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A study of aluminium brazes using hot-stage scanning electron microscopy

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Hot-stage scanning electron microscopy has been used to study the behaviour of aluminium vacuum brazes. The technique has been employed to observe the surface changes which a braze experiences on heating and to observe the formation of bonds between a braze and a workpiece. 3003 alloy pieces clad with two types of braze were studied: Al–9.3% Si–1.45% Mg alloy and an Al–7.5% Si binary alloy. The magnesium-containing alloy was found to be much more effective in forming joints than the binary alloy, which stemmed from the magnesium-containing alloy's ability to "clean" itself. At the onset of melting the surface of the braze was significantly disrupted by exudation of molten alloy. The exudation was believed to be driven by the volatilization of magnesium and would result in the original oxide layer being broken up, thus making it less effective as a barrier to wetting.

1. Introduction

Vacuum brazing is now often used in preference to flux brazing in the assembly of aluminium heat exchangers, since it avoids the problems of removing corrosive flux deposits. There are difficulties associated with the process of aluminium vacuum brazing, such as the high melting temperature of the brazes with respect to the workpieces. However, the main problem stems from the tendency of aluminium to form a tenacious oxide film which renders the material non-wetting. For successful vacuum brazing, the oxide needs to be undermined to permit wetting and flow over the workpiece [1].

Aluminium brazes are based on the aluminium–silicon eutectic system and it is now usual for the braze to be applied in the form of a thin cladding on one of the workpiece surfaces to be joined. It is generally agreed that an addition of magnesium, of the order of 1%, (wt % throughout unless otherwise stated) substantially improves the ability of the braze to form a bond with aluminium. However, what is not agreed is the mechanism which is responsible for this improvement in wettability. Terril *et al.* [2] studied the effect of a number of additions and came to the conclusion that magnesium was not exceptional in its behaviour as a "promoter". Any element capable of chemical reduction of the alumina film would facilitate joint formation. It follows that the promoter would also be able to react with water vapour and oxygen to produce a cleaner environment, but Terril *et al.* [2] maintained that the key mechanism is the reduction of the oxide film. Winterbottom and Gilmour [3] also acknowledged that magnesium will react with the aluminium oxide film, but asserted that it does not remove the oxide barrier. Instead, it renders it porous, first to the diffusion of magnesium vapour which getters the atmosphere, then to the liquid braze metal itself which wicks up to the surface of the oxide on the cladding to produce a clean, wettable layer. Anderson [4] also acknowledged that magnesium first modified the aluminium oxide film which covered the braze cladding, but at the onset of melting permitted the rupture of this film by exudation of molten eutectic.

All of these conclusions were arrived at using *post mortem* microscopy, that is investigation of material which had been cooled down from the temperature of interest. In contrast, in this work we have employed the technique of hot-stage scanning electron microscopy which allowed the direct observation of surface changes at tempera-

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ture. Studying the behaviour of Al–Si–Mg, Al–Si and Al–Mg alloys allowed a greater insight into the mechanisms of oxide displacement and joint formation.

2. Materials and techniques

The commercial braze alloys studied in this work were in the form of 0.1 mm thick claddings on the surface of 3003 (Al–1.2% Mn) alloy. Two braze alloys were used: an aluminium–9.3% silicon–1.45% magnesium alloy which contained 0.2% bismuth and an aluminium–7.5% silicon alloy. The melting range of the magnesium-containing braze extends from a ternary eutectic at 555° C to the fully molten state at 590° C. The aluminium–silicon braze has a much shorter melting range, starting at the aluminium–silicon boundary eutectic temperature of 577° C and becoming fully molten at 590° C. In addition to the commercial brazes, some experiments were conducted with 99.999% aluminium and a high purity aluminium–1% magnesium alloy sheet.

