

Dynamics of Formation of Self-Organized Mesoporous AlO(OH)·αH₂O Structure in Al-Metal Surface Hydrolysis in Humid Air

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In humid air, a nascent Al-metal surface (S) with a surface Hg²⁺ catalyst hydrolyzes in divided reaction centers (micelles) with a vigorous exothermic reaction, $\{Al+2OH^-\}+\alpha H_2O \rightarrow$ AlO(OH), $\alpha H_2O + 3e^- + H^+$. It yields amorphous AlO(OH)· α H₂O with a huge ~90% porosity with $\alpha = 0.25$. The primary driving forces of the reaction are the chemical potential μ_e between the reaction species, the mechanical stress σ induced in expansion of S, and the flow of the reaction species. They drive it in a common direction perpendicular to S. The heat released in it flows primarily along S. It disrupts and stops the directional hydrolysis if the local temperature in the micelle reaches a critical value $T_{\rm c}$ (hot spot). The hot spot cools to the operating value T_0 , and the reaction restarts and runs over to \overline{T}_{c} in a periodic manner, at a time scale of $\Delta t_{i} \sim$ 5 s, per the dynamics of hot spots, forming a self-organized mesoporous structure of 15-50-nm diameter ellipsoidal shaped particles (halo) separated through 3-5-nm pores. A pore, in continuous formation of the sample, forms in disrupted reaction during the hot spot as it cools from T_c to T_0 . The result is modeled in terms of the microstructure and dynamics of the hot spots.

I. Introduction

A MONOLITHIC solid with fine pores of 2–50-nm size forms a new class of high-technology mesoporous materials.^{1–7} It displays many unique properties and has received a great deal of attention for fundamental interest and technological applications. Its potential applications include high-performance catalysts,^{1–4} components of sensors,^{2,4} separation membranes,^{2,3} microelectronic circuits,^{3,5,7} phosphors,⁴ and hot gas filters.⁷ Porous ceramics present considerably improved mechanical, chemical, and thermal resistance over the bulk values, promising a superior structural as well as electronic material. Size, morphology, and distribution of particles through the pores largely influence their electronic structure and related properties. Moreover, a variety of pure metals, metal oxides, and other materials of confined size of the pore can be incorporated in the pores for designing a mesoporous composite material of desirably modified properties of its components.^{2–7}

A porous Al_2O_3 forms on an Al-metal surface (S) upon its hydrolysis under an anodic bias in an electrochemical cell with a liquid electrolyte.^{8,9} Recently, Jessensky *et al.*⁶ explored this idea in developing mesoporous Al membranes by S hydrolysis of an electropolished Al-metal foil in a dilute acid. The membranes have a self-ordered pattern of hexagonal pores, with a fairly well controlled, 25–40-nm, size distribution, which offer many applications. Furthermore, it is also reported that, being an active metal, pure Al metal exposed in air or water results in an instantaneous formation of a thin oxide molecular surface layer, which prevents further reaction.^{10–12} The thickness of the native layer formed spontaneously lies within 3–5 nm.¹¹ It can be increased by anodic oxidation in corrosion- and abrasive-resistant films of typically 100 μ m.¹¹ The reaction involves S hydrolysis in boehmite, AlO(OH)· α H₂O, which later decomposes into a stable dense Al₂O₃ in an integral part of the reoxidized metal surface.^{13,14}

In this series, we explored an activated self-induced S hydrolysis of a nascent Al-metal surface (with a surface Hg²⁺ catalyst) in humid air at room temperature (RT).^{13,14} It does not involve other electrolytes and gives a pure hydrolyzed product of Al metal in AlO(OH)· α H₂O (porous), a precursor of alumina or sapphire. At 300°C or above, it transforms into a porous Al₂O₃ according to the final temperature. It presents a novel chemical method, if compared with common sol–gel chemistry^{14,15} or alkoxide methods,¹⁶ for synthesizing a monolithic Al₂O₃ or derivatives. The dynamics of the Al-metal surface hydrolysis in porous AlO(OH)· α H₂O is analyzed and modeled with microstructure in this paper.

