

The wetting of carbon by aluminium and aluminium alloys

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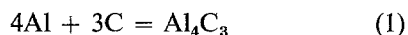
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The contact angle made by molten aluminium with vitreous carbon was measured by the sessile drop method in vacuum at temperatures up to 1100°C. The effect on wetting behaviour of the oxide layer on the molten metal was highlighted by using two samples of aluminium in different states of oxidation. The investigation involved the variation of certain parameters affecting the stability of the oxide film, e.g. the temperature, additions of Ti, Si, Cr, Be, Ca and Li to aluminium and the time held at a certain temperature. The state of the molten aluminium surface under various experimental conditions was determined indirectly by surface tension measurements.

1. Introduction

The wetting of carbon by aluminium using the sessile drop method was initially investigated by Naidich and Kolesnichenko [1] who found a wetting temperature of 1200°C. Later, Nicholas and Mortimer [2] found that wetting took place at a temperature above about 1000°C. However, the fact that the free enthalpy of the reaction



is negative ($-41 \text{ kcal mol}^{-1}$ at 660°C [3]) suggests that molten aluminium should wet carbon substrates from temperatures beginning at the melting point.

On the other hand, Manning and Gurganus [4], and Nicholas and Mortimer [2], have attempted to reduce the contact angle, θ , by alloying additions, but their results were hardly conclusive and are not easy to interpret solely on the basis of the Young equation

$$\cos \theta = \frac{\sigma_{SV} - \sigma_{SL}}{\sigma_{LV}}$$

where σ_{SV} , σ_{LV} and σ_{SL} denote the solid-vapour, liquid-vapour and solid-liquid interfacial tensions, respectively. These considerations, together with the large scatter of the experimentally determined values of σ_{LV} for aluminium (Table I), reveal the effect of the surrounding

layer of oxide on the surface properties of aluminium.

The work reported here was concerned with the detailed investigation of the effect of various factors on the wetting of vitreous carbon, i.e. the prior treatment of the metal, composition of the gaseous and liquid phases, temperature and time, all of which are liable to affect the thermodynamic and physical stability of the oxide film on aluminium and, hence, the wetting of carbon by the metal.

2. Experimental apparatus and procedure

The apparatus employed, which has been described previously [5], consisted mainly of a silicon carbide resistance furnace incorporating two windows enabling the sessile drop on the substrate to be illuminated and photographed. The experimental chamber was connected to an inert gas supply and an oil diffusion pump allowing a vacuum of up to 10^{-7} Torr. A zirconium-based getter was placed around the test specimen in order to reduce the oxygen potential of the vapour phase. Measurements were carried out either at a pressure of less than 10^{-6} Torr or using a static pressure of inert gas (helium or argon). In the latter case, the test sample on the substrate was heated at 10^{-6}

Torr to 600°C prior to the introduction of the inert gas.

The purity of the aluminium employed was 99.99%, the principal impurities present being iron, silicon, copper and manganese. Tests based on sample weights varying from 0.15 to 1.25 g indicated that fairly large sample weights of about 1 g were preferable for determination of surface tension, whereas the opposite was true for measurement of contact angle. A sample weight of about 0.6 g, however, enabled both these determinations to be carried out with sufficient accuracy. The vitreous carbon used was in the form of square plates measuring 20 mm × 20 mm × 2 mm. Both the latter and the zirconium dioxide plates were polished with 1 μm diamond and degassed for 4 h at 1200°C and 10⁻⁶ Torr.

In order to determine surface tension, σ_{LV} , from the photographic enlargements, it was necessary to determine the shape factor, β , of the drop and the radius of curvature at the origin b , both of which are related to σ as follows:

$$\sigma_{LV} = \frac{\rho g b^2}{\beta}$$

where g denotes the acceleration due to gravity and ρ the density of the liquid. The parameters β and b were calculated using the method proposed by Kozakevitch [6]. The values employed for density at various temperatures were those given by Lucas [7], i.e.

$$\rho = 2.369 - 3.11 \times 10^{-4} (T - T_m) \text{ (g cm}^{-3}\text{)}$$

where T_m is the melting point of the aluminium.

