

Figure 1 The experimental ΔH_{V_02} values [1] plotted against $(4b - 2A_x)$ values; the line represents the situation if Equation 5 (i.e., $\Delta H_{V_02} = 4b - 2A_x$) was completely successful in predicting the experimentally observed ΔH_{V_02} values. See text for significance.

be doubled. These facts may be expressed by the equation

$$\Delta H_{V_02} = 4b - 2A_x \quad (4)$$

where ΔH_{V_02} is, of course, per mole; the value of A_x is 156 k cal³. One may verify Equation 5 by means of the data given in Table I. It is clear that the ΔH_{V_02} values given by Equation 5, namely, $(4b - 2A_x)$ values, agree very well with the experimental values [1] for Ta_2O_5 , WO_3 and Y_2O_3 ; the agreement for TiO_2 , V_2O_5 and Nb_2O_5 is less than satisfactory. However, the general validity of the suggestion presented here is emphasized by Fig. 1 in which $(4b - 2A_x)$ values have been plotted against the experimental ΔH_{V_02} values; the line drawn represents the theoretical curve expected if Equation 5 were completely successful for predicting the experimental ΔH_{V_02} data. It would appear that the

agreement between the experimental and the Equation 5 values of ΔH_{V_02} is rather good, keeping in mind the scatter and uncertainties involved in the experimental determinations [1] of ΔH_{V_02} .

It should be emphasized that the Equation 5 proposed here is not really new since it is based on the original excellent suggestion of Kofstad [1] (i.e. Equation 1). It does provide, however, a follow-up of Kofstad's reasoning, especially with regard to the present proposal that the number, "167" in Equation 1 may perhaps be identified with the $-A_x$ value.

It should be pointed out here that in the present discussions the quantities being considered are *partial* molar heats of solution of oxygen since formation of an oxygen vacancy refers to a non-stoichiometric oxide [5, 6]. Also, since the proposed correlation (Fig. 1) has been obtained solely from the oxygen dissociation energy, it would follow that the partial heats of solution of the cations in the oxides considered have negligible values. This has indeed been observed for some oxides previously [5].

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Received 23 May

and accepted 1 September 1973

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Comment on "Voluminous oxidation of aluminium by continuous dissolution in a wetting mercury film"

Pinnel and Bennett [1] have used X-ray diffraction to investigate the fronds of white material which issue from the surface of aluminium wetted with mercury and exposed to moist air. Although the material had to be

heated to 750°C for 48 h to obtain an identifiable pattern, they concluded that even the "as-grown" material is γ -alumina in a microcrystalline form. The purpose of this letter is to question their conclusion, by recalling earlier studies and by presenting new evidence which may advance the understanding of the catastrophic oxidation of aluminium under these conditions.

In a comprehensive study of the material,

Watson, Vallejo-Freire, Santos and Parsons [2], using both X-ray and electron diffraction, found the "as-grown" material is amorphous even to electrons. However, after ageing in cold water for a period of months, a definite Bayerite pattern was obtained by X-ray diffraction. (Bayerite is one form of $\text{Al}(\text{OH})_3$ —alternatively written as $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$.) They also found that specimens lost up to 40% by weight on ignition. Since these observations are similar to the well-known behaviour of amorphous aluminium hydroxide precipitated from aqueous solutions, they describe the material as an amorphous aluminium hydroxide containing adsorbed water. Vedder and Vermilea [3] found more direct evidence for the presence of protons in the material in the comparison of the infra-red spectrum with that of Boehmite, $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$ or $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$.

We have repeated most of the studies of Watson *et al* [2], and can confirm their observations. Further, using electron diffraction, we have identified Bayerite in specimens aged in air for 6 months or in cold water for 2 weeks. Alternative crystallization by boiling in water for 5 min gives Boehmite, identifiable by X-ray diffraction.