The surfaces of the specimens were observed using an ISI Super III A scanning electron microscope which had been equipped with a heating stage. This device was based on the design of Cohen *et al.* [5]. Specimens were held on a stainless steel cap by two locating screws. This cap fitted over a cylindrical heater which comprised a grooved pyrophyllite core wound with tungsten wire. The heater was mounted on a pyrophyllite base and surrounded with stainless steel heat shields. The hot stage could be attached to the existing SEM stage, so that movement in the x and y directions were not impeded. Temperature measurement was by a 0.5 mm diameter sheathed chromel–alumel thermocouple held in position on the specimen surface by one of the locating screws. A number of experiments were conducted in which the observation of the interface between two pieces to be joined was achieved by clamping the two pieces in a stainless steel cap which had a recess cut in its surface.

The scanning electron microscope has a working vacuum of better than 10^{-4} torr when operated in the normal mode.

3. Results

3.1. Hot-stage experiments

3.1.1. Al–Si–Mg alloys

The scanning electron microscope was used to observe the surface changes which occurred when as-received magnesium containing cladding was subjected to a braze heating cycle. In general, the material's surface did not alter significantly until a temperature in excess of 450° C had been attained, when in some cases bright spots were observed (Fig. 1).

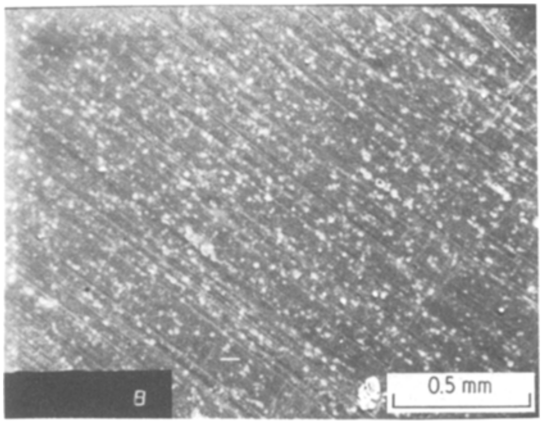

Figure 1 Al–Si–Mg braze cladding heated to ~ 500° C.

At the Al–Si–Mg ternary eutectic temperature, 555° C, a much more drastic surface change was initiated. The surface of the braze began to be disrupted by exudation of alloy (Fig. 2). The exudations gradually spread outwards (Fig. 3) over a period of several minutes at this temperature, to occupy the majority of the specimen surface area. Raising the specimen temperature to the aluminium–silicon binary eutectic temperature of 577° C and above, permitted the transformation of the surface to reach completion (Figs. 4 and 5).

On samples which had a polished surface, the transformation was much more rapid; the whole surface of a specimen would be disrupted within

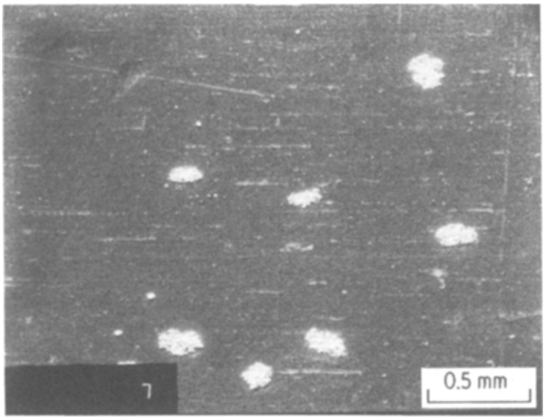

Figure 2 Al–Si–Mg braze cladding heated to 555° C. Exudation of alloy through the original surface begins.

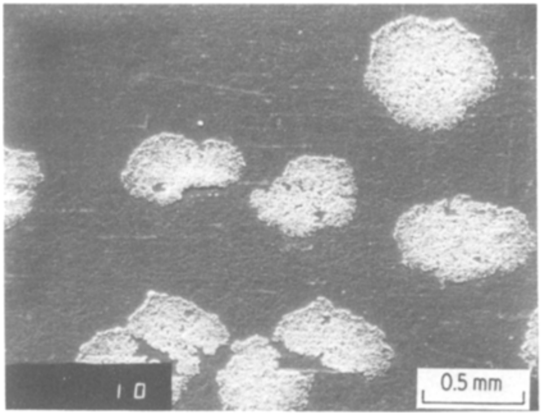

Figure 3 Al–Si–Mg braze cladding at 555° C. Disruption of the braze continues as exudations spread across the surface.

