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Wettability of SiC by aluminium and Al–Si alloys

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The variations with time of the contact angle formed by molten pure aluminium or Al–Si alloys with single crystalline SiC were measured by the sessile drop method in a vacuum of 10^{-4} to 10^{-5} Pa at temperatures ranging from 933 to 1200 K. In the Al/SiC system, a "non-wetting–wetting" transition was observed at a temperature that decreases as time increases. After holding times of about 2 h, contact angles were stabilized to acute angles even at the aluminium melting point. Although additions of silicon to aluminium were in such amounts as to prevent Al_4C_3 formation at the interface, wettability in both pure Al/SiC and Al–Si alloys/SiC systems was not observed to differ appreciably.

1. Introduction

The knowledge of features of the Al/SiC interface is of basic concern in the properties of SiC-reinforced aluminium composite materials [1, 2]. Wettability in the Al/SiC system is a major variable for the making of composites by the liquid infiltration process. Moreover, a strong thermodynamic adhesion resulting from atomic interaction at the Al/SiC interface contributes to the composite strength.

Previous studies [3] showed that the Al/SiC system exhibits a non-wetting (contact angle $\theta \gg 90°$) behaviour up to $\simeq 1223$ K, where a sharp transition to wetting ($\theta < 90°$) of SiC by liquid aluminium occurs. This kind of transition is typically found in aluminium/non-metallic refractories (carbon, Al_2O_3, TiB_2, . . .) systems. It has been attributed to the disappearance of the effect of the oxide layer on liquid aluminium at about 1223 K under high vacuum [4, 5]. At lower temperatures, this layer prevents a true metal/substrate interface from developing.

As the most interesting temperature range for composite elaboration is far below 1223 K, this study is predominantly aimed at studying wettability in the Al/SiC system within the low-temperature range: (973 to 1173 K). The experimental conditions are selected with a view to restricting or preventing the oxide layer from developing at the interface.

Our second aim was to investigate the effect of silicon addition to aluminium on the wettability in the Al/SiC system. In fact, prior alloying of aluminium allows avoidance of the development of the brittle Al_4C_3 phase at the interface [1, 2].

Some wetting experiments with the Al/Al_2O_3 system were also conducted. Results obtained with this well-known system [4–6] are used to interpret results on aluminium (and Al–Si alloys)/SiC systems.

For discussing all the results, thermodynamic data on the Al–Si–C ternary phase diagram in the temperature range investigated were needed. The isothermal section at 1073 K for the Al–C–Si system in Fig. 1a (Warren and Andersson based its construction on the known binary systems and educated guesswork [1], Viala *et al.* established it experimentally [7]) shows three fields: a three-phase field where the three phases in equilibrium are an Al–Si binary liquid (referred to as L_l), SiC and Al_4C_3, one two-phase field corresponding to the (Al–Si)liquid–SiC equilibria, and a third field corresponding to the (Al–Si)liquid–Al_4C_3 equilibria, respectively. Fig. 1b shows the variations of silicon content in the L_l phase with respect to temperature. This curve defines the break point between two composition areas where the molten (Al–Si) alloy is in equilibrium either with SiC or with Al_4C_3.

Fig. 1c shows the projection of the experimental liquidus of the Al–C–Si system on the composition plane [7]. Two specific composition points, i.e. E and τ, deserve further consideration. They correspond to two invariant reactions. When the liquidus composition reaches the ternary eutectic, E, composition at $T \simeq 849 \pm 1$ K, the invariant reaction occurs:

$$Al_s + Si_s + SiC \rightleftarrows \text{liq.}$$

When the liquidus composition reaches the τ composition at 923 K, the following ternary quasi-peritectic reaction occurs isothermally:

$$SiC + Al_s \rightleftarrows Al_4C_3 + \text{liq.}$$

2. Experiments and apparatus

The wettability is expressed as the θ angle formed by the liquid metal on the surface of the refractory (SiC or Al_2O_3) and evaluated by the sessile-drop method. The "shadow technique" was used to obtain the drop pattern. A × 30 magnification lens was used.

The investigation was carried out in an ultra-high vacuum apparatus. Fig. 2 shows a sketch of the horizontal cylindrical water-cooled double-wall-stainless-steel enclosure. The working chamber is closed at both ends by two removable disks, incorporating two viewports enabling the sessile drop on the substrate to be illuminated and photographed. A molybdenum resistance heater allowed a maximum temperature of 1873 K to be obtained. Thermal insulation is achieved through four molybdenum screens. The thermocouple