II. Experimental Procedure

A high-purity (99.99%) polycrystalline Al-metal foil (of a FCC crystal structure of lattice axis a = 0.405 nm and average crystallites of size 50 nm¹⁷) was used for the S hydrolysis in humid air at 80%–90% humidity. It was degreased, washed in distilled water, and treated with 0.1*M* HCl for 10 min followed by washing in water. Electropolishing in a 4:4:2 mixture of H₃PO₄, H₂SO₄, and H₂O caused its smooth surfaces with a roughness at 20–30 nm at a lateral scale of 10 µm. As such, a thin surface oxide passivation is still present and it does not permit their S hydrolysis in humid air at elevated temperature. Activated S hydrolysis occurs after treating the surface with Hg²⁺ cations; i.e., the specimen is dipped in an aqueous 0.1*M* Hg²⁺ solution for ~30 s and then rinsed with deionized water to remove the excess Hg²⁺ and other byproduct impurities caused during the processing.

When the specimen is placed face up in humid air, a selfinduced spontaneous exothermic reaction occurs at the nascent Al surface with air by forming a hydrolyzed product of Al atoms in AlO(OH)· α H₂O molecules at S. They grow in fibers (as long as 20–50 mm in ~30- μ m diameter¹³) in a self-organized manner in a direction perpendicular to S. As will be discussed later, the Hg²⁺ cations eventually help in thinning down the spontaneous surface oxide (SSO) layer to a specific thickness Δl below the critical value Δl_c in a stable barrier layer to inhibit the S hydrolysis at elevated temperature. The S hydrolysis thus presumably occurs at $\Delta l < \Delta l_c$ under favorable conditions of temperature and other parameters.

The microstructure was studied with a transmission electron microscope (TEM) or a scanning electron microscope (SEM) in conjunction with an energy dispersive X-ray spectrum analyzer for in situ elemental analysis. X-ray diffraction was studied with a diffractometer using filtered CoK α radiation of wavelength λ = 0.179 05 nm. A Perkin–Elmer thermal analyzer was used to study thermal transformation of the sample by DTG (differential thermogravimetric) analysis. The porosity was determined from its

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bulk density, which was measured using the Archimedes principle in N_2 gas with a Penta Pyknometer (of Quanta Chrome).

III. Results and Discussion

(1) Dynamics of Reaction of Hg²⁺ Cations on Al-Metal Surface

The surface treatment of the Al-metal surface by a surface catalyst of Hg^{2+} cations plays a crucial role in activating a self-induced S hydrolysis of it in humid air or water. According to the surface treatment, the Hg^{2+} cations react with the specimen and thin down the SSO layer, $\Delta l < \Delta l_c$, so that the reaction species of H₂O molecules from the air pass through the SSO layer to react with the nascent Al-metal surface underneath it. A value of Δl_c , in this specific example, is pretty large at 3–5 nm,¹¹ i.e., roughly, 10–20 Al₂O₃ molecular layers. Whatever the mechanism of the reaction, there is no doubt that, at an early stage of the reaction, the Hg²⁺ cations move through the SSO layer and form a thin Hg²⁺ cations into Hg metal that ultimately forms a thin amalgam film with Al atoms in the interface. Otherwise, the Hg metal does not adhere so intimately to the Al metal surface and peels off in independent Hg metal. The Hg²⁺ \rightarrow Hg co-reduction reaction

$$2Al \rightleftharpoons 2Al^{3+} + 6e^{-}$$

$$3Hg^{2+} + 6e^{-} \rightleftharpoons 3Hg$$

$$2Al + 3Hg^{2+} \rightleftharpoons 2Al^{3+} + 3Hg$$
(1)

involves a large value of the resultant chemical potential $\Delta \phi = 3\phi_1 - 2f\phi \equiv 5.877$ V. That drives the reaction so fast that it lasts only over a few seconds. The reaction Hg²⁺ + 2e⁻ \rightleftharpoons Hg has a positive $\phi_1 = 0.851$ V value while that of Al³⁺ + 3e⁻ \rightleftharpoons Al has a negative $\phi_2 = -1.662$ V value.¹⁸

The thin Al-Hg amalgam film very intimately adheres to the nascent S and induces the initial SSO layer, if any, thereon to segregate and float over the surface together with traces of Al^{3+} cations formed in reaction (1). All these surface impurities are easy to wash away along with the excess amalgam, if any, in water. A specimen so obtained has primarily a nascent S protected with a thin residual amalgamated surface, which is as thin as possible at an atomic scale and inseparably adheres to the metal surface.^{13,14} The Hg atoms, being prone to amalgamating the Al atoms, hardly leaves behind a residual SSO between the two regions. Nevertheless, one cannot ignore the SSO present in the pitting centers caused during sampling in an acidic solution. Those peel off in the course of S hydrolysis in surrounding active centers and impart a homogeneous reaction. H_2 gas, which evolves in the hydrolysis, promotes the process. The SSO peels off in the distinct characteristic color (grayish) of the specimen, inducing the hydrolysis in a product of fibers.