Contact angles were measured directly from photographic enlargements. The reproducibility of determinations was $\pm 2^\circ$ for the same specimen and 6° for separate tests.

After cooling, specimens were sectioned and subjected to micrographic examination and profile analysis using an electron microprobe.

3. Results

As already observed, the study of wetting by aluminium can be supplemented by determination of surface tension, the advantage of which is that it provides an indirect check on the surface condition of the molten metal. This being so, the effect of the degree of oxidation of the specimen, on wetting and surface tension can be observed at various temperatures. To this

*Pickled with 10% sodium hydroxide solution and then washed with nitric acid, distilled water and finally alcohol.

end, two types of aluminium specimen were employed, one having been previously pickled* and, therefore, coated with a fresh oxide layer about 20 Å thick, and the other unpickled and, therefore, coated with an oxide layer at least 100 Å thick [8].

3.1. Surface tension

Fig. 1 illustrates the results of two runs, obtained with the two types of specimen described above. The molten drop formed by the unpickled specimen exhibited virtually no fluidity, as shown by the fact that the drop did not oscillate when subjected to mechanical vibration. The fact that σ_{LV} varied with temperature in a random fashion suggests that the system was not in equilibrium.

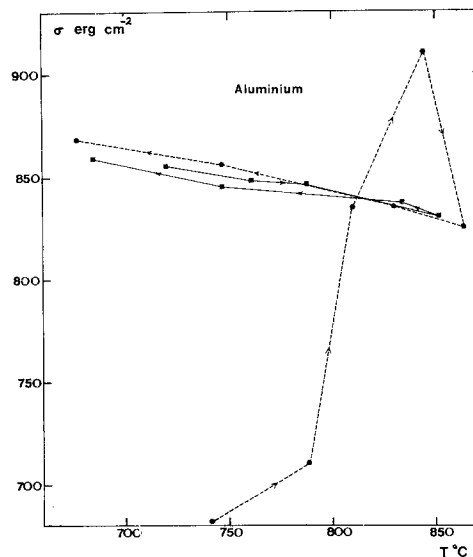


Figure 1 Surface tension/temperature cycles for Al. ● Unpickled Al; ■ pickled Al.

At a temperature of about 860°C, the drop was found to exhibit the fluidity characteristic of a molten metal, the effect of which was to bring about a rapid change in the shape of the drop. This change of shape, which was found to be reproducible to within 10°C for all the unpickled samples employed, was such that the surface tension values observed were substantially the same as those obtained with previously pickled specimens. For the latter type of sample,

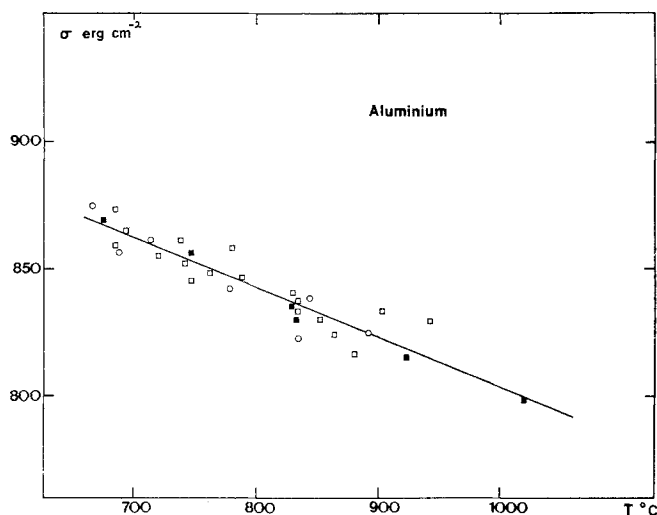


Figure 2 Surface tension versus temperature for pickled Al. □ Vacuum, carbon substrates; ■ He, carbon substrates; ○ Vacuum, ZrO₂ substrates.

the values of σ_{LV} observed with increasing temperature were virtually identical to those subsequently observed on cooling (Fig. 1).

