

690. *The Penetration of Oxide Films on Aluminium by Liquid Bismuth.*

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The wetting of mechanically abraded, electropolished, and anodised ($>700 \text{ \AA}$) aluminium plates by liquid bismuth has been studied by measurement of receding contact angles over ranges of time and temperature. Wetting was very dependent on the thickness of the oxide film and upon the time of contact with the liquid bismuth. The work suggests that wetting is preceded by physical breakdown or penetration of the oxide film. The anodised oxide film on aluminium broke down on one or two specific places and allowed bismuth to spread under it. Microscopic and metallographic examination of plates before and after wetting showed that breakdown of the oxide film, and consequent wetting, took place in areas where inclusions were trapped in the oxide film thus giving rise to a weakness. Grain boundaries, dislocations, pits, scratches, and thermal cracking of the film were not considered major causes of weakness in the oxide film on aluminium.

THE presence of an oxide film on a metal prevents immediate wetting by liquid metals because of the relative surface energies of the two phases. Wetting may occur after a time interval or on increasing the temperature, but little is known about the mechanism by which it eventually takes place. Since it is generally recognised that liquid metals should wet solid metals in the absence of a barrier film, some mechanism must be postulated to explain how the barrier film is destroyed or removed if wetting is to take place. Addison and his co-workers have studied quantitatively two types of system: in the first, the oxide is reduced by the liquid metal;¹ in the second, cationic diffusion takes place through the oxide film.² With oxide films that are thermodynamically stable to liquid metals, the mechanism of wetting is not understood, and no quantitative results or convincing mechanisms have been presented.³ We have investigated the solid aluminium/liquid bismuth system with a view to elucidating the wetting mechanism.

Aluminium lends itself to such a study because the nature of its oxide film, although complex, is well known, and because its thickness can be varied quantitatively. The oxide is protective because of its great thermodynamic stability⁴ ($-\Delta F = 340 \text{ kcal./mole}$), its high Pilling-Bedworth⁵ ratio (1.49), and its high melting point and boiling point (2015 and 2980°). Aluminium forms alloys with, or is soluble in, all the metals that melt at a lower temperature. Thus, the use of one of these metals would

¹ Addison and Kerridge, *Proc. XVIth Congr. I.U.P.A.C., Paris, 1957 (Sect. de Chimie Minerale)*, p. 145; Addison, Iberson, and Manning, *J.*, 1962, 2699.

² Addison, Addison, Kerridge, and Lewis, *J.*, 1956, 1454.

³ Wall and Milner, *J. Inst. Metals*, 1962, **90**, 395.

⁴ Richardson and Jeffes, *J. Iron Steel Inst.*, 1948, **160**, 261; Gulbransen and Andrew, *J. Phys. Chem.*, 1947, **51**, 1087.

⁵ Kubaschewski and Hopkins, "Oxidation of Metals and Alloys," Butterworths, London, 1953.

be expected to yield information about the mechanism of penetration through the oxide film. Bismuth was chosen because of its low melting point, and because the appropriate physical properties are known.⁶

The vertical plate technique, first developed by Addison,^{2,7} was used to follow quantitatively the wetting of specially prepared aluminium plates by liquid bismuth. The principles underlying the measurement of the receding contact angle, and its variation with time and temperature are well known.⁷ Variations in receding contact angle are very significant: the presence of oxide or other barrier films immediately causes a high contact angle, θ , whereas low values of θ , *e.g.*, when θ lies between about 45 and 0°, represent states where partial wetting occurs and is a mean value over the plate. Only when $\theta = 0^\circ$ is wetting complete. Results obtained from the measurement of the receding contact angle between aluminium and liquid bismuth are given together with information from a metallographic study of the wetted plates.