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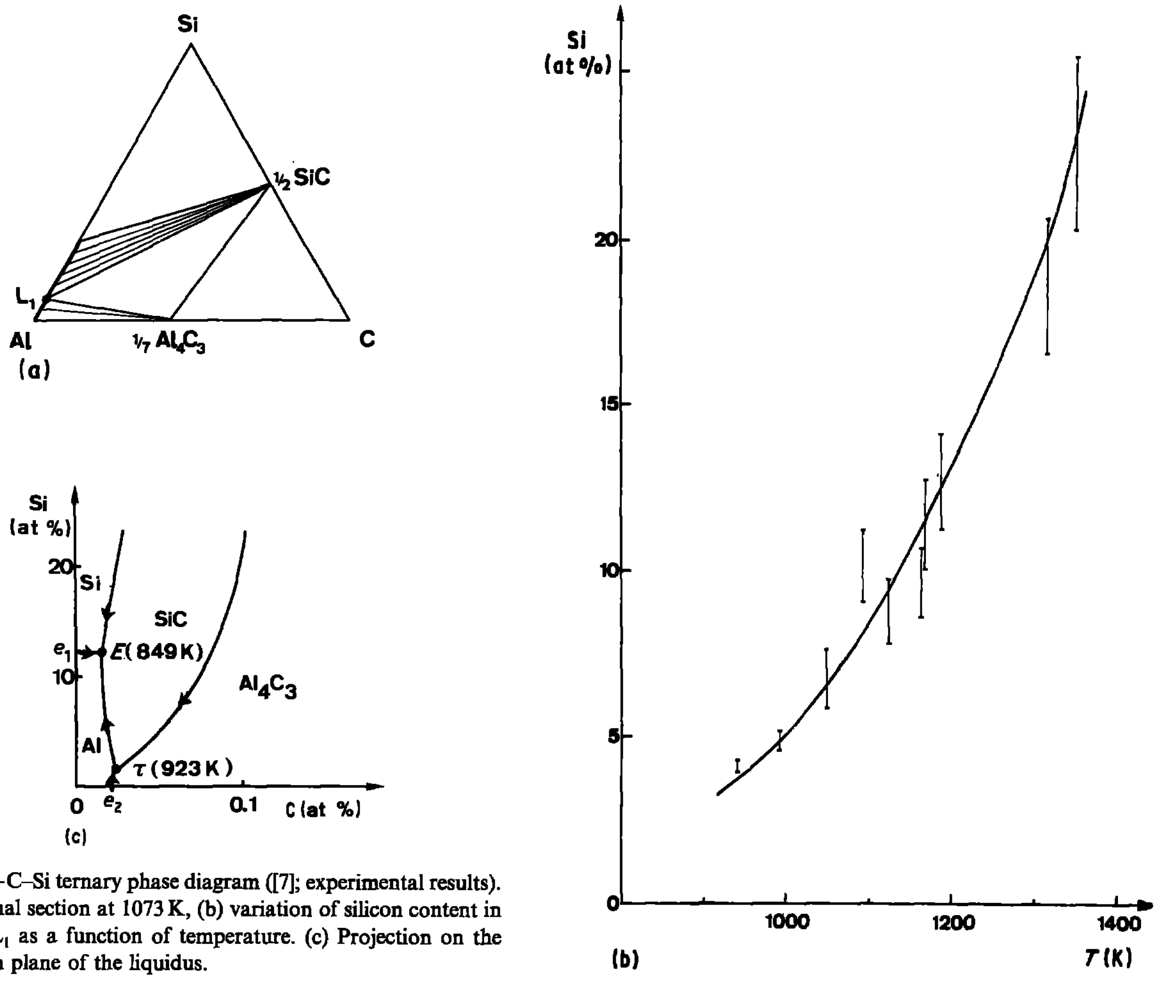

Figure 1 Al–C–Si ternary phase diagram ([7]; experimental results). (a) Isothermal section at 1073 K, (b) variation of silicon content in the liquid L_l as a function of temperature. (c) Projection on the composition plane of the liquidus.

is located under an alumina platform, bearing the drop on its substrate and allows temperature measurements within error limits of ±3 K. Vacuum is produced by three pumps (membrane, nitrogen-cooled zeolite and oil diffusion pumps) and a liquid nitrogen trap. This system allows a total pressure of less than 10^{-5} Pa and an oxygen partial pressure as low as 10^{-16} Pa at room temperature (P_{O_2} measurements were previously performed with an oxygen electrochemical gauge).

The purity of the aluminium employed was 99.9999%. Sample weight was approximately 10 mg. Aluminium specimens were previously pickled with a 10% sodium hydroxyde solution for 2 h and then washed with alcohol. The impurities content in silicon was less than 5 p.p.m.

In order to obtain homogeneous hypereutectic and eutectic Al–Si alloys, a two-step fabrication process was used: melting and holding at 1373 K for 1 h in vacuum, followed by suction of the molten metal in an alumina tube. The hypoeutectic alloys were produced by conventional melting at 1373 K in vacuum.