A number of surface tension measurements were carried out, again on pickled specimens, but this time modifying certain experimental conditions (vacuum/inert gas atmosphere, nature of substrate). The results are plotted in Fig. 2, which indicates the relevant conditions for each experimental point. It will be seen that the results obtained are substantially independent of the type of substrate employed (zirconium dioxide or vitreous carbon) and of the surrounding atmosphere (high vacuum or inert gas). These factors merely affect the rate of establishment of equilibrium, the values of σ_{LV} measured after holding at a certain temperature for a sufficiently long period (100 min) being in every case substantially the same. The line obtained by linear regression corresponds to the following equation:

$$\sigma_{LV} = 870 - 0.195(T - T_m) \text{ (erg cm}^{-2}\text{)}.$$

The precision was estimated to be within 1% with respect to σ_{LV} and within 20% with respect to the temperature coefficient.

Table I sets out the results obtained for σ_{LV} and $d\sigma_{LV}/dT$ in the case of aluminium and compares them with other experimental data. For each determination, the Table also indicates the temperature region investigated, the nature

of the gaseous phase, the purity of the aluminium employed and the experimental procedure.

It will be seen that the most recent data are in good agreement with our results in the neighbourhood of T_m . Only the value of 760 erg cm⁻² obtained by Rhee [17] using the sessile drop method seems to us to be too low; this could perhaps be explained by the fact that the samples (0.3 g) employed by Rhee were too small to enable the shape parameter β to be determined accurately.

On the other hand, there is much less agreement with regard to surface entropy, which, based on the Gibbs equation for a pure substance

$$d\sigma = -S'dT$$

is equal to the absolute values at temperature coefficient. The value we propose lies between that of 0.05 erg cm⁻² K⁻¹ found by Davies [16] and a value higher by about ten times as indicated by Körber [18]. This divergence is not surprising in view of the lack of accuracy with which surface entropy can be determined, which, in certain cases, may be due to the fact that the temperature regions investigated are fairly restricted.

3.2. Contact angle

3.2.1. Pure aluminium

Fig. 3 illustrates the variation with temperature, T , of contact angle, θ , measured after holding the

TABLE I Surface tension data on liquid aluminium.

T ($^{\circ}\text{C}$)	σ_{LV} (erg cm^{-2})	$-\frac{d\sigma_{LV}}{dT}$ ($\text{erg cm}^{-1} \text{K}^{-1}$)	Temperature range ($^{\circ}\text{C}$)	Atmosphere	Purity of aluminium (%)	Method	Author	Year
700-820	520	—	—	—	—	Capillary	Smith [9]	1914
~700	300	—	—	Ar	—	MBP	Portevin [10]	1936
712	502	—	—	—	—	Detachment	Klyachko [11]	1937
660	500	0.135	706-935	Ar	—	MBP	Zhivov [12]	1937
660	914	0.35	680-870	N_2	99.5	MBP	Pelzel [13]	1948
725 (± 15)	860	—	—	Ar	99.99	MBP	Korol'kov [14]	1960
660	865	0.14	700-1200	10^{-8} Torr	99.99	LD	Naidich [15]	1961
660	825	0.05	660-850	Ar	99.99	MBP	Davies [16]	1963
660	760	0.202	707-817	2×10^{-7} Torr	99.99	SD	Rhee [17]	1970
660	915	0.51	702-784	Ar	99.998	SD	Körber [18]	1971
660	855	0.104	700-910	Ar	99.996	MBP	Lang [19]	1973
660	870	0.195	660-1020	10^{-8} Torr	99.99	SD	This study	1973

MBP: maximum bubble pressure; LD: large drop; SD: sessile drop.

