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Joining molybdenum to aluminium by diffusion bonding

R. S. BUSHBY, K. P. HICKS, V. D. SCOTT
School of Materials Science, University of Bath, Claverton Down, Bath BA2 7AY, UK

The joining of molybdenum to aluminium and aluminium–copper alloy using diffusion bonding has been investigated. Bond strengths have been measured by means of a simple shear jig and the joint microstructures characterized by electron microscopy and electron-probe microanalysis. Successful joints were produced by using a copper foil interlayer to form a eutectic liquid during the bonding process which helped disrupt the oxide film on aluminium and promote metal diffusion across the joint interface. When bonding commercial-purity aluminium to molybdenum, the iron present as an impurity caused a ternary eutectic liquid to form and, after solidification of the liquid phase, a thin film of Al_7Cu_2Fe was left behind on the aluminium. Failure of this joint occurred at a shear stress of 75 MPa, with the fracture path contained within the aluminium. With super-purity aluminium, a binary eutectic liquid was produced and the ensuing interface reaction resulted in a multi-layered structure of molybdenum-containing phases. The bond failed at the molybdenum interface at a stress of 40 MPa. When bonding aluminium–copper alloy to molybdenum without a copper interlayer, general melting at the interface via eutectic phase formation did not occur and the interface showed only localized reaction. The joint failed by separation from the molybdenum, at a stress of 25 MPa. When, however, a copper interlayer was used, fairly thick regions of multi-layered molybdenum intermetallics formed and the remaining surface was covered by a layer of Al_7Cu_2Mo phase. Failure of this joint occurred at a stress of 70 MPa, mainly by separation at the molybdenum interface.

1. Introduction

The fabrication of engineering structures frequently involves the joining of components, often by some method of mechanical fastening or welding. Such procedures may, however, introduce undesirable stress concentrations into the system, with the possibility of damage and component failure during service, or they may result in some structural discontinuity which affects the thermal and/or electrical characteristics. The aim of the present work was to develop a method for joining molybdenum to aluminium which avoided these problems.

Unfortunately, information directly applicable to the bonding of molybdenum to aluminium appears to be lacking and, indeed, only limited data are available on the joining of molybdenum to any type of material [1]. Nevertheless, some results have been published on the diffusion bonding of aluminium to aluminium-based composites [2] which would appear to have some relevance, in particular the identification of problems associated with the barrier oxide on aluminium and with the differential thermal contraction of the bonded joint. The study demonstrated that successful bonds could be achieved using modest pressures at elevated temperature, provided that a suitable interlayer such as copper was employed to promote the bonding process. Consequently, because somewhat similar problems were to be expected when joining molybdenum to aluminium, it was decided to use a similar approach. In this paper, we describe experiments on the diffusion bonding of molybdenum to aluminium and to an aluminium–copper alloy, with and without a copper interlayer, and relate the shear strength of the joints with the associated microstructures.

2. Experimental procedure

2.1. Materials

The molybdenum samples consisted of commercial-purity plate, 50 mm × 50 mm × 1.5 mm thick. These were bonded to 6 mm thick plate of (a) commercial-purity (CP, 99 wt %) aluminium, (b) super-purity (SP, 99.99 wt %) aluminium, and (c) aluminium–5 wt % copper alloy. The surfaces to be bonded were first ground smooth to a 1200 grit finish and washed in acetone, whilst the bonding interlayer, high-purity 10 μm thick copper foil, was cleaned by immersion for several seconds in 10 vol % H_2SO_4 followed by washing in acetone. Each bonding experiment was carried out with aluminium or aluminium alloy plates positioned either side of the molybdenum in order to provide suitably sized specimens for shear testing of the joint. Steel shims were placed on the outside of this

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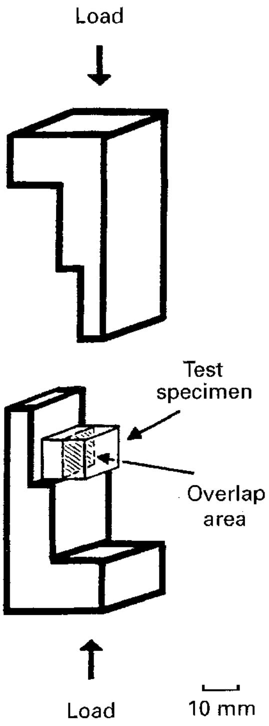

Figure 1 Schematic diagram of the shear jig.

sandwich-type assembly to prevent the aluminium adhering to the platens of the bonding rig.

2.2. Diffusion bonding

Bonding was carried out in air using a furnace attached to an 1195 Instron testing machine. The specimen sandwich assembly was placed between the Instron platens and positioned in the furnace, which was preheated to 555 °C. The choice of temperature was based upon previous bonding studies [2] and was measured via thermocouples mounted in each platen. The specimen was loaded to a pressure of 10 MPa. At the start of the bonding experiment, a temperature drop to 530 °C was noted due to heat loss when the specimen was inserted, but it returned to 555 °C within 10 mins. After 60 min, the specimen was removed and allowed to cool in air. Samples were cut from the central bonded area for microstructural analysis and shear testing.

