JOURNAL OF MATERIALS SCIENCE 7 (1972) 1016–1026

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

M. R. PINNEL, J. E. BENNETT
Bell Telephone Laboratories, Columbus, Ohio 43213, USA

Aluminium, in its normal passivated state, does not react with mercury, i.e., it is not attacked and does not wet or readily dissolve. When the passivating surface layer is removed from high-purity aluminium, the metal can be easily wetted by mercury and upon exposure to air a spontaneous and rapid growth of a fibrous or ribbon-like product emanates from the wetted surfaces. In this work it was observed that the reaction product had little mechanical strength and readily disintegrated into a molecular-scale powder. It was identified as γ-Al_2O_3 which even after heating for 48 h at 750°C was still of the order of 60 to 70 Å in average particle size. By consideration of the Al-Hg phase diagram, thermodynamic data, and further experimental observations, a mechanism for the phenomenon has been proposed. The probably unique situation which exists at room-temperature in the Al-Hg system enables a spontaneous reaction to take place between the aluminium dissolved in the wetting mercury film and the water vapour and oxygen present in the atmosphere. The influences of several variables on the reaction product morphology and relative reaction rate were investigated. Also, other mercury-metal systems were investigated for possible similar reactions.

1. Introduction

The problem of the interaction between liquid and solid metals has long been recognized [1, 2]. Studies have been conducted toward understanding the corrosive behaviour of such molten metals as Mg, Zn, Hg, Cd, Pb, Sn, Ga, In, Bi, and the alkali metals on common ferrous and nonferrous alloys [2, 3]. More recently attention has been directed toward the study of embrittlement of solid metals by liquid metals and liquid-metal solutions, Ga and Hg being given particular attention [4-6]. In general, these interactions are found to be destructive or detrimental to the properties of the solid metal. Few advantageous applications of the interactions between solid and liquid metals can be found in the literature. Two significant exceptions to this are noted. The first is amalgam metallurgy which uses the amalgamation of certain metals with mercury to extract relatively pure metals from low grade ores [7]. The other is intermediate phase synthesis from a binary liquid – solid metal system [8-10]. This technique uses the high diffusivity and transport properties of the liquid to aid in the continuous uniting of the two elemental constituents for the formation of an intermediate phase. In this paper the authors describe an unusual interaction between aluminium and mercury at room-temperature (25°C), propose a model for the reaction, and point out possible technological implications.

2. Description of the interaction between aluminium and mercury

When a piece of high purity (99.99 %) aluminium is wetted with mercury and air-exposed, a spontaneous and rapid growth of a fibrous or ribbon-like nature emanates from the wetted areas. A typical example of this growth is shown in Fig. 1. It is white in colour and often has a diaphanous appearance. This peculiar interaction has long been known [11, 12] but, to the authors' knowledge, the reaction product has not been clearly identified or characterized and the formation process has not been elucidated. In this work the material has been identified as

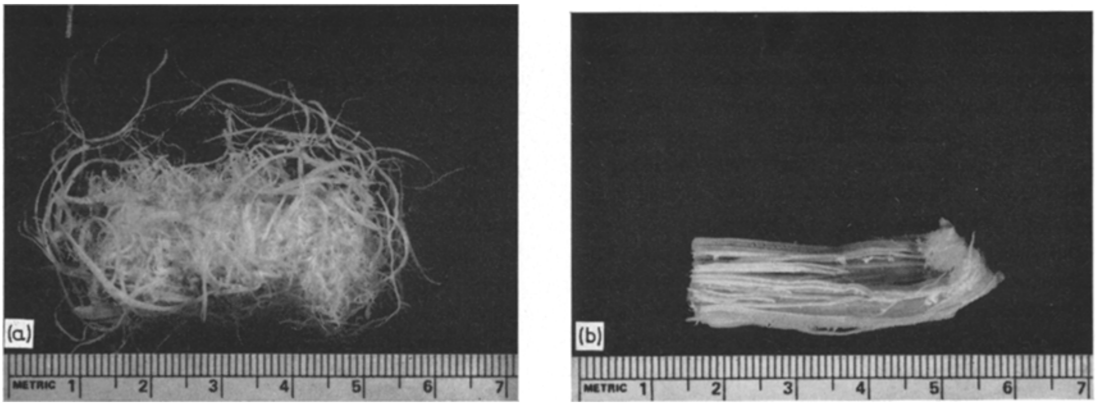

Figure 1 Typical "fibres" of aluminium–mercury–water vapour reaction product from mercury-wetted and air-exposed aluminium.

γ-aluminium oxide and the mechanism for its formation is presented in the following section.

3. Formation mechanism

The mechanism for the formation of γ-aluminium oxide utilizes the spontaneous reaction between a wetting mercury film on aluminium and the water vapour and oxygen present in the atmosphere. Under normal circumstances a piece of air-exposed aluminium has a stable and passive oxide layer which has been described as amorphous and which has been variously estimated at 20 to 100Å in thickness [13, 14]. In this state the aluminium is not wetted by mercury and no interaction between the two elements can occur. However, when the passivating layer is fractured in the presence of mercury, the mercury wets the exposed "clean" aluminium surface and an interaction between the two pure elements is possible.

