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Reactions between mercury-wetted aluminium and liquid water

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The reaction of solid aluminium with liquid water has been studied by several investigators. In this paper, the reaction between mercury-wetted aluminium and liquid water is described. At 25 and 90 °C, the reaction products were identified by X-ray diffraction analysis as bayerite, β-$Al_2O_3.3H_2O$, and boehmite, α-$Al_2O_3.H_2O$, respectively. The transitions of these hydrates to γ-Al_2O_3 upon heating were indicated by endothermic peaks on DTA thermograms and weight-loss measurements by TGA.

The wetting mercury film acts as a medium for rapid transport of aluminium in solution from the solid–liquid interface to the liquid–vapour or liquid–liquid interface. This unique condition produces readily identifiable materials since it avoids some of the difficulties encountered by other investigators in their attempts to study the reactions of air and liquid water directly with aluminium foil or bulk samples.

1. Introduction

The rapid formation of a protective barrier layer on solid aluminium under ambient conditions is well recognized. This layer is less than 100Å thick and is usually described as amorphous [1-3]. Investigations to characterize and identify it are hampered by the proportionately small amount of material which forms on a given quantity of solid metal. The authors previously reported on the reaction that occurs when mercury-wetted aluminium is exposed to *air* [4]. Under such conditions, a spontaneous and rapid growth of a fibrous or ribbon-like product emanated from the wetted surfaces. The voluminous product, which readily disintegrated to powder, was identified as γ-Al_2O_3 and not an amorphous hydroxide as described by others [5, 6].

The reaction of solid aluminium and liquid water has been studied by several investigators [6, 9]. In addition to the initial barrier layer, a layer of aluminium hydroxide is formed which may grow to several microns at 100°C. Vedder and Vermilyea presented a mechanism for the reaction between solid aluminium and liquid water which consisted of three essential steps: 1. amorphous Al_2O_3 formation; 2. dissolution of the Al_2O_3 to form soluble species; and 3. precipitation of aluminium hydroxide (AlOOH) from the solution [6]. In the present paper, the authors describe the reaction between *liquid water* and mercury-wetted aluminium. This approach takes advantage of the wetting mercury film which acts as a medium for rapid transport of aluminium atoms from the aluminium–mercury interface to the mercury–water interface; thus, adequate quantities of reaction products from these unique conditions can be readily obtained for various detailed analyses. However, these unique conditions may not necessarily result in products identical to those obtained by direct reaction of mercury with liquid water.

2. Description of the interaction between mercury-wetted aluminium and liquid water

The experimental procedure in this investigation was quite similar in the initial stages to that previously reported for studying the interaction of mercury-wetted aluminium and moist air [4]. The normal passivating layer of a typical aluminium sample (~ 0.25 g) was chemically stripped by lowering the sample into a beaker containing sequential layers of dilute hydrochloric acid (HCl) and mercury. The HCl removed the oxide layer and the mercury was then able to wet the entire surface. The HCl was flushed off the mercury layer by distilled water which, in turn, was decanted off the mercury layer. The specimen was then removed from the mercury pool and placed in a clean beaker containing distilled water.

At room temperature (23 to 25° C) a reaction did occur but it was much less dramatic than that of the spontaneous emanation observed in air [4]. The evolution of hydrogen was almost immediately detectable but it was approximately one day before the water became cloudy with reaction product. The experiment was terminated after 460 h by removing the mercury-wetted aluminium sample. Upon removal and exposure of the residual aluminium sample to air, the fibrous product spontaneously started growing from its surface. The water in the beaker was allowed to evaporate at room temperature and the reaction product was air-dried to a white powder. Products of both reactions, i.e., from in the water and after removing the aluminium from water, were analysed by differential thermal analysis and by X-ray diffraction prior to, and after, the DTA evaluations. The two products were different. However, immersion and reaction in liquid water had no effect on the subsequent air reaction; the reaction product in air again was γ-Al_2O_3.

Another aluminium sample was acid-stripped and mercury-wetted in the same manner and then allowed to react with liquid water maintained at 90° C. Under this condition, the reaction proceeded rapidly as evidenced by the vigorous evolution of hydrogen and the prompt clouding of the water. In a matter of days (1 week) the reaction proceeded to completion and the entire aluminium sample (0.25 g) was consumed. The beaker and contents were kept at 90° C until the water had evaporated and the reaction product dried. As with the material from the room temperature reaction, the dried cake readily crumbled into white powder which was evaluated by DTA and X-ray diffraction.

