

Wettability of Aluminium-Magnesium Alloys on Silicon Carbide Substrates

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Abstract

Wettability between the liquid matrix and the reinforcement is important for the processing of Metal Matrix Composites (MMCs); the contact angle can be measured with the sessile drop method. However, for the wetting angle of liquid Al-Mg alloys on ceramics, it is difficult to obtain an accurate measurement because aluminium is easily oxidized and the rate of evaporation of Mg is high. Here an oxide stripping device is used to provide an aluminium alloy droplet with minimal oxide on the surface when the droplet makes initial contact with the substrate. Results are reported for contact angle (θ) versus time for Al-2.1, 3.9, 9.1 and 14.2 wt.%Mg alloys with sintered SiC substrates. The samples were quenched from the test temperature. Magnesium is playing a key role in the adhesion, or otherwise, of the droplet to the substrate. Magnesium is probably migrating to the surface of the droplet and evaporating or forming a 'crusty' layer on the surface over time. When viewed from above, 'halo' regions, initially showing interference colours, develop on the substrate around the base of the droplets. These are probably associated with Mg (and Al) diffusing from the droplet across the surface of the substrate.

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INTRODUCTION

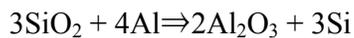
Ceramic reinforced/Al alloy Metal Matrix Composites (MMCs) are a family of advanced materials with attractive properties including high strength, high specific modulus, low coefficient of thermal expansion, good wear resistance, low density and good thermal conductivity. The most important consideration in the fabrication of MMCs by liquid metal routes is the issue of compatibility between the reinforcement and the matrix.¹ This compatibility has two related aspects, wettability at the liquid metal-ceramic interface and reaction between the two constituents. Both wettability and reactivity determine the quality of the bond between the two materials and therefore greatly influence the final properties of the composite. The non-wettability of ceramic reinforcement by liquid aluminium is a major consideration in the fabrication of aluminium matrix-ceramic composites below 1000K since the liquid aluminium is readily covered with an oxide layer. In most cases wettability is poor, and, therefore, an external pressure is required to force the liquid metal into the preform.^{e.g.2} Application of the required pressure is an additional cost. One approach to reduce the pressure required in the process, thereby making it more economical, is to select alloying additions that promote wetting of the reinforcement by the liquid metal.^{e.g.3}

The standard method for the evaluation of wettability is the sessile drop method⁴, which has been used to measure the wettability of a range of Al based alloys on SiC,⁵⁻¹¹ of pure Sn on SiC,^{9,12} of pure Al or Al-alloys on Al₂O₃,¹³⁻¹⁵ on MgO,¹⁶ on graphite and on AlN.^{17,18} It is, however, difficult to obtain an accurate and repeatable measurement of the wetting angle of liquid Al-Mg alloys on ceramics, especially under vacuum, because the rate of evaporation of Mg is high above the melting temperature.¹⁹ In the experiments described here an argon

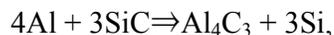
atmosphere is used to reduce the rate of evaporation in comparison with that which would be obtained under vacuum. It cannot, however, be avoided.

Liquid aluminium has a layer of Al_2O_3 on its surface since it has an extremely high affinity for oxygen. However, when Mg is present, a spinel (MgAl_2O_4) and/or a Mg containing oxide (MgO) layer may also be present.²⁰ Delannay et al.²¹ reported that if alloying additions to aluminium are more reactive than Al itself, Al in its oxide will be replaced by the active alloying addition. The formation of spinel is probably due either to absorption of Mg in the interface and/or to large negative free energies of formation. For the formation of MgAl_2O_4 , $\Delta G(1073\text{K}) = -1852\text{kJ/mol}$ and for Al_2O_3 , $\Delta G(1073\text{K}) = -1377.6\text{kJ/mol}$.²²