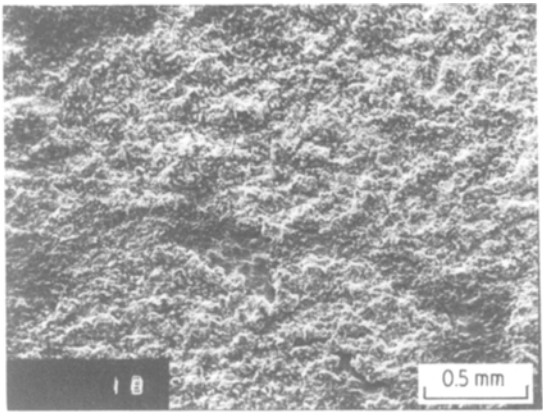

Figure 5 Al–Si–Mg braze cladding at 590° C. The original surface has been completely disrupted.

2 min of the ternary eutectic temperature being achieved. This seemed to indicate that surface cleanliness and oxide thickness may affect the alloy's ability to "clean" itself.

3.1.2. Al–Si alloys

The surface changes observed on heating specimens clad with Al–7.5% Si braze alloy were much less dramatic. The surface was merely rumpled even at 590° C (Fig. 6). Only on cooling did the material change appreciably, solidification of the braze producing a cellular pattern on the surface (Fig. 7).

3.1.3. Al–Mg alloys

Heating an aluminium–1% magnesium alloy produced effects similar to those observed in the Al–Si–Mg braze alloys. The onset of melting at approximately 640° C produced grain-boundary grooving and islands of exuded material. Inspection of the regions at room temperature using a high tilt angle revealed that growths of new material had lifted up the original surface, breaking it up in the process (Fig. 8).

3.1.4. Braze–aluminium interfaces

Attempts to join aluminium clad with Al–Si–Mg braze to a piece of polished aluminium were recorded by means of hot-stage microscopy. Figs. 9 to 12 illustrate a typical sequence. At room temperature the braze cladding, bottom left in Fig. 9, was difficult to discern. However, on heating to above 450° C the braze alloy zone became very apparent (Fig. 10). Above 555° C the braze zone became disturbed and was brought into more intimate contact with the aluminium "workpiece" (Fig. 11). On cooling, areas of bonding

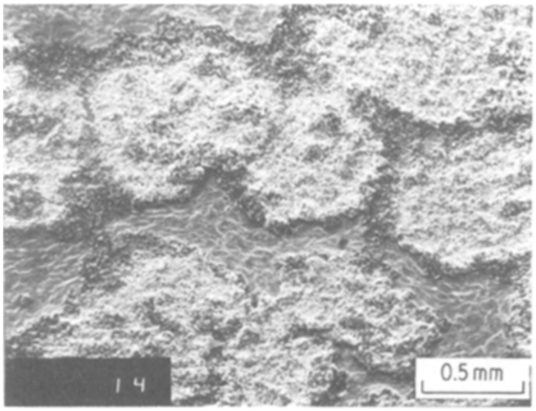

Figure 4 Al–Si–Mg braze cladding at 577° C.

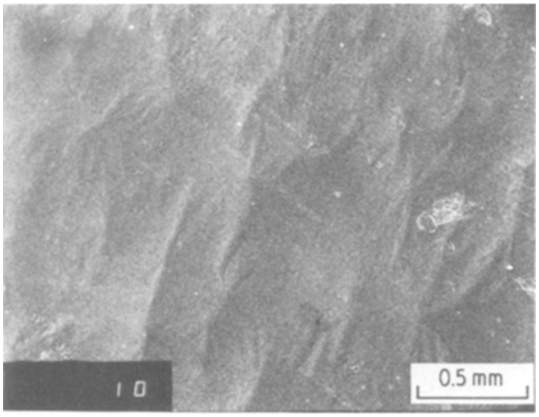

Figure 6 Al–Si braze cladding at 590° C. Only minor surface rumpling apparent.