EXPERIMENTAL

Measurement of Receding Contact Angle.—Thin plates of aluminium were drawn vertically through the surface of the liquid bismuth. The downward forces on the plate resulting from surface tension, buoyancy, and gravity were measured by a magnetic balance that has been described previously.⁸ The bismuth was filtered at just above its melting point through a grade 0 sintered-glass disc into a glass vessel heated to the experimental temperature by an electrothermal heating mantle. The aluminium plate, approximately $3.2 \times 1.2 \times 0.04$ cm., was suspended from the magnetic balance by a thin Pyrex-glass capillary. Before, and during, the experiment an inert gas was passed through the apparatus. The aluminium plate was lowered into the bismuth and withdrawn 0.1 inch at a time. The net downward force on the plate was balanced and measured each time. The cycle of immersion and withdrawal of the plate was repeated at 5-minute intervals. The contact angle was calculated from the equation

$$2(t + w) \gamma \cos \theta = (F - w + tw\rho)g,$$

where t and w are the thickness and width, in cm., of the plate, l = length, in cm., of plate immersed in the bismuth, γ = surface tension of liquid bismuth,⁹ $378 - 0.069(T - 273)$ dynes/cm., ρ = density of bismuth, $10.03 - 0.003(T - 273)$ g./c.c.,¹⁰ θ = receding contact angle, and F = force recorded by magnetic balance.

Material.—Bismuth. The metal was supplied by the Consolidated Mining and Smelting Co., of Canada Ltd. The maximum content of metal impurities was Ca, 0.1; Cu, 3.0; Al, 0.1; Fe, 0.2; Mg, 0.1; Pb, 0.1; Si, 0.1; Ag, 2.0; Ni, 0.5; Cd, 1.0 p.p.m. Non-metallic impurities were removed during filtration, the solubility of, *e.g.*, oxygen¹¹ being 0.17 p.p.m. at 273°.

Inert atmosphere. An oxygen-free mixture of 10% by volume of hydrogen and 90% by volume of nitrogen was dried¹² by passing it through a column of type 5A Linde molecular sieves.

Aluminium. Rolled sheet of 4-mm. thickness was supplied by the Aluminium Company of Canada, of superpurity grade (99.98%), having the following metallic impurities: Cu, 50; Mg, 80; and Ni, 80 p.p.m. For one experiment, lower-purity Alcan 2S aluminium was used, it contained the following metallic impurities: Cu, 0.2; Fe, 0.52; Si, 0.14; Mg, 0.01; Mn, 0.05; V, 0.1; Ti, Zn, Cr, <0.01%.

Preparation of Plates.—The following surface treatments were used.

(a) This was mechanically polished to 3/0 emery under kerosene and degreased in trichlorethane.

(b) As in (a), followed by electropolishing for 2 min. at 24 v in a solution of 15% perchloric acid in acetic acid followed by washing in water and alcohol.

⁶ "Liquid Metals Handbook," 2nd edn., NAVEXOS P-733, U.S. Govt. Printing Office, Washington, 1952.

⁷ Addison, Kerridge, and Lewis, *J.*, 1957, 2861.

⁸ Allday and Raynor, *J. Sci. Instr.*, 1962, 39, 519.

⁹ Addison and Raynor, unpublished results.

¹⁰ Bircumshaw, *Phil. Mag.*, 1931, 12, 596.

¹¹ Horsley, *J. Nuclear Energy*, 1957, 6, 41.

¹² Addison, Iberson, and Raynor, *Chem. and Ind.*, 1958, 96.

(c) Anodised ¹³ in 3% ammonium tartrate solution to give film thicknesses of 140, 210, 280, 420, and 700 Å.

(d) Anodised ¹⁴ in 15% sulphuric acid to give a film thickness of 14 μ.

(e) As in (d) but sealed by immersion in boiling water for 30 min.

Before being anodised, each plate was chemically etched for 10 min. at 70–80° in a solution containing 80% of orthophosphoric acid, 14% of acetic acid, and 6% of nitric acid.