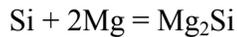
Two different chemical interactions are expected between SiC and an aluminium matrix.²³ The first is the interaction of liquid aluminium with the oxide film present on the surface of the SiC reinforcement:



and the second is the dissolution of the SiC given by:



Formation of magnesium silicide is possible if Si from the above reactions combines with Mg present in the Al melt²⁴:



Yaghmaee and Kaptay²⁵ have examined the stability range of SiC in ternary liquid Al-Si-Mg alloy and shown that a certain minimum critical Si content is needed in the melt to avoid the formation of Al₄C₃ at the interface. The critical Si-content has been found to increase both with temperature and with the Mg-content of the melt. Results from Ferro and Derby²⁶ reinforce the fact that there is a critical level of Si required to suppress the formation of Al₄C₃.

Wettability in most ceramic/metal systems for Metal Matrix Composites is poor but alloying additions can be used to improve wettability. The additions fall into three categories:

- (i) those that reduce the surface tension of the melt;
- (ii) those that decrease the solid-liquid interfacial energy;
- (iii) those that induce wettability through chemical reaction.

The role of magnesium has been reviewed by Hashim et al.²⁷ Magnesium acts as a surfactant, reducing the surface tension of the liquid in comparison with that of pure aluminium.²⁸ The reduction is sharp for the first 1 wt.% Mg addition. Magnesium can also act through reducing the solid-liquid interfacial energy, aiding the reaction at the surface of the ceramic and forming new compounds at the interface. Levi et al.²⁹ suggested that bonding was achieved for an Al-Mg alloy based composite through the formation of a MgAl₂O₄ layer by reaction at the solid-liquid interface. Other workers have also highlighted the role of MgAl₂O₄ in modifying the oxide layer which covers the surface of the liquid aluminium³⁰⁻³⁸.

The aim of the experiments described here is to measure the contact angle versus time for a series of Al-Mg alloys on SiC, using an oxide stripping device as the sessile drop is produced

so that the effect of oxide layers on the surface is minimized. The effects of oxygen cannot be avoided as there will be a native SiO₂ layer on the SiC substrates and, even in five-nines argon, there will be more than enough oxygen (or water vapour) to oxidize both Mg and Al, according to the Ellingham diagram. In addition, the presence of the Ti getter is not sufficient to prevent oxidation occurring. However, with the oxide stripping device, the aim is for the droplet to be momentarily *almost* oxide free so that as the droplet comes into contact with the substrate the instantaneous contact angle represents that between the alloy and the SiC with a native SiO₂ layer. We do not argue here that we have avoided the effects of oxygen but rather that we have obtained results which can be compared with others in the literature and which do provide some insight into the behaviour of Mg in the alloy. The distribution of the elements in the samples (in particular the Mg) is investigated with Energy Dispersive Analysis in the Scanning Electron Microscope.

EXPERIMENTAL METHOD

Materials

The target alloy compositions for the experiments were Al-2, 4, 9 and 14 wt.%Mg. 99.98% pure Al was melted in a graphite crucible in a controlled atmosphere electrical heating furnace and Mg alloying additions having purity of 99.7% or better were added. The alloys were analysed using Inductively Coupled Plasma Emission Spectroscopy (ICPES) showing the actual compositions to be: 2.1, 3.9, 9.1 and 14.2 wt% Mg. For convenience the alloys will be referred to as 2, 4, 9, and 14 wt% Mg in the text. The alloys were cast into a 20mm diameter chill cast ingot. The sintered 6H α -silicon carbide (SiC) for the substrates was supplied by Wacker, Walton-on-Thames, Surrey, and had composition 98.5 wt% SiC, 1.0 wt% free carbon

and 0.3 wt% Al plus trace amounts of oxygen and nitrogen. Note that there will be a very thin layer of silica on the surface.