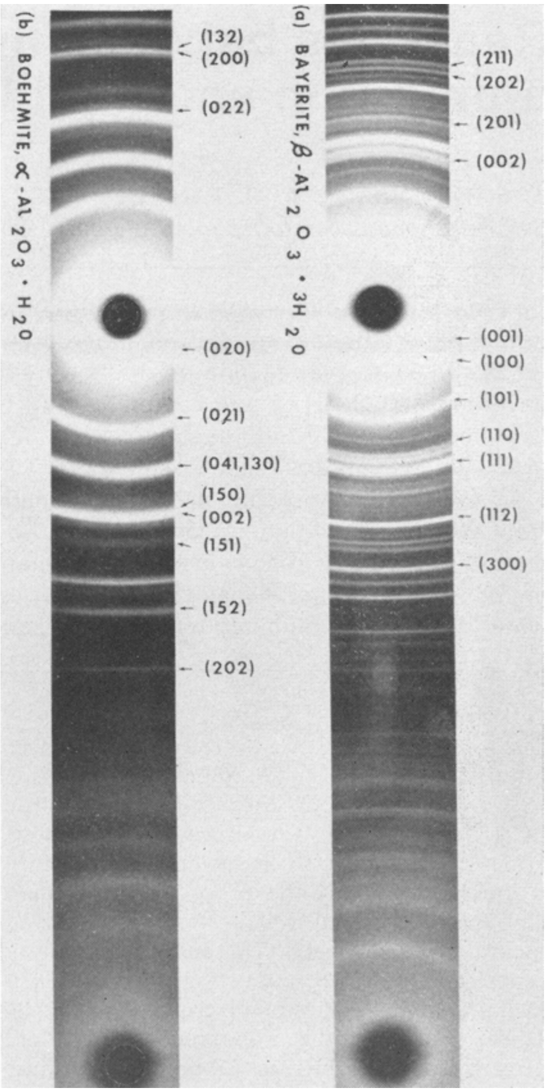

Figure 1 Debye-Scherrer X-ray patterns (Cu$K\alpha$, 45 kV, 35 mA) of products from mercury-wetted aluminium–liquid water reactions at (a) 25° C and (b) 90° C.

3. X-ray analysis of reaction products

The products of the reactions between mercury-wetted aluminium with water at 25 and 90° C were analysed by X-ray diffraction; the Debye-Scherrer powder patterns are shown in Fig. 1. The 25° C product was identified as β-$Al(OH)_3$ or bayerite, and the 90° C product was identified as α-AlOOH or boehmite; they are also designated as the beta-trihydrate, β-$Al_2O_3.3H_2O$, and the alpha-monohydrate, α-$Al_2O_3.H_2O$, respectively. The formation of boehmite films on aluminium by reaction with water and steam has been well documented by Altenpohl [9]. The formation of bayerite films at low temperatures has not been as widely noted but it has been reported by Keller and Edwards [10]. Table I lists pertinent characteristics of various forms of alumina and alumina hydrates.

It is clear from the X-ray patterns that the products produced by these reactions were well crystallized. Bernard and Randall [8] obtained very diffuse X-ray patterns from films produced in reactions above 80° C and could not conclude that they had produced pure boehmite. Similarly, Vedder and Vermilyea [6] in their studies of the

TABLE I Characteristics of some forms of alumina and alumina hydrates.

Alumina form	Formula	Mineral name	Crystal symmetry	Lattice constants (Å)			Specific gravity
				a	*b*	*c*	
Alpha-alumina	αAl_2O_3	Corundum	Trigonal	4.76	—	12.991	4.0
Gamma-alumina	γAl_2O_3	—	Cubic	7.9	—	—	7
Alpha-monohydrate	$\alpha Al_2O_3.H_2O$	Boehmite	Orthorhombic	3.78	11.8	2.85	3.0
Beta-monohydrate	$\beta Al_2O_3.H_2O$	Diaspore	Orthorhombic	4.73	9.36	2.82	3.4
Alpha-trihydrate	$\alpha Al_2O_3.3H_2O$	Gibbsite	Monoclinic	8.62	5.06	9.69	2.42
Beta-trihydrate	$\beta Al_2O_3.3H_2O$	Bayerite	Hexagonal	5.01	—	4.69	2.5

reaction between H_2O and aluminium at 50 to 100°C, identified the reaction product as "pseudoboehmite" by its infra-red spectrum but could not support that conclusion by X-ray diffraction. They characterized pseudoboehmite as a poorly crystallized defect structure which contains more hydroxyl ions than correspond to the formula AlOOH, i.e., the compound may vary from 1.5 to 2.5 H_2O per Al_2O_3.

The results of this investigation clearly show that the reaction of mercury-wetted aluminium with liquid water forms different products at temperatures of 25 and 90°C, and that both products are well crystallized.