Since aluminium would have been etched first, a NaOH solution could not be used for alloy pickling purposes. Fresh surfaces were obtained by cutting samples just before initiating the experiments. SiC plane substrates are made up of the hexagonal structure single crystals (α-SiC). The ESCA observation of

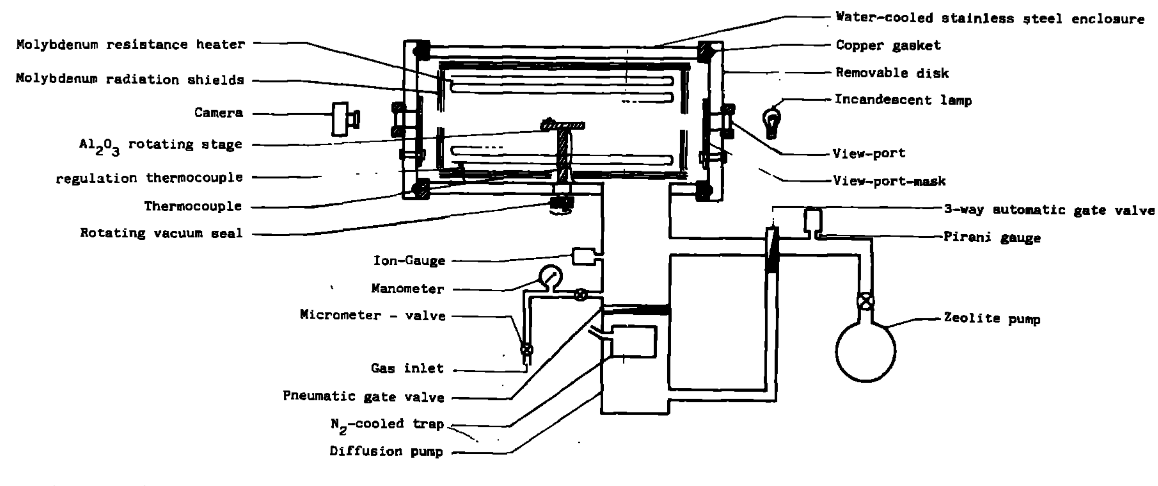

Figure 2 Sketch of the apparatus.

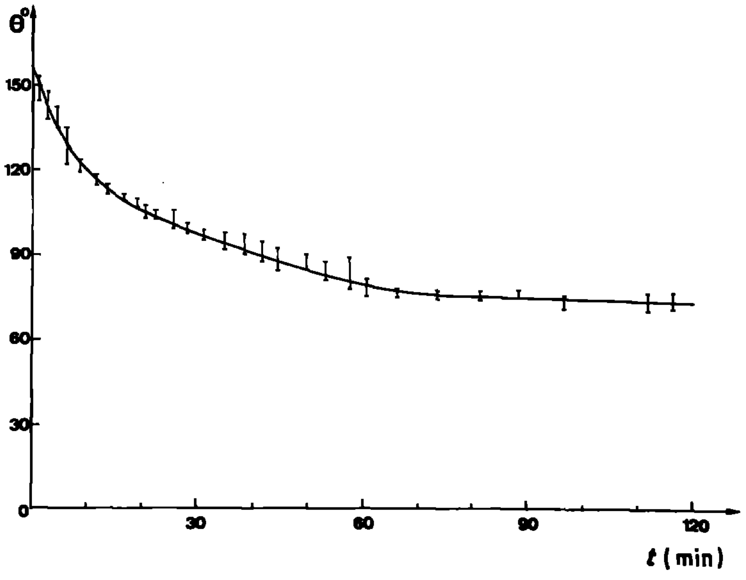

Figure 3 Variation of contact angle with time for the Al/SiC system at 973 K. $P = 10^{-4}$ to 5×10^{-5} Pa.

the SiC substrate showed evidence of an oxide film that developed by oxidation in air at room temperature. To eliminate this detrimental condition, the SiC surface of random orientation was polished with 0.1 μm diamond lading compound just before putting the substrate into the furnace. Moreover, the polishing action produced a smooth surface (roughness measurements performed with a Talysurf 10 were found to range from 0.02 to 0.035 μm only).

The sapphire substrate was previously polished (to a roughness below 0.02 μm) and heat treated at 1373 K for 1 h.

As soon as the ultra-high vacuum condition is established within the work chamber, the temperature was rapidly increased to $T_m - 50$ K, then gradually up to the melting point (T_m) and measured. When the metal-drop was well shaped, contact-angle changes with time were observed until a stable condition developed. The precision of measurement of θ was $\pm 3°$. This procedure is repeated at increasing fixed temperatures ($T \leqslant 1173$ K). All contact angles measured were advancing angles.

3. Results

Fig. 3 shows contact angles θ for the Al/SiC system at 973 K as a function of time. This curve pattern exhibits the three areas of variation of θ with respect to time that were observed in our experiments: the first showing a sharp slope, the second typified by a slighter slope, and the third where the value of θ is nearly constant.

