

Diffusion in evaporated films of magnesium-aluminium

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VACUUM deposition can easily produce metal films of uniform thickness. When two such metal films are deposited, one over the other, and the resultant double layer film is annealed, diffusion will occur at the common interface, resulting in the formation of either a solid solution or intermetallic compounds or both. The presence of the diffusion layers can be confirmed by electron-diffraction or X-ray diffraction or deduced from other measurements, such as electrical resistance or adhesion (Weaver and Hill, 1959).¹

These methods can give only a qualitative picture and cannot normally give the rate of growth of the diffusion layer and hence the diffusion coefficient of the system. Techniques used for determining diffusion coefficients in bulk diffusion couples are inapplicable to the study in evaporated thin films, since it is impossible to section them, and the quantity of material available is not sufficient for chemical analysis. In thin films it is much more convenient to measure the time required for one film to be completely penetrated by atoms of the other metal. This can be done simply by measuring the variation of reflectivity with time and this technique has been used by Schopper (1955)² for study of diffusion of lead into gold and by Weaver and Brown³⁻⁵ (1962, 1963, 1968) for study of diffusion in evaporated film of gold-aluminium, gold-lead and silver-aluminium.

Magnesium forms two intermetallic compounds with aluminium, corresponding approximately to the formulae Mg_3Al_2 and Mg_2Al_3 respectively. The presence of Mg_2Al_3 (or β -Al-Mg) has previously been observed in a precipitated phase during the ageing of Al-Mg alloys (Trehan et al., 1965).⁶

Experimental

Metal films were evaporated on to glass microscope slides which had been carefully cleaned with 'Teepol' and polished with lens tissue before being placed on a jig about 20 cm above the evaporating heaters in the vacuum evaporation chamber. This jig could be rotated so that the slides could be brought vertically above each evaporating heater in turn, thus ensuring uniformity

SYNOPSIS

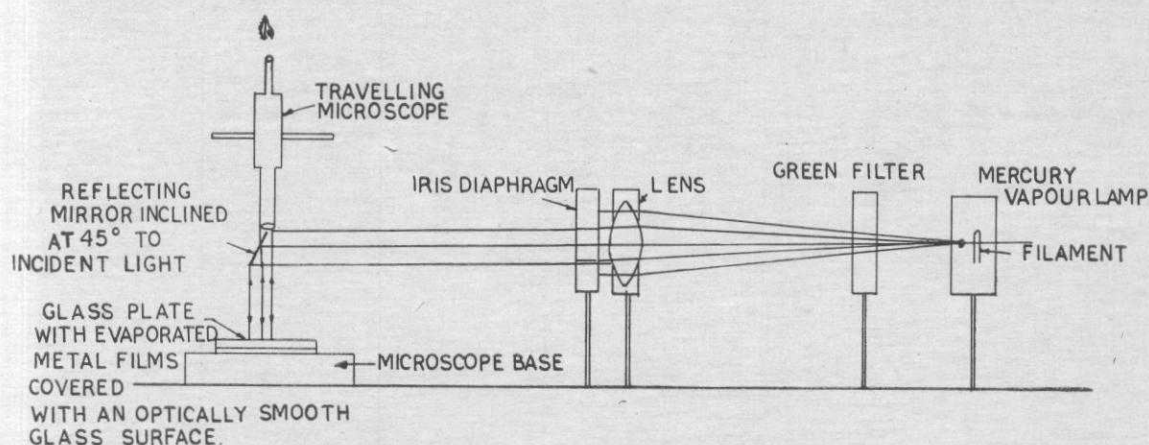
Measurements of optical reflectivity have been used to investigate diffusion and formation of intermetallic compounds in thin-film diffusion couples of magnesium-aluminium. The couples were formed by the successive evaporation of magnesium and aluminium in vacuum, on to glass substrates. The specimens were annealed at different temperatures up to 250°C and reflectivity measured at both the free surface (aluminium-side) and the glass substrate (magnesium side). Marked changes in reflectivity were noted on both the aluminium and the magnesium surfaces which have been attributed to the formation of β -AlMg (Al_3Mg_2) due to diffusion. The diffusion appears to take place by a vacancy mechanism, rather than by grain boundary mechanism.