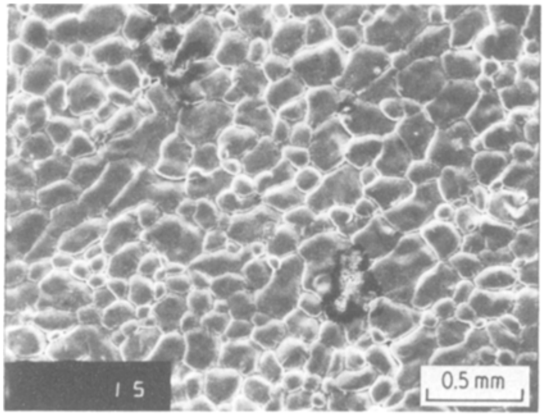

Figure 7 Al–Si braze cladding at 550° C. Cellular solidification of the braze becomes apparent at the surface.

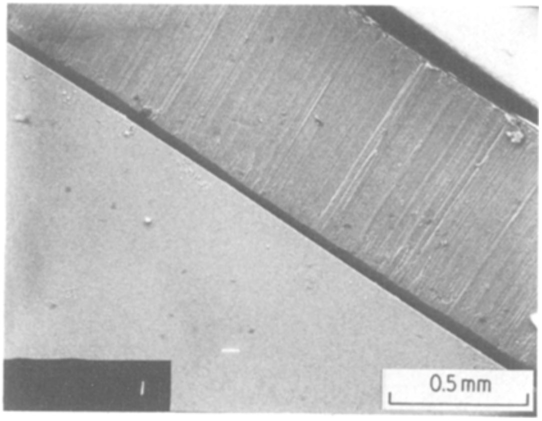

Figure 9 Interface between pure aluminium and 3003 alloy clad with Al–Si–Mg braze (bottom left).

were revealed, such as the one depicted in Fig. 12. The braze has started to spread out from the original area of penetration and appears to have tunnelled under the surface of the aluminium workpiece, displacing the oxide as it does so.

In experiments of this type which used an Al–Si braze cladding, bonding with the aluminium was not established. In addition, the braze did not become highlighted during heating, nor was it significantly disrupted until cooling.

3.2. Specimen microstructures

The microstructures corresponding to the surface changes in the Al–Si–Mg braze alloy were observed by studying cross-sections of specimens (Figs. 13 to 15). At room temperature the braze alloy exists as a distribution of Si and Mg_2Si precipitates within a primary aluminium matrix (Fig. 13). Heating to just above the ternary eutectic temperature caused partial melting of the alloy and void formation in addition to the disruption of the surface (Fig. 14). Fig. 15 shows the microstructure produced by cooling from the full brazing temperature, namely primary aluminium phase and an aluminium–silicon eutectic structure.

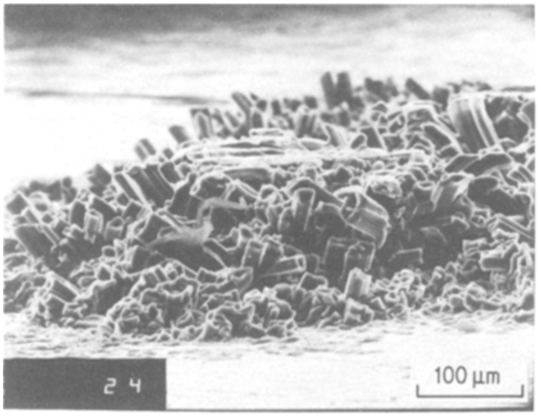

Figure 8 High tilt angle micrograph of Al–1% Mg alloy which has been heated to 640° C. A raft of the original surface has been lifted up by exudation of new material.

4. Discussion

A number of authors (e.g. [3, 4]) have asserted that the presence of magnesium will "modify" the aluminium oxide film which exists on the surface of the braze material. The transformation of the highly protective alumina film to a porous magnesium-based oxide at temperatures above 400° C permits the escape of magnesium vapour to the furnace atmosphere where it can getter the environment of contaminants such as oxygen and water vapour. Effects which were observed in the

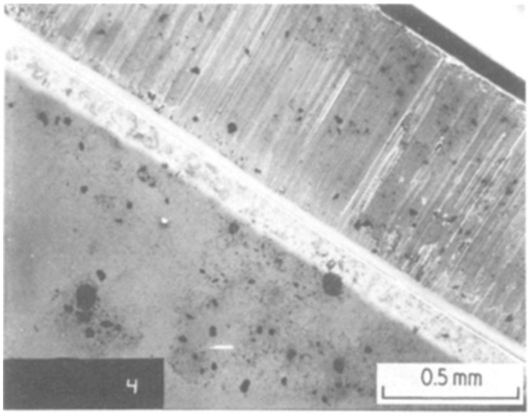

Figure 10 As Fig. 9, heated to 450° C.