More than 100 min were generally required to obtain a constant angle. The constant values of θ (referred to as θ_{st}) were obtained from single fixed temperature curves in order to show θ_{st} as a function of temperature.

Since the liquid infiltration process is more concerned with θ values after short holding times, contact angles measured after the first 15 (and 60) min, noted θ_{15} (θ_{60}), were also plotted.

3.1. The Al/SiC system

θ_{15} changes with respect to temperature are shown in Fig. 4. This curve was plotted from results of seven separate experiments conducted on the Al/SiC system.

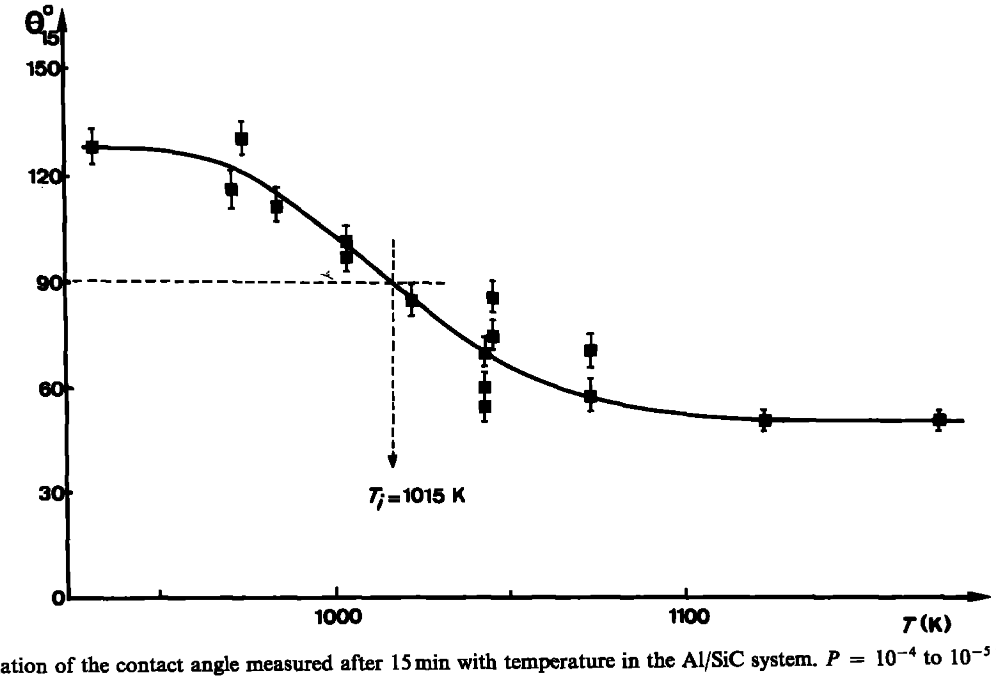

Figure 4 Variation of the contact angle measured after 15 min with temperature in the Al/SiC system. $P = 10^{-4}$ to 10^{-5} Pa.