of film thickness. The slides were then exposed to a high voltage glow discharge for about 10 minutes during the pumping cycle. The ultimate vacuum attained before evaporating the metal films was of the order of $2-5 \times 10^{-5}$ Torr, as measured by an ionization gauge. Two slides were placed on the jig at one time in such a way that while one of the slides was fully exposed, the other was only partially exposed to metal vapour so that steps could be formed on it for thickness measurements by multiple beam interferometry [Tolansky (1948),⁷ Weaver and Benjamin (1956),⁸ (1958),⁹] in a set up diagrammatically shown in Fig. 1.

Magnesium was evaporated first from a molybdenum boat, followed on top by aluminium, which was evaporated from a spiral of stranded tungsten wire. There was a delay of 1-1½ minutes between the two evaporations. High purity metals were used and any volatile impurities were removed by using a shutter over the crucibles for the first few seconds, before the metals were allowed to condense on the glass slides.

The slides were aged in a hot air oven, thermostatically controlled to $\pm 1^\circ C$ at the appropriate ageing temperatures. Reflectivity measurements were made at regular intervals. The reflectometer (schematically shown in Fig. 2) used a mercury discharge tube as a source of monochromatic light, and reflectivity was measured by comparing the intensity of light reflected by the slide

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1 Interferometer for thickness measurement (schematic)

under examination with the intensity of the undeviated beam, as received by a photo multiplier cell.

Results

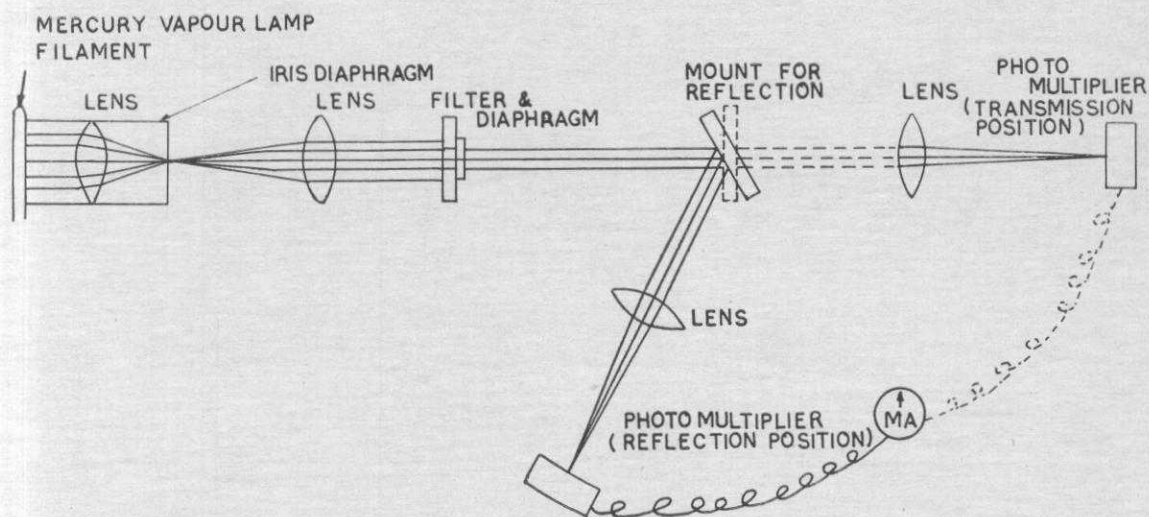
Reflectivity changes on ageing for different lengths of time at different temperatures were measured both at the magnesium surface (through glass) and at the aluminium surface. A dark-violet filter was used with the photomultiplier for getting best reflectivity measurements.

