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The wettability of silicon carbide by liquid aluminium: the effect of free silicon in the carbide and of magnesium, silicon and copper alloy additions to the aluminium

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Results from the sessile-drop method are reported for the effects on wetting angle, θ, of free silicon in the silicon carbide substrate and of alloy additions of silicon, copper or magnesium to the aluminium drop for the temperature range 700–960 or 1040 °C in a titanium-gettered vacuum ($10^{-4}/10^{-5}$ torr; 1 torr = 133.322 Pa). Wetting angle, θ, was reduced by a factor as large as 2.8 for pure aluminium on reaction-bonded, compared with sintered silicon carbide, attributable to partial dissolution by the aluminium of the 18 wt% free silicon present in the reaction-bonded material. For wetting of reaction-bonded silicon carbide, the addition of 5 wt% silicon, copper or magnesium to the aluminium gave contact angles that decreased in the sequence Si→Cu→Mg, with the magnesium addition being the only one to result in wetting (i.e. $\theta < 90°$) for all conditions studied. These results may have implications for design of conditions for joining or promotion of infiltration of silicon carbide parts, preforms or arrays with aluminium alloy melts.

1. Introduction

Wettability as manifest in the contact angle, θ, has long been recognized as a critical parameter in determining the solderability or brazability of a material by a fusible alloy or the ability of a melt to infiltrate a porous preform or array of another material. Particular interest at present centres on the need to develop brazes suitable for joining of ceramics and to identify conditions that promote formation of metal-matrix composites by infiltration of ceramic preforms or fibre arrays. Silicon carbide was selected for study because of its availability in several varieties and consolidated forms suitable as substrates for sessile-drop measurements of contact angle with aluminium based melts. Pure aluminium and binary alloys containing 5 wt % silicon, copper and magnesium were selected as molten (matrix) materials for the study.

2. Experimental procedure

The aluminium used in the study was of 99.99% purity, while the copper, silicon and magnesium used for 5 wt % alloying were at least 99.9% pure. These were added to molten pure aluminium vacuum melted in an alumina crucible, and resulting alloys were chill cast into slab ingots 15 mm × 50 mm in section and 150 mm long. Pieces weighing 0.2–0.3 g with parallel faces ground flat were used for the sessile drop experiments. The substrate material was reaction-bonded silicon carbide (Tenmat Ltd) which contains 18% free silicon as the bonding agent. Some experiments were carried out also with samples of sintered silicon carbide which does not contain free silicon. These were employed as cylindrical discs 14–16 mm diameter by 5 mm height sliced from rod. One flat surface of each disc was ground with emery papers and then polished down to 0.25 µm diamond finish prior to each wetting experiment.

The sessile drop apparatus is illustrated in Fig. 1. It was based on a horizontal resistance-heated mullite tube furnace of internal diameter 25 mm and length 675 mm. Water-cooled flanged ends included windows for illumination and observation of the molten sample located on the substrate at the centre of the hot zone of the furnace. Vacuum pumping down to $10^{-4}/10^{-5}$ torr (1 torr = 133.322 Pa), was achieved with a rotary pump/diffusion pump combination via one of the end flanges. Temperature up to 1100 °C was controlled to within ± 2 K at the location of the sample and calibrated against the furnace setting by separate trials using a sheathed Pt–13% Rh/Pt thermocouple located at the same position as the specimen. A titanium sponge getter was located adjacent to the specimen during runs to minimize the oxygen partial pressure there.