Apparatus

A schematic of the sessile drop apparatus is given in Figure 1. It consists of a transparent silica work tube positioned vertically in a resistance furnace and a vacuum unit. The silica tube has dimensions of 50mm OD, 46mm ID and 800mm length. It is sealed at both ends with "O" ringed end caps. The middle of the furnace has two observation windows. A ceramic (mullite) tube having one end drilled to 1mm diameter was used as a crucible and positioned on the centreline of the silica tube.

The central feature of the apparatus is that the alloy is melted in the ceramic tube and is then forced out as a droplet onto the ceramic substrate by gas pressure. The orifice on the ceramic tube is designed so that the oxide skin is stripped from the surface of the droplet as it emerges. This is similar to previous oxide stripping mechanisms³⁹⁻⁴². The droplet which is therefore in contact with the ceramic substrate does not have the normal alumina skin interfering with the measurements. Evidence that the droplet is virtually oxide free will be presented later. To avoid the stripped droplet oxidizing as it emerges, argon gas (99.999%) is fed in from below and drives any remaining oxygen in the atmosphere in the tube upwards (as it is heavier and displaces gas upwards). Vertical positioning is critical to the successful operation of the apparatus. The vertical positioning mechanism allows careful placement of the substrate in relation to the bottom of the ceramic tube. In most of the published works,^{5,7-13} the sessile drop

rests on the substrate during heating up of the furnace. It is therefore difficult to determine the precise contact time which should be quoted for a particular temperature. In the present work, however, a droplet of molten metal is gently dropped onto the substrate through the hole in the ceramic tube when the predetermined temperature is reached. An advantage of the present apparatus is that the silica tube, with its contents, can be quickly drawn downwards out of the apparatus, hence quenching the sample. This enables a fast quench in comparison with the published works,^{5,7-13} where it takes time to get the sample out of the furnace, again introducing uncertainty about the precise contact time which should be quoted.

Methodology for a Wetting Experiment

The SiC material was slit with a diamond saw to dimensions 12x12x5mm for wettability studies. The samples were then mounted, ground with 400, 600, 800, 100 and 1200 mesh SiC papers and polished with 6, 3 and 1 μm diamond paste. Alloy pieces approximately 0.5g in weight were cut from pre-alloyed ingot material and placed in the ceramic tube.

The SiC substrate piece was placed on an alumina boat with the polished surface upwards. The rest of the alumina boat was filled with titanium sponge to act as a getter for residual oxygen in the environment. The alumina boat was placed in the middle of the length of the furnace in line with the observation windows. This was achieved by raising the alumina rod manually. Horizontal leveling of the SiC surface was achieved with the aid of a travelling microscope placed in front of the observation window. Spacers at the position "Z" in Fig. 1 were used to tilt the silica tube to make the surface horizontal. Prior to the experiment, valves A, B, D and E were turned on and the system was flushed for 1/2 hour with high purity (99,999 %) argon. Then valves A, B, D and E were turned off and the system was evacuated down to 10^{-3} mbar

vacuum. Argon was then introduced to the system until atmospheric pressure was reached followed by flushing with argon for further 1/2 hour. This procedure was repeated 4 times to ensure the system was fully cleaned of oxygen. Then the valves A and E were turned off and valve C turned on to allow argon to flush through the top of the silica tube. The furnace was heated at a linear heating rate of 10°C/min. As the temperature reached 750°C, a droplet of the molten alloy sample in the ceramic tube is pushed out through the orifice using gas pressure onto the SiC substrate. The gas screw injection valve allows this to be done gently and in a controlled way. As the droplet is pushed through the 1mm diameter orifice in the ceramic tube, fresh aluminium surface, with no oxide film, is created. The Al droplet appears shiny when viewed through the observation window and indeed the reflection of resistance wires can be seen on the surface of the droplet. This is evidence that the objective of having a virtually oxide free droplet is achieved. It is difficult to obtain an image demonstrating this but the reflection of the resistance wires can just be seen in Fig. 2a. For comparison, when the experiment is carried out in a vacuum of 10^{-3} mbar with no argon flushing (and hence with some oxygen present in the atmosphere), immediately after the droplet emerges it is much duller in appearance (compare Figs. 2a and 2b) and gave higher contact angles as compared to the Ar flushed sample. (Note that it is not possible to carry out the experiment in air at atmospheric pressure or in oxygen at atmospheric pressure as the droplet is too 'wrinkled'.)