(a) Reflectivity changes at the magnesium surface

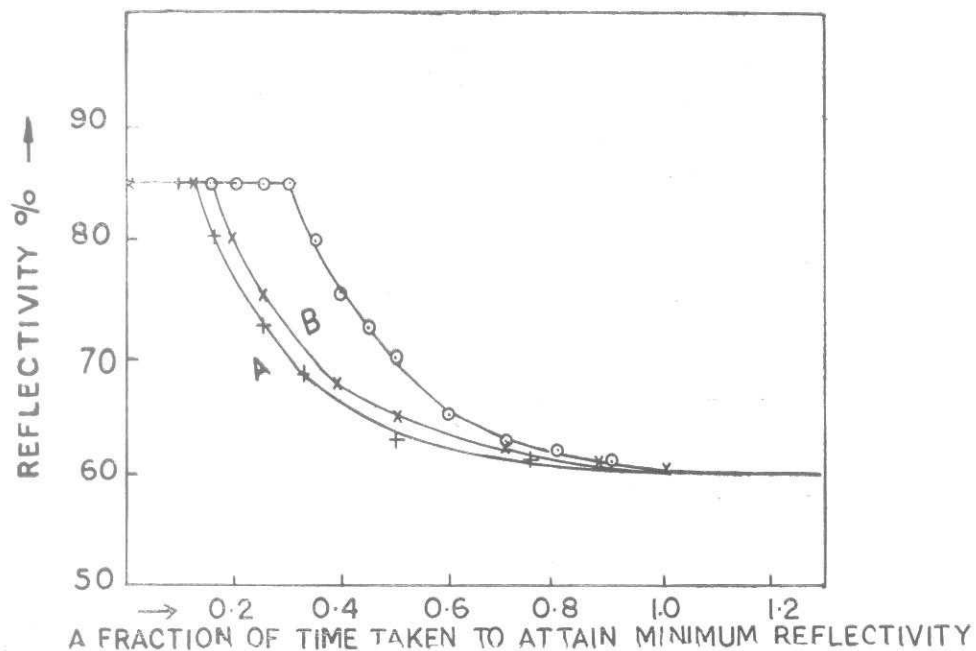
Graphs of change of reflectivity with ageing time on the magnesium surface are shown in Fig. 3. These

values were obtained by measurements at the under surface (glass side) of the magnesium films, the thickness of which varied between 400 Å and 1600 Å. Each film was overlaid with excess aluminium and anneal was done at 200°C. It may be noted that the curves coincide at the beginning and the ends but their shapes differ even when they are adjusted to a normalized time scale. The reflectivity changes from about 85% to 60%, which cannot be explained on the basis of the solid solubility of aluminium in magnesium (<3%)¹⁰ at the temperature of study. The length of the initial graph showing no change in reflectivity increases with increase in thickness.

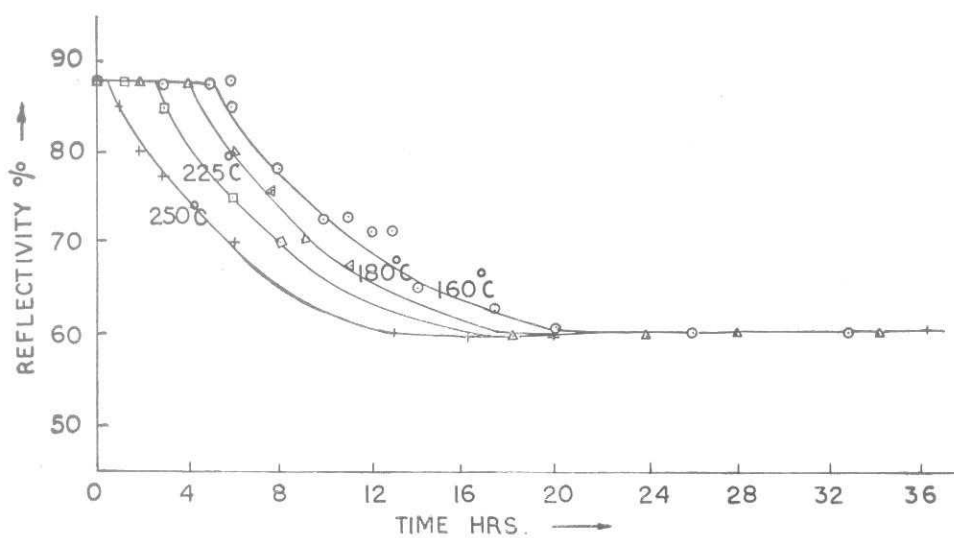
According to Schopper's theory¹¹ of a progressive change in surface composition, curves of reflectivity in samples with different thicknesses of magnesium should coincide when plotted against time as related to the



