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The reaction of liquid metals to form intermetallics

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The formation of intermetallic compounds of high melting point, by reaction between liquid metals at low temperatures, was studied for a number of binary systems, in particular Al–Sb, Mg–Sb, Mg–Bi and Na–Bi.

Two regimes of behaviour on mixing were found:

(1) Catastrophic exothermic reaction between the liquid metals leading to rapid formation of the compound.

(2) Non-catastrophic reaction, characterized by the formation of solid intermetallic barrier layers between the reactive liquids.

Non-catastrophic mixing was investigated by means of equipment which produced a horizontal interface between the two liquid metals. The structures of the interfacial compound layers, and the kinetics of the interdiffusion process, were examined by x-ray microanalysis and metallography. The results are compared with a simple model of the diffusion process. It is concluded that two distinct types of rate controlling intermetallic layer may exist between the molten reactants; either a thin stable layer through which reactants may pass by solid state diffusion, or a much thicker but perforated layer undergoing continuous local remelting and reformation. It is suggested that an important factor determining the layer type adopted by a particular binary system is the composition range of the intermetallic compound.

The factors influencing whether catastrophic or non-catastrophic reaction occurred were also determined by thermal and metallographic investigation of different systems under different mixing conditions. It is concluded that catastrophic reaction is only possible in systems for which the enthalpy of mixing is sufficient in the liquid state to raise the temperature of the product alloy above its liquidus.

1. Introduction

It has been known for many years that exothermic reactions may occur catastrophically between liquid metals, to produce intermetallic compounds. In the 19th century, amalgams of mercury and the alkali metals, containing intermetallics of relatively high melting point, were produced by low temperature reaction between the liquid metals.

Recent interest in direct reaction by mixing liquid metals has included attempts to produce finer dispersions of intermetallics in the microstructure of the resulting alloy than would occur in a conventionally cast alloy of the same overall composition. The hope was that on mixing the reactant metals, at a temperature well below the liquidus of the alloy produced, the resultant undercooling with respect to this temperature would induce widespread rapid nucleation and growth of intermetallic precipitates. A number of such experiments with ternary systems have been carried out [1, 2].

In the present investigation, binary systems were used in order to simplify the kinetics and thermodynamics of the reactions, to gain an understanding into the type of mechanisms limiting the reaction rate in some cases, and allowing catastrophic reaction in others. Preliminary experiments indicated that it was apparently not possible to induce catastrophic reaction by mixing liquid aluminium and antimony in stoichiometric proportions (to produce the intermetallic AlSb only). The microstructure of the resulting specimens revealed extensive regions of unreacted aluminium and antimony separated by joined-up AlSb particles. In contrast to this, catastrophic reaction occurred very readily in the Na–Bi system, whereas the Mg–Sb and Mg–Bi systems exhibited behaviour intermediate between these extremes, being capable of either catastrophic or non-catastrophic reaction, depending on the mixing conditions.

2. Experimental Procedure: 1

2.1. Non-catastrophic reaction

The non-catastrophic reaction was investigated using the device shown in Fig. 1. Made of graphite, the equipment was operated within a furnace, bringing two liquid metals into contact, with a horizontal interface between them. This was achieved by a 180°

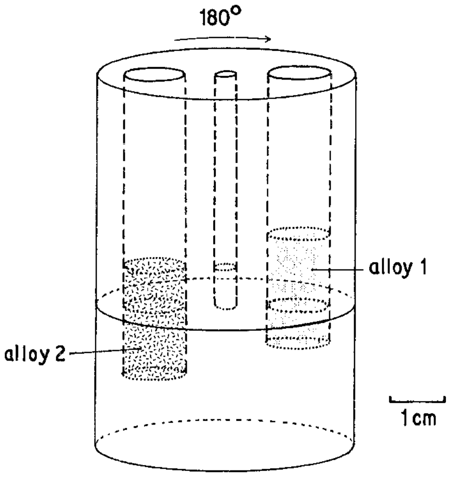

Figure 1 Device for producing a planar interface between two alloys.

rotation of the upper cylinder with respect to the lower one, chopping each alloy into two portions, creating fresh surfaces just before formation of the interface, thus ensuring that it was oxide-free. When arranged so that the less dense alloy ended up above the denser one, this configuration ensured intermixing by diffusion only (density differences would then favour solute-rich liquid on either side of the interface remaining in its vicinity, rather than sinking or floating away).

2.2. Al–Sb system

Interfaces were created between pure aluminium and pure antimony, using the device described above, then cooled rapidly after various times at constant temperature. The metallographic feature common to all the specimens was an unbroken intermetallic (AlSb) layer running along the interface. The layer was of variable thickness, apparently comprised of particles joined by thin bridges of intermetallic (Fig. 2). The bulk alloys on either side of the interface contained primary intermetallic particles whose size and number decreased with increasing distance from the interface. Higher experimental temperatures increased the volume fraction of these particles at any given distance from the interface, and longer experimental times increased the distance from the interface at which significant quantities of intermetallic were found. Quenching specimens from the experimental temperature (done in a much smaller version of the device in Fig. 1, modified to prevent water entering), had little effect on the scale of the interfacial layer, but significantly reduced intermetallic particle sizes in the bulk alloys on either side of it.