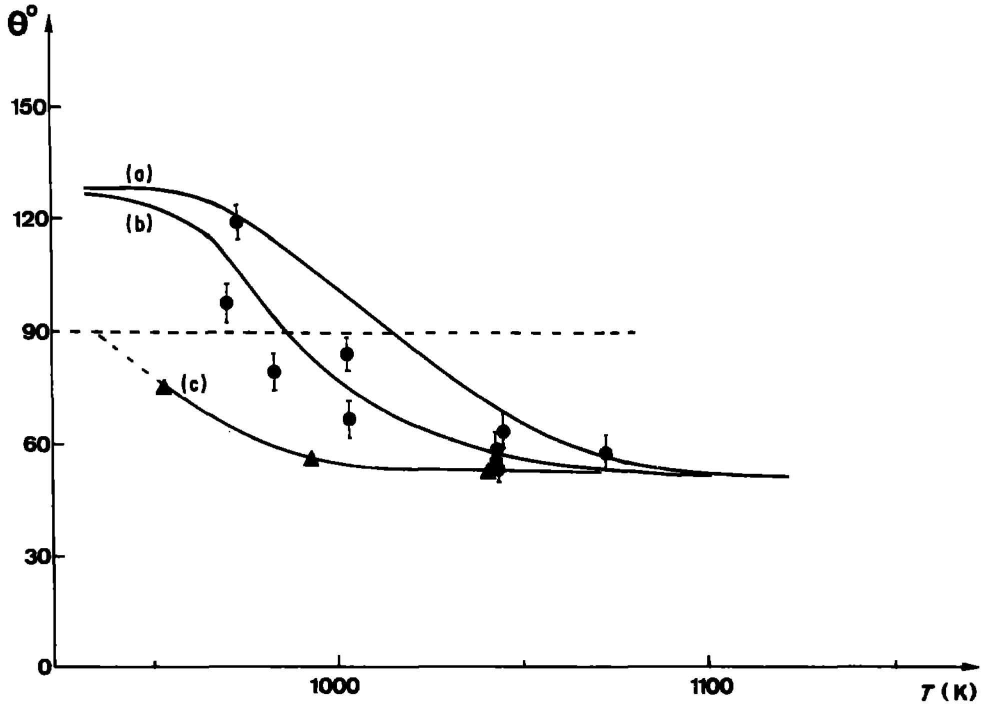

Figure 5 Variation of contact angles (a) θ_{15} (b) θ_{60} and (c) θ_{st} measured after 15 min, 60 min and $\simeq 2$ h, respectively, with temperature in the Al/SiC system. ($P = 10^{-4}$ to 10^{-5} Pa.)

Three temperature ranges, in which the wetting of the SiC substrate by aluminium differs significantly, are shown. In the first temperature range from 933 to about 973 K, contact angles are very high ($\simeq 130°$). A contact melting was observed in all experiments. This phenomenon takes place at the bottom of the aluminium samples 10 K below the melting point in line with the phase diagram (point τ in Fig. 1c). That denotes the existence of an actual Al/SiC interface, but the θ value scattering observed in this area would denote that the oxide film surrounding the aluminium has not yet completely disappeared [8].

Within the range 973 to 1073 K, contact angle decreases appreciably. The "non wetting–wetting" transition occurs at $T_i \simeq 1013$ K. The θ values are still scattered. In the third temperature range, i.e. over 1073 K, contact angles are about 50°. The θ values scattering lies within the experimental error.

The variations of contact angles θ_{60} and θ_{st} with temperature are plotted in Fig. 5 compared to those of θ_{15}. Transition temperature decreases with increasing holding times and ultimately the θ_{st} curve does not show the transition, as wetting has already occcurred at the melting point in the curve. The scanning electron micrograph in Fig. 6 shows the bottom of the solidified aluminium drop on its SiC substrate after heat treatment up to 1173 K (× 420).

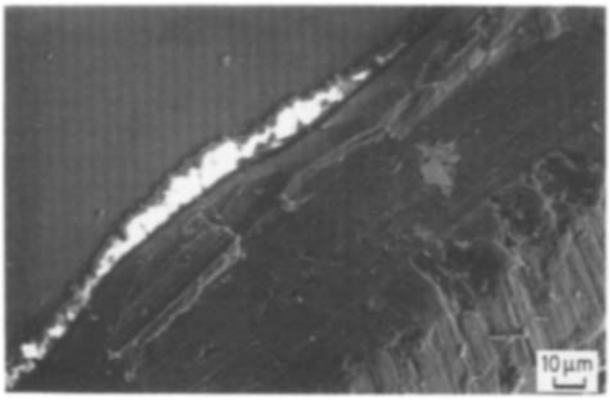

Figure 6 Scanning electron micrograph showing the bottom of the solidified aluminium drop on its SiC substrate after heating to 1173 K (× 420).

A reaction product was observed following the drop solidification shrinkage which was identified as alumina, resulting from an attack on Al_4C_3 by air moisture.

With a view to considering the effect of SiC surface oxidation, a wetting experiment on an oxidized SiC surface was performed. The SiC substrate was oxidized in air for 1 h at 1173 K. The thickness of the oxide film was evaluated as $\simeq 25$ nm [9]. Table I shows contact angles for the Al/SiC and Al/oxidized SiC systems. The holding time at each temperature and the relevant temperature are indicated. The values of contact angle obtained at 973 and 1003 K are constant and higher than those measured at the same temperature and holding time with the Al/SiC system. 120 min were required at 1043 K to obtain a value of contact angle similar to that measured in the Al/SiC system.

The SiC oxidation appears to have an adverse effect on the wetting of SiC by aluminium.

TABLE I Contact angle values in the Al/SiC and Al/oxidized SiC systems at different holding times and temperatures

Temperature (K)	Holding time (min)	Contact angle, θ (deg)	
		Al/SiC	Al/oxidized SiC
973	15	120	133
	60	106	133
1003	15	100	130
	60	75	125
1043	15	70	121
	60	58	80
	120	53	44