2 Reflectometer (schematic)



3 Change of reflectivity at magnesium surface on ageing at 200°C ; magnesium thickness: A 400 Å + — +
 B 650 Å x — x
 C 1600 Å o — o



Al ~ 500 Å, Mg ~ 400 Å
 o — o 160°C, Δ — Δ 180°C, □ — □ 225°C, + — + 250°C

4 Reflectivity at aluminium surface

total time in which maximum fall in reflectivity occurs. Since the curves in Fig. 3. do not coincide, it appears that Schopper's theory is not applicable in the present case.

Since light waves can penetrate a small distance within a metal, the advancing atoms can be detected before they reach the surface. It may be seen that there is an abrupt and sharp change in reflectivity. This would suggest that there is a sharply defined advancing front, which approaches the surface at a certain rate (the diffusion rate), since small amounts of aluminium in magnesium are not known to cause any appreciable lowering of reflectivity. These considerations, coupled with the low solubility of aluminium in magnesium, suggest that the reflectivity changes are caused by a sharply defined phase boundary, rather than to a gradual change in concentration which would occur if atoms in the magnesium lattice were being gradually replaced by aluminium atoms.

Kirkaldy¹² (1958) has shown that the motion of such a phase boundary should follow the parabolic law $X^2 = D't$, where X is the distance the boundary moves from the initial interface in time t , and D' is the diffusion coefficient of the boundary. It has been shown by Weaver and Brown (1963)⁴ that D' does not vary to the film thickness.

To determine the activation energy, different portions of the same slide were aged at different temperatures in the range 160° to 250°C. The curves of reflectivity are shown in Fig. 4. The diffusion coefficient, D' , will vary with temperature according to the Arrhenius equation :

$$D' = D_0' \exp(-E/RT)$$

where E is the activation energy of diffusion in cal/mole, R is the universal gas constant and T is the temperature in the Kelvin scale (absolute temperature). Therefore,

$$\log_{10} \left(\frac{1}{D'} \right) = \log_{10} \left(\frac{1}{D_0'} \right) + E/2.3 RT$$

where $D' = d^2/t_2$, d being the thickness of the metal film and t_2 the time taken for reflectivity to drop to the minimum value.

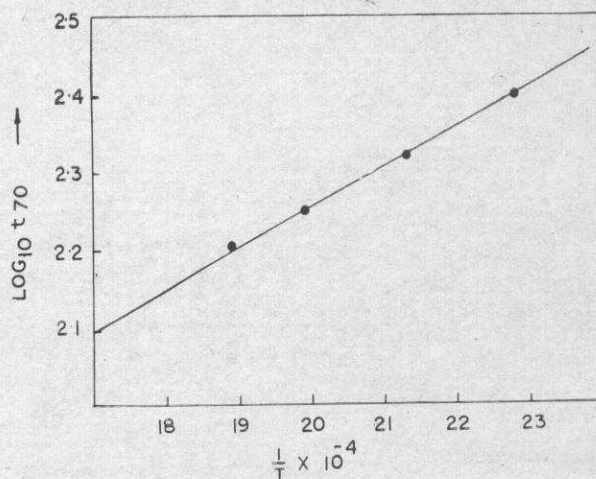
But the curves for different portions of one slide have practically the same shape, even though the time scale varied widely. If we take t_{70} as the time for the reflectivity to drop to a fixed level of 70%,