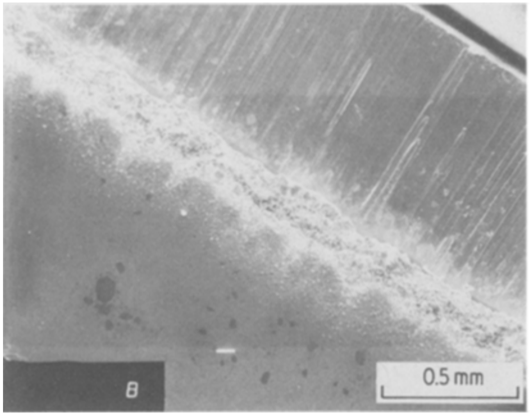

Figure 11 As Fig. 9, heated to 555° C.

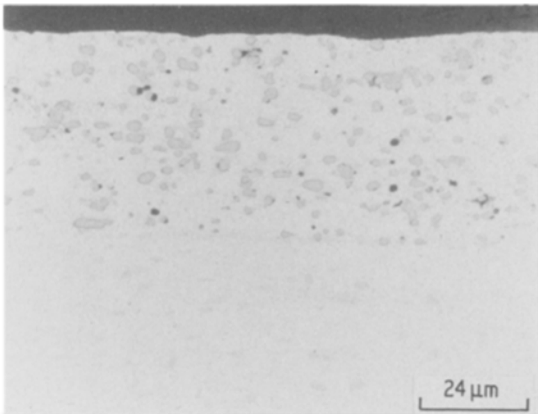

Figure 13 Microstructure of Al–Si–Mg braze cladding as-received.

hot-stage experiments on magnesium-containing alloys may be related to this phenomenon. It is conceivable that the bright surface spots (Fig. 1) and the highlighting of the braze zone (Fig. 10) are indicative of the reaction between diffusing magnesium and either the oxide or the atmosphere.

The benefit of this phenomenon is difficult to assess; although the magnesium vapour can take oxygen and water vapour out of the system, it is inevitable that the oxide on the braze will still be increasing its thickness as it is heated to the brazing temperature. However, the hot stage experiments show that at the onset of melting the magnesium present in the alloy initiates a more violent surface change. Figs. 2 to 5 show that material exudes through the original surface. A consequence of this is that the original oxide-covered surface is dislodged and fragmented (Fig. 8). The likely mechanism for this exudation process, put forward by Anderson, is one of volume expansion associated with the melting of an Al–Si–Mg ternary eutectic liquid. This suggestion is borne out by the examination of cross-sections. The cross-sections also reveal that void formation occurs, but it is not clear whether this assists in the disruption of the surface.

Once the original surface has been disrupted by the exudation of liquid, Anderson suggests that the surface is likely to re-solidify due to the loss of magnesium and this could account for the crystal "columns" observed in Fig. 8. After this process has occurred the barrier to wetting produced by the original oxide and surface contaminant layer will have been minimized. However, braze flow will only be appreciable above

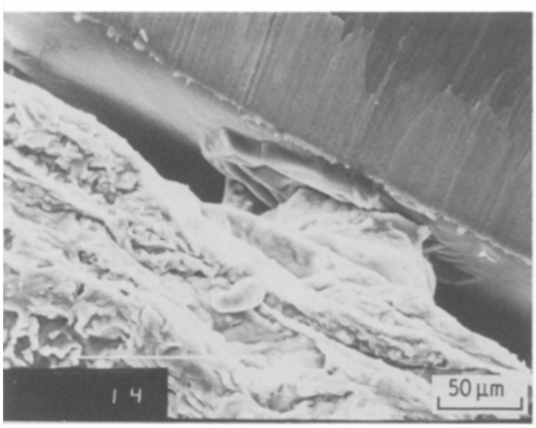

Figure 12 As Fig. 9, cooled from 590° C. Bonding between the braze and aluminium has begun, with tunnelling of the braze beneath the oxide film occurring.