Before each run the substrate carrying its metal sample in the furnace was carefully aligned horizontally on an alumina boat (containing the titanium sponge getter) in the furnace using an external spirit level and observation with respect to crosswires in a

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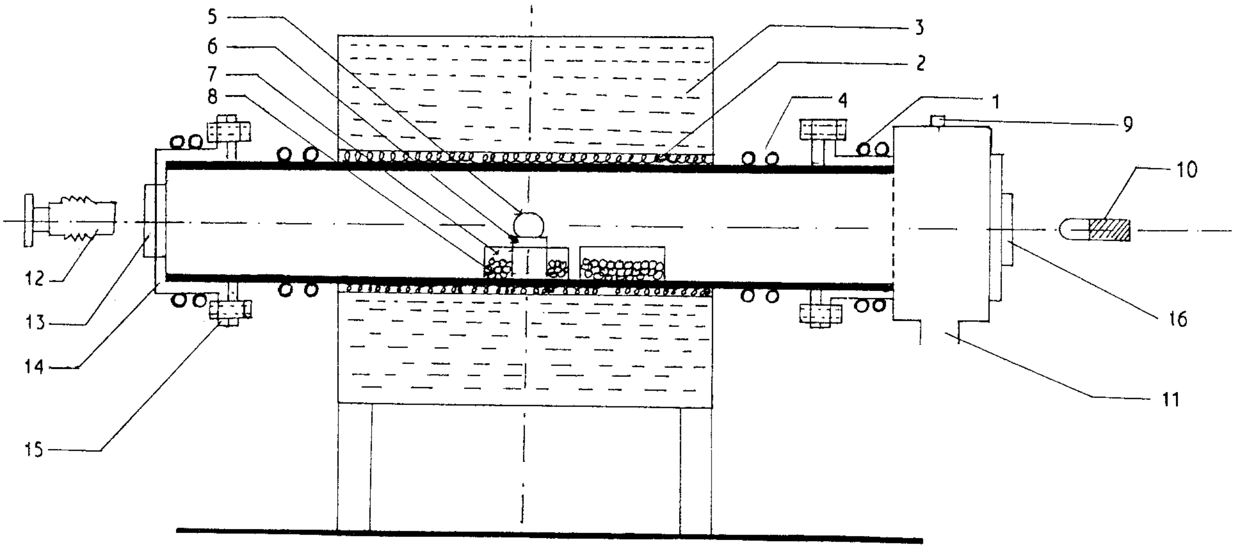

Figure 1 Schematic drawing of the sessile-drop apparatus used for the measurements: (1) furnace tube, (2) nichrome wire heating element, (3) insulation, (4) cooling pipes, (5) sessile drop, (6) SiC substrate, (7) alumina boat containing, (8) titanium sponge, (9) air admittance valve, (10) fibre optic illuminator, (11) exit to diffusion and rotary pumps, (12) camera unit, (13) observation window, (14) water-cooled end flange, (15) location of O-ring seal to furnace tube, (16) illumination window.

travelling microscope. The furnace was then sealed and evacuated to $10^{-4}/10^{-5}$ torr. Heating was then carried out to $\simeq 400\,°C$ for 30–60 min to facilitate degassing, followed by raising to the run temperature at $20\,K\,min^{-1}$. Photographs of the resulting sessile drop were taken on small-grained high-contrast PAN F film at intervals at the run temperature using an Olympus camera with a 300 mm focal length objective lens focused on the specimen. A clear image on the back plate of the camera was obtained by adjusting the camera bellows length. On completion of the run the furnace was switched off to allow the sessile drop to solidify, bonded to the substrate.

Four-dimensional characteristics of the photographed drops were determined from negative films by means of a travelling microscope, i.e. maximum diameter, $2X$, base diameter, $2R$, maximum height, Z, and distance, Z_{90}, between apex of drop and its maximum diameter line Fig. 2. When the contact angle, θ, was acute its value was determined from $\theta = 2\tan^{-1}(Z/R)$ where Z and R are the radius and height of the drop, respectively. When θ was obtuse its value was determined from tables provided by Bashforth and Adams [1] by the procedure described by Selcuk [2].

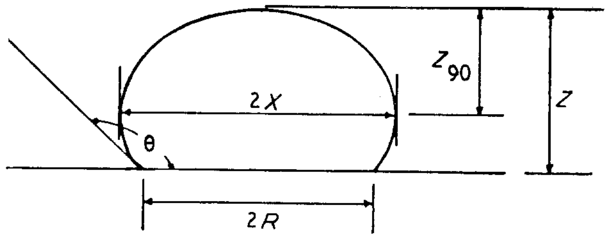

Figure 2 Definition of dimensional parameters used to determine contact angle, θ, of a sessile drop.