2.3. Mg–Sb and Mg–Bi systems

Similar experiments to those involving Al–Sb, carried out in these two binary systems, again yielded unbroken intermetallic layers running the length of the interface, but their structure was very different from that of the AlSb layer. They were of much greater and almost uniform thickness, containing no very thin regions (see Figs. 3 and 4). These intermetallic layers each appeared to be divided into two sub-layers with an approximately planar interface between them (this was particularly noticeable in the Mg–Bi system).

The solute content on either side of the interface decreased with increasing distance from it (in qualitative agreement with the results for Al–Sb) as shown by the sequence; primary intermetallic → eutectic → primary magnesium (or antimony) on both sides of the interface in Fig. 5.

2.4. Interpretation

The striking differences between the observed interface structures of the Al–Sb and Mg–Bi (or Mg–Sb) systems but the close similarities between their bulk concentration profiles away from the interfaces are reconciled by considering the following model:

Suppose that small scale turbulent mixing occurs in a narrow interfacial region when the liquid metals are first brought into contact. Nucleation and growth of intermetallic in this region takes place rapidly until a

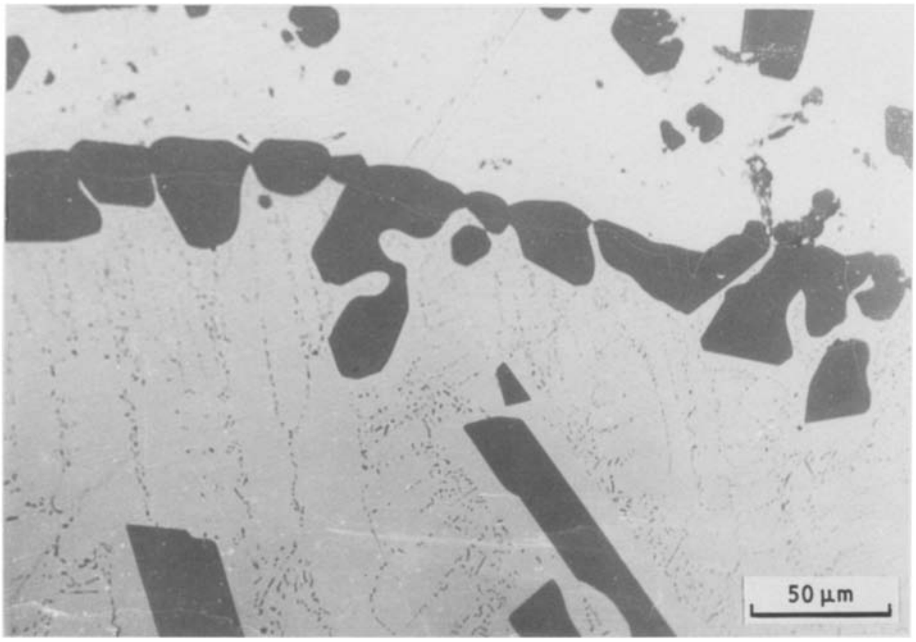

Figure 2 AlSb specimen, air cooled after 90 min at 750° C.

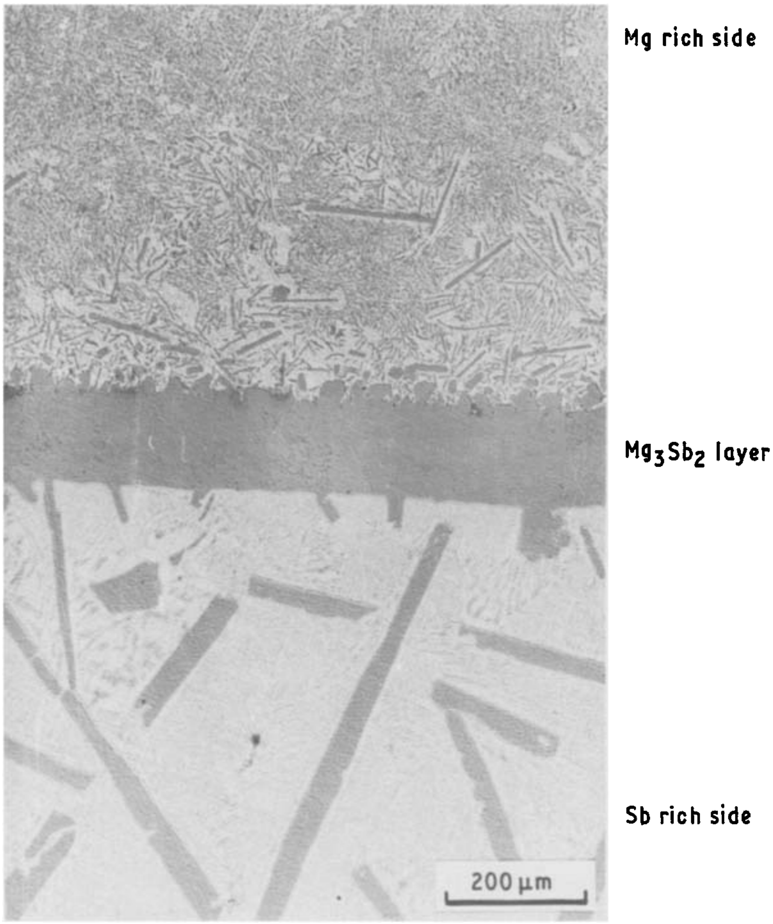

Figure 3 Intermetallic layer formed in interface device, between liquid magnesium and antimony; specimen air cooled after 5 min at 670°C.