The validity of reaction (1) is confirmed in a separate experiment by co-reducing a Hg²⁺ salt (solid) into a pure Hg metal (liquid) by milling it with Al chips or granules in a closed reactor. An efficient Hg²⁺ \rightarrow Hg co-reduction reaction also occurs if Al chips are ground in an aqueous Hg²⁺ solution. The pure Hg metal is easily recovered since it is automatically segregated by its large density $\rho = 13.6$ g/cm³. It does not adhere to the byproducts or the remaining Al metal after the reaction. This is analyzed with the characteristic chemical tests¹⁹ as follows.

(i) A freshly prepared specimen with a thin Al–Hg amalgam film at an Al plate, as described above, is immersed in HCl (12*N*). The Al metal dissolved, Al + 3HCl \rightarrow AlCl₃ + $\frac{3}{2}$ H₂, in part of the specimen, leaving behind a silver white Hg metal. No such Hg metal is recovered from residual Al chips after the bulk reaction with a Hg salt in the other case.

(ii) In another experiment, the specimen was immersed in HNO_3 . The HNO_3 dissolved both the components of the amalgam and A1 metal in a clear solution. On adding an ammonia solution, a white precipitate appears in mercury(II) amidonitrate,

$$2Hg^{2+} + NO_3^- + 4NH_3 + H_2O \rightarrow HgO \cdot Hg \swarrow ^{NH_2}_{NO_3} + 3NH_4^+$$
(2)

confirming the Hg^{2+} cations to be present in the solution in the amalgam.

(2) Process and Dynamics of the Al-Metal Surface Hydrolysis

As demonstrated in diagrams (a) and (b) in Fig. 1, as soon as it is put in humid air at RT, the nascent Al S with an atomically thin Al–Hg surface film sets up a weak activation barrier E_a between the reaction species of Al atoms (A) at the surface and the OH⁻ or O²⁻ anions (B) from the air over it. The chemical potential μ_e between A and B initiates their reaction against the E_a energy barrier in a specific AB direction perpendicular to S (Fig. 1(b)). The reaction is more efficient with OH⁻ anions, which involve a relatively small E_a value. It persists over a long time scale of minutes and permits its measurement with a continuous S hydrolysis on nascent S. This is not feasible with O²⁻ anions , under these conditions, which form a highly stable nonporous Al₂O₃ surface layer on the nascent reaction surface that instantaneously stops the reaction.

Other forces, which support the unidirectional reaction, are the mechanical stress k induced in expansion of S during the reaction and the flow of the reaction species. Both of them occur in a common AB direction and assist the directional S hydrolysis along it. A noninterrupted migration of Al³⁺ cations (from the Al surface) through the AB interface performs a noninterrupted growth of hydrolyzed Al metal in AlO(OH)· α H₂O, with ΔH_f° = -1971.6 kJ/mol being the standard enthalpy of formation.²⁰ This occurs in divided reaction centers (micelles) on S nucleated in divided reactions of Hg²⁺ cations on it according to its granular structure (grain size \sim 50 nm), which determines the structure of micelles or the reaction through channels at S. As described earlier,¹³ on a nascent Al S, Hg²⁺ cations form directional Al-Hg reaction thorough channels perpendicular to S. They collimate a directional S hydrolysis of the specimen of the nascent Al S in humid air. κ affects the kinetics of the S hydrolysis through the creation of additional active sites for the S hydrolysis during the reaction.

The heat released in the highly exothermic S hydrolysis reaction in micelles flows primarily along the Al-metal S (good thermal conductor). It disrupts directional S hydrolysis in the perpendicular direction if instantaneous temperature in the micelle increases to a critical value T_c , well above its average value, T_{av} , during the reaction. Per the average reaction rate,¹³ a model temperature profile of ABH is predicted in Fig. 2(a). It governs the drift velocity v_z of the reaction species along AB, as schematically



Fig. 1. Schematic diagram of Al-metal surface hydrolysis in humid air: (a) the pure metal surface before the reaction and (b) expansion of it in the formation of its hydrolyzed product.