2.3. Microstructural analysis

Metallographic sections through the joint were prepared by grinding on successively finer grades of diamond abrasive down to 1 μm, finishing on a fabric cloth with colloidal silica. They were investigated first by light microscopy (LM) and then by scanning electron microscopy (SEM). Electron-probe microanalysis (EPMA) was carried out to determine the chemical composition of microstructural features. A minimum of six measurements were taken from each feature and the data corrected using a conventional ZAF routine [3]; all EPMA data quoted in this paper were reproducible to within 2% relative. Differential scanning calorimetry (DSC) was employed to analyse material which was expelled from the joint during some of the bonding experiments; this involved heating the material at 5 °C min^{-1} from 100–600 °C and recording the temperatures where phase transformations occurred.

2.4. Shear tests

Specimens, 10 mm × 10 mm, were cut from each joint and tested in shear using the jig illustrated in Fig. 1. The load to failure was recorded and divided by the area of joint overlap to provide a value for the shear strength; the experimental scatter was typically ± 5 MPa. The failure surfaces were examined using SEM and EPMA.

3. Results

3.1. Molybdenum to CP aluminium

During bonding, the pressure progressively decreased with time by some 50%, due to deformation of the aluminium. Upon removal of the specimen from the bonding rig, it was apparent that, although the aluminium had been deformed by 10%, the molybdenum and aluminium plates readily separated with no visible evidence of any bond having been established.

3.2. Molybdenum to CP aluminium with copper interlayer

A marked decrease in applied pressure occurred after ~ 10 min into the bonding experiment, as indicated by point A in the pressure versus time curve, Fig. 2. On removal of the specimen, it was noted that a bead of liquid had been ejected from the joint. The joint remained intact upon cooling, and measurement showed that the aluminium had undergone ~10% deformation during the bonding operation.

The microstructure of the bead consisted of three phases, A, B and C, see Fig. 3a. EPMA results are given in Table I, first as weight per cent and then as atomic per cent (normalized). The data show that the phases A, B and C have compositions consistent with

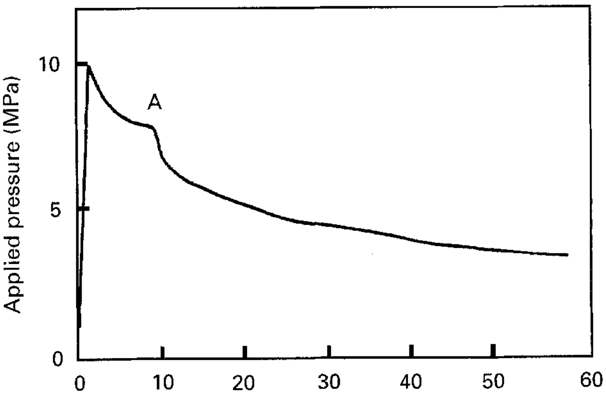

Figure 2 Pressure versus time curve for the molybdenum/CP aluminium joint with a copper interlayer.

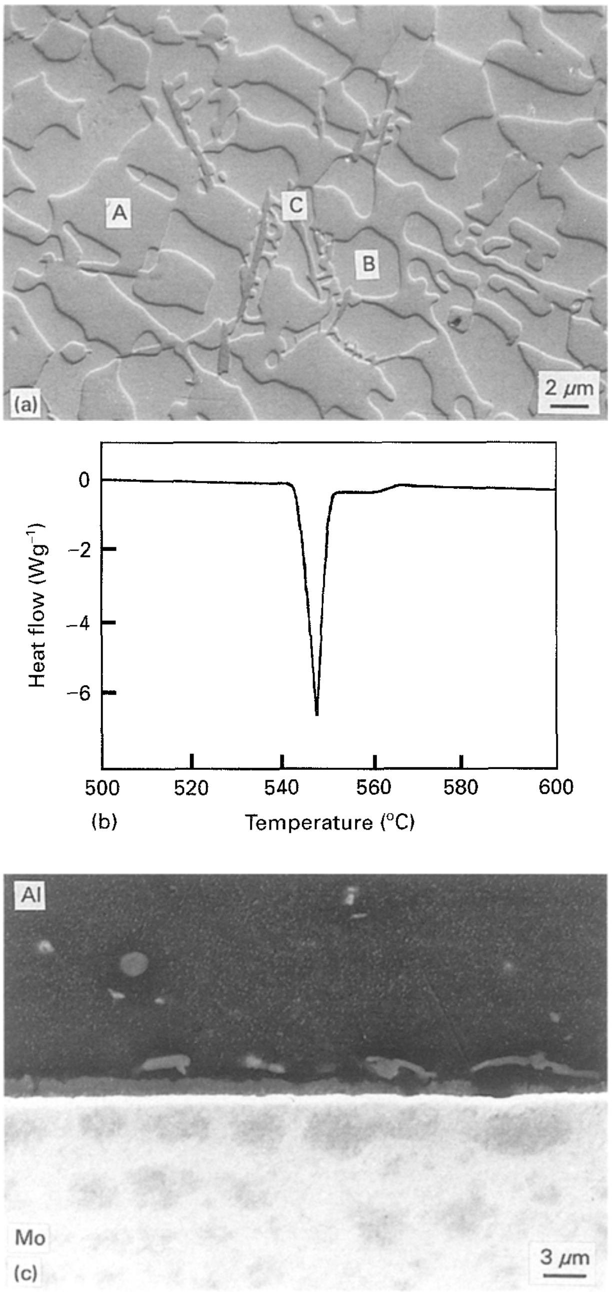

Figure 3 Molybdenum/CP aluminium joint with a copper interlayer: (a) microstructure of the bead, LM; (b) DSC trace from bead; (c) microstructure of the joint, SEM.