RESULTS AND DISCUSSION

Nature of the Oxide Film on Aluminium.—The oxide film normally present is transparent, glassy, and amorphous, and consists of groups of two molecules of Al₂O₃.¹⁵ The film does not increase in thickness significantly after the initial rapid formation, the final thickness being variously reported as from 20 to 100 Å at room temperature,^{16–18} the best values being 80–100 Å. When an amorphous film is heated for 4 hours at 500° or 1 hour at 600°, crystalline η-Al₂O₃ can be detected by electron diffraction.^{17,18} The oxide film on electropolished aluminium is about 20–30 Å thick and is amorphous,¹⁹ as is the oxide on

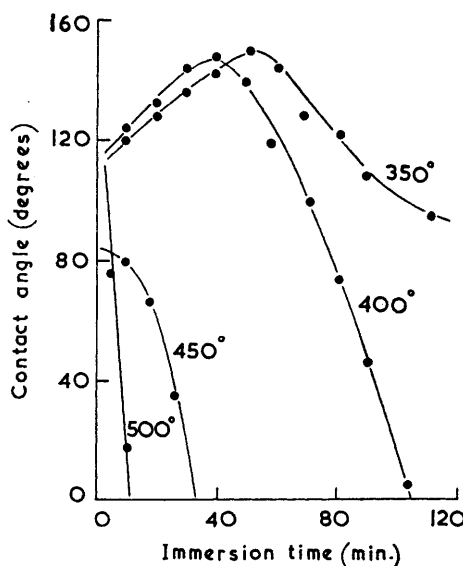


FIG. 1. The wetting of abraded aluminium by bismuth.

aluminium anodised in ammonium tartrate.¹⁸ The oxide film on aluminium anodised in sulphuric acid is anhydrous alumina containing up to 13% of sulphur trioxide as sulphate. The oxide is about 14 μ thick, and consists of numerous pores in a hexagonal array. Each pore is about 200 Å in diameter and extends down to within 500 Å of the metal surface.²⁰ Sealing the surface causes the oxide to swell and hydrate to form γ-Al₂O₃·3H₂O.

Wetting Behaviour.—The variation of receding contact angles with time and temperature for a plate of mechanically abraded aluminium against bismuth is shown in Fig. 1.

¹³ Hunter and Fowle, *J. Electrochem. Soc.*, 1954, **101**, 481.

¹⁴ Spooner, *J. Electrochem. Soc.*, 1955, **102**, 156.

¹⁵ Wilsdorf, *Nature*, 1951, **168**, 600.

¹⁶ Haas, *Z. anorg. Chem.*, 1947, **254**, 96; Cabrera and Hamon, *Compt. rend.*, 1947, **224**, 1713; Cabrera and Mott, *Reports Progr. Phys.*, 1948—9, **12**, 163; Andrushchenko and Dankor, *Compt. rend. Acad. Sci., U.R.S.S.*, 1948, **62**, 353; Wilsdorf, ref. 15; Keller, Hunter, and Robinson, *J. Electrochem. Soc.*, 1953, **100**, 411; Preston and Bircumshaw, *Phil. Mag.*, 1936, **22**, 654; Vernon, *Trans. Faraday Soc.*, 1927, **23**, 117.

¹⁷ de Brouchère, *J. Inst. Metals*, 1945, **71**, 131; Thomas and Roberts, *J. Appl. Phys.*, 1961, **32**, 70.

¹⁸ Hunter and Fowle, *J. Electrochem. Soc.*, 1956, **103**, 482.

¹⁹ Hart, *Proc. Roy. Soc.*, 1956, **A**, **236**, 68; Welsh, *J. Inst. Metals*, 1956, **85**, 129.

²⁰ Brooker, Wood, and Walsh, *Brit. J. Appl. Phys.*, 1957, **8**, 347.

From the curves, it is seen that the time of immersion before wetting takes place ($\theta = 0$) decreases as the temperature increases. At 350° , complete wetting never occurred, and above 500° , wetting was almost instantaneous. The steepness of the curves shows that once wetting had started, it was soon complete.

The wetting of electropolished aluminium plates was very different: at all temperatures between 350 and 500° , wetting was instantaneous and contact angle-time curves were unobtainable.