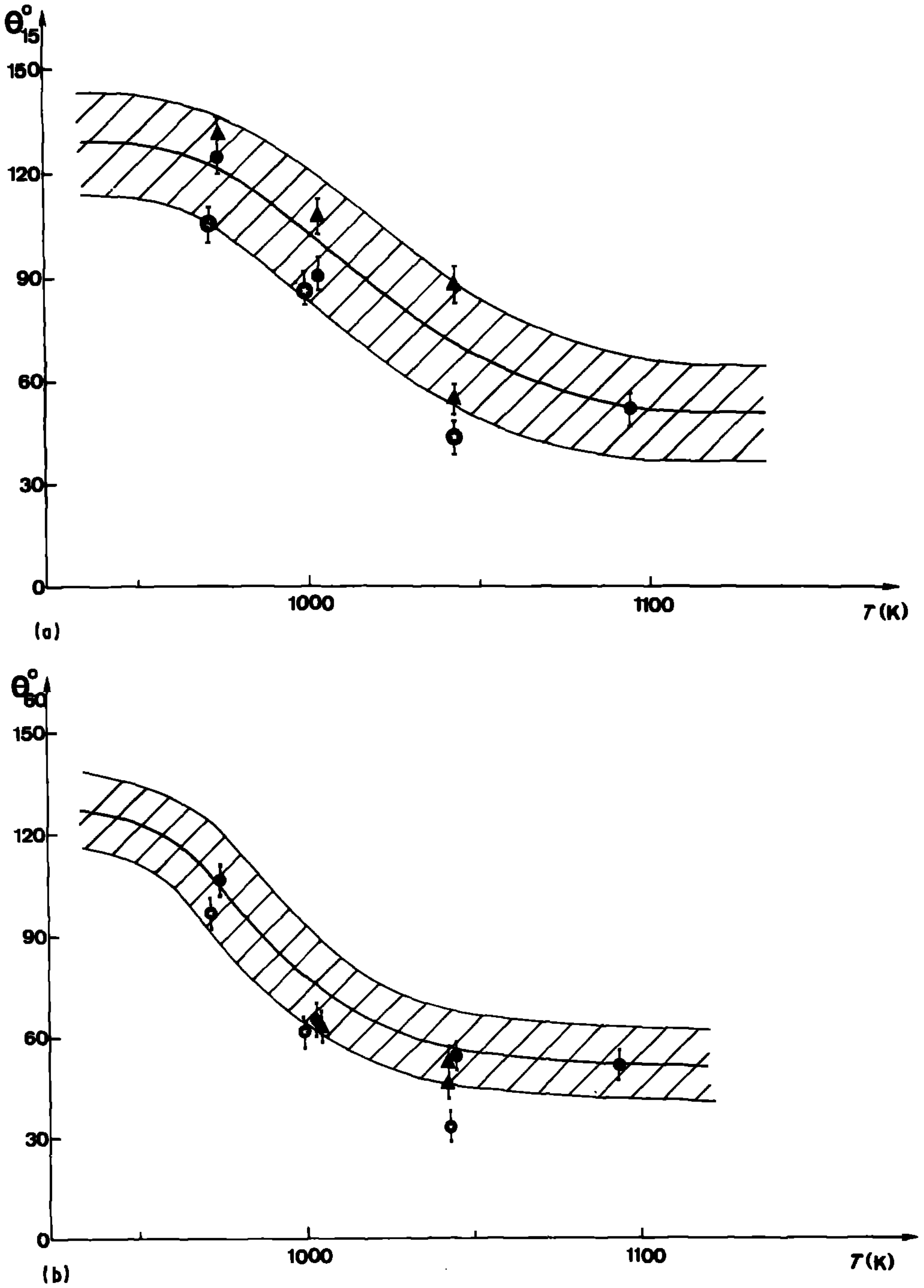

Figure 7 Effect of additions of silicon to aluminium on wettability (a) contact angles θ_{15} measured after 15 min plotted against temperature: (●) Al–5 wt % Si/SiC, (▲) Al–12 wt % Si/SiC, (○) Al–18 wt % Si/SiC, compared to those obtained with the pure Al/SiC system and its uncertainty range (hatched area); (b) as (a), but for contact angles measured after 60 min.

3.2. Al–Si alloys/SiC systems

The effect of various additions of silicon to aluminium on contact angle was investigated. Several wetting experiments were run with three Al–Si alloys: i.e. hypoeutectic (5 wt % Si), nearly eutectic (12 wt % Si) and hypereutectic (18 wt % Si).

For all alloys, contact melting was observed to occur by ≃ 15 K below the Al–Si eutectic temperature, in good agreement with the Al–C–Si ternary phase diagram (point *E* in Fig. 1c).

The θ_{15} and θ_{60} contact-angle changes with temperature for the Al–Si alloys/SiC systems compared to those for the pure Al/SiC system are plotted in Figs 7a and b, respectively. The hatched areas refer to uncertainty ranges of contact-angle values observed with the Al/SiC system. Wetting is not significantly affected by the addition of silicon but is slightly improved for 18 wt % Si alloys at high temperatures. The scanning electron micrograph in Fig. 8 shows the bottom of a solidified Al–18 wt % Si drop in contact with SiC substrate (×350). The specimen has been heated to 1043 K. No reaction product could be seen by means of drop solidification shrinkage. This observation is in agreement with Fig. 1b since the Al–18 wt % Si alloys are found to lie within the "Al_4C_3 non-formation" composition region within the investigated temperature range.