TABLE I EPMA data from an expelled bead, CP aluminium to molybdenum, with copper interlayer

Element	Phase A		Phase B		Phase C	
	(wt %)	(at %)	(wt %)	(at %)	(wt %)	(at %)
Al	98.0	98.6	47.3	68.5	49.9	70.2
Cu	2.1	1.4	51.1	31.5	34.9	20.8
Fe	–	–	–	–	13.2	9.0

Al(Cu), $CuAl_2$ and Al_7Cu_2Fe, respectively. Bulk analysis revealed that the bead contained ~0.5 wt % Fe but no molybdenum. DSC analysis indicated an endotherm at 545 °C, Fig. 3b.

A metallographic section of the joint, Fig. 3c, showed a reaction zone consisting of particles and a thin (~1 μm) layer. The exact composition of the layer was difficult to establish because of its size relative to the spatial resolution of the EPMA technique, but it is believed to be Al_7Cu_2Fe, as was found to be the case where the film was appreciably thicker; the structure of the joint is depicted schematically in Fig. 11a, see below. In the aluminium, particles ~10 μm in size were present which contained iron; these were probably Al_3Fe phase. Copper was detected in the aluminium up to ~50 μm from the interface, but not in the molybdenum. No molybdenum was found in the aluminium and no aluminium in the molybdenum.

Shear testing of the joint resulted in extensive plastic deformation of the aluminium at a stress of 75 MPa. The bond interface remained, however, intact.

3.3. Molybdenum to SP aluminium with copper interlayer

During bonding, a rapid decrease in pressure took place in the first few minutes. A bead of liquid was again expelled from the joint and, overall, the aluminium experienced ~50% reduction in thickness.

Analysis of the microstructure of the bead, Fig. 4a, showed the presence of $CuAl_2$ and aluminium, characteristic of the divorced aluminium–copper eutectic. DSC indicated an endothermic reaction at 548 °C, Fig. 4b.

A metallographic section through the joint, Fig. 4c, reveals a reaction zone, ~20 μm thick, consisting of three layers, labelled D, E and F. The EPMA data are given in Table II. According to these figures, the composition of layer D is close to Al_3Mo, a phase reported in early work [4, 5] but not in more recent studies [6, 7]. Closer inspection of layer D shows, however, that it contains fine-scale phases which are beyond the resolution of the electron probe. The majority of the layer, the light-grey phase, is believed to be Al_8Mo_3, the phase referred to in the later work, whilst the dark-grey regions are Al_4Mo; the small white particles are probably molybdenum. Hence, averaging these compositions would explain why that of layer D was close to Al_3Mo. Layer E was single-phased and had a composition corresponding to Al_4Mo, whilst that of layer F was close to Al_6Mo; both phases contained ~1 at % copper. The sequence of layered phases is shown schematically in Fig. 11b, see below. As well as finding copper in the Al–Mo phases, it was also detected in the aluminium for a distance of ~50 μm from the interface. No aluminium or copper was found in the molybdenum.

Shear testing of the joint resulted in some plastic deformation of the aluminium, at a stress of 40 MPa, and this was soon followed by rapid failure. The fracture surfaces were fairly smooth and EPMA showed that the aluminium side, Fig. 5a, contained aluminium and molybdenum, consistent with Al_8Mo_3, as found for layer D. On the molybdenum side, Fig. 5b no aluminium or copper was detected.