With anodised aluminium plates, contact angle-time curves were found to be unreplicable at all temperatures; plates with the same surface treatment behaved in totally unpredictable ways. Contact angles never reached zero and wetting was either patchy or non-existent. With the anodised oxide films (140 \AA — 14μ), visual observations were made at intervals and metallographic sections were prepared from a number of the plates. With the very thick oxide films (14μ), penetration was frequently rapid and took place in only one or two selected areas. The bismuth then spread rapidly ($\frac{1}{2}$ inch in a few seconds) under the oxide film, raising it or causing it to wrinkle (Plate 1). With most plates there was some edge attack but no spreading of bismuth under the oxide film at these points. The Table summarises the observations of the wetting behaviour. Where wetting did not occur, immersion was continued for up to 72 hours.

Mechanism of Penetration.—Electropolished aluminium. The ease of wetting can

Wetting behaviour of aluminium plates treated in various ways.

Treatment of plate	Thickness of oxide *	Wetting behaviour			
		350°	400°	450°	500°
Electropolished	$20\text{--}30 \text{ \AA}$	Immediate	Immediate	Immediate	Immediate
Abraded	$80\text{--}100 \text{ \AA}$	None	Slow	Slow	Rapid
Anodised	140 \AA	None	Partial	Partial	Partial
	210 \AA	None	None	Partial	Partial
	280 \AA	None	None	None	Partial
	420 \AA	None	None	None	Slight pitting
	700 \AA	None	None	None	Pitting
Anodised	14μ	None	None	None	Spread under film
Sealed	14μ	None	None	None	Spread under film

* The thickness of the film is unlikely to be increased significantly by oxidation from small amounts of oxygen dissolved in the bismuth (0.17 p.p.m. at 273°). Its concentration remains constant in all experiments, and the rate of its desorption from solution on to the aluminium surface thus decreases as the temperature increases.²¹

readily be explained by a process of penetration of liquid bismuth through the few layers of aluminium oxide molecules, which have neither structure nor the strength of thicker, more compact films. Bismuth atoms would thus readily pass through the amorphous oxide.

Abraded aluminium. A similar process accounts for the wetting of mechanically abraded aluminium. The increase in thickness ($\sim 80\text{--}100 \text{ \AA}$) is reflected by the temperature-dependence of wetting. The non-wetting at 350° might be due to the lower mobility of associated bismuth atoms.²²

Anodised aluminium. The anodised oxide films were all thicker than films formed by electropolishing or abrasion, films less than 140 \AA thick being impossible to obtain.¹³ Thus, the absence of complete wetting can probably be accounted for by the increased thickness of the oxide film. However, the wide variation of wetting behaviour indicates a factor not common to all the plates, and another mechanism, involving defects, must be postulated to account for this. The spreading of liquid bismuth under the oxide film was only associated with the thicker anodised films (14μ). It is due to the shearing and lifting of the strong oxide film from the base metal and subsequent capillary action, rather

²¹ Addison, J., 1945, 98.

²² Jouniaux, *Bull. Soc. chim. France*, 1932, **51**, 677.

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than to spreading by dissolution of the base metal. Similar shearing behaviour has been observed by Edeleanu²³ when aluminium with thick oxide films is strained. Edge attack occurs because of weakness in the oxide film arising from the oxidation mechanism. Outward growth of oxide by cationic diffusion causes "cleft-like" weaknesses at edges at which attack may take place.

Source of Defects.—Penetration through the face of the plate must occur because of defects in the oxide film, which may arise from one of the following sources. The following tests were carried out in a vacuum furnace at 500°.

(a) *Scratches and pits.* Drops of bismuth were placed on plates with mechanically induced defects made with a steel scribe. There was no immediate attack, suggesting that the damaged oxide film soon healed on exposure to the atmosphere. Attack eventually took place after 9 hours. Gross deformation by bending through 180° causes cracking and consequent penetration of bismuth.