continuous intermetallic layer is formed between the reactants, isolating them from one another. As soon as this has occurred, diffusion of solute away into the bulk liquids on either side of the layer will cause the solid to start remelting from both sides in order to maintain the alloy compositions on the liquidus at the solid/liquid interfaces. The expected composition profiles are shown in Fig. 6. This thinning process will continue until one of two situations occurs: (1) The layer becomes thin enough (or the liquid concentration gradients become low enough) that solid state diffusion can supply reactants through it at a sufficient rate to maintain the liquidus composition at the solid/liquid interface without further thinning. Indeed subsequent thickening will then occur as the concentration gradient in the liquid decreases with time, reducing the requirement for supply of solute through the layer. (2) Solid state diffusion is unable to supply reactants fast enough at any finite layer thickness, and thinning continues until the layer perforates.

In other words, it is found that the morphology of the intermetallic product layer formed between two

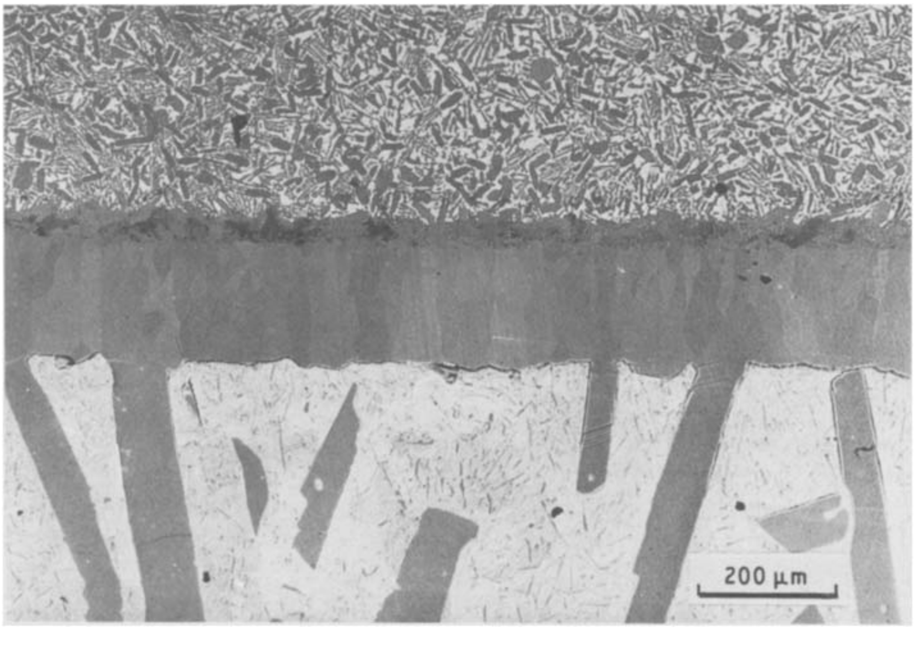

Figure 4 Specimen produced in interface device, using bismuth and Mg–Bi eutectic, air cooled after 5 min at 560° C.

liquid reactant metals, under conditions of diffusion control, is determined (in all but the very early stages of mixing) by the requirement for supply of solute across the layer to balance the diffusion of solute away into the bulk liquids on either side. In fact the flux across the solid layer is not exactly equal to the flux away into the liquid, as some thickening of the layer will occur, but the discrepancy between these fluxes can be shown [3] to become negligible after a very short time.

For a given binary system, therefore, at a given time after mixing, the demand for solute supply through the product layer is fixed by the concentration profiles and diffusion coefficients in the liquids on either side of it. If the product layer is unbroken, this solute must be transported by solid state diffusion. The solid state diffusion coefficient is also fixed (by the choice of system), so the concentration gradient in the solid layer is the only parameter which may be adjusted to ensure the flux is sufficient to meet the demand for solute supply into the liquid. Since the solid intermetallic compositions are fixed at the two solid/liquid interfaces (as indicated by the appropriate phase diagram), altering the concentration gradient in the solid layer can only be done by altering its thickness. It may be that this required thickness is several, or even tens of atoms thick, in which case it is quite possible to envisage such an unbroken solid state diffusion layer existing between the liquids. If, however, the solid state diffusion coefficients or the composition variation across the layer are sufficiently small, the physically impossible situation of a solid layer of subatomic thickness is predicted. The paradox in such a case is that permanent contact between the liquids would be impossible, as they would react to form solid, but permanent presence of an unbroken solid layer would be impossible, as it would remelt until its thickness was subatomic. This is resolved by considering the solid layer in such a case as unstable – continuously perforating locally, but almost immediately reforming as liquids intermix, while remelting and perforating in other regions.

The mathematical analysis of the conditions for a solid state diffusion layer to exist was carried out for an idealised symmetrical system, as outlined below: The model assumes that:

(i) The process is diffusion controlled – by diffusion through the intermetallic layer and away into the bulk liquid, i.e. that interface processes are relatively rapid.