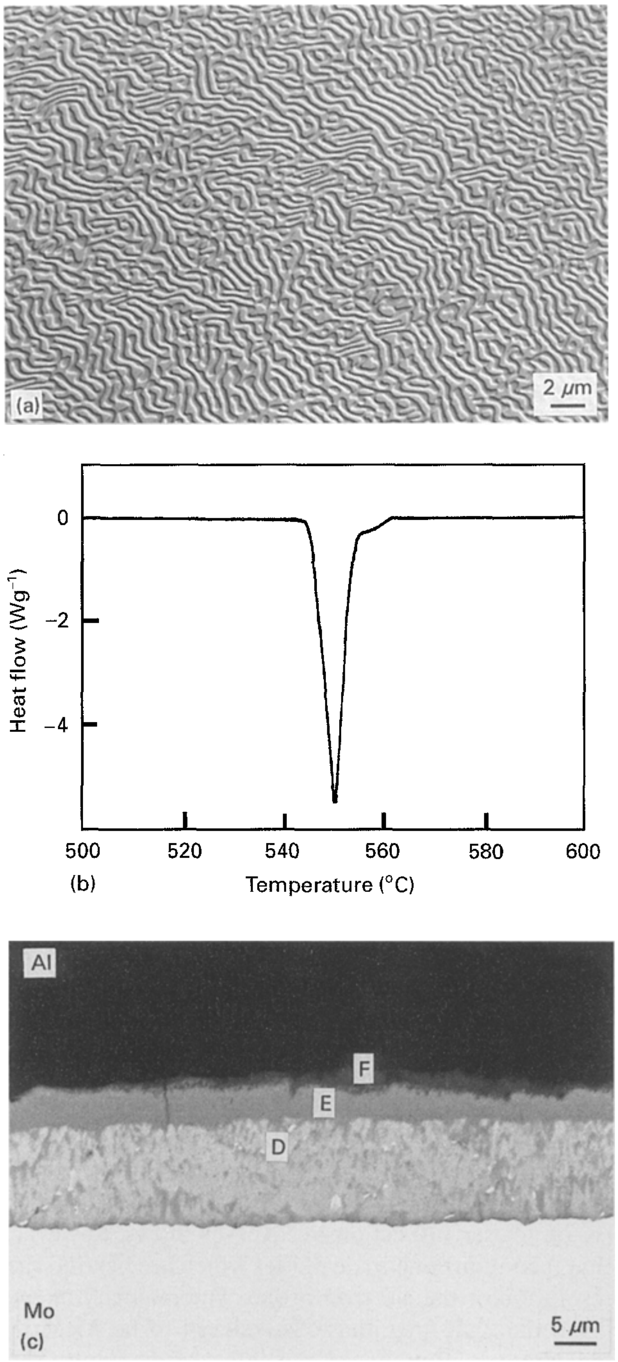

Figure 4 Molybdenum/SP aluminium joint with a copper interlayer: (a) microstructure of the bead, LM; (b) DSC trace from bead; (c) microstructure of the joint, SEM.

TABLE II EPMA data from the joint, SP aluminium to molybdenum, with copper interlayer

Element	Layer D		Layer E		Layer F	
	(wt %)	(at %)	(wt %)	(at %)	(wt %)	(at %)
Al	48.0	75.5	56.6	81.5	68.5	87.0
Mo	53.9	23.6	42.4	17.2	34.4	12.2
Cu	1.3	0.8	1.7	1.1	1.5	0.8

3.4. Molybdenum to aluminium alloy

The purpose of this experiment was to establish whether there was sufficient copper present in the alloy itself to form a eutectic liquid covering the interface without the use of copper interlayer.

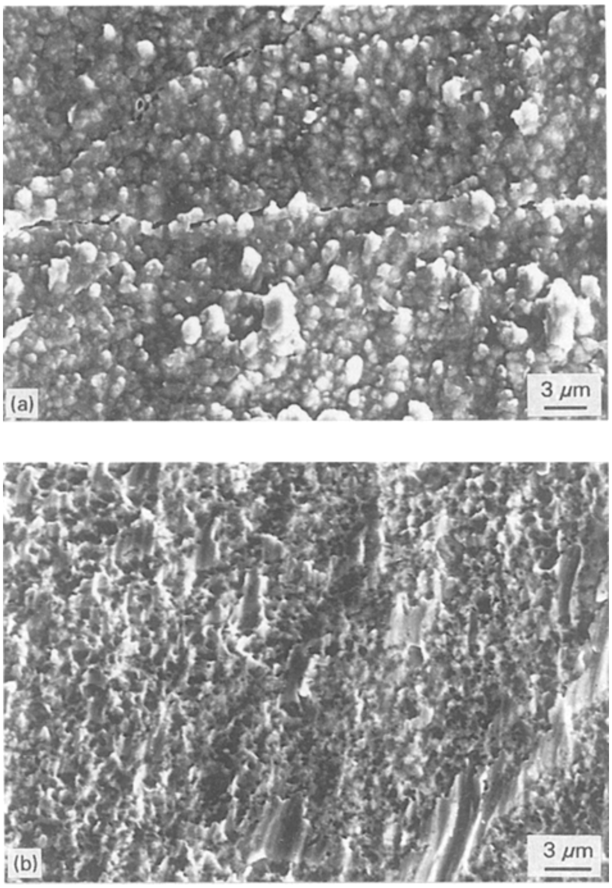

Figure 5 Molybdenum/SP aluminium joint with copper interlayer, fracture surfaces, (a) aluminium side and (b) molybdenum side, SEM.

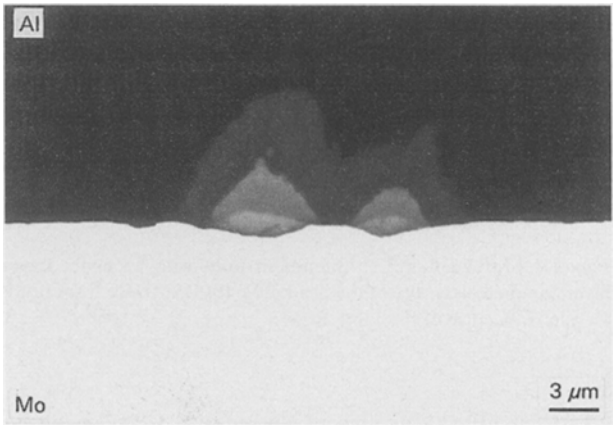

Figure 6 Molybdenum/aluminium alloy, microstructure of the joint, SEM.