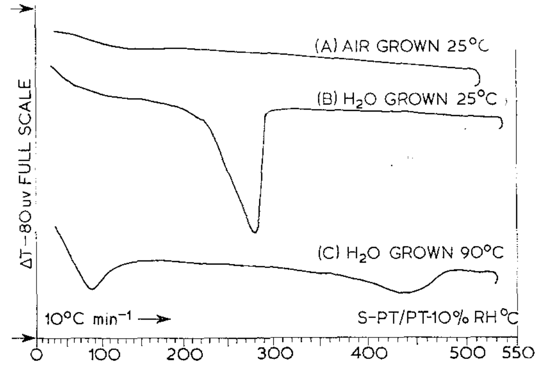

Figure 2 DTA thermograms of products from reactions of mercury-wetted aluminium with moist air or liquid water.

4. Thermal analysis of reaction products

Additional information on the reaction products and their behaviour with increasing temperature was obtained by differential thermal analysis in normal air environment. The equipment used in this study was a CSI-Stone DTA System which consisted of an RC 202A recorder-controller, a P-202 furnace platform, and an F202LT furnace. The sample holder was an SH-202-13Pt with ring-type differential thermocouples of Platinel II and a reference thermocouple of Pt/Pt–10% Rh. Samples and reference material, pure α-Al_2O_3, were contained in small platinum pans which fit inside the ring-type differential thermocouples. The temperature axis was calibrated using the melting points of 99.99% pure tin (232°C) and lead (327°C).

In Fig. 2 are thermograms obtained by heating at 10°C min^{-1} in air the reaction products of mercury-wetted aluminium with (A) air at 25°C, (B) liquid water at 25°C, and (C) liquid water at 90°C. The starting materials, as identified by X-ray diffraction, were molecular-scale γ-Al_2O_3 [4], bayerite, and boehmite, respectively. Sample and reference weights were 5 mg except for A; the voluminous character of the air-grown product permitted only a 1 mg sample to be used. After heating the samples to 500 to 550°C and cooling to room temperature, all samples were found to have converted to well-crystallized γ-Al_2O_3.

Thermogram 2A shows no evidence of phase transformations over the temperature range investigated. A shallow endothermic reaction near 100°C is due to evaporation of adsorbed water. In thermogram 2B, the large endothermic peak at 280°C is due to the loss of water of hydration upon the apparent conversion of β-$Al_2O_3.3H_2O$ directly to γ-Al_2O_3. In thermogram 2C, there is a peak again due to loss of adsorbed water near 100°C and then an endothermic transition at 440 to 450°C due to loss of water of hydration upon conversion of α-$Al_2O_3.H_2O$ to γ-Al_2O_3. The relative sizes of the peaks of 2B and C indicate the greater endothermic reaction due to the loss of more water of hydration with β-$Al_2O_3.3H_2O$, as would be expected.

From 2B it appears that the β-$Al_2O_3.3H_2O$ converts directly to γ-Al_2O_3 with no intermediate transition of β-$Al_2O_3.3H_2O$ to α-$Al_2O_3.H_2O$. A sample of β-$Al_2O_3.3H_2O$ was heated in the DTA apparatus up to completion of the bayerite transition (300°C) and then cooled to room temperature. In this instance, X-ray diffraction analysis of the sample after DTA showed it to be composed of both α-$Al_2O_3.H_2O$ and γ-Al_2O_3. In order to aid in resolving the mechanisms of the transitions, samples of the three as-prepared materials were evaluated by thermogravimetric analysis (TGA). Weight losses were determined with a Cahn automatic recording microbalance by heating individual 5 to 10 mg samples at 10° C min^{-1} up to 500° C under flowing nitrogen gas. The air-grown material showed a continuous loss in weight from room temperature to 250° C. A total weight change of 37% was 95% completed by 150°C; no abrupt changes were discernible above that temperature. This loss is attributed to water adsorbed by this voluminous high surface-area material. The absence of transitions above 150° C further confirms that the air-grown material was γ-Al_2O_3. The TGA curve for boehmite, α-$Al_2O_3.H_2O$, showed a gradual weight loss beginning near 80° C and continuing up to 400 to 425° C. This gradual weight change agrees fairly well with the course of the DTA curve (2C) for this material. The measured weight loss of 15.4% is in very good agreement with the theoretical amount (15%) for the monohydrate → gamma conversion. For bayerite, β-$Al_2O_3.3H_2O$, the weight loss was relatively more abrupt; primarily occurring between 140 to 240° C, it also correlated fairly well with the DTA curve (2B). With this material there was a continued gradual weight loss above 240° C to about 400° C. The measured weight loss for the abrupt transition was 27% which is slightly larger than the theoretical value (23.6%) for the trihydrate → monohydrate transition; however, the total weight loss of 33.8% agrees with the theoretical loss (34.6%) of 3 moles of water.

In view of the X-ray and thermal analysis data, it is concluded that bayerite transforms upon heating by an overlapping two-step process bayerite → boehmite → gamma. The evidence indicates that the DTA peak near 280° C (2B) represents the completion of the first step; the second transition, however, begins below this temperature and is so gradual that it is not detected with DTA. The overlapping nature of the two processes does not permit much boehmite to exist at any given time and its transition to gamma is masked by the coinciding and more endothermic bayerite to boehmite transition.