Fig. 2. (a) Model temperature (*T*) profile in the local heating and cooling in a micelle in the Al-metal surface (S) hydrolysis in humid air. The hydrolysis stops at the mobile hot spots at H and H' at $T \ge T_c$. (b) Drift velocity v_z of the reaction species of Al³⁺ cations perpendicular to S. The straight line (dashed) indicates the flow of the hot spots.

shown in Fig. 2(b). A value of T_{av} as large as 350 K has been observed in this experiment. At $T \ge T_c$, the micelles involved in the exothermic S hydrolysis reaction become hot spots H and disrupt the reaction by arresting the uniaxial drift of the AI^{3} cations from S along AB. Actually, at $T \ge T_c$, 2AlO(OH)• α H₂O \rightarrow $Al_2O_3 + (1 + 2\alpha)H_2O$ thermal decomposition occurs and deposits in a hard Al2O3-surface film (amorphous) over hot S and that inhibits further S hydrolysis.

This is clearly demonstrated by the DTG thermogram of recovered AlO(OH)·aH2O from S hydrolysis of a nascent Al metal

in humid air in Fig. 3. The thermogram consists of a thermal desorption peak in desorption of αH_2O (or of any interstitial gas) at \sim 340 K, which follows a similar peak at \sim 405 K in molecular dissociation of the specimen into Al₂O₃ with a total of 21% loss in its mass per its molecular structure with $\alpha = 0.25$. In contrast to other reports,⁶ the result unambiguously confirms that Al hydrolysis in an aqueous electrolyte or in humid air does not give a hydrolyzed Al-metal product of Al₂O₃ directly. IR analysis confirms the as-received product to be a metastable AlO(OH) $\cdot \alpha H_2 O.^{14}$ We performed several experiments of S hydrolysis of Al metal in humid air at different temperatures from 273 to 380 K and found that an effective reaction occurs only at $T_{\rm av} \leq 320$ K. It stops if $T_{\rm av}$ increases above 350 K due to the heat produced in the exothermic S hydrolysis reaction of OH⁻ anions on Al atoms.

Our results are consistent with the studies of electrochemical behavior of Al metal with a thin SSO layer.¹² According to these studies, the rate of H₂ evolution in the hydrolysis behaves as a nonlinear function of temperature in this region. The SSO thermal stability, microstructure, and surface chemistry govern the process. AlO(OH), which transforms to Al₂O₃ in this region, modifies the reaction dynamics according to other parameters. This is one of the regions in which protection efficiency of SSO against the hydrolysis varies in different environments.^{10–12} A newly formed SSO layer thus can be described as the best in a product of pseudoboehmite.

In the proposed model, the H spots move with the flow of heat (phonons) along S and cease the drift of Al³⁺ cations in directional S hydrolysis in its perpendicular direction along AB. These Al³⁺ cations are lost to the Al surface and are prerequisite for the discontinuous (porous) growth of hydrolyzed Ål metal into $AlO(OH) \cdot \alpha H_2O$. Only the Al^{3+} cations, which cross the interface through the barrier $E_{\rm a}$ in a single noninterrupted step, contribute a noninterrupted S hydrolysis in the AB direction. After a certain time interval Δt_i , with $\Delta t_i = 0$ at $T = T_c$, the H spot cools down to the operating value T_0 and S hydrolysis occurs again. As schematically shown in Fig. 2(b), this occurs in successive steps in a periodic interval Δt_i . From the TEM micrograph of the sample, in Fig. 4(a), it appears that a single, separated AlO(OH) $\cdot \alpha H_2O$ particle by a pore (which forms in a subsequent disrupted reaction step) forms in a single noninterrupted reaction. The particles, in an ellipsoidal shape of diameter D = 15-50 nm, are self-organized through pores in a specific fashion according to directional S hydrolysis. An average diameter in pores between particles is 3-5 nm. The electron diffractogram corresponding to TEM, in Fig. 4(a), has a broad halo in Fig. 4(b) of radius d = 0.235 nm, an intrinsic characteristic of an amorphous structure.^{21,22}



Fig. 3. (a) DTG thermogram of a porous AlO(OH) α H₂O, $\alpha = 0.25$, measured by heating it at 0.33 K/s. The dashed curves are the guidelines for two components in the two-step thermal desorption transformation of AlO(OH) aH₂O in Al₂O₂.



Fig. 4. (a) TEM and (b) corresponding electron diffraction in a mesoporous AlO(OH) α H₂O powder from hydrolysis of Al metal in humid air, and the Al-metal surfaces in SEM (c) before and (d) after treating with Hg²⁺ cations to form a thin amalgam surface layer.