During bonding, the applied pressure progressively decreased with time, although it did not show the sudden decrease associated with the expulsion of liquid from the joint.

The microstructure of the joint, Fig. 6, shows small isolated regions of reaction, ~10 μm in size, which covered ~10% of the interface; between these regions no phase was visible. Each region contained three layers, EPMA indicating that their compositions were similar to those illustrated in Fig. 4c, i.e. Al_8Mo_3, Al_4Mo and Al_6Mo; again 1–2 wt % copper was detected in each phase.

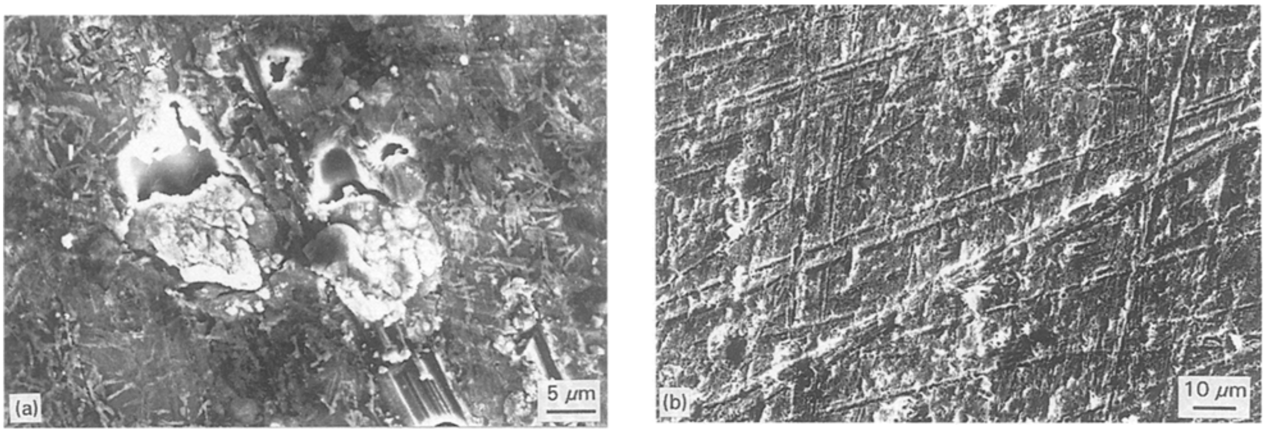

Figure 7 Molybdenum/aluminium alloy joint, fracture surfaces, (a) aluminium side and (b) molybdenum side, SEM.

When the joint was shear tested, failure took place at the bond interface at a stress of 25 MPa, without any plastic deformation of the aluminium. The fracture surfaces were fairly rough. Particles of intermetallic with a composition close to Al_8Mo_3 were indentified on the aluminium side, Fig. 7a, but no second phases were found on the molybdenum side, Fig. 7b.

3.5. Molybdenum to aluminium alloy with copper interlayer

The pressure versus time curve was similar to that obtained for bonding CP aluminium to molybdenum using a copper interlayer (see Fig. 2) and, again, liquid was ejected from the joint during the course of the bonding experiment. Overall, the aluminium alloy experienced a 10% reduction in thickness.

The microstructure of the bead was closely similar to Fig. 4a, as obtained from the bead formed in the experiment using SP aluminium, i.e. $CuAl_2$ and aluminium in proportions consistent with the divorced Al–Cu eutectic. The DSC trace confirmed this with an endotherm at 548 °C, similar to Fig. 4b.

A section through the joint, Fig. 8, showed large (~ 50 μm) regions of reaction covering $\sim 50\%$ of the interface, each comprising layers labelled G, H and J, and between them a thin (~ 2 μm) layer (K) was visible. EPMA data, see Table III, showed that layer G was similar in composition to layer D, see Table II, i.e. Al_8Mo_3. However, the high level of copper (~ 8 wt %) in the central layer (H) suggested that it was a ternary phase, $Al_{18}Mo_3Cu$, although there are no published data to confirm its existence. The layer, J, had, however, a composition which matched the $Al_{12}Mo$ phase shown on the Al–Mo equilibrium diagram, see Fig. 9. EPMA data from the thin layer, K, indicated that it was also a ternary phase, Al_7Cu_2Mo, an intermetallic probably isomorphous with Al_7Cu_2Fe, see Section 3.2. The structure of the joint is illustrated schematically in Fig. 11d, see below.

During the shear test, failure took place in the region of the bond interface at a stress of 70 MPa, but there was no plastic deformation of the aluminium. The fracture surfaces were fairly rough, with areas corresponding to Al_8Mo_3 and Al_7Cu_2Mo on the aluminium side, Fig. 10a, and patches of Al_7Cu_2Mo on the molybdenum side, Fig. 10b.

