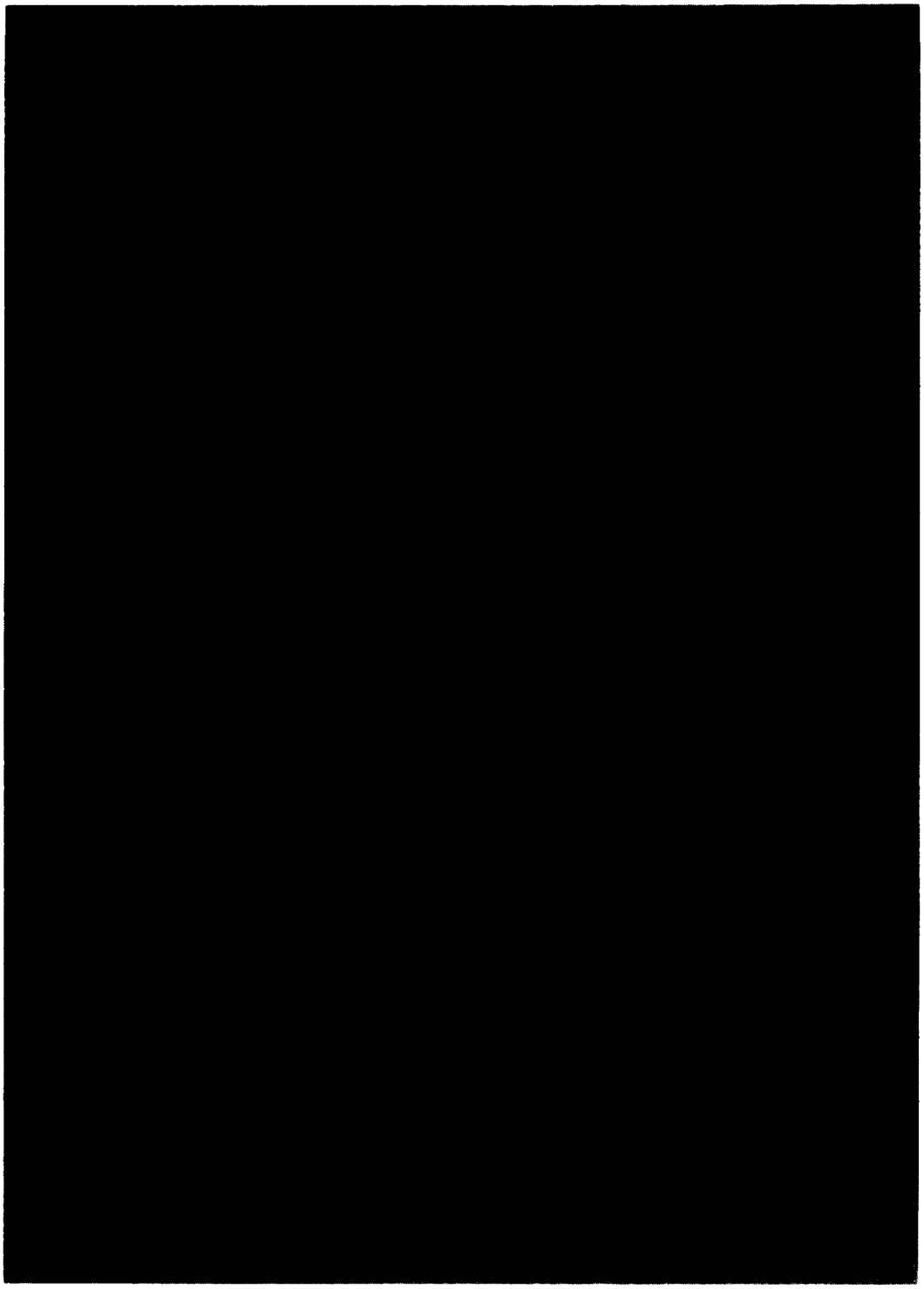


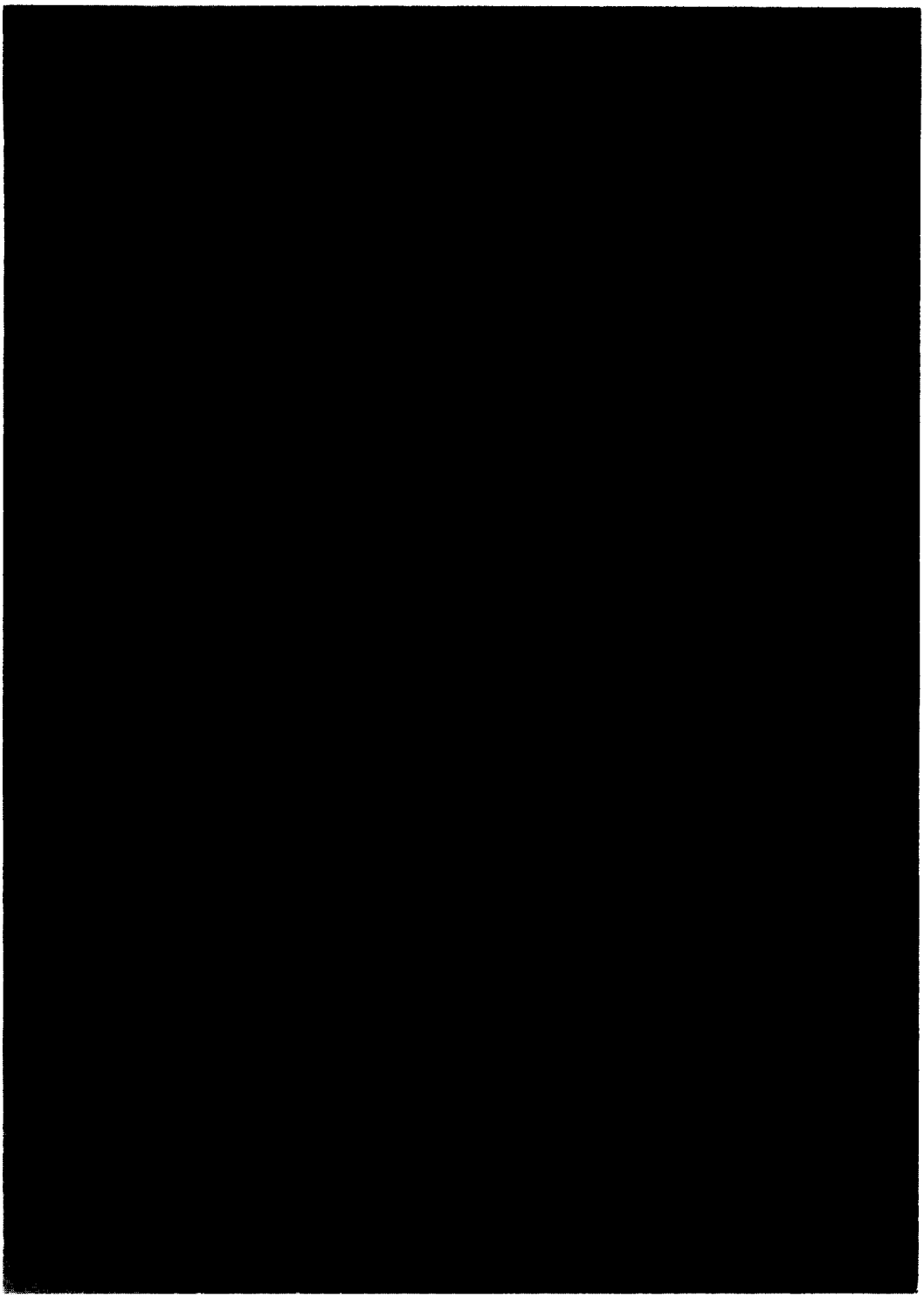












in the micrograph are unanodized aluminum (identified by selected area diffraction patterns). The pore density in this alumina was not affected by an increase of the voltage to 30 V (see Fig. 6). The average radius and pore density in these films are still 3.4 nm and 673×10^9 pores/cm^2, respectively, but fewer aluminum particles are left after the anodization process. Some pores, however, are more or less distorted. By anodization of an aluminum film of 30-nm thickness for 2 min at 20 V in a bath of 5 wt% sulfuric acid, pores of 1.7-nm radius were obtained (see Fig. 7). The pore density of this alumina is 157×10^{10} pores/cm^2 which is twice that of the aluminas shown in the micrograph in Fig. 5.

By anodization of 30-nm-thick aluminum films for 2 min at 45 V in 3 wt% oxalic acid, low density, small and shallow pores having a radius of 1.5 nm were obtained (see Fig. 8). When an aluminum film of about the same thickness was anodized for 2 min at 20 V in a mixture of 5 wt% sulfuric acid and 1 wt% d-tartaric acid, well-defined cylindrical parallel pores having an average radius 1.4 nm and a pore density of 179×10^{10} pores/cm^2 were obtained (see Fig. 9).

CONCLUSION