The equilibrium diagram for the aluminium–mercury binary system as given by Hansen [15] is shown in Fig. 2. The system is a simple eutectic with the eutectic temperature practically

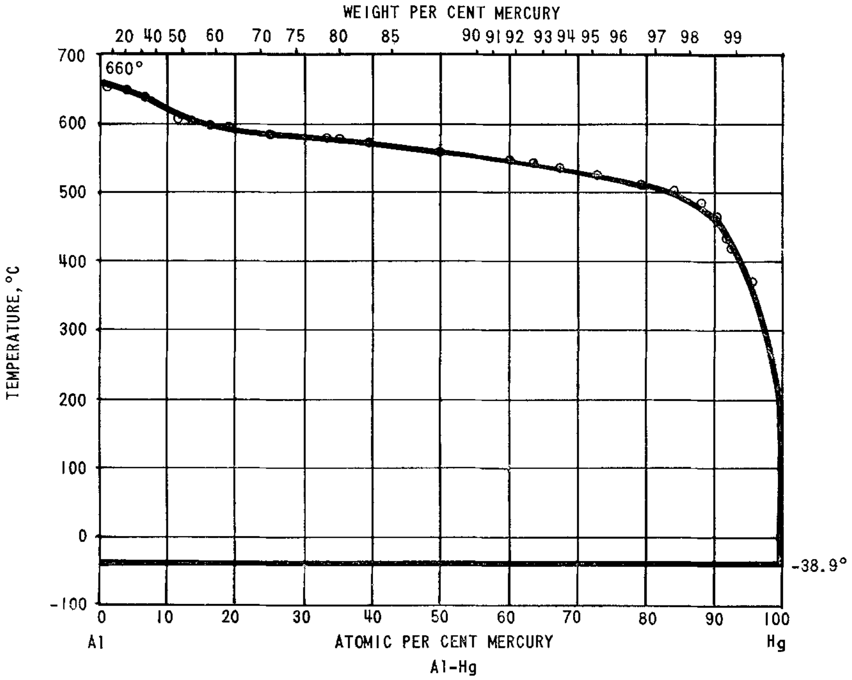

Figure 2 Aluminium – mercury equilibrium diagram (after Hansen [15]).

identical to the melting-temperature of mercury. Liquid mercury is insoluble in solid aluminium but a small solubility of aluminium in liquid mercury does exist (approximately 0.002 wt % at room temperature). Hence, at room-temperature (25° C) at a mercury-aluminium interface an equilibrium exists between a very dilute liquid solution of aluminium in mercury and pure aluminium. At the aluminium-mercury interface, aluminium is drawn into solution to satisfy equilibrium requirements. However, it is thermodynamically more favourable for the aluminium to exist as an oxide or hydroxide than as free atoms in mercury solution.

TABLE I Thermodynamic data (25°C) for aluminium oxide, aluminium hydroxide and water [16]

	ΔH^f (kcal/mol)	ΔG^f (kcal/mol)
Al_2O_3	− 399.09	− 376.87
$Al(OH)_3$	− 304.80	− 272.90
H_2O (g)	− 57.80	− 54.64
H_2O (l)	− 68.32	− 56.69

The available thermodynamic data on the free energy of formation for aluminium oxide and hydroxide are listed in Table I. On the basis of these data, several reactions are thermodynamically possible and they are listed below together with their respective free energy change of reaction.

$$2Al + 3/2O_2 \rightarrow Al_2O_3 + 377 \text{ kcal/mol} \quad (1)$$

$$2Al + 3H_2O\,(g) \rightarrow Al_2O_3 + 3H_2 \uparrow + 212 \text{ kcal/mol} \quad (2)$$

$$Al + 3/2O_2 + 3/2H_2 \rightarrow Al(OH)_3 + 273 \text{ kcal/mol} \quad (3)$$

$$Al + 3H_2O\,(g) \rightarrow Al(OH)_3 + 3/2H_2 \uparrow + 103 \text{ kcal/mol} \quad (4)$$

Alternatively, the water may act catalytically in the following sequence of reactions

$$\begin{gathered} 3H_2O\,(g) \rightarrow 3H_2O_{(ads)} \\ 2Al\,(Hg) + 3H_2O_{(ads)} \rightarrow Al_2O_3 + 6H_{(ads)} \\ 6H_{(ads)} + 3/2O_2 \rightarrow 3H_2O_{(ads)} \quad (5) \end{gathered}$$

Experimental results indicate that the reaction product is the oxide rather than the hydroxide, thus Equations 1, 2 or 5 are applicable. In spite of the fact that the formation of the oxide via Equation 1 is the most favoured thermodynamically, the fact, which will be detailed later, that moisture has a pronounced influence on the reaction indicates that Equations 2 and/or 5 represent the primary reactions taking place. These overall reactions actually consist of an additional step, namely the dissolution of aluminium in mercury,

$$Al(s) \rightarrow Al(Hg) \quad (5a)$$

followed by the reaction of the dissolved aluminium with water vapour as given by Equations 2 and 5. These bulk phase thermodynamics will be modified for a dilute solution of Al in Hg; however, this difference has been neglected.