$$t_2 = k t_{70}$$

Substituting for t_2

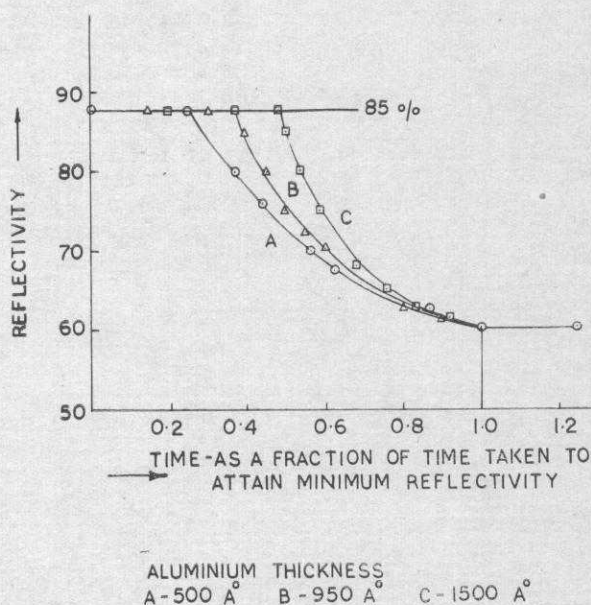
$$\log_{10} t_{70} = K + E/2.3 RT \quad \text{where } k \text{ is a constant.}$$

The value of t_{70} could be determined with greater accuracy than the total ageing time. The effect of variations in diffusion coefficient for different samples