Alumina films prepared by anodization of foils or films of aluminum contain pores which are essentially parallel cylinders uniformly distributed but closed at one end by a nonporous film. The nonporous film closing the pores can be eliminated by etching in phosphoric acid solution. Pores which penetrate the foil over its entire thickness are thus obtained. The etching process makes the shape of the pores more cylindrical but enlarges their diameter. The size and density of the pores can be controlled by selecting appropriate preparative conditions. In this work, pores larger than 6 nm were obtained by anodizing 2.5-μm-thick aluminum sheets in a 5 or 10 wt% sulfuric acid bath at 0°C at different voltages followed by etching for several minutes in a 48 wt% phosphoric acid. Higher pore densities were obtained by lowering the applied voltage. Pores with radii less than 6 nm were obtained by anodizing 30–60-nm-thick aluminum films at different voltages in a 5 wt% sulfuric acid bath at 0°C. In the anodization process, low temperatures and low concentrations of sulfuric acid were used because they favor the formation of small pores. The applied voltage did not affect the pore density in the thin alumina films but fewer aluminum particles were left in the alumina films at the higher voltages. A bath containing a mixture of an electrolyte (sulfuric acid) which produces a porous alumina and an electrolyte (tartaric acid) which produces a nonporous alumina produced a film having small pores. These pores were more densely and more uniformly distributed than pores in films produced with sulfuric acid alone.

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