The kinetic requirements for this reaction to proceed spontaneously are apparently more than satisfied on the top surface of the mercury pool (the mercury solution-air interface); hence, molecules of γ-aluminium oxide are formed at this interface. This reaction mechanism is depicted in Fig. 3 for a scratch wetted with mercury on a bulk piece of aluminium. The oxide formation depletes the solution of aluminium causing a departure from equilibrium at the aluminium-mercury interface. To satisfy equilibrium more aluminium is drawn into solution. The reaction is thus continuous until all the aluminium has reacted, provided the supply of water vapour is sufficient and the aluminium-mercury interface is not disturbed in such a way as to cause dewetting If the surface dewets, the aluminium forms its passive oxide layer and no further reaction can occur.

A point worth clarifying is the role of mercury in this reaction and the several important functions it performs. First, it serves to keep the bulk aluminium "active" by wetting the surface and thereby preventing intimate contact of aluminium and oxygen to form a passivating

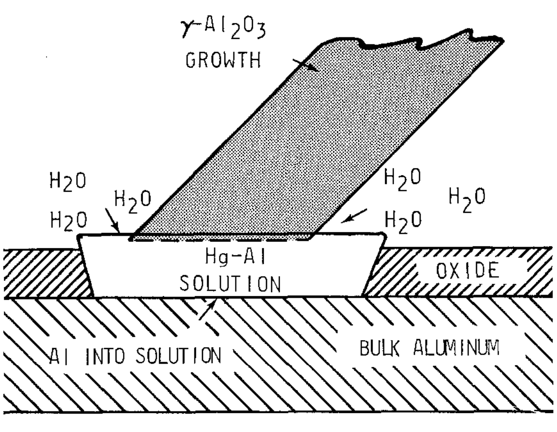

Figure 3 Physical schematic of the growth of the γ-aluminium oxide "fibres".

oxide layer. Secondly, its phase-equilibrium requirements serve to remove atoms from the bulk aluminium. Thirdly, since mercury is a liquid at room temperature it serves as a rapid transport medium to bring the aluminium atoms to a source of water vapour and provides the interface for continuously combining aluminium and water vapour on the molecular scale. However, the mercury itself is not depleted in the reaction; hence it plays a catalytic role.

This type of reaction should not be confined to the aluminium–mercury system alone. Any element which forms a liquid solution with mercury, which has a sufficiently large negative free energy of formation of its oxide or hydroxide, and which has an otherwise uncomplicated binary phase diagram with mercury may react similarly. What is meant by an uncomplicated phase diagram is one which has no intermediate phases. The formation of an intermediate phase at the element-mercury interface could prevent the continuation of the oxidation or hydroxylation reaction by placing a solid-state diffusion-controlled step in the removal of element atoms from the bulk sample into mercury solution. Several examples of other binary systems are presented in a later section of this paper.

4. Experimental verification and discussion

The experimental efforts centred on four areas, including: (1) identification of the reaction product and characterization of some of its physical properties, (2) influence of temperature, moisture and other processing variables on the growth-rate, (3) processing of the as-grown γ-Al_2O_3 into other forms of Al_2O_3, and (4) investigation of possible similar reactions in other systems.

4.1. Identification and characterization

The physical appearance of the reaction product varied as a function of the growth conditions. The details of these various conditions are specified in the next section and it is sufficient to mention at this point that two basic forms were noted. One form was white, opaque, and fibrous in appearance when viewed by the unaided eye or by low-power optical microscopy as shown in Fig. 1. Fig. 4 shows the same material when viewed at higher magnification in a scanning electron microscope. It appears to be layered, flaky, porous, and non-crystalline on a microscopic scale. The second form of reaction product grew as large continuous sections and had a diaphanous appearance as shown in Fig. 5.

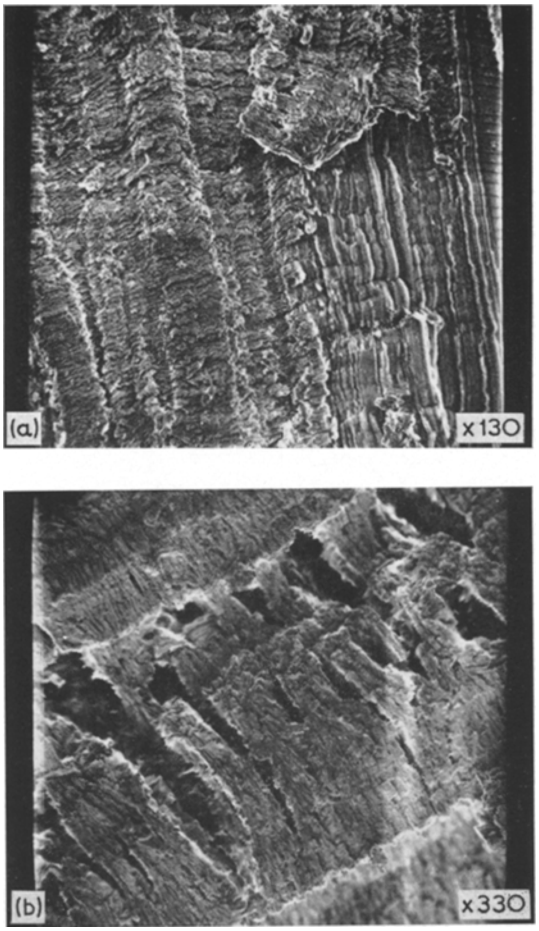

Figure 4 Typical "fibres" of the reaction product as viewed with secondary electrons on the scanning electron microscope.