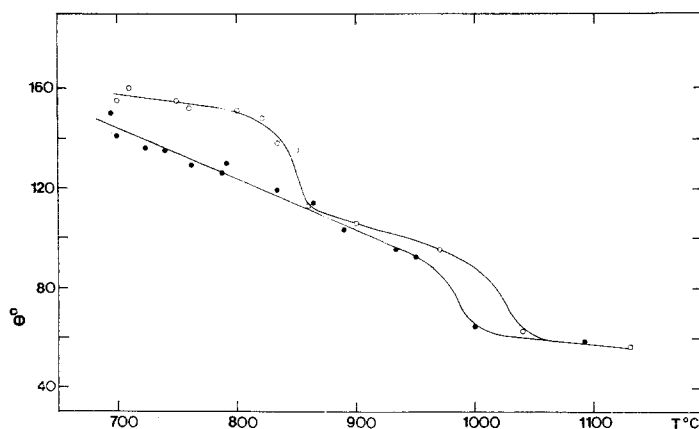


Figure 3 Variation of contact angle with temperature for the Al-C system. ○ Unpickled Al; ● pickled Al.

specimen at temperature for 100 min. The curve obtained for unpickled aluminium samples features three temperature regions in which the wetting of the carbon substrate differ significantly.

The first temperature region, from 660 to 860°C, is associated with contact angles of about 150°. These are of the same order of magnitude as the values obtained at 800°C by Naidich and Kolesnichenko [1] ($\theta = 157^\circ$) and by Nicholas and Mortimer [2] ($\theta \cong 145^\circ$). Microprobe examination did not point out the formation of carbide at the liquid/solid interface.

Towards 860°C ($\pm 10^\circ\text{C}$), the contact angle reduced appreciably and approached about 110°. There was then little change up to about 1000°C. Observation of the interface formed from 860°C upwards indicated the presence of carbide in quantities which increased with the time for which the specimen was held at temperature.

At about 1000°C the liquid wetted the solid and the contact angle decreased very rapidly from 95 to 65°. A layer of carbide about 20 μm thick was observed at the liquid/solid interface.

The second curve in Fig. 3 refers to specimens of aluminium which were previously pickled but nevertheless coated with a thin oxide layer (about 20 Å). This curve shows only two temperature regions and θ varies monotonically with respect to T up to about 1000°C.

Microprobe examination revealed the formation of carbide as from 800°C. This type of specimen also exhibited wetting at about 1000°C, accompanied by the formation of a thick carbide layer at the interface. This latter

result agrees with experimental data obtained by Nicholas and Mortimer [2]. Naidich and Kolesnichenko [1], however, found that the sharp change in contact angle accompanying the formation of carbide occurred at 1200°C. This difference might be due to an excessively rapid increase of temperature, thus emphasizing the importance of the rate of establishment of equilibrium in the system, which is itself determined by temperature. This is illustrated by the fact that 60 min were required at 850°C to obtain a constant contact angle, as against only 30 min at 900°C.

3.2.2. Aluminium alloys

With a view to rounding off the experimental data obtained on wetting of a carbon substrate by aluminium, the effect of various alloying elements on contact angle was studied. Preliminary results confirmed those of Manning and Gurganus [4], who have reported that wetting is not significantly affected by the addition of small quantities (2 to 3% wt/wt) of surface-active elements such as bismuth and lead.

Table II shows contact angles for pure aluminium and various aluminium alloys containing titanium, silicon, chromium, beryllium, calcium and lithium under the same experimental conditions. The time held at a certain temperature, the relevant temperature and the atmosphere employed are indicated in each case. A static pressure of argon of 760 Torr was employed in the case of elements exhibiting high vapour pressure, e.g. calcium and lithium. The time held at temperature was in every case

TABLE II Contact angles of aluminium alloys on carbon substrates.

Alloy/composition (% wt/wt)	Time held at temperature (min)	Atmosphere	Contact angle (degrees) at temperature, °C			
			700°C	800°C	900°C	1000°C
Al	30	10 ⁻⁶ Torr	160	140	102	77
	30	Ar	160	150	140	110
	100	10 ⁻⁶ Torr	140	125	102	65
Al-Ti 0.1	30	10 ⁻⁶ Torr	135	127	95	68
Al-Si 19	30	10 ⁻⁶ Torr	150	124	90	58
Al-Cr 0.5	30	10 ⁻⁶ Torr	155	144	103	68
Al-Be 0.8	30	10 ⁻⁶ Torr	~170	~170	~170	~170
Al-Ca 11	15	Ar	87	77	—	—
Al-Li 6	15	Ar			~29 at 640°C	

limited to 30 min in order to obviate any substantial change in composition during the test.