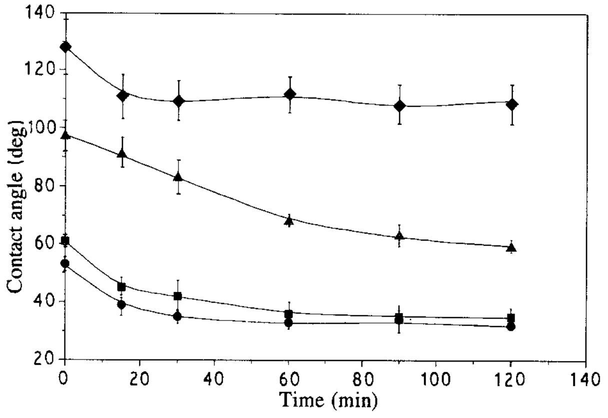

Figure 3 Contact angle, θ, as a function of time, *t*, of holding at temperature for 99.99% aluminium in contact with reaction bonded silicon carbide at $10^{-4}/10^{-5}$ torr (◆) 700 °C, (▲) 780 °C, (■) 870 °C, (●) 960 °C.

3. Results and discussion

Fig. 3 shows θ as a function of time for pure aluminium on reaction-bonded SiC for the four temperatures investigated. For each temperature, θ decreases with time, the effect being particularly marked at 780 °C for which a transition from non-wetting to wetting behaviour occurs within the first 15 min. Such reductions in θ with time at temperature were also found in previously reported sessile drop studies on Al/SiC [3–9] and are typical of contact (angle) behaviour for liquid metal/ceramic systems [10–12]. They have been variously attributed to limited reaction with, and dissolution of, the ceramic by the liquid metal and losses of oxide or other surface films or alloying elements from the sessile drop itself. For a given time of holding, θ decreases with increasing temperature, the transition from non-wetting to wetting behaviour occurring at a holding temperature between 700 and 780 °C for times of holding between 30 and 120 min and between 780 and 870 °C for times up to 15 min. Reported wetting transition temperatures, T_t, range between 700 and 1200 °C for aluminium on SiC [3, 4, 6, 7] compared with 900 or 1000 °C for B_4C [13], 740 °C for TiC [14, 15], 900 to > 1000 °C for carbon [16–18], 800 °C for SiO_2 [9, 19], 860 or 900 °C for AlN [14, 15, 20], 1000–1100 °C for BN [20–23], 1000 °C for Si_3N_4 [20], 700 to 1000 °C for TiB_2 [14, 15, 24], 1200 °C for ZrO_2 [25], 1060 or 1100 °C for MgO [26, 27] and 900–1300 °C for Al_2O_3 [3, 5, 14, 15, 16, 28–35]. Our results for θ as a function of temperature after 30 min hold are compared in Fig. 4 with the corresponding results of Köhler [3], Laurent *et al.* [4] and Shimbo *et al.* [6]. The results of Köhler and Shimbo are in mutual agreement, while the results of Laurent correspond more closely with ours. Köhler and Shimbo used 99.99% and 'high-purity' aluminium, single-crystal and pressureless-sintered SiC, in vacuums of 2×10^{-6} (gettered with zirconium) and 10^{-5} torr, respectively. Laurent used 99.9999% Al on single-crystal SiC in ultrahigh vacuum ($10^{-6}/10^{-7}$ torr with P_{O_2} down to 10^{-18} torr). The implication appears to be that the free silicon present in the reaction-bonded SiC used for our experiments at 10^{-4} torr has promoted a degree of wetting observed for aluminium previously only under the conditions of ultrahigh purity and ultralow oxygen partial pressure achieved by Laurent.