Particles in Fig. 4(a) have a shell structure as can be seen in close observation of their surfaces, which suffer throughout from a lack of uniform contrast. A few white images are present in region A in the peeling-off part of thin surface walls in some particles. An average 3–5-nm thickness (δ) is estimated by images of the cross section in broken surface walls. A shell particle of an average 30-nm diameter thus encloses \sim 40% shell volume at $\delta \sim$ 4 nm in approximation of its spherical shape. It covers a major part of observed porosity $\Phi \sim 90\%$ in the sample (Table I). SEM micrographs (c) and (d), in Fig. 4, give an idea of the Al-metal surfaces used in the S hydrolysis. A microstructure (Fig. 4(d)) of micelles, 30-100-nm diameter, is developed on treating the surface (Fig. 4(c)), after the electroplating, in a Hg^{2+} solution. Porous anodic SSO films in a reaction of Al metal with H₃PO₄ had similar micelles.¹¹ The sample in Fig. 4(d) has been boiled in water to inhibit the hydrolysis, with an enriched SSO layer, which allowed the measurement. Otherwise, this sample hydrolyzes very rapidly, making examination of the structure difficult.

Table I.Structure, Bulk Density, and Porosity in theSamples Obtained by Al-Metal Surface Hydrolysis in HumidAir at Room Temperature Followed by
Annealing at Selected Temperatures

Sample	Annealing	Structure	Density [†] (g/cm ³)	Porosity (%)
	As received	Amorphous	0.23 (2.25)	90
	2 h at 600 K	Amorphous	1.80 (3.67)	51
	2 h at 900 K	Crystalline	1.95 (3.67)	47

[†]The theoretical values of the density, given in the parentheses, are taken from Refs. 14 and 17. For a lack of data, the theoretical value for the amorphous phase is taken to be the same as that for the crystalline phase.

The encapsulated shell inside the particle is formed by trapping H_2 gas during its formation by S hydrolysis of the Al metal. H_2O molecules (from the air) dissociate at the nascent Al-metal surface and produce H_2 gas, part of which gets trapped inside the growing particles in micelles perpendicular to S. The H_2 gas encapsulated in the particles (which behave as H_2 -gas-filled balloons) assists their directional growth perpendicular to S in the open air according to its low pressure. The pores between the particles mediate a rather free growth of sample in separated particles driven by the above driving forces. An elongated ellipsoidal shape of particles is indicative of their directional growth along their major axes in the direction of μ_e (AB). Dynamics of pores along S during the H spots are cooling from T_c to T_0 and that



Fig. 5. Model surface hydrolysis of (a) a refreshed Al-metal S into (b) a hydroxyl product in a reaction with H_2O molecules through a thin SSO laver. The product behaves as a weak acid.



Fig. 6. Model of activated hydrolysis of a nascent Al-metal surface (with a thin amalgam layer) in AlO(OH) • AH₂O in humid air.

perpendicular to S in the subsequent S-hydrolysis step attenuate this particular particle structure as follows.

Al-atomic density in Al metal is decreased roughly by a factor $f \sim 5$ upon its hydrolysis in AlO(OH)· α H₂O. This involves a volume expansion of it by an order of magnitude per the diminished bulk density $\rho = 0.23 \text{ g/cm}^3$ in AlO(OH)· α H₂O from $\rho = 2.70 \text{ g/cm}^3$ in the Al metal (Table I). As mentioned above, the hydrolysis induces a mechanical stress τ in the specimen during its S hydrolysis as a possible origin of forces between the neighboring pores (discontinued hydrolysis) and/or the particles (continuous hydrolysis). As the S hydrolysis takes place at the entire pore bottom simultaneously, the material can only expand in the vertical direction so that the existing pore walls are pushed symmetrically upward in the same direction as the particles growing in a noninterrupted S hydrolysis. The dynamics of the pores, therefore, attenuates the dynamics of an ordered pattern of self-organized AlO(OH)·aH2O particles through the pores. Three driving forces of the directional reaction are (i) μ_e , (ii) the longitudinal component of the mechanical stress κ_{zz} , and (iii) the flow of the reaction species. All of them drive the observed pattern of the reaction in a common direction perpendicular to S.