4. Discussion

The thick oxide layer surrounding the unpickled aluminium appears to be mainly responsible for the high contact angles ($\theta > 150^\circ$) observed between T_m and 860°C (Fig. 3) and for the random variation of σ_{LV} in this temperature range (Fig. 1). The fact that this type of metal exhibits no fluidity up to 860°C shows that the oxide layer prevents the establishment of equilibrium of the liquid phase. The metal only becomes fluid from 860°C and this coincides with (i) reproducible values of σ_{LV} and (ii) values of θ which are substantially the same as those obtained with pickled aluminium.

The above results, combined with the fact that Al_4C_3 is formed at the aluminium-carbon interface at 800°C in the case of pickled specimens, but only from 860°C in the case of unpickled specimens, indicate that at 860°C the compactness of the thick oxide layer seems to disappear. This transformation permits the establishment of equilibrium between aluminium and the external phase (gaseous or solid), whereas in the case of pickled specimens the establishment of equilibrium occurs as soon as the melting point is reached.

Several explanations may be advanced to explain the reduction in the compactness of the oxide layer observed at 860°C. One possible mechanism, originally suggested by Taylor [20] in the case of sodium and subsequently by Brennan and Pask [21] for aluminium, is based on "solubility of oxide particles in the molten metal". Brennan and Pask suggest that the "disappearance" of the oxide layer observed at about 870°C may be ascribed to a sharp

increase in the solubility of the oxide in aluminium arising from a structural transformation in the thin film. However, this structural transformation, accompanied by the formation of the suboxide AlO in the form of a spinel, is thought to occur at a temperature of between 900 and 1000°C [21], which is higher than the temperature of 870°C determined by Brennan and Pask. The mechanism suggested would, therefore, appear to relate more to the second transformation observed, i.e. the occurrence of wetting at a temperature of about 1000°C.

A further mechanism may be envisaged, which involves the formation of a gaseous substance, Al_2O , according to the equation



The partial pressure at 860°C of the volatile substance Al_2O is approximately 10⁻⁶ Torr [3], i.e. very close to the pressure in the experimental chamber. Hence, defects may occur in the solid film as a result of a partial deoxidation of the oxide phase as from 860°C. This mechanism does not, however, provide an explanation for the fact that, in the case of a pickled specimen, equilibrium is established immediately at the melting point at which the equilibrium pressure of Al_2O is very low.

Consideration also has to be given to a physical effect which may contribute to the loss of compactness of the oxide layer, arising from stresses which may occur at the metal-oxide interface owing to a relatively substantial change in the volume of the specimen on melting (~7% [7]). The subsequent temperature rise can only increase any such stresses in view of the considerable difference in the coefficients of expansion of aluminium and alumina [22].

Neither of the two mechanisms suggested

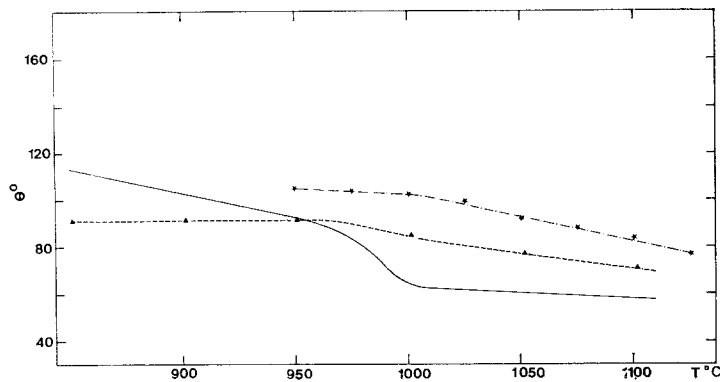


Figure 4 Contact angle versus temperature for pickled Al. — Al on carbon (present work); ★ Al on sapphire [23]; ▲ Al on sapphire [21].

provides a satisfactory explanation of the transformation observed. The loss of compactness of the oxide film can only be explained by a combination of both these mechanisms, in conjunction with the suggested effect of increase in volume.