3.3. Al/Al_2O_3 (sapphire) system

A wetting experiment was performed with the Al/Al_2O_3 system under the same experimental conditions. The variations of contact angle with holding time at

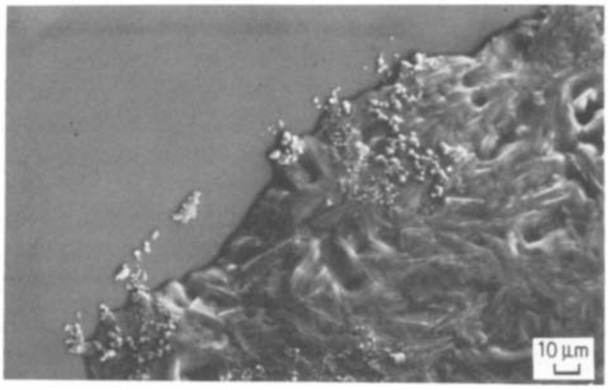

Figure 8 Scanning electron micrograph showing the bottom of an Al–18 wt % Si drop on its SiC substrate after heating to 1043 K (× 350).

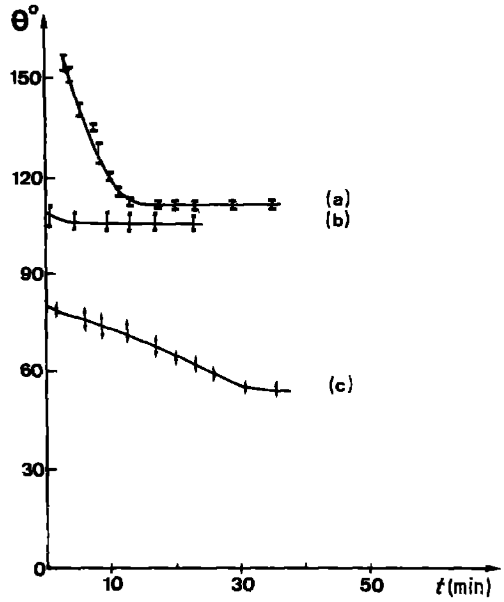

Figure 9 Variation of contact angle with time for the Al/Al_2O_3 system: (a) at 973 K; (b) at 1003 K; (c) at 1223 K. $P = 5 \times 10^{-4}$ to 5×10^{-5} Pa.

three increasing temperatures (973, 1003 and 1223 K) are plotted in Fig. 9. Here, aluminium melting on the Al_2O_3 substrate occurred at 933 ± 3 K. The contact angle measured at 973 K decreases rapidly before reaching a constant value after 15 min. The contact angle is virtually unaffected by time at the next holding temperature (1003 K). One explanation for these two quite dissimilar wetting behaviours is that an Al/Al_2O_3 interface does actually exist through the oxide layer at 973 K. Therefore an equilibrium condition is observed to rapidly develop at 1003 K. The last kinetic curve (at 1223 K) does not show a stabilization of contact angle. θ values show a regular pattern with respect to time up to about 30 min. This kinetic wetting behaviour is due to corrosion of the substrate by aluminium which occurs from 1173 K upwards in accordance with Pask and Champion's observations [5, 6]. (A typical ring can be observed through the sapphire by optical microscopy in the Al/Al_2O_3 interface.)

4. Discussion

The kinetic wetting curves obtained with the Al/SiC and Al–Si alloys/SiC systems exhibited three areas of variation of θ with respect to time. The first area, typified by a rapid θ decrease, can be observed in the Al/Al_2O_3 system when the specimen is held at 973 K (Fig. 9). This wetting behaviour, combined with the fact that a contact melting is observed with the Al/SiC and Al–Si/SiC systems at temperatures lower than the melting point indicates that already at low temperature an actual interface develops between metal and substrate through the oxide film.

The second area typified by a smaller slope is observed, both with (in Al/SiC system) and without