(b) *Thermal cracking.* There was no evidence of thermal cracking of the oxide film owing to stresses arising from the fact that the coefficient of expansion of aluminium oxide is one-fifth that of aluminium.

(c) *Grain boundary attack.* The purity of the metal was such that no impurities were precipitated at grain boundaries. Anisotropy of film growth on different crystal faces is considerable (up to 30% on Al-3% Mg alloy²⁴), but neither this nor grain boundaries are likely to be areas of preferential attack with aluminium of this purity. The presence of impurities segregated at grain boundaries was shown to give rise to preferential attack in less pure aluminium, e.g., Alcan 2S, with 0.75% metallic impurities (Plate 2). There was no evidence that these impurities affected the oxide film and caused any weakness.

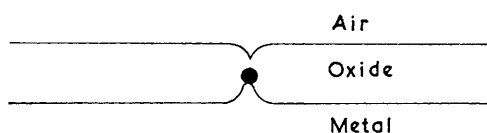


FIG. 2. Anodic film with dimple due to unoxidised particle on aluminium cone.

(d) *Foreign particles.* Particles picked up by the aluminium during rolling or polishing were shown not to damage the oxide film. When a drop of bismuth was placed over visible foreign particles, penetration was no faster than normal.

(e) *Dislocations.* These are not etch pitted²⁵ and consequently are unlikely to affect oxidation behaviour.

(f) *Inclusions.* Inclusions are large and of two types: Fe_2O_3 that has been precipitated out at subgrain boundaries, and certain second-phase constituents such as Fe-Al-Si alloys; the latter is less likely, because "superpurity" aluminium has a low silicon content. Compared with the oxide film, these constituents are good electrical conductors and, during the course of anodising, oxidation of the aluminium will proceed at varying rates in the vicinity of the constituent. The result is the appearance of a conically-shaped asperity "capped" by the particle (Fig. 2). This has been detected by electroplating with copper, when deposition only occurs above the inclusion.²⁶ Plate 1 shows part of a thick (14 μ) anodised aluminium plate where the bismuth has dissolved or loosened an inclusion, leaving the circular hole in the oxide film. A section through such a hole is shown in Plate 3. The surface density of these holes was approximately the same as the number of pits in wetted aluminium plates and of the same order as the number of inclusions seen on the surface. Attack of aluminium by carbon tetrachloride proceeds in a similar way and is dependent upon the nature of the oxide film.²⁷

²³ Edeleanu and Law, *Phil. Mag.*, 1962, **7**, 573.

²⁴ Herenguel and Lelong, *Compt. rend.*, 1951, **232**, 2218.

²⁵ Barber, *Phil. Mag.*, 1962, **7**, 1925.

²⁶ Cooke, *Plating Mag.*, 1962, **49**, 1157.

²⁷ Stern and Uhlig, *J. Electrochem. Soc.*, 1952, **99**, 381, 389.

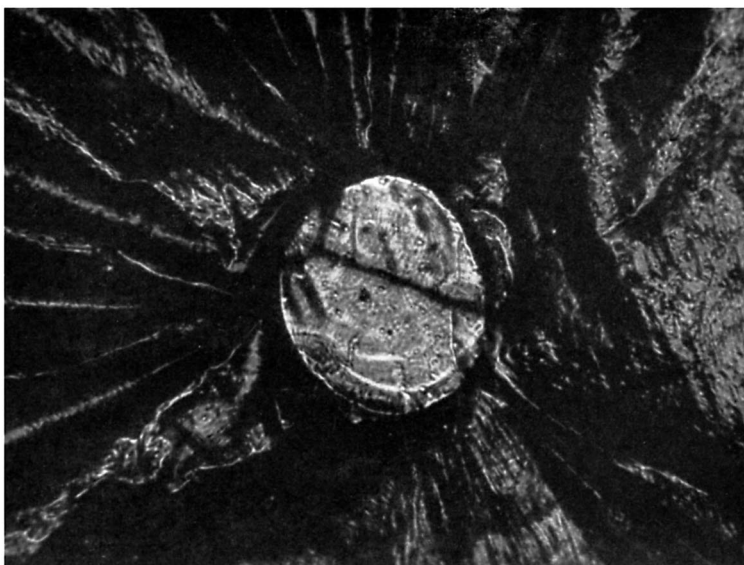


PLATE 1. Circular hole in a wrinkled oxide film (14μ) where an inclusion has been loosened or dissolved away. ($\times 50$.)