In spite of the differences in physical appearance of the reaction product, both forms possessed minimal mechanical strength. They could be easily pulverized into a fine powder by agitation in a container. This indicates the lack of strong bonding in the as-grown condition. Hence, preparation of particles of the reaction product approaching molecular scale may be feasible. In any case, the pulverized material from both as-grown forms appeared to be identical and subsequent X-ray analysis verified this similarity of composition and structure.

Initial identification of the reaction product was attempted through the use of an X-ray diffractometer and an electron microprobe. The

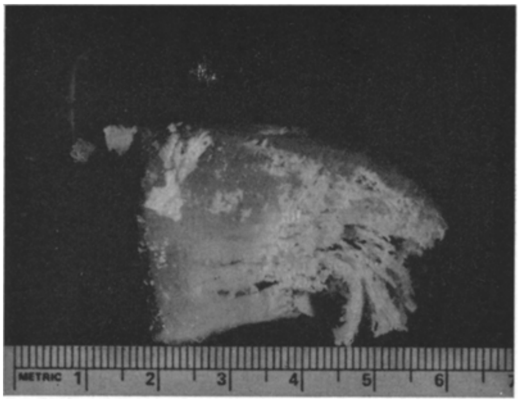

Figure 5 Example of the diaphanous form of aluminium-mercury-water vapour reaction product.

results were inconclusive. The diffractometer trace of the pulverized sample showed only a single broad band (approximately 4 degrees (2θ) half-intensity breadth) of low intensity X-radiation centred at 20 degrees (2θ). This "amorphous" peak was attributed to the 20% collodion binding solution used to form the powder specimen. A sample of the reaction product was isostatically compacted to densify the material and form an X-ray specimen without the use of a binder. This specimen gave no indications of any diffracted X-ray intensity, suggesting that the aluminium - mercury - water vapour - oxygen reaction product is amorphous, or of such small particle size as to produce insufficient diffraction conditions for detectable peaks. The quantitative data from the electron microprobe were also inconclusive, showing substantial scatter in aluminium concentration due to specimen charging. This scatter coupled with the inability of the microprobe to detect oxygen made distinction between an oxide and hydroxide impossible.

Debye-Scherrer X-ray powder patterns were tried and met with favourable results. Tragacanth gum was used as the binder since its diffracted X-ray intensity is relatively weak and at a sufficiently low angle as not to interfere with the principal lines of most allotropic forms of aluminium oxide, aluminium oxide hydrate, and aluminium hydroxide.

The powder pattern of the as-grown material had two broad bands of low intensity diffracted X-radiation, in addition to the lines from the tragacanth gum. Conclusive identification of a phase cannot be made on the basis of only two diffraction lines. This is particularly true in this instance where the line positions are not accurately resolved due to extensive line broadening. However, using an estimate of the centre of the intensity bands and comparing them to the known line positions and relative line intensities for the various allotropic forms of aluminium oxide, oxide hydrate, and hydroxide, it was found that only the gamma (γ) and eta (η) forms of aluminium oxide provide a possible match. Analysis of the powder following certain heat-treatments confirmed that when the material was more perfectly crystallized into larger particles it was the gamma form of aluminium oxide. Hence, it may be concluded that the product of the reaction is γ-Al_2O_3. The extensive line-broadening is due to the almost molecular size of the Al_2O_3 particles in the as-grown condition.

Density determinations were made on five pieces of the as-grown diaphanous material similar to that shown in Fig. 5. The pieces were first sectioned into orthogonal shapes for facility of volume determination by measurement with a scale. Weight measurements were made on a Mettler analytical balance which is accurate to 0.1 mg. The average density was found to be 1.30×10^{-2} g cm^{-3} compared to a theoretical density of 3.7 g cm^{-3} for γ-Al_2O_3 [17]. A ratio of these two densities shows the reaction product to be only 1/350th of the theoretical density. This is consistent with the molecular particle size and almost non-existent mechanical strength of the material. Density measurement could not be made on the fibrous form due to the inability to make volume determinations.

4.2. Processing variables

The influences of several variables on the reaction-product morphology and reaction rate were investigated. The variables of interest included the method of stripping the passivating oxide layer, temperature, and the absence or presence of moisture.

The first method applied for stripping the passivating oxide layer on the aluminium was mechanical. The aluminium specimen was simply scratched while it was submerged in a container of mercury. The scratched region exposed unoxidized aluminium to mercury and it immediately became wetted. Upon removal of the sample from the mercury pool and exposure to atmosphere, the white fibrous type of reaction product emanated from the wetted regions. The growth rate was sufficiently rapid to be observable with the unaided eye.

Chemical stripping was employed to wet the entire specimen surface rather than localized scratched regions. A block of aluminium was placed into a beaker through sequential layers of dilute hydrochloric acid (HCl) and mercury. The HCl stripped the oxide layer and the mercury was then able to wet the specimen surface. The HCl was flushed off the mercury layer with water prior to removal of the sample. This prevented any acid from remaining on the specimen and altering the reaction product once growth was initiated. The specimen was removed from the mercury pool and placed in a clean beaker. Growth of the diaphanous form of reaction product emanated from all surfaces of the specimen almost immediately. The growth rate was again sufficiently rapid to be detectable with the unaided eye.