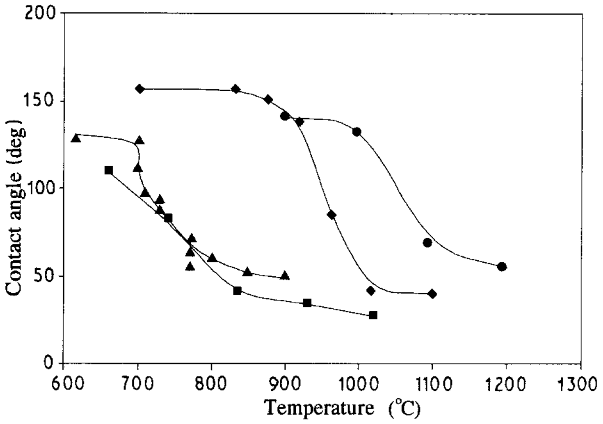

Figure 4 Contact angle, θ, as a function of temperature after 30 min holding for aluminium in contact with silicon carbide. (◆) Köhler [3]: 99.99% Al, single-crystal SiC, 2×10^{-6} torr (zirconium-gettered). (●) Shimbo *et al.* [6]: "high purity" aluminium, sintered SiC, 10^{-5} torr. (▲) Laurent *et al.* [4]: 99.9999% Al, single-crystal SiC, $10^{-6}/10^{7}$ torr ($P_{O_2} \rightarrow 10^{-18}$ torr). (■) Present work: 99.99% Al, reaction-bonded SiC, $10^{-4}/10^{-5}$ torr (titanium-gettered).

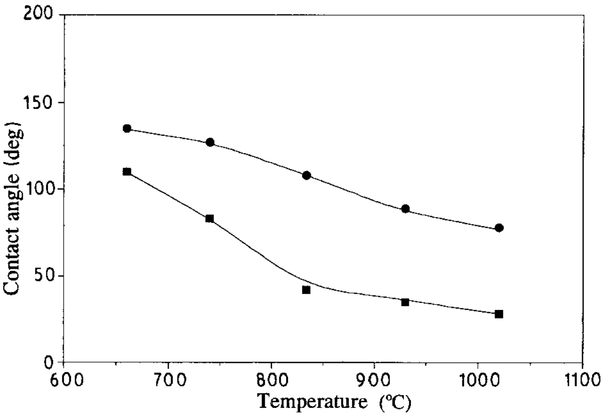

Figure 5 Contact angle, θ, plotted against temperature (30 min hold) for pure aluminium in contact with silicon carbide at $10^{-4}/10^{-5}$ torr. (●) Reaction-bonded SiC, (■) sintered SiC.

This interpretation is supported by our results for aluminium on sintered SiC (containing essentially no free silicon) at 10^{-4} torr and compared with our results for reaction-bonded SiC in Fig. 5. Fig. 5 indicates that θ is higher on sintered SiC than on reaction-bonded SiC at all temperatures up to 1040 °C, such that T_t after 30 min hold is increased from ≃ 760 °C to ≃ 960 °C in the absence of the free silicon present in reaction-bonded SiC.

Figs 6–8 show our results for the effect of time of holding on θ for Al-5 wt % Si, Cu and Mg, respectively, on reaction-bonded SiC at 700, 780, 870 and 960 °C. These again show that wetting is promoted by increasing temperature and time of holding. Fig. 9 compared the effect of temperature on θ after 30 min hold for pure aluminium and the three alloys. This shows that addition of 5% Mg is effective in reducing θ at all temperatures, while 5% Si or Cu are effective (silicon barely so) only at 700 and 780 °C (they actually increase θ at 870 and 960 °C). Notably, the 5% Mg addition achieves wetting even for the shortest time and lowest holding temperature studied. Reports of the effects of alloying on wettability of SiC by aluminium appear to have been limited to effects of silicon by Laurent *et al.* [4] and of silicon, copper and some transition metals by Choh and Oki [36]. Laurent *et al.* found that 5 or 12 wt % Si had no significant effect on θ over the temperature range 680–820 °C (15 or 60 min hold) while 18 wt % Si gave indications of some