This conclusion contrasts with the hypothesis advanced by Brennan and Pask [21], who suggest that the oxide layer disappears completely at about 870°C. Comparison of our results for the system aluminium-carbon and those obtained for the system aluminium-alumina (Fig. 4) shows that contact angle is unaffected by the nature of the substrate employed up to about 1000°C. This result, together with the fact that wetting is observed to occur in the case of both systems at the same temperature (1000°C), would appear to indicate that the oxide layer is still present on the surface of the molten metal up to this temperature and

that the transformation observed at 860°C affects only the compactness of the layer.

Additionally, at 1000°C ($\pm 50^\circ\text{C}$ depending on the prior treatment of the specimen, rate of temperature rise and the experimental atmosphere) the carbon substrate is rapidly wetted by the aluminium, the contact angle falling from above 95° to about 65°. This sharp reduction in contact angle, in conjunction with the simultaneous formation of a thick layer (20 μm) of aluminium carbide, indicates that a change in the nature of the interface also occurs at around this temperature. Comparison of results obtained for aluminium which has (Fig. 4) or has not (Fig. 5) been previously pickled would appear to indicate that the wetting observed at this temperature in the case of both systems is ascribable to the same effect. This effect could arise from solution of the oxide layer in the molten aluminium and/or from the production of Al_2O according to reaction [2]

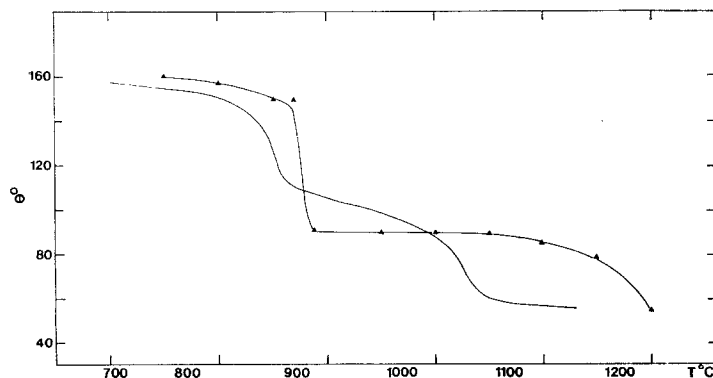


Figure 5 Contact angle versus temperature for unpickled Al. — Al on carbon (present work); ▲ Al on sapphire [21].

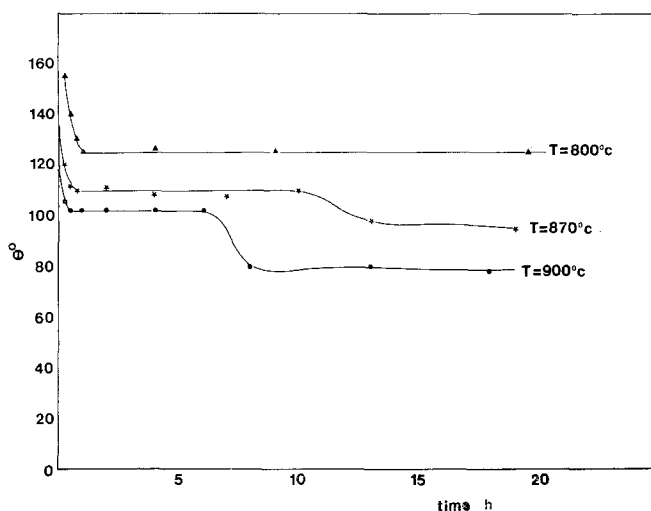


Figure 6 Contact angle versus time. Pickled aluminium on carbon.

as observed by Brennan and Pask [21], Wolf *et al.* [24] and Champion *et al.* [23]. Examination of Figs. 4 and 5 indicates that at temperatures above about 1000°C the contact angle made by aluminium on alumina assumes values of less than 90° . The molten metal could, therefore, infiltrate through defects in the oxide layer and, in the case with which we are concerned, lead to contact between the molten metal and the solid substrate and, hence, to the formation of considerable amounts of aluminium carbide. In these circumstances, the contact angle observed is a "dynamic" angle depending on the rate of the reaction. In effect the contact angle of 104° of Al over the Al_4C_3 substrate, measured by Belyaev and Zhemchugina [25] at 1000°C in vacuum, is much higher than an angle of 65° that we have determined at this temperature.