As the temperature increases, the solubility of aluminium in mercury increases. Hence, it may be expected that an increase in temperature would cause an increase in the reaction rate. Experimentally it was found that an increase in temperature decreased the reaction rate and that a temperature of approximately 125°C was sufficient to stop the reaction. This may be attributed to the fact that the reaction is dependent on the presence of adsorbed water vapour and elevated temperatures inhibit this reaction by eliminating the water vapour at the mercury–air interface.

The influence of moisture was further investigated in a qualitative manner. The growth rate was observed when a mercury-wetted specimen was exposed to normal room atmosphere conditions (25°C, 45 to 60 rh). An identical specimen was observed while being maintained in a beaker which had a small amount of water in the bottom and which was covered with a moist towel (increased rh). The growth rate was substantially more rapid in the latter case. This provides some additional support to the conclusion that the reactant with aluminium is water vapour, either directly or as a catalyst, and that Equation 2 or 5 is the chemical equation for the observed reaction.

A specimen was fully submerged in a beaker of water so that it was essentially isolated from a source of oxygen. A reaction did occur, but the rate of growth of a reaction product was significantly slower than for the two previous conditions. Subsequent X-ray analysis identified this reaction product as beta aluminium hydroxide [β-Al(OH)$_3$], type B. The corresponding Debye-Scherrer pattern is given in Fig. 6. The different reaction products point to the strong influence of environment in determining which reactions occur and to the fact that Equation 5 rather than Equation 2 may define the primary reaction which occurs under normal atmospheric conditions.

Finally a specimen was placed in a container under flowing (1 litre/min) moist nitrogen (90% rh). This provided a condition of adsorbed water vapour but no oxygen. The typical atmospheric reaction did occur; however, the rate of growth was somewhat slower than in any previous atmospheric condition tested. Thus it may be that both reactions defined by Equations 2 and 5 actually occur in the formation of γ-Al$_2$O$_3$ from an Al-Hg solution.

4.3. Thermal processing of the reaction product

The aluminium–mercury–water vapour reaction product was subjected to a series of thermal treatments to determine the conditions necessary to transform it into other forms of aluminium oxide. A sequence of Debye-Scherrer powder patterns for pulverized samples of reaction product which were heated in air at a series of temperatures is given in Fig. 7. Long-time (110 and 72 h) heating at low temperatures (400 and 600°C, respectively) caused little alteration in the reaction product which was detectable by X-ray analysis. The morphology of the γ-Al$_2$O$_3$ is apparently stable to at least 600°C. However, a temperature of 750°C for 48 h was found sufficient to crystallize (coarsen the particle size) of the γ-Al$_2$O$_3$ and provide a conclusively identifiable powder pattern (Fig. 7c). At a temperature of 950°C for 50 h, the γ-Al$_2$O$_3$ begins to transform to alpha aluminium oxide, α-Al$_2$O$_3$. A considerable quantity of γ-Al$_2$O$_3$ is still present following this heat-treatment, however, as evidenced in Fig. 7d. In their work on the kinetics of the gamma-to-alpha alumina phase transformation, [18] Steiner *et al* found no trace of α-alumina after heating γ-alumina for 12 h at 900°C but some degree of sharpening and shifting of certain X-ray peaks could be observed indicating the beginning of a phase transformation at this lower temperature.

The most significant point to be noted from the X-ray results on the heat-treated powders of this investigation is the broadness of the diffraction peaks. Peak broadness can be due to a variety of causes but in this instance the only reasonable possibility for the extreme broadness is very small particle size. An *estimate* of the size of very small particles can be made through the use of the Scherrer formula and the measured peak width [19]. The formula is given as:

$$t = \frac{0.9\lambda}{\mathrm{B}\cos\theta_{\mathrm{B}}} \qquad (6)$$

where t = particle thickness (Å), λ = incident radiation wavelength (Å), θ_{B} = angle of diffracted peak, B = peak width at an intensity equal to half the maximum (radians) after correction for instrumental broadening. The Warren method was employed to correct for instrumental broadening where the corrected value of B is given as:

$$B^2 = B_{\mathrm{M}}{}^2 - B_{\mathrm{S}}{}^2 \qquad (7)$$

and B_{M} = measured specimen peak width, B_{S} = measured peak width of coarse grain standard for a peak having a 2θ value near that of B_{M}. A nickel (1 1 1) peak with $2\theta = 44.5°$ was used as the standard for the measured (400) peak of γ-Al_2O_3 at a 2θ value of 45.8°.

On the basis of measured peak widths from X-ray diffractometer traces (Debye patterns were not used since peak widths are not clearly resolved) and Equation 6, the γ-Al_2O_3 powder formed by the 750°C heat-treatment has an average particle size of 68Å. This is indicative of the truly molecular scale γ-Al_2O_3 produced by this reaction. Consistent with this, the 950°C heat-treatment produced γ-Al_2O_3 with an average particle size of 90Å. This indicates that further coarsening of gamma occurs during the higher temperature heat-treatment prior to the transformation of alpha.