A CCD camera unit was set up in front of the observation window to record the image of the metallic drop. This unit consists of a CCD camera with a telephoto lens fitted to enlarge the image. Images of sessile drops at rest on SiC were taken at 5, 15, 30 and 60 minute intervals timing from the point at which the drop was established on the SiC. After 60 minutes, the silica tube with its contents was plunged down out of the furnace to quench the droplet. After quenching, the system is let up to atmosphere and the sample removed from the tube. One

sample was prepared without quenching to check whether any effects are due to condensation from the atmosphere during quenching. In that case, after dropping the Al-2wt%Mg melt onto the surface of the SiC, 15 minutes contact time was allowed then the furnace was switched off and the apparatus left to cool with the sample inside.

Measurements of Contact Angles

Images from the CCD camera were processed directly by using an AutoCAD 2000 computer software program which calculates the contact angle automatically. The selected images were scanned and magnified approximately 12X by using the computer. This was done by drawing a reference line at the bottom of drop and a tangent line from the apex of the angle. The validity of the resulting θ 's obtained from AutoCAD was established by comparing with results from the Bashforth and Adams tables^{4,9} for selected samples. All values of θ were correct to within an error of $\pm 2^\circ$.

Analysis of Sessile Drop Samples after Quenching

Some sessile drop samples adhered to the substrate and some did not. The samples were firstly examined with a stereomicroscope (Olympus SZX12) and then in a SIRION Field Emission Gun Scanning Electron Microscope (FEGSEM) with Energy Dispersive X-ray Analysis (EDX). Analysis was carried out on both the drop surface and on the 'halo' region around the drop on the SiC surface. Samples were sectioned transversely to examine the interior of the droplet. For transverse sections, the droplets (and SiC substrates where these were still adherent) were cut with an ACCUTOM-2 slitting wheel and then mounted, ground with SiC paper, polished with 6 and 3 μ m diamond and finished with a colloidal silica polishing cloth.

Between each step the sample was ultrasonically cleaned in ethyl alcohol for two minutes and rinsed in the same. The EDX analyses were at 20 keV apart from in the 'halo' region where results were obtained at 10 keV. With 10keV the penetration depth of the electron beam into the surface is less than for 20keV and thus the EDX results will be from the thin layer on the SiC surface which was leading to the interference colours in the 'halo' region, rather than from the substrate beneath.

RESULTS

Contact Angle

The results of contact angle measurements as a function of contact time at 750°C are shown in Fig. 3.

The contact angle, θ , decreased initially with increasing contact time and then stabilised. The overall changes were small. The contact angle decreased with increasing Mg content in the aluminium, with wetting (i.e $\theta < 90^\circ$) achieved for 9Mg and 14Mg additions.

Scanning Electron Microscopy of the Surface of the Droplet

Figure 4 shows an SEM image of Al-2wt%Mg on SiC substrate after a short contact time. The droplet is relatively shiny when viewed by eye.

The surface appearance for a higher Mg content droplet is shown in Fig. 5. The surface is now less smooth. When viewed by eye the droplet surface appears dull and dark.

Table 1 gives the summary of the EDX results for the drop surfaces. In EDX scans no elements were found other than Al, Mg and Si. The surface is not a flat, polished surface and therefore there is considerable inherent error. The results are therefore given to two significant figures but are illustrative of trends. Note that the starting alloy does not contain Si. Note also that we have concentrated on obtaining data for those samples where the droplet has remained adhering to the substrate. Further information on the 14%Mg is given in the section on the transverse samples. The EDX analysis is for a small square area rather than a point.