Since the suggested mechanism by which the molten metal could enter into contact with the solid substance is a kinetic process, it may be expected that the same process should be observable at temperatures below 1000°C provided the specimen is held at the temperature concerned for an extended period. Thus, it can be seen from Fig. 6 that, where the temperature is held for long enough periods, the contact angles observed at 870°C and 900°C are significantly less (by 13° and 22° , respectively) than those observed after short periods at temperature. On the other hand, the fact that both the angles concerned are observed to be the same at 800°C would apparently indicate that, at this

temperature, the rate at which the molten metal enters into contact with the solid substrate is very low.

The explanations advanced with regard to the transformations observed are consistent with the results obtained on the alloys investigated. Thus, only those alloying elements which affect the compactness of the oxide layer were found to have any significant effect on the contact angle (Table II). For instance, the addition of beryllium, which lowers the permeability of the oxide layer, gives a very large contact angle which is virtually not affected by temperature or time held at this temperature. On the other hand, calcium and lithium lead to rapid dislocation of the oxide film and react strongly with the substrate to bring about wetting.

Results obtained by Manning and Gurganus [4] at low temperatures for unpickled aluminium alloys on graphite, boron carbide and beryllium substrates, respectively (Table III), prompt the same conclusions. Of the alloying elements investigated by Manning and Gurganus, only magnesium, an element which could reduce the compactness of the alumina layer, brought about a significant reduction in the contact angle of aluminium on the three substrates employed.

5. Conclusions

1. The surface tension and surface entropy of specimens of molten aluminium determined by the sessile drop method in a 10^{-6} Torr vacuum or in an atmosphere of helium, up to 1000°C ,

TABLE III Manning and Gurganus [4] results on contact angles of aluminium alloys on graphite, boron carbide and beryllium substrates.

Alloying element	Composition (% wt/wt)	Atmosphere	Contact angle (degrees) on		
			Graphite	B ₄ C ₃	Be
Cu	1.62	10 ⁻⁵ Torr	134	148	148
	5.04		132	—	—
	9.82		127	136	136
Mg	1.39	He	145	154	150
	4.52		131	—	—
	9.98		115	110	109
	20.00		—	—	68
Si	2.58	10 ⁻⁵ Torr	146	140	125
	10.38		—	130	140
Pb	0.94	10 ⁻⁵ Torr	> 130	—	—
Bi	0.90				
Mn	1.24				

were found to be respectively 870 (± 10) erg cm⁻² at T_m and 0.195 (± 0.04) erg cm⁻² K⁻¹.

2. The rate at which the aluminium comes into contact with the vapour or solid phase, as the case may be, depends on the nature of the prior treatment of the metal. Where a thin, fresh layer of oxide is present, contact occurs rapidly, and seemingly as soon as the melting point of aluminium is reached, by diffusion through the oxide layer. In the case of specimens aged in air, contact is not observed until about 860°C, when the thick oxide film present appears to lose its compactness.

3. None of the mechanisms considered provides a satisfactory explanation of the transformation. Only if a physico-chemical and a physical effect are considered in conjunction can the observations be explained qualitatively.

4. The reactivity between Al and C appears to be weak at temperatures below 1000°C. The presence of an oxide film at low temperatures is a supplementary barrier in this case. Above 1000°C, the oxide layer appears to have no further effect. Molten aluminium is able to infiltrate through the defects in the oxide layer and wet the substrate to form a thick film of carbide.

5. Only those alloying elements which affect the compactness of the oxide layer were found to bring about any significant change in contact angle.

6. The experimental conditions, particularly

the prior treatment of the metal, the atmosphere employed, the temperature and time held at a certain temperature, have a decisive effect on the wetting of carbon by aluminium.

7. The simultaneous determination of surface tension and contact angle, made possible by the judicious choice of the weight of sample employed, would appear to be of real interest with a view to the indirect examination of the surface state of an oxidizable metal.

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