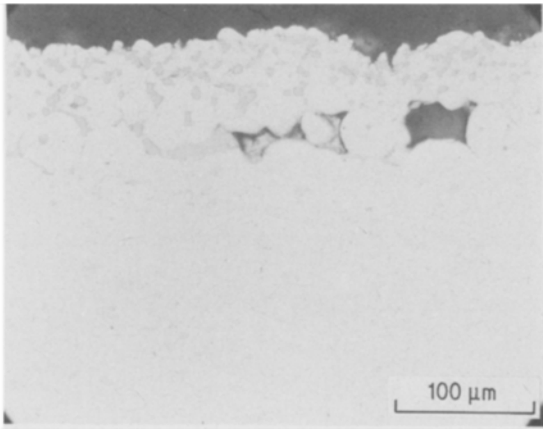

Figure 14 Microstructure of Al–Si–Mg braze which has been cooled from a temperature of 562° C. Note partial melting of alloy.

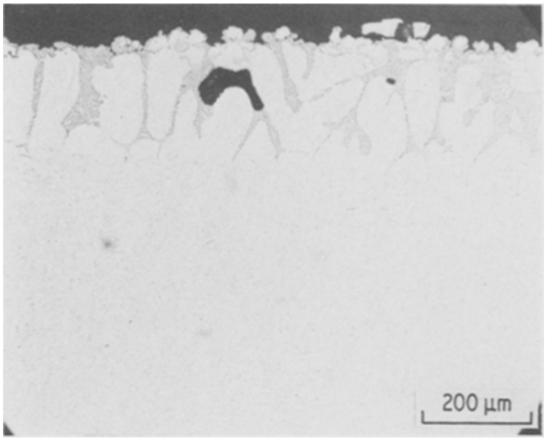

Figure 15 Microstructure of Al–Si–Mg braze which has been cooled from a temperature of 590° C.

577° C, when most of the braze becomes molten, so a slow heating rate or poor vacuum quality may cause the advantage to be lost.

Polished surfaces were disrupted much more easily than as-received braze surfaces, which may be due to the polished surface having a thinner oxide or contaminant layer. The implication of this observation is that the use of braze materials which are badly cleaned or carelessly stored may mean the difference between success and failure in joint formation.

Al–Si braze surfaces were not cleaned by the exudation of material which suggests that it is the volatility of the magnesium which provides the driving force for surface disruption of Al–Si–Mg brazes. Since the surface oxide on an aluminium–silicon braze remains apparently undisturbed, wetting should be much more difficult to achieve and this is experienced in practice.

Experiments studying joint interfaces have shown that after the initial disruption of the braze, the alloy must become fully molten and penetrate two oxides; the oxide which has re-formed on the braze and the oxide which exists on the unclad workpiece. Fig. 12 reveals that, despite the magnesium evolution from the braze, liquid has to spread out underneath the workpiece oxide from the initial area of penetration. The extent of the joint formation is then dependent on the ability of the liquid to sweep out the braze and workpiece oxides from the joint. This will probably depend on vacuum quality and cleanliness of the original pieces.

5. Conclusions

The success of aluminium vacuum brazing is dependent on the disruption of the oxide layer present on the braze. Magnesium-containing alloys are more effective than binary aluminium–silicon alloys at causing oxide disruption, due to a process of exudation of braze alloy. At the onset of partial melting of the alloy, liquid is pushed up through the original braze surface, the driving force being provided by volatilization of magnesium in the eutectic liquid. The breaking up of the original oxide which this achieves may then permit wetting to proceed once the braze becomes fully molten.

The wettability of an aluminium workpiece by braze alloy can also be limited by the oxide on the workpiece. This oxide must be penetrated by the liquid braze, which then spreads out underneath the oxide, lifting it away from the metal as it does so.

Acknowledgement

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