The alpha X-ray peaks are sharper than those noted for gamma. Application of Equation 6 yields an α-Al_2O_3 particle size of approximately 250Å. This is consistent with the coarsening that may be expected during the phase transformation.

4.4. Other Hg-metal systems

Several other mercury–metal systems were

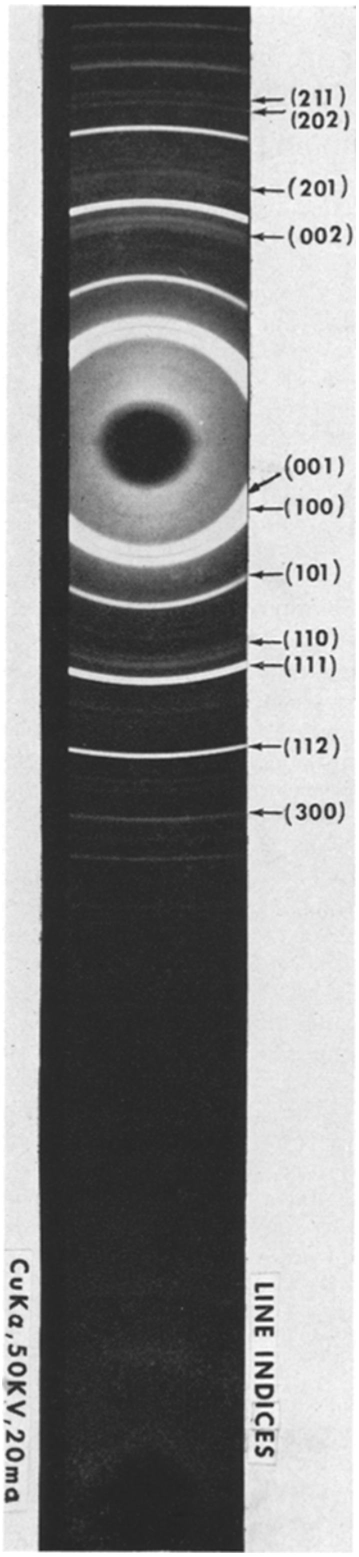

Figure 6

Figure 6 Debye-Scherrer X-ray powder pattern of aluminium–mercury–water reaction product grown from a specimen submerged under water. The pattern is identified as beta aluminium hydroxide, β-$Al(OH)_3$ (also known as Bayerite) ASTM X-ray data card 12-457.