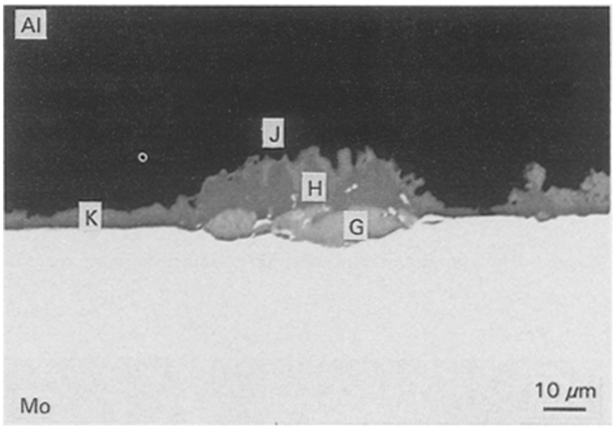

Figure 8 Molybdenum/aluminium alloy with a copper interlayer: microstructure of the joint, SEM.

TABLE III EPMA data from the joint, aluminium alloy to molybdenum, with copper interlayer

Element	Layer G		Layer H		Layer J		Layer K	
	(wt %)	(at %)	(wt %)	(at %)	(wt %)	(at %)	(wt %)	(at %)
Al	48.4	76.0	56.5	80.8	76.6	92.8	44.7	71.0
Mo	51.9	22.9	35.9	14.4	19.7	6.7	18.5	8.5
Cu	1.7	1.1	7.9	4.8	1.0	0.5	30.5	20.5

4. Discussion

It was evident that all the joints formed between aluminium and molybdenum by diffusion bonding remained intact after cooling, despite the fact that large strains were produced due to differences in thermal contraction of the two metals. In all but the CP aluminium experiment, shear failure of the joint occurred by separation at the molybdenum interface rather than in the aluminium. The following discussion relates the development of the bond to (a) overcoming the oxide film diffusion barrier, and (b) the characteristics of the diffusion layers subsequently formed.

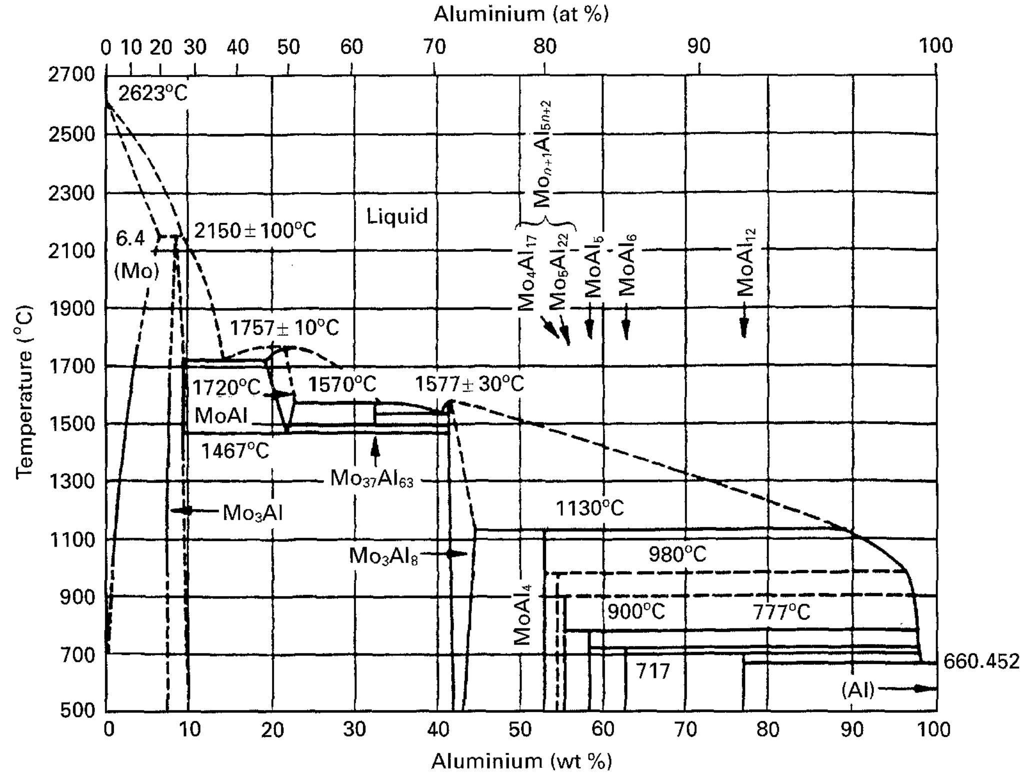

Figure 9 The aluminium–molybdenum equilibrium phase diagram [7].