Dynamics of Formation of $AlO(OH) \cdot \alpha H_2O$ Molecules (3)

In general, all metal oxides react with H₂O in the surface.^{23,24} The degree of the reaction (hydrolysis) varies from case to case according to their chemistry. As demonstrated in Fig. 5, a metal surface thus reacts with H₂O via a thin oxide layer of its own and extends its hydrolysis in a metastable hydroxyl product, which behaves as a weak acid.²³ An activated reaction occurs in absence of the surface barrier layer. In humid air, a nascent Al-metal surface (with a thin surface amalgam) dissociates H₂O molecules (from the air) at the surface into OH⁻ and H⁺ ions. The OH⁻ anions react on Al atoms at S in successive steps and cause its S hydrolysis in AlO(OH) $\cdot \alpha H_2O$ in a self-controlled manner. This is shown schematically in Fig. 6. The intermediate $[Al(OH)_2]^+$ reaction species in Eq. (3b) transforms into a stable AlO(OH) molecule just by releasing a proton H⁺ only. Since it involves a minor redistribution of its local properties of internal energy and electronic charges, it occurs fast before another OH^- group recombines to it and forms a stable Al(OH)₃ molecule. Further, an AlO(OH) molecule so deduced takes up a controlled amount of water of hydration from the medium in a subsequent step of the reaction with H_2O and ultimately converts into AlO(OH)· αH_2O . This grows very fast in AlO(OH)·aH₂O molecular fibers. It does not dissociate, giving a weak acid behavior.

As mentioned above, the H₂ gas being produced in the intermediate reactions in Eq. (3) gets easily locally trapped within the nascent AlO(OH) $\cdot \alpha$ H₂O molecules in the divided reaction centers. The volume in the gas enclosed inside a group of molecules grows as a shell by accumulation of more and more H₂ molecules (from the reaction) as a function of their growth into a particle in a continuous reaction. Obviously, the gas drives directional molecular growth perpendicular to the reaction surface per its initial internal pressure and other driving forces.

(4) Modeling of the Discontinuous Al Surface Hydrolysis

Mathematically, the temperature profile of micelles in Fig. 2(a) can be represented by a presumed empirical function,

$$T = \alpha [T_i + \beta t^n] - (1 - \alpha)(T_c - \Delta T) \exp\{-(t/\tau)^n'\}$$
(4)

where T_i is the initial temperature and $\alpha = N_1/N_0$ and $(1 - \alpha) =$ N_2/N_0 are the fractions of the micelles N_0 shared in the internal heating (N_1) and cooling (N_2) processes in the regions of ABH and BH', respectively. Other parameters in this relation are the correlation constant β , the exponents *n* and *n'*, and the relaxation time τ . The exponential function in the second term represents a well-known thermal or structural relaxation of a physical property P in general.^{21,22} Here, it describes simply the release of the excess temperature $\Delta T = T_c - T$, overshooting the operating value T_0 by internal heating in the first term, as a function of time t by Tapproaching T_0 .

Equation (4) is rewritten for the average heating process in a sample of N_1 heating micelles as

$$T = \frac{N_1}{N_0} \left[T_i + \beta t^n \right] \tag{5}$$

which reduces to

$$T = T_i + \beta t^n \tag{6}$$

for a single micelle or for a system of a single micelle, N_1 and its equivalent; $\alpha N_0 = 1$. It represents a parabolic T profile, as shown in Fig. 2(a), with an arbitrary value of $\beta = (30 \text{ K})/s^n$ with $n = \frac{1}{2}$ and the initial experimental temperature $T_i = 295$ K. It gives a rise in T over T_i by 67 K with a final value of T = 362 K within t =5 s of the reaction begun at t = 0. That can be treated as the $T_{\rm c} =$ 362 K value, which is a consistently larger value if compared with the average $T_{av} = 320$ K value measured at S during the S hydrolysis.