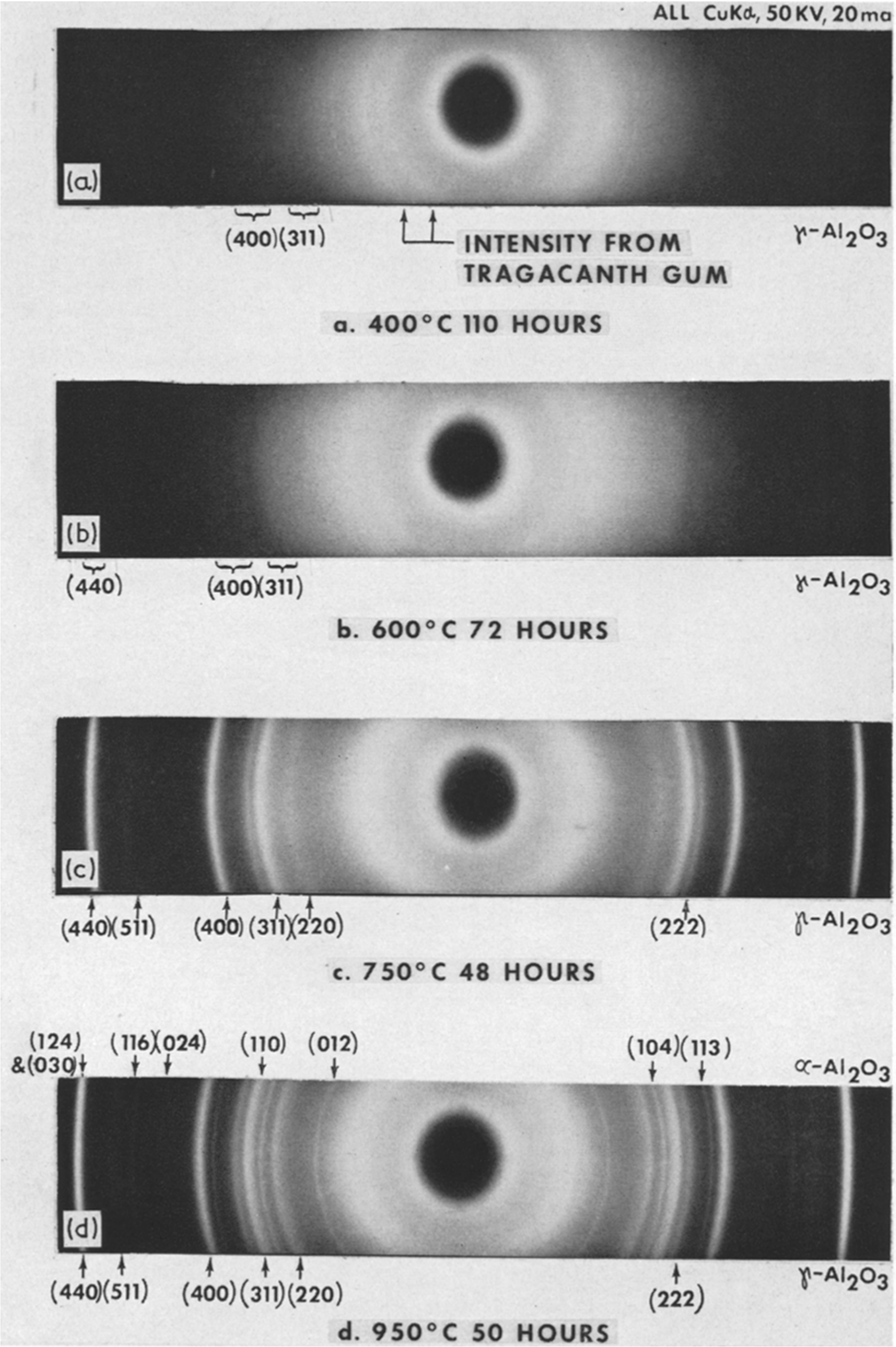

Figure 7 Debye-Scherrer X-ray powder patterns of thermally treated aluminium–mercury–water vapour reaction product.

investigated in order to determine any possible generality in this type of reaction. The bismuth–mercury system was chosen because of the similarity of its phase diagram to that of aluminium–mercury as shown in Fig. 8. The equilibrium composition at 25°C is a liquid solution of pure bismuth in mercury. The phase diagram indicates the room-temperature solubility of bismuth in mercury to be approximately 2 wt %. However, no reaction similar to that observed for aluminium was detected. The free energies of formation of bismuth oxide and bismuth hydroxide are substantially less negative than that for aluminium oxide and aluminium hydroxide [22] and apparently kinetic factors are such that bismuth will not spontaneously and continuously oxidize from a mercury solution in the same manner as aluminium does. The system thus remains metastable in the amalgamated (liquid mercury solution) state.

The magnesium–mercury system was the third binary that was investigated. Conflicting data on the free energies of formation of magnesium oxide and magnesium hydroxide exist with one reference citing a substantially smaller negative value than that for aluminium [23] and a second citing a larger value [24]. In either event the reaction is thermodynamically favourable and the point of interest was whether or not the kinetic factors for this system would permit spontaneous and continuous formation. The significant difference between this and the other

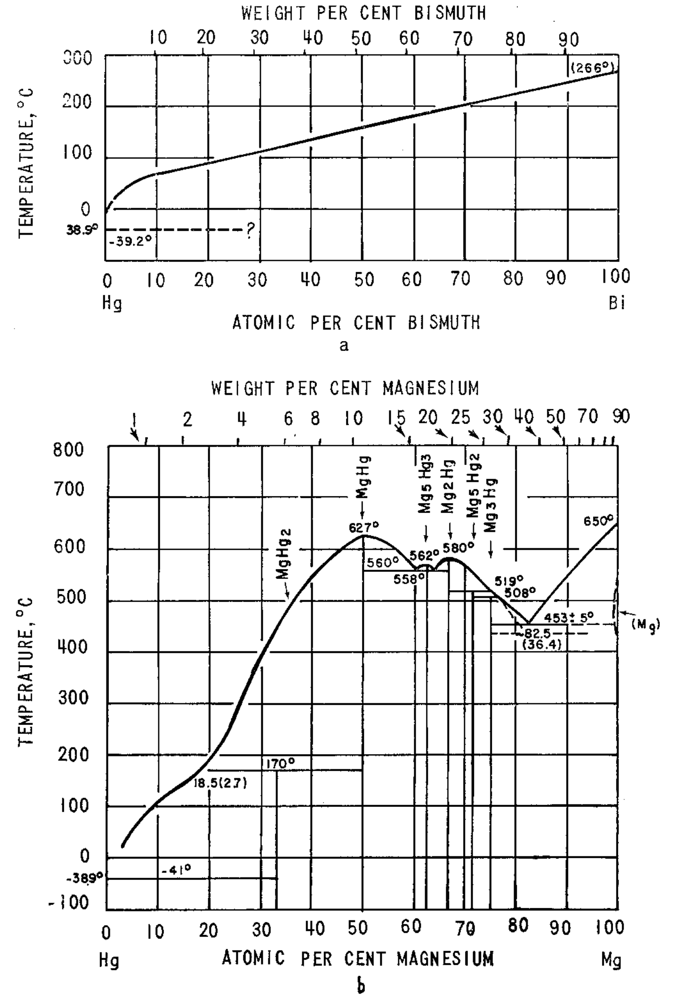

Figure 8 (a) Bismuth–mercury equilibrium diagram (after Hansen [20]). (b) Magnesium–mercury equilibrium diagram (after Hansen [21]).

two binaries is the existence of intermediate phases which are stable at room-temperature as shown in the phase diagram, Fig. 8.