In order to establish unequivocally the presence of protons in the "as-grown" material, and study their nature, we have carried out a comparative n.m.r. study of the material, three forms of hydroxide, and the chemisorbed residual hydroxides on a sample of γ -alumina. Specimens for resonance were contained entirely within the rf coil, and consisted of at least 100 mg of material contained in thin-walled 7 mm glass tubes which could be evacuated and then filled with dry nitrogen before resealing. The proton resonance was observed in a field of about 1650 G at a frequency of 7 MHz. The measurements were made using a fast passage technique so that the absorption line and not its derivative was obtained directly. The detecting apparatus was a marginal oscillator and the output from this unit was directly connected to a PDP-8 computer so that continuous averaging techniques could be used. Fig. 1 shows the composite line found in the "as-grown" material, and the removal of the narrow component by evacuation and heating. The width of the narrow line is broadened by the technique used. An independent study of this region by a high resolution bridge method shows its true width to be a few hundred milligauss; such a width and behaviour is normally attributed to physically-

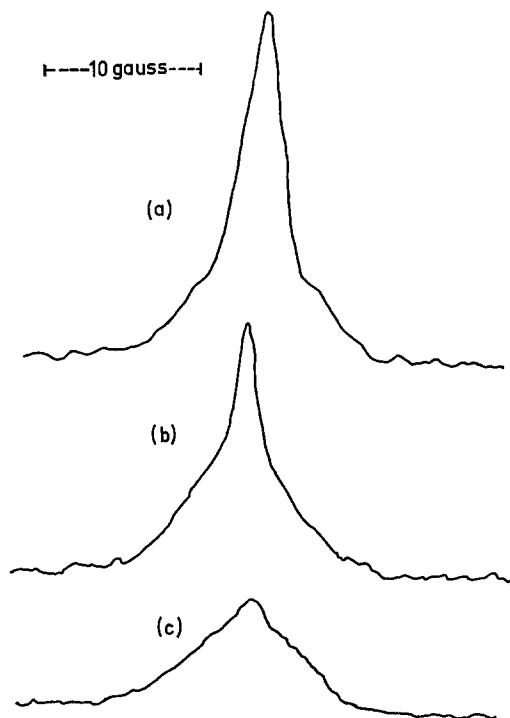


Figure 1 Proton magnetic resonance spectra of the product of the Al/Hg/moist air reaction. (a) As-grown; (b) after 10 min pumping at room temperature; (c) after 20 min pumping at 100°C.

bound water molecules. The half-height width of the broad component, measured after evacuation at 100°C for about 20 min, is given in Table I, along with those measured for the comparison materials after similar pre-treatment. Since the area under an absorption line is proportional to the number of protons in the rf coil, we also compare in Table I the areas under the absorption lines for an equal mass, after treatment, of each substance. These values are mutually consistent with the respective molecular formulae of Gibbsite ($\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$) and Boehmite, but unexpectedly low for Bayerite. The area under the line for Gibbsite or Boehmite may then be used as a calibration of the response to a known number of protons, the proton content of the other substances evaluated, and used to obtain a molar ratio of alumina/water. By assuming that the weight loss on evacuation at 100°C was due to loss of water only, this molar ratio may also be calculated for the untreated specimens. The results of this procedure are summarized in Table II. Whereas Bayerite is reputedly stable at 100°C, a considerable

TABLE I N.M.R. measurements

Material	Formula	Line width (gauss)	Relative area/mg	
			Experimental	Formula
Natural gibbsite	$\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$	10.0	2.3	2.3
Synthetic bayerite	$\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$	8.1	1.4	2.3
Synthetic boehmite	$\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$	9.1	1	1
γ -alumina	Al_2O_3	6.0	0.2	0
Precipitated amorphous aluminium hydroxide (before recrystallization to pure boehmite)	?	8.9	1	
Al/Hg/moist air				
1	?	7.3	1.4	
2	?	7.4	0.7	
3	?	7.2	1.0	

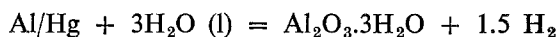
 TABLE II Molecular ratios $\text{H}_2\text{O}:\text{Al}_2\text{O}_3$

Material	After treatment	Untreated
Bayerite	1.4	2.8
Al/Hg/moist air		
1	1.5	2.9
2	0.7	2.4
3	1.0	2.4

deviation from stoichiometry is evident here. The material grown on the Al/Hg surface has a variable water content, particularly after the drying procedure, suggesting that the equilibrium value at that temperature had not been established. A less rigorous outgassing would probably suffice to remove only the "narrow-line" water. If the protons of the treated material are to be described as hydroxyls chemisorbed at the surface of γ -alumina, a surface area of over $1500 \text{ m}^2 \text{ g}^{-1}$ would be required to give the lowest ratio found for the specimens studied. (This assumes an area per hydroxyl of $19 \times 10^{-16} \text{ cm}^2$, as determined from the known BET area of the actual γ -alumina included in the study.) Because of this high value, and because γ -alumina has never been found to rehydrate to Bayerite or Boehmite [4], we believe that the material is best described as an amorphous aluminium hydroxide. Its recrystallization processes will be as complex as that of any of the hydroxides of aluminium and, for example, very precise conditions would be required to obtain γ -alumina by heating [5].