This kinetic analysis reveals that the time interval Δt_i of overshooting of T in a micelle in the S hydrolysis lies at a scale of s. The overshooting of the internal T in a micelle to T_c stops the S



Fig. 7. X-ray powder diffractograms of (a) as-received AlO(OH) α H₂O and that annealed 2 h at (b) 600 and (c) 900 K in air. The diffraction peaks of recrystallized γ -Al₂O₃ in (c) are marked by their (*hkl*) values.

hydrolysis at it. This cools back to T_0 by releasing the ΔT per the second term in Eq. (4), which in a more realistic form is rewritten as

$$\Delta T = \Delta T_{\rm c} \exp\{-(t/\tau)^{n'}\}\tag{7}$$

with ΔT_c being the optimal value of ΔT . As schematically shown in Fig. 2(a), curve HB' represents a monotonically decreasing signal of the release of excess ΔT in Eq. (7), i.e., relaxation of phonons excited in high-energy levels, with *t*. The curve of HB' is reproduced with n' = 0.6 and $\tau = 25$ s in Eq. (7). Similar values for *n*' and τ appear in a structural relaxation of excitons or phonons or in a local structure in amorphous or crystalline solids.²² A comparison of the results with the phonon-assisted tunneling of small polarons, which successfully describes the motion of muons or protons, implies a hopping rate²⁵

$$\tau^{-}(T) = v_0 \exp\{-\Delta E/kT\}$$
(8)

with

$$v_0 = A_i T^{-1/2} \tag{9}$$

$$A_i = \mathbf{J}^2 (4\eta^2 \Delta E/k)^{-1/2} \tag{10}$$

where **J** is the tunneling matrix and ΔE is the difference between the adjacent energy levels.

In this formalism, the dynamics of the two processes, which occur one after another in a periodic interval $\Delta t_i \sim 5$ s, are interdependent. As a result, T_c , in Fig. 2(b) (dashed line), regularly decreases with t in the periodic S hydrolysis in micelles by a periodic variation in v_z of the reaction species. The straight line represents a linear decrease in T_c with t and the S hydrolysis automatically stops as its final value reaches T_0 . The $\Delta T_c = T_c - T_0$ dictates the driving path or potential for S hydrolysis. That vanishes at $\Delta T \sim 0$ and stops the S hydrolysis.

(5) Microscopic Structure of $AlO(OH) \cdot \alpha H_2O$ Particles

The AlO(OH)· α H₂O particles, D = 15-50 nm (Fig. 4(a)), have a prominent X-ray diffraction halo (Fig. 7a) at wavevector $q_1 =$ 6.8 nm⁻¹ {defined by $q_i = (4\pi \sin \theta)/\lambda$ } and two weak halos at $q_2 = 26.9$ nm⁻¹ and $q_3 = 44.5$ nm⁻¹. The $q_2 = 26.9$ nm⁻¹ halo compares well in the position with the electron diffraction halo in Fig. 4(b). A large peak-width $D(2\theta_{1/2}) \sim 10^\circ$ or larger in these halos signifies an amorphous structure of the sample. For a time being, if we assume a crystalline structure of it, then a Debye– Scherrer analysis²⁶ of $D(2\theta_{1/2})$ values predicts a crystallite size $r \leq 0.8$ nm (diameter), which is smaller than the critical $r^* \geq 3.8$ value for a stable AlO(OH)· α H₂O crystallite calculated with the relation²⁰

$$\frac{1}{2}r^* = \frac{2\sigma}{\Delta G_{\rm v}}\tag{11}$$

with $\sigma = 0.70 \text{ J/m}^2$ (its surface-energy density) and $\Delta G_v = 0.74 \times 10^9 \text{ J/m}^3$ (the change in the Gibbs free energy on its formation). In the absence of the absolute values, the values of σ and ΔG used are the same as those for a pure Al₂O₃.²⁰ The average *r* value deduced from $D(2\theta_{1/2})$ comes to be even smaller than the average size, $d = V^{1/3} \cong 0.75$ nm, of its single crystal unit cell of volume *V*. The crystal unit cell, of a monoclinic structure, consists of eight molecules, lattice parameters a = 0.886 nm, b = 0.506 nm, c = 0.983 nm, and $\beta = 94^{\circ}34'$.¹⁴ In fact, a single crystal unit cell is never stable. A stable crystallite of size *r** consists of several crystal unit cells.

According to the Bragg's relation, the halo q_1 lies at $d = \lambda/(2 \sin \theta) \sim 1.0$ nm. This is a larger value than is possible for an interplanar distance d_{hkl} in this series. All the results ultimately have a single implication that the sample is not in a crystalline state. It has an amorphous structure of small configurations or microscopic domains of AlO(OH) $\cdot \alpha H_2O$ molecules of $r = d \sim 1$

nm in size.²⁷ Most likely, a strong surface reflection of the X-ray beam occurs from their confined surfaces and results in the prominent diffraction halo $q_1 \approx 6.5 \text{ nm}^{-1}$. The other two halos, which are characteristically week in intensity, are common^{21,22} and refer to average atomic reflections with two prominent pair distribution functions of atoms in an amorphous AlO(OH)·aH2O structure.