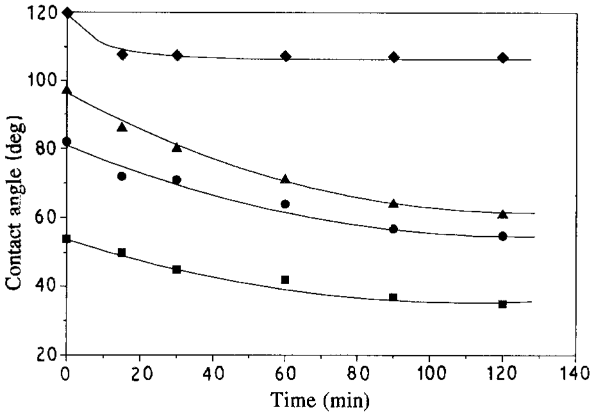

Figure 6 Contact angle, θ, plotted against hold time at temperature for Al-5 wt % Si in contact with reaction-bonded SiC at $10^{-4}/10^{-5}$ torr. (◆) 700 °C, (▲) 780 °C, (●) 870 °C, (■) 960 °C.

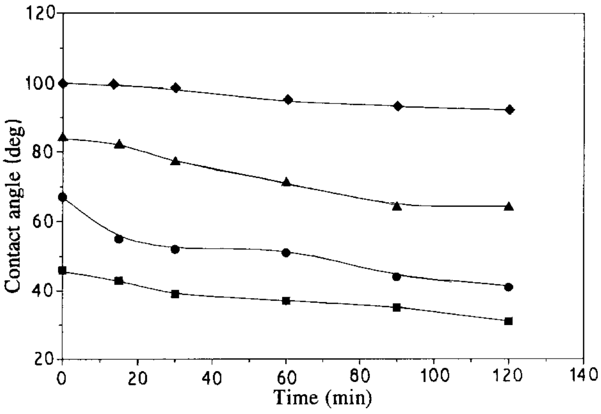

Figure 7 As Fig. 6 but for Al–5 wt % Cu.

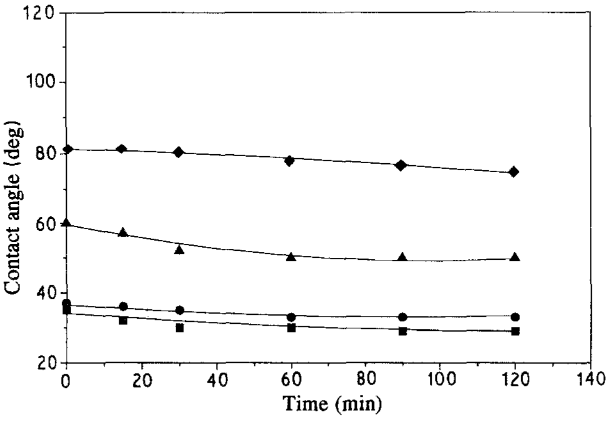

Figure 8 As Fig. 6 but for Al–5 wt % Mg.

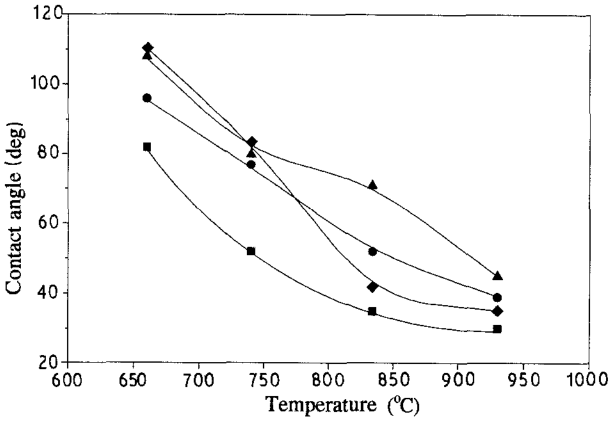

Figure 9 Contact angle, θ, as a function of temperature after 30 min hold in contact with reaction-bonded silicon carbide at $10^{-4}/10^{-5}$ torr. (◆) 99.99% Al, (▲) Al–5 wt % Si, (●) Al–5 wt % Cu, (■) Al–5 wt % Mg.