(ii) The concentration profile in the liquid is characterised by a Boltzmann substitution, that is; $c = f(\lambda)$, where $\lambda = Xt^{-1/2}$ (X = distance from the interface, t = time).

Referring to Fig. 6 and letting the half-thickness of the intermetallic layer be x, equating the accumulation of solute at the interface with the fluxes to and from it;

$$(c_{S2} - c_{l2})\frac{dx}{dt} = D_l\frac{dc}{dx_l} - D_S\frac{dc}{dx_S} \qquad (1)$$

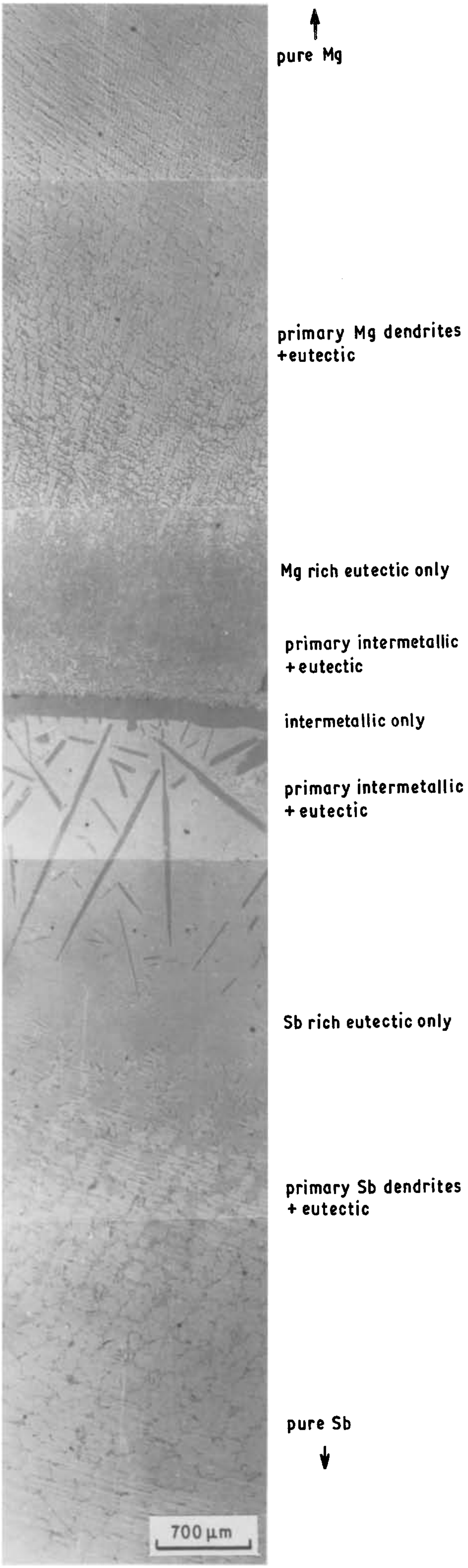

Figure 5 Same specimen as in Fig. 3, but showing the composition variation on either side of interface.

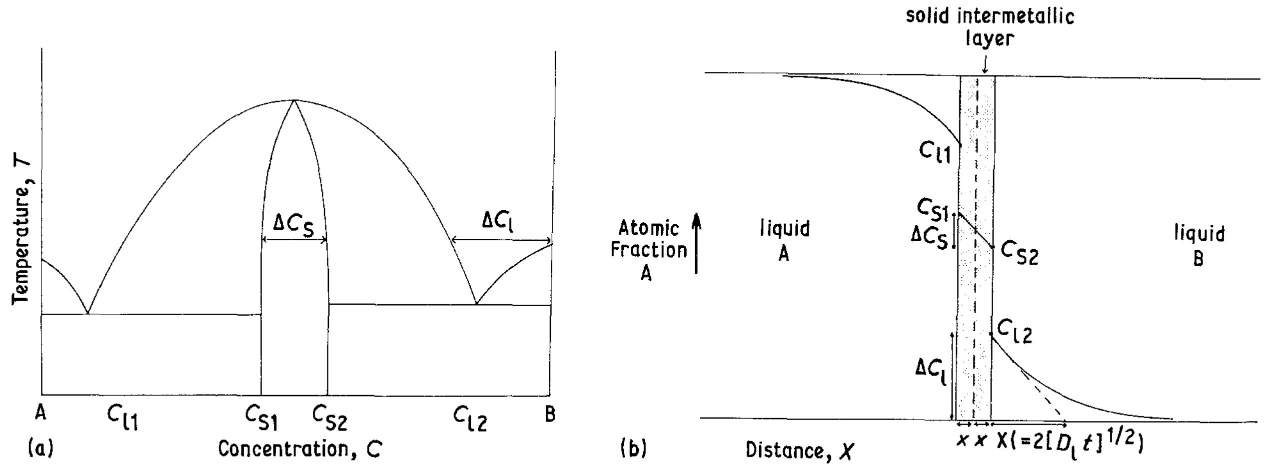

Figure 6 (a) Idealized phase diagram for barrier layer calculation. (b) Concentration profiles within interface and in liquids on either side of it.