Some additional DTA results are illustrated in Fig. 3. They show the effects of various treatments upon alumina produced by the mercury-wetted aluminium-moist air reaction at 25° C. Thermogram 3A is of the as-grown material, molecular-scale γ-Al_2O_3, and is included for reference (same as 2A). A sample of the as-grown material was heated to 750° C in air to produce well crystallized γ-Al_2O_3. As expected, the DTA plot upon reheating the sample at 500° C showed no evidence of any reaction (3B), and subsequent X-ray analysis confirmed it. It is significant to note that thermograms 3A and 3B are almost identical, supporting the conclusion that the alumina grown in this manner at 25° C is γ-Al_2O_3 [4].

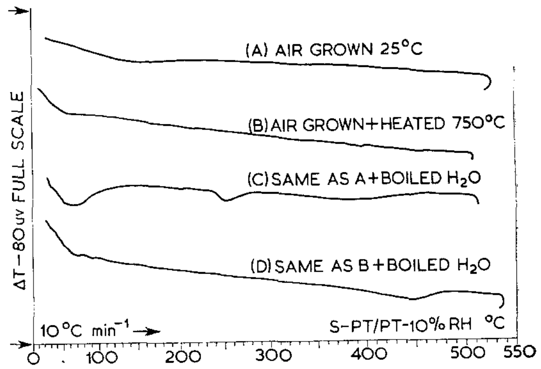

Figure 3 DTA thermograms after indicated treatments of the mercury-wetted aluminium-moist air reaction product.

Thermogram 3C was obtained with a sample which had been air-grown, boiled in water for 3 h and then dried in air. This treatment, according to Vedder and Vermilyea [6], produces pseudo-boehmite. However, X-ray diffraction analysis of this material indicated that it was a mixture of boehmite with traces of bayerite. Differential thermal analysis, thermogram 3C, showed the loss of adsorbed water near 100° C, a small peak at 250 to 260° C, and a very gradual endothermic reaction in the vicinity of 400° C; the latter peaks correspond to the bayerite and boehmite transitions to γ-Al_2O_3 as indicated previously in Fig. 2. The slightly lower transition temperatures in this sample may be due to the mode of preparing the starting material. Altenpohl [9] showed that DTA peaks for the boehmite transition ranged from 300 to 550° C depending upon the manner in which it was produced. The sizes of the two peaks in 3C are significantly smaller than either of the corresponding individual peaks in 2B and 2C, yet the sample and reference weights were the same for all three. It is suspected that much of the air-grown molecular-scale γ-Al_2O_3 remained as such even after boiling, thus leading to only small peaks for the correspondingly smaller proportion of bayerite and boehmite which retransformed in 3C.

Thermogram 3D was obtained with a sample which had been air-grown, heated to 750°C to form well crystallized γ-Al_2O_3, boiled in water for 3 h, and then air-dried. The X-ray pattern of this material revealed that it was boehmite and residual γ-Al_2O_3. Accordingly, the only transition indicated in 3D is that for boehmite to γ-Al_2O_3 near 450°C.

5. Summary and conclusions

In a previously reported investigation [4] it was stated that the product of the reaction between mercury-wetted aluminium and moist air was γ-Al_2O_3 rather than a hydroxide or hydrate. This conclusion was based on the results of X-ray diffraction analysis which showed two broad bands of X-ray intensity. More conclusive evidence has now been generated with DTA analysis of this material and comparison with a similar reaction in liquid water. More specifically, both the unaltered air-grown product and the air-grown product which had been heat-treated at 750°C to produce well crystallized γ-Al_2O_3 showed identical thermograms with no endothermic or exothermic reactions indicated. The reaction of mercury-wetted aluminium with liquid water at 25 and 90°C produced β-Al_2O_3.$3H_2O$ (bayerite) or α-Al_2O_3.H_2O (boehmite) respectively. The transitions of these hydrates to γ-Al_2O_3 were clearly indicated by endothermic peaks on DTA thermograms and weight loss measurements by TGA. Additional boiling water treatment of air-grown material produced a mixture of boehmite and bayerite and not pseudoboehmite as has been observed by others [6].

The presence of the wetting mercury film has an important role in these reactions. It acts as a medium for rapid transport of the dissolved aluminium from the solid–liquid interface to the liquid–vapour or liquid–liquid interface. The intimate and continued contact of the reactants at the liquid–vapour or liquid–liquid interfaces permits the reactions to occur rapidly until completed or disturbed. This unique condition produces readily identifiable materials since it avoids some of the difficulties encountered by other investigators in their attempts to study the reactions of air and liquid water directly with aluminium foil or bulk samples.

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