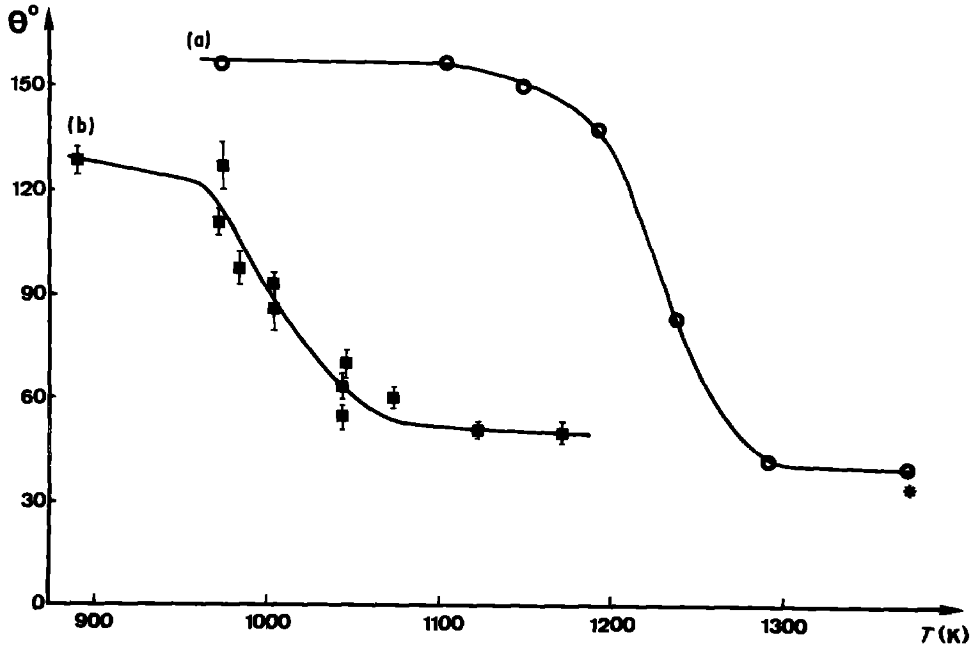

Figure 10 Variation of contact angle with temperature for the Al/SiC system (measurements after 30 min): (a) according to Köhler [3], $P = 2$ to 8×10^{-4} Pa; (b) present work, $P = 10^{-4}$ to 5×10^{-5} Pa. (*) Value of contact angle measured by Naidich at 1373 K ($P \simeq 5 \times 10^{-3}$ Pa [13]).

(in Al–18 wt % Si/SiC and Al–12 wt % Si/SiC ($T <$ 1163 K) systems) Al_4C_3 formation. This area of contact-angle variation with time is similar to that observed with the Al/Al_2O_3 system when the system is reactive, i.e. at 1223 K. The only reaction common to the three systems investigated is an ordinary dissolving reaction: SiC dissolving into Al or Al–Si alloys and Al_2O_3 dissolving into aluminium.

Wettability improvement due to the development of a new phase was emphasized in previous work [10, 11] on metal/refractory systems. From above results, the same does not hold true for the Al/SiC system since the dissolving kinetic typifying the Al/SiC system is observed to be unaffected by Al_4C_3 development. Al_4C_3 phase might grow as a discontinuous layer, according to observations by Viala [12]. The third region (θ constant values) corresponds to saturation of liquid in SiC.

The variation of contact angle with temperature for the Al/SiC system measured by Köhler [3] and our experiments are plotted in Fig. 10. (The contact angle is measured upon completion of a 30 min holding time at each temperature.) The curve obtained by Köhler shows a flattened section at low temperature which may be ascribed to an aluminium oxide film preventing an actual Al/SiC interface from developing. In Köhler's experiments, the inhibiting effect of the oxide layer on wetting begins to disappear from 1123 K upwards. Therefore the "non wetting–wetting" transition occurs at 1233 K in the Köhler's curve whereas our curve shows the transition at 1003 K. Beyond the transition, both curves show a flattened section along which contact angle retains similar values within the limits of experimental error.

Naidich measured a contact angle of 34° at 1373 K and 1 to 7 $\times$ 10^{-3} Pa for the Al/SiC system [13]. The contact angles are found to be in good agreement in the high-temperature range, as wetting is no longer affected by the oxide film.

5. Conclusion

The wettability of SiC single crystals by aluminium and Al–Si alloys was investigated in the 973 to 1173 K temperature range under experimental conditions (low total pressure, low oxygen partial pressure, fresh metallic surfaces) allowing an actual molten metal–substrate interface to develop as early as at the melting point of aluminium (or Al–Si alloys).

In all cases (pure aluminium or Al–Si alloys), the common reaction occurring at the interface (SiC dissolving into aluminium) leads to changing contact angles for about 30 to 120 min depending on the temperature.

In the case of the Al/SiC system, spreading of the aluminium drop is observed to occur concurrently for both Al_4C_3 development and the dissolving reaction. The "non-wetting–wetting" transition temperature decreases with increasing holding time and for comparatively long times ($\simeq 2$ h), no transition exists at all: aluminium wets SiC even in the vicinity of its melting point ($\theta \simeq 75°$ at $T = 950$ K).

Wettability in metal/refractory systems was found to be improved by the development of a new phase. Here, the development of Al_4C_3 compound at the initial Al/SiC interface has no measurable effect on the wetting behaviour in this system: additions of silicon to aluminium allow avoidance of Al_4C_3 development which would promote reactions, but do not affect wettability.

Oxidation of SiC substrates appears to affect detrimentally the wetting by liquid aluminium. Further studies are currently underway in our laboratory for the purpose of quantifying this effect.

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