where

$$\frac{\mathrm{d}c}{\mathrm{d}x_\mathrm{l}} = -\frac{\Delta c_\mathrm{l}}{2(D_\mathrm{l}t)^{1/2}} \qquad (2)$$

and

$$\frac{\mathrm{d}c}{\mathrm{d}x_\mathrm{s}} = -\frac{\Delta c_\mathrm{s}}{2x} \qquad (3)$$

The subscripts l and s refer to the liquid and solid respectively. Solving Equation 1 gives;

$$\frac{\left(\dfrac{x}{t^{1/2}} - A \pm (A^2 + 2B)^{1/2}\right)^{[A/\pm(A^2+2B)^{1/2}]-1}}{\left(\dfrac{x}{t^{1/2}} - A \pm (A^2 + 2B)^{1/2}\right)^{[A/\pm(A^2+2B)^{1/2}]+1}} = \frac{t}{T} \qquad (4)$$

where

$$A = -\frac{(D_\mathrm{l})^{1/2}\,\Delta c_\mathrm{l}}{2(c_{\mathrm{S}2} - c_{\mathrm{l}2})}, \quad B = \frac{D_\mathrm{S}\Delta c_\mathrm{S}}{2(c_{\mathrm{S}2} - c_{\mathrm{l}2})} \qquad (5)$$

If reasonable, initial values of x and t are chosen, Equation 4 predicts that the layer thickness will rapidly become a close approximation to the predictions of a much simpler model in which the fluxes through the solid and liquid are equated (i.e. the discrepancy between these fluxes, due to layer thickening, becomes negligible).

The layer thickness is then given by;

$$x = \frac{B}{|A|}t^{1/2} = \frac{D_\mathrm{S}\Delta c_\mathrm{S}}{(D_\mathrm{l})^{1/2}\Delta c_\mathrm{l}}t^{1/2} \qquad (6)$$

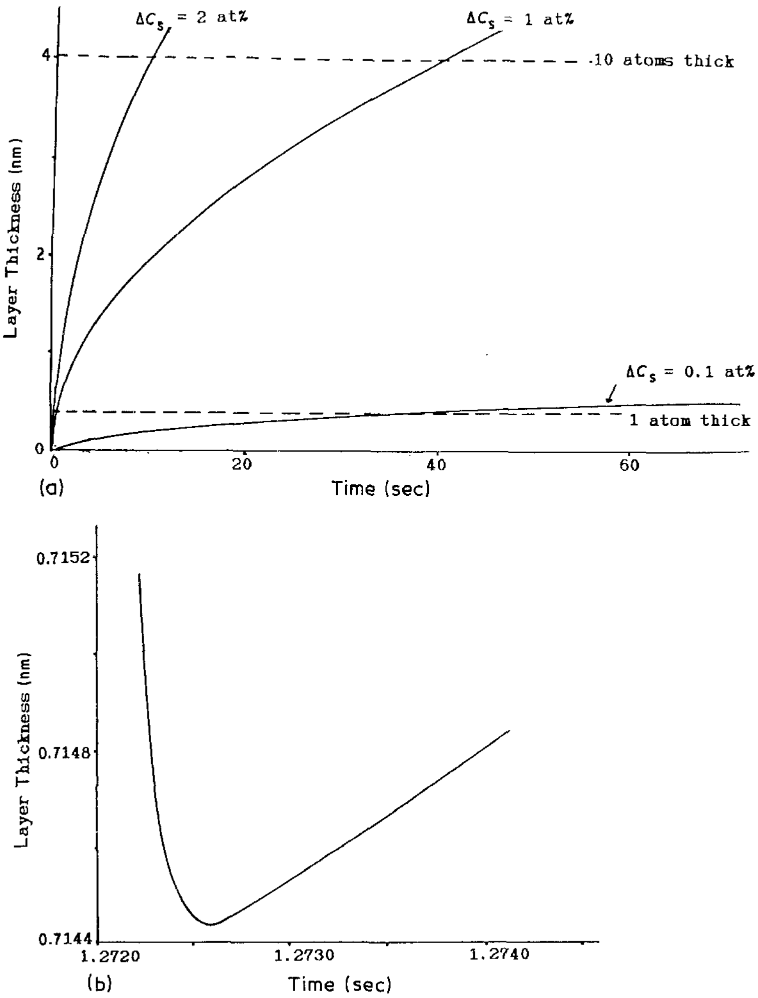

Figure 7 (a) Layer thickness against time plots from simple model of the interface, showing how different values of Δc_s can drastically alter the time taken to achieve a given layer thickness. (b) Plot of layer thickness against time (assuming Δc_s = 1 at %) from Equation 4, of the point where an initially thick layer reaches a minimum thickness, i.e. where solid state diffusion starts to take control. As can be seen from the above plot, this changeover is extremely rapid, taking place in a few thousandths of a second.