All three diffraction halos marginally shift at lower $q_1 = 6.3$ nm⁻¹, $q_2 = 23.7$ nm⁻¹, and $q_3 = 42.5$ nm⁻¹ values on thermal desorption transformation of AlO(OH)·aH2O into an amorphous Al_2O_3 at 600 K in Fig. 7(b). The latter recrystallizes in γ - Al_2O_3 (Fig. 7(c)), at 900 K, in an O_4F_{3DM} cubic crystal structure with the standard lattice parameter $a_0 = 0.79$ nm value.¹⁷ A halo still appears at modified $q_1 = 5.4$ nm⁻¹ in modified microscopic domains in part of the amorphous phase which is still present. The three samples maintained a high 90%-47% porosity (Table I).

IV. Conclusions

Nascent Al-metal surface, catalyzed by a thin atomic surface film by a surface catalyst of ${\rm Hg}^{2+}$ cations, instantaneously S hydrolyzes in a porous AlO(OH) $\cdot \alpha H_2O$, with as much porosity as 90%, in humid air at RT. It has an ordered pattern of halo particles in an ellipsoidal shape, 15-50-nm diameter, by a self-organizing process in operation during the hydrolysis. It is suggested that the heat evolved in this exothermic reaction and the dissipation of it along the Al-metal S form moving hot spots H of the reaction in divided reaction centers (micelles). The H disrupts the spontaneous reaction at temperatures $T \ge T_c$, with T_c being the critical value. A value of $T_c \sim 362$ K is estimated using a proposed kinetic model of the reaction. The reaction restarts after the H cools back to the operating point T_0 . It occurs by directional S hydrolysis in successive steps in the direction of the chemical potential (normal to S) between the reaction species. An expansion of S during its hydrolysis induces a mechanical stress κ in this direction. It acts as repulsive forces between the particles and/or the pores, which, therefore, form one after another in a self-organized sequence in this direction.

The AlO(OH)·aH2O sample is X-ray amorphous with a prominent X-ray diffraction halo at wavevector $q_1 = 6.8 \text{ nm}^{-1}$ and two usual weak halos at $q_2 = 26.9 \text{ nm}^{-1}$ and $q_3 = 44.5 \text{ nm}^{-1}$ in two prominent pair distribution functions of the atoms. The small-angle halo q_1 most likely ascribes to a surface reflection of the X-ray beam from the surface of a specific substructure of AlO(OH)·aH2O in microscopic domains. An average diameter of the domain is determined to be ~1.0 nm by the $d = \lambda/(2 \sin \theta)$ value of the diffraction halo. It is significantly bigger over the average value, $d = V^{1/3} \approx 0.75$ nm, of a crystal unit cell (that contains eight molecules) of AlO(OH)·aH2O of volume V.14

A kinetic model is proposed of the S hydrolysis of a nascent Al metal into a metastable AlO(OH)·aH2O compound. According to the model, an AlO(OH) $\cdot \alpha H_2O$ molecule in this example forms by a local reaction of OH⁻ and Al³⁺ ions at S in successive steps followed by a local redistribution of atoms within the system. This is a reaction-rate-limited process. It can give a number of metastable phases out of a dynamic equilibrium of it per the dynamics of the reaction species. The most stable phase in this series is $Al(OH)_3{}^{*}\alpha H_2O.^{16}$ It does not appear in this particular process under present conditions. The formation of the metastable AlO(OH) $\cdot \alpha H_2O$ phase is feasible in this example per its large value $\Delta H_{\rm f}^{\circ} = -1971.6$ kJ/mol of enthalpy of formation if compared with $\Delta H_{\rm f}^{\circ} = -1288.6 \, \text{kJ/mol for Al(OH)}_{3} \cdot \alpha H_2 O$. A confined Al³⁺–OH⁻ surface-reaction interface in S hydrolysis in air has a self-controlled reaction at which only the intermediate

AlO(OH) $\cdot \alpha H_2O$ phase forms. A bulk reaction with a sufficiently large Al³⁺–OH⁻ interface in other methods results in the equilibrium Al(OH)₃· α H₂O phase.^{13,16} In general, the results are useful for understanding and modeling (i) formation of self-ordered structure and (ii) underlying mechanisms of physical processes in porous materials and for designing (iii) their electronic devices and components.

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