When mercury-treated aluminium is reacted with liquid water rather than moist air, at room temperature the initial product is amorphous, recrystallizing to Bayerite [6]. The

evolution of hydrogen is tacitly assumed. There is obvious evolution of gas and since this can be ignited, the reaction may be written

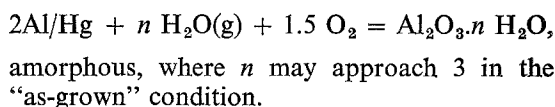


However, this equation has also been quoted [2] as applicable to the moist air reaction, without evidence. We constructed a small, constant volume, constant humidity apparatus to detect any pressure change consequent to reaction. This consisted of a small glass bucket hanging in a tube containing the water supply and attached to a capillary manometer. The specimens on which reaction had been started were placed in the bucket, and the starting pressure in the system adjusted to atmospheric by briefly opening a tap. Using this apparatus, we have established:

1. that the pressure *decreases* in the system during reaction, by as much as 10 cm; this reduction was confirmed to be in the partial pressure of oxygen by using an oxygen analyser based on the paramagnetism of oxygen;

2. that the reaction can proceed at water vapour pressures down to 4.5 mm (over ice), but cannot be sustained at 3.5 mm (over a saturated solution of potassium acetate at 20°C).

The reaction must then be written as



The dual nature of the reaction in gas and liquid phases is suggestive of an electrochemical basis for both. In the vapour phase, a minimum vapour pressure of water may be needed to

TABLE III Standard potentials (25°C)

Mg ²⁺ /Mg	-2.38
Al ³⁺ /Al	-1.66
Ga ³⁺ /Ga	-0.52
Bi ³⁺ /Bi	+0.23
O ₂ /OH ⁻	+0.40
Hg ₂ ²⁺ /Hg	+0.80
O ₂ , H ⁺ (10 ⁻⁷ M)/H ₂ O	+0.82

create a cell by multilayer adsorption of water at the relevant interface.

Aluminium also dissolves in gallium to form liquid alloys at room temperature [7]. We have found that such alloys produced on an aluminium substrate are quite stable in moist air, although they are extremely reactive with liquid water [7], with evolution of hydrogen. In this liquid phase reaction, the grey precipitate was largely very finely divided aluminium and gallium, from which could be separated a white product, giving the X-ray pattern for Boehmite, after drying at 100°C. The failure of the aluminium dissolved in gallium to react in moist air is evidence for some specificity in the action of mercury. We suggest that mercury functions as an efficient cathode for the reduction of oxygen. The behaviour of other mercury/metal systems reported by Pinnel and Bennett [1] appears consistent with this proposal. Thus, the failure of the bismuth-mercury system to show such oxidation may be due to the relative positions of bismuth and mercury in the electrochemical series. The relevant values of standard potentials are given in Table III. Watson *et al* [2] remarked on the similarity in morphology of anodic films on aluminium and the growth on aluminium/mercury, but their mechanism of growth due to upward pressure of hydrogen supposedly evolved

cannot be correct. We suggest that the growth is anodic. The mercury/aluminium couple recurs at intervals over the surface leading to a discontinuous film.

Acknowledgements

We are pleased to acknowledge the assistance of Dr J. V. Sanders with electron microscopy, and of Dr D. Mainwaring with the preparative procedures of the comparison materials. We also thank Dr Mainwaring for discussions on the relationship between the various aluminium hydroxides, and Dr J. McAndrew for the sample of natural Gibbsite from Myalla, Tasmania.