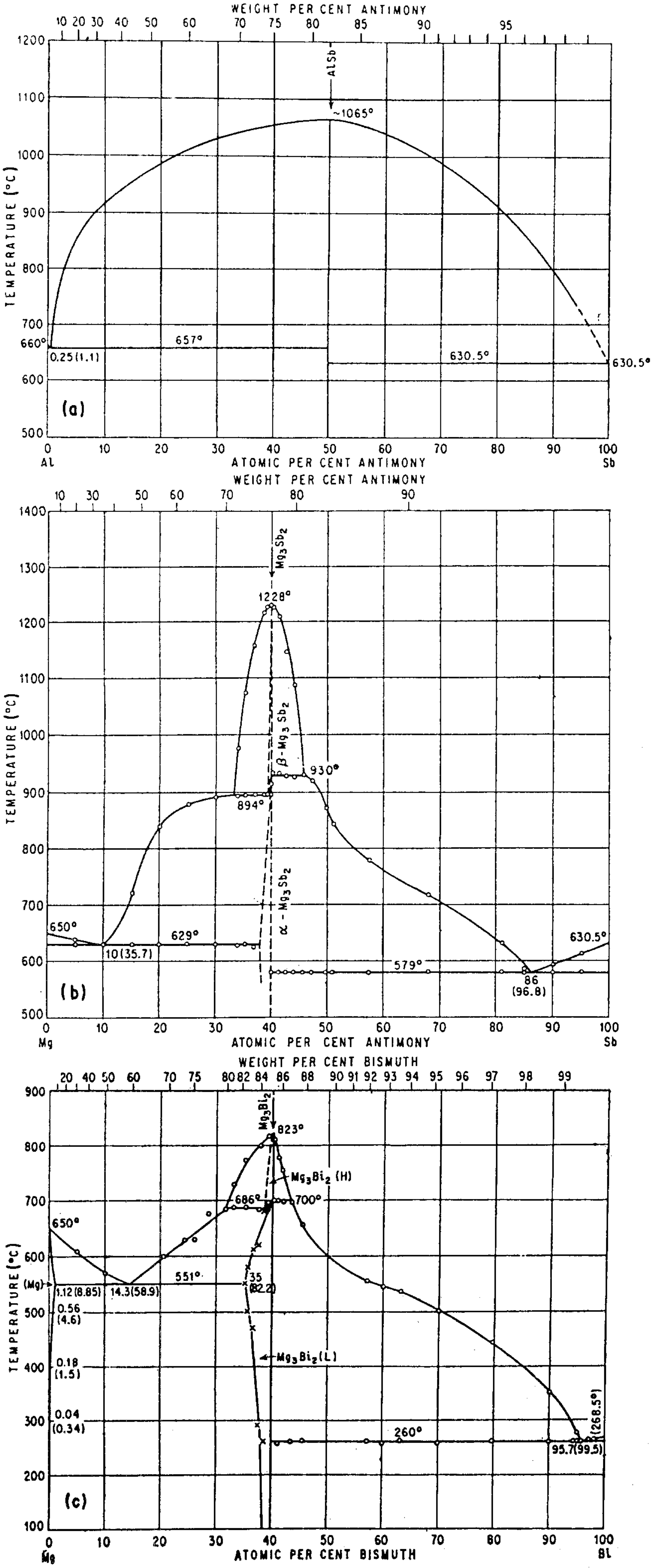

Figure 8 (a) The Al–Sb phase diagram, (b) the Mg–Sb phase diagram, (c) the Mg–Bi phase diagram.

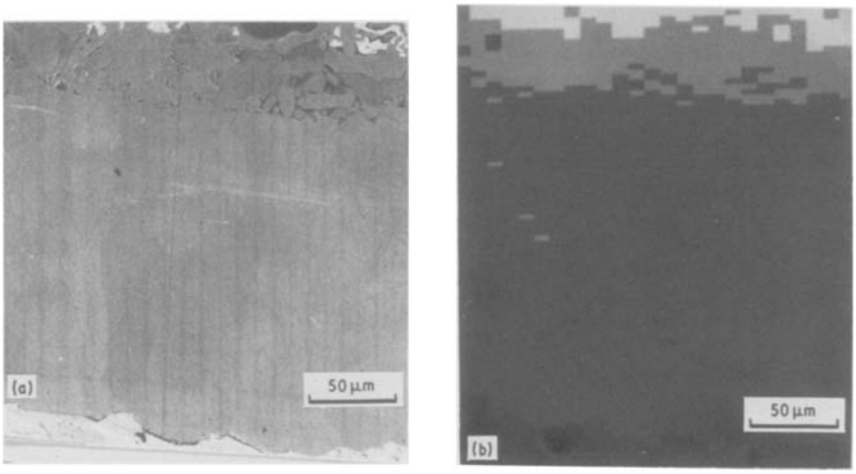

Figure 9 Interface layer in Mg–Bi specimen (air cooled after 5 min at 560° C), with corresponding composition scan of layer. (a) Part of the intermetallic layer in which the composition scan was made. Contamination of the surface of the specimens where the electron beam has scanned clearly shows up its path as a number of parallel lines. (b) Composition map of the same area on the same scale as (a). The light grey areas mark intermetallic of > 60 at % Mg, the dark areas < 60 at % Mg, while the white areas represent Mg-rich matrix and the black areas show Bi-rich matrix.

2.5. Discussion

The implications of the above analysis are, assuming realistic values for the other parameters, that the value of Δc_s must be of the order of atomic fraction 0.01, or 1 at %, for stable layer thicknesses of a few atoms or more to be achieved within experimental times (see Fig. 7).