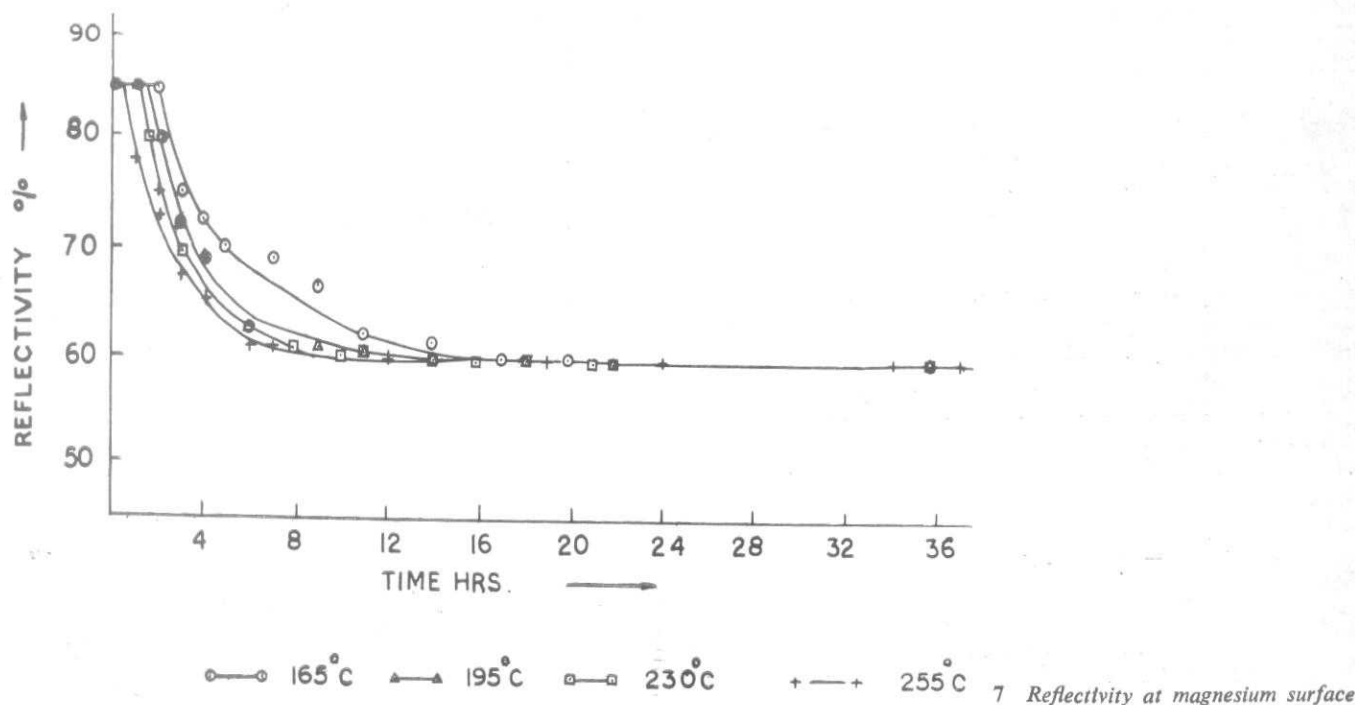


5 Activation energy plot

and of errors in thickness determination were eliminated by using specimens made from different portions of the same slide. The experimental error was thus reduced to about $\pm 1.5\%$. Plotting $\log_{10} t_{70}$ against $1/T$ gives separate straight lines for each film thickness, but they all have the same slope (Weaver and Brown, loc. cit.) Fig. 5 gives the plot obtained for a magnesium thickness of 400 Å from the gradient of which



6 Change of reflectivity at aluminium surface on ageing at 200°C



(corresponding to $E/2.3R$) the activation energy has been calculated to be 23.7 KCal/mole.

(b) Reflectivity changes at the aluminium surfaces

Reflectivity changes were measured at the aluminium (top) surface in several films having different thicknesses over the substrate magnesium films. Results obtained on ageing at about 200°C for different thicknesses of the aluminium film in the range 500 Å to 1500 Å are shown in Fig. 6, plotted against fraction of time taken for maximum drop in reflectivity. The length of the initial plateau increased with thickness of aluminium film and the results obtained resemble those for diffusion of aluminium into magnesium (Fig. 3). It, therefore, seems likely that in this case also the reflectivity changes are due to the movement of a sharply defined phase boundary. This is also supported by the fall of reflectivity from 88% to 60%, which cannot be accounted for by the small solid solubility of magnesium in aluminium (< 3%) at the temperature of study, viz. 200°C.

Fig. 7 shows the changes in reflectivity occurring when different portions of the same slide (i.e. samples having the same thicknesses of magnesium and aluminium) were aged at different temperatures between 160° and 250°C. From a graph of $\log_{10} t_{70}$ plotted against the reciprocal of T (absolute temperature) the activation energy was calculated to be 23.4 K Cal/mole.

(c) Electron diffraction investigation

The aluminium surface of the double layer was also examined by reflection electron diffraction at various stages of the ageing process. Initially the pattern (Fig. 8)

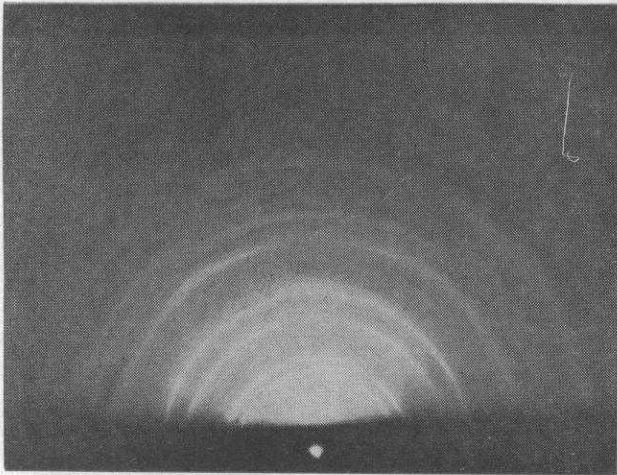
showed the presence of aluminium rings only. No change in the pattern, except a slight haziness, was observed till the reflectivity reached its minimum value. At this stage the surface showed a pattern (Fig. 9) consisting of aluminium rings mixed with another phase. In the process, the reflectivity had dropped by 28% and no further change in reflectivity took place.

These results show that reflectivity changes are associated with compound formation, since the diffraction pattern changed only when a sizeable quantity of the new phase reached the surface. The ring diameters of the new phase corresponded to a cubic lattice having $a_0 = 4.70 \text{ \AA}$.