It was observed that a reaction similar to that found for aluminium does occur in the magnesium-mercury system. The growth of a layer, shown in Fig. 9, proceeds spontaneously upon removal of a mercury-wetted piece of magnesium from the mercury pool. The reaction proceeds violently and is of very short duration compared to the aluminium reaction. The layer shown in Fig. 9 was from a reaction which lasted less than 5 seconds. There are two possible reasons for the short duration of this reaction. One of the intermediate phases may form at the magnesium – mercury interface and prevent further dissolution of magnesium into mercury by placing a kinetically slow solid state diffusion-controlled step in the reaction. Or it may be that the reaction proceeds so violently that the magnesium surface is dewetted and passivated by a stable oxide layer. Evidence for the latter mechanism exists in that beads of mercury can be seen on the *top surface* of the reaction product layer (Fig. 9).

The magnesium reaction product was identified by X-ray diffraction as magnesium hydroxide, $Mg(OH)_2$. A diffractometer trace, via the large peak broadening, indicated that the particle size was still small (of the order of 100Å).

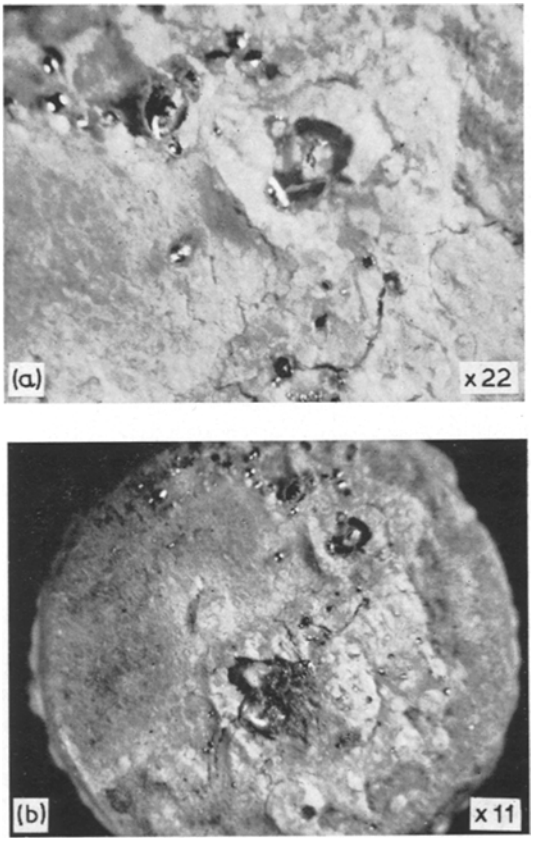

Figure 9 Magnesium hydroxide $Mg(OH)_2$ layer formed on mercury-wetted and air-exposed magnesium.

5. Summary and conclusions

After exposure to mercury, an unusually rapid and continuous oxidation of aluminium in air at room temperature has been observed. The product of the reaction has been identified as gamma aluminium oxide, γ-Al_2O_3. By consideration of the Al-Hg phase diagram and further experimental observations, a mechanism for the phenomenon has been proposed. In this system there exists a probably unique situation at room-temperature. There is a metastable equilibrium between pure but passivated aluminium and pure liquid mercury. Once the metastable equilibrium is disturbed by damage or removal of the passivating surface oxide, the mercury insulates the aluminium from direct oxidation by the atmosphere but does permit the rapid dissolution–oxidation reaction to proceed. The wetting mercury film acts as a medium for rapid transport of the aluminium from the solid–liquid interface to the liquid–vapour interface.

This phenomenon has significant implications in several technical areas. It has been seen that a metal, which is not wetted by mercury under normal circumstances, will be wetted when a clean metallic surface is provided. Another important aspect is that wetting has occurred on the surface of a metal which is negligibly soluble in mercury at room temperature. These facts imply that wetting of almost any metal may be achieved under the proper conditions.

The transport behaviour of mercury as observed here is analogous to that seen in studies on mercury contact materials [25]. There, mercury appeared to promote reactions among dissolved constituents which resulted in the formation of Cu_3Sn single crystals and tin-rich layer growths on the contact metal surfaces.

Rapid hydroxide formation was also observed on magnesium and similar growth may be attainable in other metal-Hg systems. Oxidation of metals dissolved in mercury is well known; mercury becomes “dirty” owing to oxidation of dissolved base metals. Room temperature and the atmospheric partial pressures of oxygen and water vapour may not be the optimum conditions for other metal-Hg systems but manipulation of these variables may enable control of the process.

Control of this growth process in any metal-Hg system would have technological applications Since the growths on aluminium readily disintegrate into a fine powder, large scale controlled processing should enable the production of copious quantities of high purity, submicron Al_2O_3 powder.

Consolidation of this material by isostatic pressing and sintering has been utilized Theoretical density is what can be expected by consolidation of molecular-sized particles. Scanning electron microscopy on fracture surfaces of an initial sample revealed no evidence of porosity. Superior mechanical properties and surface smoothness should be obtainable with this material.

Acknowledgements

The authors gratefully acknowledge the assistance and contributions to this work by the following: D. E. Heath and D. J. Speelman for obtaining the X-ray data, G. V. McIlhargie for photographic assistance, and N. H. Winquist for the scanning electron microscopy.

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Received 6 December 1971 and accepted 28 February 1972.