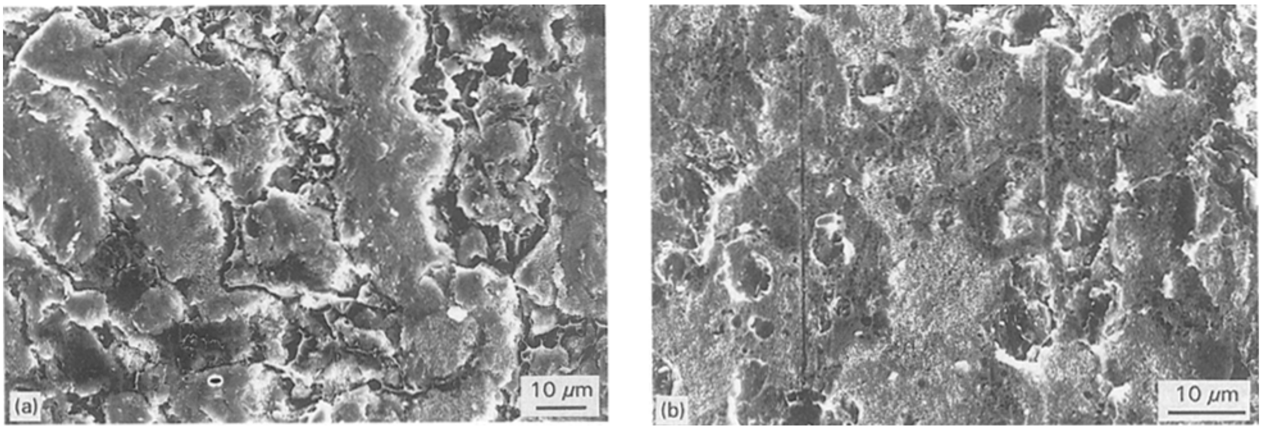

Figure 10 Molybdenum/aluminium alloy joint with a copper interlayer: fracture surfaces, (a) aluminium side and (b) molybdenum side, SEM.

4.1. Formation of liquid at the interface and the oxide film on aluminium

The experiments on diffusion-bonding commercial-purity (CP) aluminium to molybdenum showed that a copper interlayer was required to form a satisfactory joint. Without the interlayer the oxide film on the aluminium proved to be a major barrier to diffusion, more so than the oxide film on molybdenum which, because of its lower stability [8], would have caused little inhibition of the diffusion-bonding process. The role of the copper interlayer may be explained as follows. When present, an eutectic liquid metal was formed at the interface during the bonding process, as evinced by a drop in applied pressure after ~ 10 min, see Fig. 2, and by the expulsion of metal from the joint in the form of a bead. Examination of the solidified bead using DSC showed melting at 545 °C, Fig. 3b, whilst its microstructure, Fig. 3a, revealed an eutectic containing 0.5 wt % Fe and 32.5 wt % Cu, in accordance with published data [9]. It is considered that the iron was introduced into the system as an impurity in the CP aluminium. The fact that molybdenum was not found in the bead suggests that it was not involved in the liquefaction process. It may thus be argued that the formation of liquid eutectic at the joint, coupled with the applied pressure, caused disruption of the oxide film on aluminium. Fragments of the oxide were then swept away as the liquid spread over the interface and increased the extent of metal-to-metal contact. Our observations showed that the majority of the liquid alloy was ejected from the joint during this process. The remaining liquid solidified isothermally as copper diffused away from the joint and a thin layer of Al_7Cu_2Fe phase was left at the interface. This

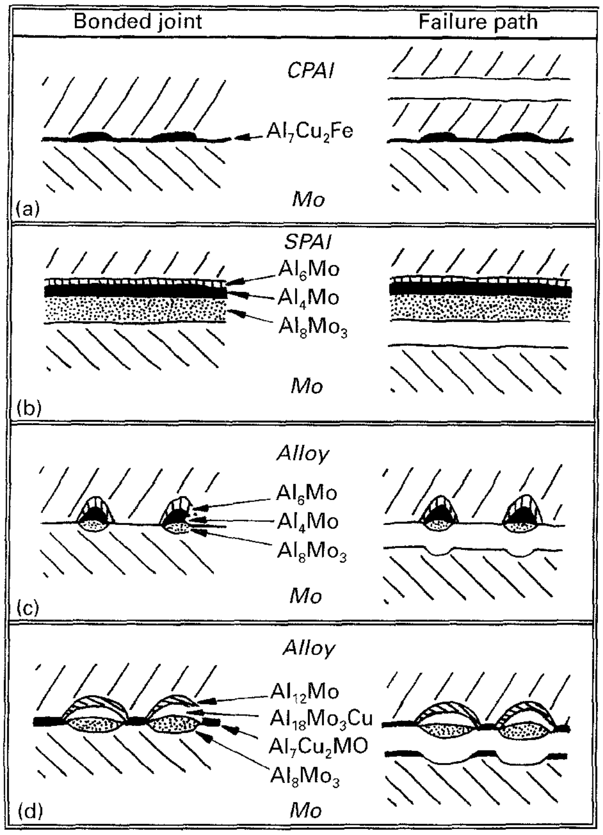

Figure 11 Schematic diagrams showing the microstructures of bonded joints and failure paths after shear testing: (a) molybdenum/CP aluminium with a copper interlayer; (b) molybdenum/SP aluminium with a copper interlayer; (c) molybdenum/aluminium alloy; (d) molybdenum/aluminium with a copper interlayer.

mechanism of oxide disruption agrees with previous findings on liquid-phase bonding of aluminium and aluminium-based composites [2].