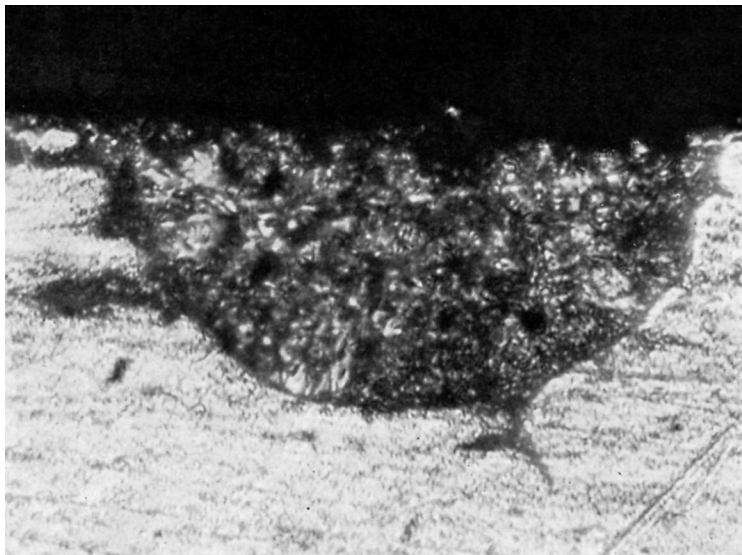


PLATE 2. Section through area where bismuth has attacked the aluminium (Alcan 2S). Grain boundary attack can be seen. ($\times 20$.)

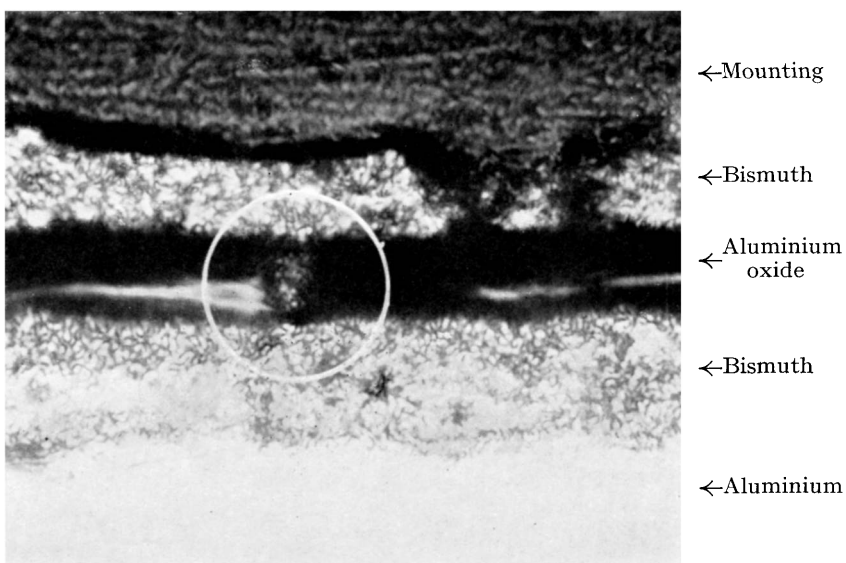


PLATE 3. Section through a hole in oxide film showing how the bismuth has penetrated through the hole (circled) and spread along the aluminium/oxide interface. ($\times 50$.)

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Sealing the anodised oxide film ($14\ \mu$) gave no additional protection; although this was contrary to expectation, it suggests that the inclusion is large enough to prevent the hydrated oxide from entirely covering it.

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