The levels of magnesium on the surface of the drop are always higher than the original magnesium content of the alloy. For the 2 wt%Mg alloy at 5 mins, the surface concentration is about 8wt%, by 15 mins the concentration has risen to an average of about 50wt%. With further increase in hold time to 30 mins the levels drop again to about 11 or 12 wt%. The 9wt% alloy sample gives a surface concentration of 17wt% at 5 mins holding in comparison with about 8wt% (taking an average of three areas) for 5 mins with a 2 wt%Si sample. Note that silicon is found at levels of a few wt% even though it is not present in the original alloy.

Adherence of the Droplet to the SiC Surface

Droplets of Al-2wt%Mg with contact times of 5, 15 and 30 minutes, and Al-9wt%Mg with 5 minutes contact time stayed adhering to the SiC surface whereas for the remaining samples (Al-9wt%Mg with 15, 30, 60 minutes contact time and Al-14wt%Mg with 5, 15 and 60

minutes contact time) the droplet broke off during gentle handling. For the Al-14wt%Mg samples the droplet in fact breaks off in two pieces, an overlying droplet and then a 'flake' which was situated between the droplet and the substrate and which corresponds in shape to the 'crater' which forms on the surface of the substrate (i.e. it could be fitted back into the crater).

The 2wt% Mg alloy droplets showed very clear 'haloes' on the SiC surface in the immediate vicinity of the drop (see Fig. 6).

There is some evidence of a halo for 5 minutes contact time for the 9 wt% Mg droplet. At 15 minutes and 30 minutes the region around the droplet simply appears dark (rather than shiny) in the stereomicroscope. For 60 minutes, a 'zone' of some kind is evident. For the 14 wt% Mg droplet, no interference film colours are visible. At 5 minutes, there is a dark 'reaction zone'. With the 15 minute sample, the whole surface appears dark, with similar behaviour for 60 minutes. The samples were examined by using Field Emission Gun Scanning Electron Microscope (FEGSEM) and Energy Dispersive X-Ray (EDX) analysis in the 'halo' region. The haloes were apparently due to very thin interference films. Therefore, the voltage of the electron beam was reduced to decrease the penetration depth. The EDX was carried out at 10keV. (When the voltage was dropped from 15keV to 10 keV, the percentage of magnesium in the EDX result increased significantly, suggesting it is concentrated in the surface film and therefore that 10keV is an appropriate analysis voltage). The EDX analysis is for a small square rather than a point.

Table 2 gives the EDX results for the halo region. Note that carbon will be present because the substrate is SiC but it is not included in the analysis.

Mg generally increases as the distance from the edge of the droplet increases (with one exception – one of the two radial positions analysed for 2wt%Mg 15mins 750°C). The levels are high (and in some cases very high – up to 97wt%) in comparison with the wt% of magnesium in the droplet alloy. For the 9wt% and 14wt% Mg droplets the levels of magnesium in the halo region are much *lower* than for the 2wt%Mg specimens. There is in some cases a measurable amount (a few wt%) of Al in the halo region, generally decreasing with distance from the edge of the droplet.

For the 14wt%Mg 750°C samples the droplet has detached leaving a crater (e.g. Fig. 7).

The region on the edge of the crater was analysed in more detail for all three Al 14wt%Mg samples (i.e. 5 mins, 15 mins and 60 mins hold at 750°C). For the 5 mins. hold sample, the values for Mg and Al in the ‘scalloped edge’ are in some cases very high (e.g for one region 19.2 wt% Mg and 80.3% wt% Al). In other parts of the scalloped edge, values are much lower (e.g. 0.5 wt% Mg and 2.4 wt% Al) but not zero. As the analysis moves outside the scalloped edge across the surface of the SiC at 10 micron intervals the values are typically tending towards 1.1 wt% Mg and 0.7 wt% Al at 30 µm from the scalloped edge. For the 60 mins. hold sample this has increased to typically 2-3 wt% for both Mg and Al.