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Received 9 July

and accepted 16 July 1973

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Authors' reply to "Comment on 'Voluminous oxidation of aluminium by continuous dissolution in a wetting mercury film'"

We appreciate the comments of Bruce and West [1] concerning our paper "Voluminous oxidation of aluminium by continuous dissolution in a wetting mercury film" [2]. Although their NMR study of this intriguing phenomenon was interesting to us, we did not find their results conclusive. They conclude that the "as-grown" material is best described as an amorphous

aluminium hydroxide rather than molecular size γ -alumina on the basis of (1) their NMR results which imply that a surface area of over 1500 m² g⁻¹ would be required to obtain a sufficient quantity of physically adsorbed water molecules to account for the number of protons observed, (2) a statement from their Ref. [4] that γ -alumina has never been found to rehydrate to Bayerite or Boehmite, and (3) a statement from their Ref. [5] that very precise conditions would be required to obtain γ -alumina by heating any form of aluminium hydroxide.

As we reported [2], heating the "as-grown"

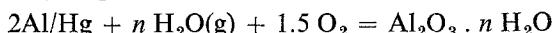
material in air at 750°C for 48 h produced well-crystallized γ -Al₂O₃ with an average particle size of 68 Å. Using this size, a density of 3.7 g cm⁻³ for γ -Al₂O₃, and assuming a spherical shape, the calculated minimum surface area would be 240 m² g⁻¹. As indicated by the X-ray data, "as-grown" particles are substantially smaller than 68 Å and certainly would not be spherical so that a surface area in the order of 1500 m² g⁻¹ as required by Bruce and West is not unrealistic. (Even spherical particles in the order of 10 to 15 Å would yield such a surface area.)

As reported in our more recent paper [3], rehydration of well-crystallized, 68 Å γ -alumina to Boehmite was accomplished by boiling in water for 3 h. This was verified by both X-ray diffraction and DTA results. Thus, the results of Bruce and West that the "air-grown" product was converted to Bayerite by cold water immersion for 2 weeks or to Boehmite by boiling water immersion for 5 min are not at all verification that the starting material must be a hydroxide.

Finally, we did not find very precise heating conditions to be required to convert the "air-grown" Al/Hg reaction product to well-crystallized γ -Al₂O₃ [2]. In fact, almost any temperature between 600 and 900°C for some period of time should accomplish this. Additionally, both Bayerite and Boehmite were readily converted to γ -Al₂O₃ (verified by X-ray diffraction) [3] by heating at 10°C min⁻¹ to 550°C in a DTA apparatus. Thus, the ability to convert or ease of conversion of any of these materials to well-crystallized γ -Al₂O₃ is not conclusive evidence toward identifying the character of the starting material.

Therefore, based on the aforementioned points and the results of DTA and TGA evaluation [3] of the moist air and water grown Al/Hg reaction products, we are still led to the conclusion that the moist air grown material is best described as a molecular scale γ -Al₂O₃ with physically adsorbed water and not water of crystallization.

The suggestion by Bruce and West that the reaction in both gas and liquid phases has an electrochemical basis is very plausible and we certainly agree that mercury has a unique and specific action with aluminium. However, we must point out that we found the moist air reaction also occurs in moist nitrogen as previously reported [2]. Thus, to ascribe the single equation



to the reaction is still questionable in our minds both from the true nature of the reaction product and from the specific action of water vapour and oxygen in forming it.

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Received and

accepted 16 October 1973

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Surface preparation of MgO single crystal substrates

The surface condition of the magnesium oxide single crystal substrate in the epitaxial growth of ferrite is known to have an adverse effect on film quality. As-cleaved or as-sawn substrate surfaces are unsuitable because of cleavage and mechanical damage (see Fig. 1). We have found that a short manual polish of approximately 2 min with 400 and 600 silicon carbide papers followed by 1 h polishing treatments using a polishing machine with each of the following grades of diamond paste, 14, 6, 3, 1 and 0.25 μ m, yields surfaces which are markedly smoother. Only shallow

grooving and small surface protuberances are observed when these surfaces are examined in the scanning electron microscope. These surface features can be removed by chemical polishing. The most satisfactory chemical polish has been found to be orthophosphoric acid maintained at 170°C, with the specimen immersed for periods from 10 sec to 3 min. The surfaces produced in this way are flawless apart from minor pits (Fig. 2).

Some uncertainty exists regarding the most successful final polishing treatment of substrates for ferrite and garnet films. In some investigations a final treatment with Syton is claimed to be the most satisfactory technique for preparation of