reduction in θ over the range 680–770 °C. This was explained on the basis that 5 and 12 wt % Si additions are not sufficient to destabilize Al_4C_3 formation as a reaction product under these conditions while 18 wt % Si is sufficient. Choh and Oki found that 8 wt % Si reduced the incubation time for interaction between aluminium and SiC at 1000 °C from 205 s to 20 s, but did not subsequently change the overall reaction rate constant. Addition of 5 wt % Cu in contrast did not change the incubation time but halved the rate constant. The corresponding effects of added copper on θ do not appear to have been reported. The effect of Si in increasing θ at 870 and 960 °C in Fig. 9 was outside the temperature range studied by Laurent *et al.* while the minimal effect of silicon at 700 and 780 °C is consistent with their findings for 680–820 °C.

The enhancement of wettability of ceramics by molten aluminium resulting from magnesium additions has been noted repeatedly [37–43]. In particular, Oh *et al.* [38] found that the threshold pressure for infiltration of molten aluminium into SiC particulate compacts at 800 °C was unaffected or increased by additions of 2% Si or Cu to the melt but was reduced by additions of 2% Mg. They note that this behaviour correlates with the free energy of formation, ΔG_f, of the oxide of the alloy addition: the larger the negative ΔG_f, the larger the threshold pressure. Subsequently, Aghajanian *et al.* [42, 43] reported that spontaneous infiltration of molten Al–5 wt % Si into a loose bed of particulate alumina occurred in a nitrogenous atmosphere above a critical concentration of magnesium addition to the alloy which decreased with increasing temperature of infiltration. Copper additions, in contrast, were found to retard infiltration. Addition of an alloying element can be expected to enhance wetting if it reduces the surface tension of the melt, reduces the interfacial energy and/or promotes chemical reaction at the melt/ceramic interface [44]. The effect of magnesium the surface tension of liquid aluminium has been determined by Pelzel [45], Korolkov [46], Lang [47] and Garcia-Cordovilla *et al.* [48]. All show that surface tension is reduced by magnesium addition, the most recent study [48] showing that this occurs whether or not the aluminium surface is oxidized. The effect of magnesium on the interfacial reaction between liquid aluminium and solid SiC, or between liquid aluminium and the layer of silica with which the SiC is normally covered [9], has yet to be investigated. Oh *et al.* [38] suggest that low wetting angles between liquid Al–Mg alloys and SiC could result from chemical reaction between dissolved magnesium and the SiO_2 film or underlying SiC to form forsterite (Mg_2SiO_4), spinel ($MgAl_2O_4$) or mullite ($3Al_2O_3 \cdot 2SiO_2$). The role of such interfacial reactions in promoting wettability between aluminium-based melts and SiC remains to be established.

4. Conclusions

1. Free silicon present in reaction-bonded silicon carbide is effective in promoting wetting by liquid aluminium in the temperature range 700–1040 °C and a titanium-gettered vacuum of $10^{-}4/10^{-5}$ torr as manifest by a significant reduction in contact angle θ compared with silicon carbide containing no free silicon.

2. The wettability achieved thereby in a titanium-gettered vaccum of $10^{-4}/10^{-5}$ torr is comparable to that obtained by Laurent *et al.* for ultrapurity aluminium on single-crystal silicon carbide containing no free silicon in ultrahigh vacuum with a residual oxygen pressure down to 10^{-18} torr.

3. The addition of 5 wt % Mg to aluminium results in wetting ($\theta < 90°$) of reaction-bonded silicon carbide at all holding times and temperatures in the range 700–960 °C at $10^{-4}/10^{-5}$ torr.

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