A flake of material has broken off from the base of the droplet. EDX results for the crater and for the base of the detached flake give very high Si levels (approaching 100 wt.%). Some Al and Mg can be detected on the scalloped edge alongside the Si. The crater represents a region

where the alloy droplet has reacted with the SiC substrate (the depth of the crater is about 1 mm).

For the sample which was prepared without quenching the halo still exists. It is less shiny than for the as-quenched sample.

Scanning Electron Microscopy of Transverse Sections Through Droplets

After the initial FEGSEM examinations of haloes and of droplet surfaces, the 14wt%Mg droplets were sectioned perpendicular to the droplet/SiC interface. Note that these droplets had detached from the substrate. Fig. 8 shows a cross-section for Al 14wt%Mg for 5 mins holding. The 5 mins and 60 mins samples in fact show non-wetting contact angles even though the *in situ* contact angle measurements were less than 90° (Fig. 3). This is thought to be due to shrinkage during solidification, with the triple point shrinking back from its position at temperature. The figures in boxes on Fig. 8 are the EDX results for wt% Mg and Si raster analyses (approximately 40 µm x 40 µm) at the positions shown. As far as possible porosity was avoided. The balance is in each case Al.

For the 5 min hold sample (Fig. 8), the magnesium level is less than the original alloy level of 14wt% except in two positions on the surface of the droplet. The concentration near the base of the droplet is decreasing. In the immediate vicinity of the base the Si level suddenly rises. The interface at the base of the droplet is relatively flat suggesting that the droplet has broken off along a line corresponding to the original surface of the substrate whereas the ‘flake’ mentioned earlier (which has also broken off) is from beneath the droplet within a reaction zone in the SiC itself. Si is present in some positions on the surface of the droplet. There is

significant porosity, particularly in the surface regions, with what appear to be gas bubbles breaking the surface.

The 40x40 μm raster analyses were too coarse to examine phenomena near the triple point in the corner of the droplets in detail. Point analyses were therefore carried out at 1 μm , 4 μm and 8 μm in from the corner (moving diagonally into the droplet). The results for the right hand corner in Fig. 8 were, respectively, (with the balance Al):- 14.1 wt%Mg and 0.8 wt% Si; 14.5 wt% Mg and 0.8 wt% Si; 14.9 wt% Mg and 0.6 wt%Si. For the left hand corner the equivalent values are:- 27.5 wt% Mg and 16.1 wt%Si; 24.0 wt% Mg and 12.4 wt% Si; 19.0 wt% Mg and 8.5 wt% Si. There is therefore significant evidence for the right hand corner (if not for the left hand corner) that Si has migrated into the droplet from the substrate and that Mg is congregating in the corner.

In the 15 min sample , no silicon was detected. Mg levels are again lower than the original alloy composition of 14 wt% apart from the position at the very top of the droplet where the level is 19 wt% (higher than in the previous sample). There appears to be less porosity than in the previous sample. The analysis near the triple point was again carried out in greater detail as described for the 5 min. sample above. The results were similar to those for the left hand corner of the 5 mins hold sample i.e. Mg levels close to the overall alloy composition of 14 wt % and Si levels at around 1 wt%.

Every Mg reading for the 60 mins hold sample is below the original level for the alloy. The single exception is a measurement taken actually within a hole to see if there is evidence that the hole was formed by evaporation of Mg. The level of Mg in the hole is relatively high at

25wt%. There is evidence of Si within the hole and at one other position in the surface region. There is some suggestion of Mg depletion on the sides of the droplet (typically 6 or 7wt%Mg) in comparison with the top of the droplet (12wt%). The detailed analysis near the triple point was carried out as described for the 5 mins hold sample. The values were typically 7-10 wt% Mg and 0.1 -0.6 wt% Si i.e. the Mg level is significantly lower than the original alloy composition. The reading at the interface with the substrate and in the centre of the droplet is similar to the previous sample at 10 or 11 wt%. At what would have been the triple point it is now 7 wt%Mg i.e. it has decreased from 10 wt%Mg between 15 mins and 60 mins.