From the phase diagrams for Al–Sb, Mg–Sb, and Mg–Bi (Fig. 8), it can be seen that this criterion for Δc_s is satisfied by the intermetallic in the latter two cases, but not in the former case.

It is thus suggested that the interface layer existing between liquid magnesium and bismuth (or antimony) is of the solid state diffusion type, i.e. it is a few atoms thick, and uniform but not perforated. The much thicker layers observed metallographically, result from growth of intermetallic on this initially thin layer during bulk solidification of the specimen on cooling. This view is supported by the two layer substructure of these interfaces as shown both metallographically and by a microprobe composition scan (see Fig. 9) showing layers of compositions equivalent to c_1 and c_2.

The intermetallic layer between aluminium and antimony must perforate, however, as its Δc_s value is so small that it would paradoxically need to be of subatomic thickness in order to transport reactants fast enough by solid state diffusion. Thus the AlSb layer is visualized as a relatively thick but perforated disc, with the positions of the perforations continuously changing. This is because effusion of reactants through them leads to local solute enrichment sufficient to block them with intermetallic, while previously thicker regions melt back and perforate as solute diffuses away from them into the bulk liquid.

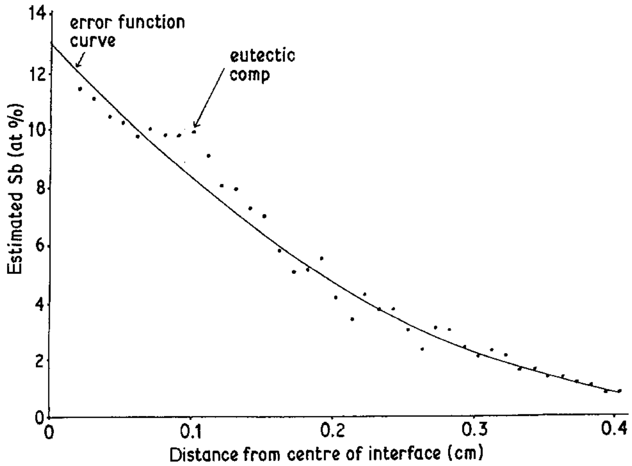

Figure 10 Plot of the average antimony concentration in strips spaced 100 µm apart on the Mg-rich side of the interface for the specimen shown in Fig. 5. In addition to these points, an error function curve is also plotted in the above graph, for Mg–Sb at this temperature (and assuming that $D_l = 8 \times 10^5\ \mathrm{cm}^2\ \mathrm{sec}^{-1}$). As can be seen, this theoretical curve is in very close agreement with the experimental points, particularly at large distances from the interface.

Both these interface mechanisms, however, lead to similar concentration profiles in the bulk liquid away from the interface, since they both maintain a constant composition (the liquidus composition) at the interface. An experimental plot of concentration versus distance from the interface is given in Fig. 10, for Mg–Sb, along with the curve predicted by the above diffusion controlled model for the appropriate temperature and time. It can be seen that there is good agreement between the theoretical and experimental curves.

3. Experimental Procedure: II

3.1. Catastrophic Reactions

Experiments were carried out involving the pouring together of liquid metals, in stoichiometric proportions to produce the intermetallic only, and measuring the temperature rises occurring on mixing. As indicated earlier, the Al–Sb system would not react catastrophically, even when vigorously mixed, and alloys produced in this way rapidly became impossible to stir, while undergoing only small temperature rises of the order of tens of degrees. Subsequent examination of the microstructure of these specimens revealed intermetallic layer formation, the layers surrounding unreacted regions of both metals (see Fig. 11).

The other systems investigated, however, including Mg–Sb and Na–Bi, readily reacted catastrophically, maintaining high fluidity during reaction, and undergoing temperature rises of many hundreds of degrees in times of the order of a second or less, reaching maximum temperatures well in excess of the appropriate intermetallic melting point (see Fig. 12).

The Mg–Sb specimens were examined metallographically, on cooling, and found to consist entirely of the intermetallic Mg_3Sb_2, with a fairly coarse-grained structure.

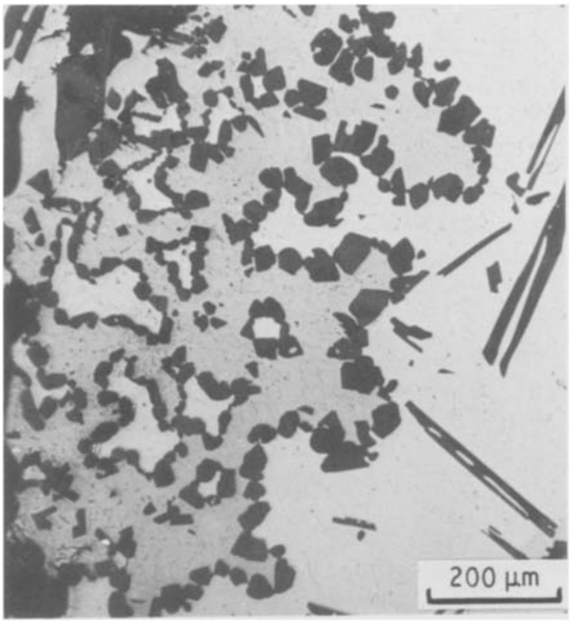

Figure 11 Microstructure of a specimen produced by vigorous mixing of aluminium and antimony in equiatomic proportions at 750° C.