The removal of oxide by liquefaction at the joint interface was evident also in the bonding experiments on super-purity (SP) aluminium and Al–Cu alloy when a copper interlayer was used. In these cases, however, a binary eutectic was formed which melted at a temperature of 548 °C, rather than the Al–Cu–Fe eutectic produced with CP aluminium which melted at 545 °C. As we shall discuss in the following section, the subtle difference in eutectic composition (0.5 wt % iron) had a marked effect on subsequent diffusion reactions.

4.2. Diffusion reactions and the efficacy of the joints

In the case of CP aluminium bonded to molybdenum using a copper interlayer, a continuous layer of liquid was formed at the interface and, after much of it was ejected, the remainder became enriched in iron as copper diffused away into the bulk aluminium. Based upon previous observations [2], it is argued that the iron-rich layer was formed after ~20 min and remained little changed during the rest of the bonding experiment, see schematic diagram, Fig. 11a. The fact that no molybdenum could be detected on the aluminium side of this interface layer indicated that the intermetallic layer was impervious to molybdenum diffusion. Upon shear testing, the bond remained intact and the aluminium plastically deformed at a stress of 75 MPa, a value consistent with the shear strength of the CP aluminium [2].

Results obtained on the bonding of SP aluminium to molybdenum were in contrast to those found in the experiment on CP aluminium. Now, appreciable diffusion of molybdenum into aluminium occurred, forming continuous layers of Al_8Mo_3, Al_4Mo and Al_6Mo, see Fig. 11b. It was significant that no Al_7Cu_2Fe layer had formed, not surprising in view of the high purity of the aluminium. Indeed, the absence of the Al_7Cu_2Fe layer supports our contention that, when present, it inhibits molybdenum diffusion into the aluminium. During shear testing of the joint, the aluminium started to yield and, when the stress reached 40 MPa, separation occurred at the interface between molybdenum and the Al_8MO_3 intermetallic layer, as depicted diagrammatically in Fig. 11b.

The experiment on bonding Al–Cu alloy to molybdenum showed that there was insufficient copper to produce a liquid phase covering the entire interface, as evinced by the lack of an expelled bead. There were, however, some isolated regions where the above multilayer structure of Al–Mo phases had formed, although most of the interface (~90%) was, essentially, unreacted. An explanation for the occurrence of these isolated regions is that liquid eutectic had formed here, probably associated with the presence of $CuAl_2$ particles in the aluminium at the interface. Indeed, the distribution of $CuAl_2$ particles in the aluminium is consistent with that of the reacted Al–Mo regions. Furthermore, the fact that the thickness of the Al–Mo layers, Fig. 11c, is similar to that produced in the SP aluminium experiment, Fig. 11b, indicates that such localized melting must have occurred in the early stage of bonding. The shear test of the joint demonstrated that the molybdenum/Al_8Mo_3 interface was again a weak link, as depicted schematically in Fig. 11c, and that the unreacted interface was even weaker, the net result being a joint with a shear stress of only 25 MPa.

When a copper interlayer was introduced into the Al–Cu alloy/molybdenum diffusion couple, Al–Cu eutectic liquid was produced at the joint and the microstructure showed that the whole interface had reacted, indicative that the aluminium oxide film had now been effectively removed. Around 50% of the interface contained isolated regions of a multi-layered structure which bore some resemblance to that identified above, except that the central phase consisted of $Al_{18}Mo_3Cu$ and not the copper-containing Al_4Mo phase, see Fig. 11d. Another difference in the interface microstructure was the presence of an Al_7Cu_2Mo layer covering the remainder of the interface. It may, therefore, be argued that the combination of Al–Cu alloy and copper interlayer has resulted in the retention of Al–Cu eutectic liquid at the joint for some considerable time because copper diffusion away from the joint has been inhibited by the high level of copper in the alloy. Owing to the long contact time of molybdenum and liquid, some molybdenum has become absorbed, resulting in the formation of the Al_7Cu_2Mo

layer. It follows that the high level of copper was responsible for the presence of $Al_{18}Mo_3Cu$ in the multi-layered structure instead of the Al_4Mo phase. The joint was seen to fail at 70 MPa with fracture following, essentially, the molybdenum/Al_8Mo_3 interface and passing through the Al_7Cu_2Mo layer, see Fig. 11d. Since it has been demonstrated in the SP aluminium experiment that the bond between molybdenum and the Al_8Mo_3 layer is relatively weak, it may be concluded that here much of the strength of this joint has been provided by the Al_7Cu_2Mo layer.

5. Conclusion

It has been demonstrated that satisfactory joints may be produced between aluminium and molybdenum by diffusion bonding using a copper interlayer. The most effective joint was made using CP aluminium, with failure taking place through the aluminium at a shear strength of 75 MPa. With SP aluminium, extensive formation of Al–Mo intermetallic layers during the bonding operation led to failure at the molybdenum interface at a shear stress of 40 MPa. Studies on Al–Cu alloy showed that a copper interlayer was again necessary to achieve a good bond with molybdenum and, whilst the fracture path was more complex because of the resulting complex microstructure, a bond strength of 70 MPa was achieved.

Acknowledgements

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