DISCUSSION

Mechanism to Account for the Above Results

Fig. 9 shows a mechanism which might account for the results.

The Mg is either diffusing to the surface of the droplet and evaporating off or evaporating into gas bubbles rising within the droplet (there is some gas porosity in the transverse sections and an analysis in one of the holes showed relatively high Mg). The question is then whether the halo region is forming by diffusion across the surface from the droplet or whether it is due to condensation from the atmosphere. Condensation is unlikely because the drop and the substrate are at the same temperature. The Mg vapour pressure above the dilute solution would be too low to lead to condensation of pure elemental Mg. This then leads to the possibility that the haloes result from diffusion across the substrate surface. It might then be expected that the Mg concentration on the surface of the substrate would be highest near the droplet. In fact, it

increases with distance away from the droplet. However, this might be accounted for if the supply of Mg is being inhibited by the progressive formation of an oxide/spinel layer on the droplet. Note that the haloes disappear with hold time at temperature almost certainly because the surface layer is thickening (hence appearing darker) and hence the interference colours are disappearing.

Mg is thought to promote wetting by reacting with oxygen in the silica on the surface of the SiC⁸. The diffusion of the Mg across the surface oxide layer on the SiC may then be 'paving the way' for the advance of the wetting alloy. The argument against this is that it is actually the high Mg droplets which give the lowest contact angle but these have the lowest Mg in the halo region. Al may also be involved in the reaction (forming MgAl₂O₄) because both Mg and Al are found at low levels near to the triple point position on the surface of the SiC just outside the scalloped edge of the crater for the 14 wt% Mg samples. The values for the Al and Mg increase at 30 μm from the edge with hold time (comparing the 5 min sample with the 60 mins sample). Mg does not form a carbide but may react with the SiC to form a silicide Mg₂Si ($\Delta G^\circ = -73.1 \text{ kJ/mol}^{43}$). In Fig. 9, Al is shown as diffusing from the droplet across the SiC surface at the triple point because the levels of Al *decrease* with distance from the droplet as would be consistent with diffusion.

Residual oxygen in the system (as identified earlier) will tend to react with the surface of the droplet giving either an Al₂O₃ surface film (for the low Mg content droplets), or MgO or the spinel MgAl₂O₄ (for the higher Mg content droplets). This would account for the darkening of the surface of the droplet with time and with the higher Mg contents. The Al₂O₃ film in the early stages of holding will tend not to be complete and therefore this might then explain why

the Mg level is higher in the halo region for the 2 wt% Mg than for the higher Mg content droplets. For longer holds with higher Mg contents, the surface of the droplet is darker and 'crusty', suggesting there is a thicker film which may be inhibiting the evaporation of Mg from the surface.

What is clear is that with increasing Mg concentration in the original droplet and increasing hold time at temperature, extensive reaction is occurring at the interface between the droplet and the SiC. It is likely that the reactions include:



The free Si is then transferring into the droplet (and is hence detected in the EDX analysis of the cross-section) and the formation of the brittle Al_4C_3 (although it has not been possible here to prove that Al_4C_3 is present) leads to the detachment of the droplet from the substrate. If the reaction is extensive, the flake forms. The Si now dissolved in the droplet can form Mg_2Si (and indeed this precipitate will form even with low quantities of Mg and Si present in the alloy provided there is a stoichiometric balance of Mg and Si (the stoichiometric ratio of Mg:Si is 1.73:1)⁴⁴ then the excess Si beyond that soluble in the Al will either precipitate as Si particles or diffuse to the surface of the droplet. Wetting is only achieved for the 9 and 14 wt% Mg samples and therefore there is an intimate connection between this interfacial reaction and the wetting. Note that the spreading kinetics are significantly faster than when no Mg is present.²⁶

Contact Angle

Although the addition of 2 or 4-wt%Mg reduced the contact angle of aluminium, the non-wetting condition was still present in these alloy/SiC systems (i.e $\theta > 90^\circ$). The wetting condition (i.e $\theta < 90^\circ$) was achieved only for 9 and 14-wt%Mg additions in the present work.