3.2. Interpretation

The temperatures reached by catastrophic reaction could not be due to the latent heat of solid formation, as this would not allow temperatures higher than the intermetallic melting point to be achieved. For this reason, the enthalpy of mixing in the liquid state was considered as the source of the temperature rise. Simple estimations of these enthalpy of mixing values, in conjunction with the heat capacities of the reacting liquids, enabled approximate values for the temperature rises expected due to enthalpy of mixing to be obtained. This was done for the systems Mg–Sb, Na–Bi, and Al–Sb, and temperature rises of approximately 1000° C, 1500° C, and 130° C respectively were predicted on mixing the liquid elements in stoichiometric proportions, at temperatures in each case several hundred degrees below the highest point on the liquidus. For the Mg–Sb and Na–Bi systems, therefore, enthalpy of mixing could easily raise the temperature of the system to hundreds of degrees above the intermetallic melting point, with no solidification necessary. This would not be possible for Al–Sb, since the relevant enthalpy of mixing is very small.

4. Conclusions

The above results are consistent with the experimental findings that Al–Sb would not react catastrophically, whereas temperatures well in excess of the intermetallic melting point were observed on mixing in the Na–Bi and Mg–Sb systems.

It is suggested that the enthalpy of mixing is the factor which determines the possibility of catastrophic reaction in a given system. If this enthalpy is large enough to raise the temperature of the system above the melting point of the intermetallic, no solidification will occur, and the reaction will be catastrophic. If it is small, however, intermixing of the liquids will not itself cause large temperature rises, and instead nucleation of solid product will occur in the intermixed regions, leading to intermetallic barriers of the type described earlier, isolating the reactants from one another, controlling the rate of subsequent reaction, and, in the case of Al–Sb, providing mechanical strength (making further intermixing by stirring impossible). In view of this, it seems unlikely that rapid nucleation of intermetallics will occur in binary systems, on mixing the reactive liquid elements. Thus it does not appear that the possibility, mentioned in the introduction, of producing very fine dispersions of intermetallics by reaction between liquid metals, will be realised in systems for which the reactions are controlled by the mechanisms proposed here.

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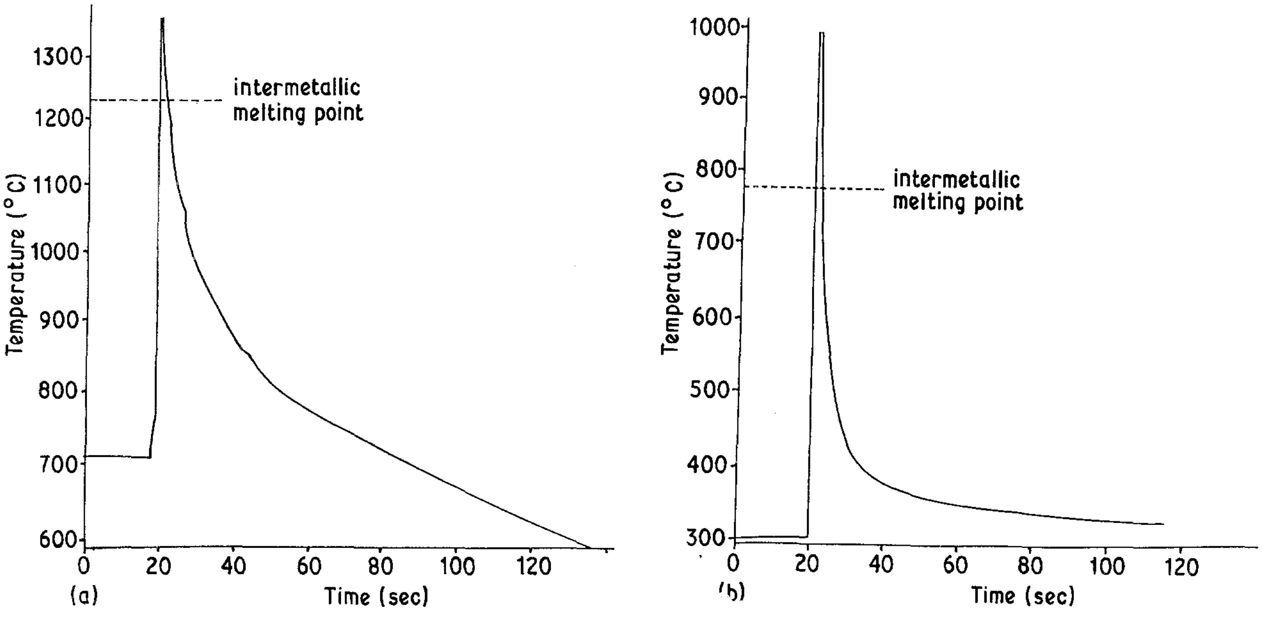

Figure 12 Catastrophic temperature rises accompanying reaction mixing for (a) Mg–Sb and (b) Na–Bi.

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