SUMMARY AND CONCLUSIONS

The wetting of SiC by aluminium-magnesium alloys has been investigated with a sessile drop apparatus that strips the surface oxide from the molten alloy droplet so that, at least at the instant of initial contact, it is not interfering with the measurements. The measurements have been carried out at 750°C for times up to 60 minutes and for alloys ranging in magnesium content from 2 wt% to 14 wt%. A mechanism has been proposed to account for the results as follows:

- 1) Immediately on contact with the substrate, magnesium in the droplet is migrating to the surface of the droplet including evaporating into bubbles which rise to the surface of the droplet. Magnesium is likely to be evaporating from the surface of the droplet.
- 2) There may be some diffusion of Al and Mg from the triple point across the surface of the SiC in the immediate vicinity of the droplet and this may be contributing to the wetting.
- 3) A wetting contact angle is only achieved for the higher Mg contents (9 and 14 wt%) and for these samples extensive reaction is occurring at the interface with the SiC (to a depth of ~ 1 mm for the most extreme case). The droplet then has a brittle interface with the substrate and easily breaks off.

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FIGURE CAPTIONS

Figure 1. Schematic of the experimental apparatus. The left hand diagram shows the droplet under observation. The bottom diagram shows the droplet being squeezed out through the orifice in the ceramic tube onto the substrate; the oxide layer on the molten aluminium is stripped off the surface of the droplet as it emerges from the orifice. The right hand diagram shows the apparatus after the silica tube and its contents have been quickly drawn out downwards and the droplet quenched in the process.

Figure 2. Image of sessile Al-2Mg droplet on SiC (a) using the argon atmosphere, (b) with a vacuum of 10^{-3} mbar (and hence some oxygen present).

Figure 3. Contact angle, θ , versus time for the Al-Mg alloy/sintered SiC system in argon at 750°C

Figure 4. SEM image of Al-2wt%Mg alloy for 5minutes contact time on SiC substrate

Figure 5 SEM image of Al-14wt%Mg for 30 mins. contact time.

Fig. 6 Stereomicroscope images of (a) Al-2wt%Mg for 5 minutes, (b) Al-2wt%Mg for 15 minutes, (c) Al-2wt%Mg for 30 minutes, (d) Al-9wt%Mg for 5 minutes, (e) Al-14wt%Mg alloy for 5 minutes contact time on the SiC substrate

Fig. 7 Crater in the Surface of the SiC Substrate for the 14 wt% Mg 5 mins 750°C sample after the droplet (and the flake beneath it) have broken off.

Fig. 8 Montage of SEM Micrographs of Transverse Section through Al14wt%Mg Droplet after Holding for 5 mins on a SiC Substrate at 750°C. Figures in White Text Boxes Show the EDX Raster Analyses for Mg and Si in the positions indicated. The Balance is Al in Each Case. Analysis Voltage 20keV.

Fig. 9 Proposed mechanism for interaction of the Al-Mg alloy droplet with the SiC substrate

TABLES

Table 1 EDX Results for the Surfaces of Droplets of Al-Mg Alloys of Various Mg Contents Obtained in Wetting Experiments on SiC with a Holding Temperature of 750°C and Holding Times as Indicated (Analysis Voltage 20keV).

Table 2 EDX Results for the 'Halo' Region around the droplet on the surface of the SiC (Analysis Voltage 10keV)