Discussion

The shape of the experimental curves clearly shows that the changes in reflectivity occurring at both the magnesium and aluminium layers are due to moving phase boundaries. The fact that the reflectivity of the phase formed at both the aluminium and the glass (magnesium) surface has the same value of 60% indicates that only one phase is principally formed during the diffusion process. The diffusion of both aluminium and magnesium into this phase appears to be the rate controlling factor.

Only two intermetallic compounds are known to form in the aluminium-magnesium system¹³, β Al-Mg (or approximately Al_3Mg_2) and the γ Al-Mg corresponding to Al_2Mg_3 . β Al-Mg has been reported to be hexagonal ($a_0 = 11.38 \text{ \AA}$, $c_0 = 17.87 \text{ \AA}$) by Reiderer (1936)¹⁴ and complex cubic ($a_0 = 28.3 \text{ \AA}$) by Perlitz (1944)¹⁵, and by Saulnier and Mirand (1960).¹⁶ In an earlier paper⁶, the author had observed the precipitation of a similar phase (cubic $a_0 = 4.7 \text{ \AA}$) in the ageing of Al-Mg alloys.



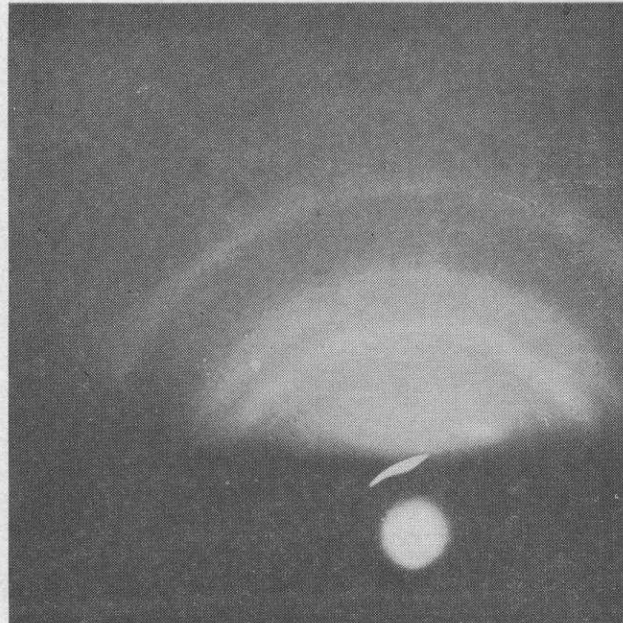
8 Electron diffraction pattern showing initially the presence of aluminium rings only

Detailed structural studies of the β -phase in the Al-Mg system by the present author (to be published) indicate that the β -Al-Mg phase in fact has a cubic lattice but has a lattice parameter $a_0 = 4.70 \text{ \AA}$. Thus the phase observed on the aluminium surface was the β Al-Mg (or Al_3Mg_2) intermetallic compound. It is possible that some γ Al-Mg (Al_2Mg_3) may also have been formed but its quantity was so small that it could not be detected by electron diffraction.

Weaver and Brown³⁻⁵ have shown that in the case of diffusion couples of gold-aluminium, gold-lead and silver-aluminium, the mechanism of diffusion in thin films is the same as in bulk materials, viz., vacancy diffusion. The initial precipitation of the intermetallic phase occurs due to the diffusion of atoms of one metal into the other to fill up the vacancies (of the order of 1-2%) generally associated with evaporated films.¹⁷ Once this phase has precipitated its further growth and movement of the phase boundary are controlled by the diffusion of both Al and Mg into this phase due to the presence of vacant lattice sites near the interfaces. It has been shown by Bessett, Mentar and Pashley (1950)¹⁸ that thin films formed by evaporation have large numbers of dislocations. These dislocations in thin films can act as ideal sinks for vacancies (Le Claire, 1953).¹⁹ In a bulk metal, dislocations can easily supply the large number of vacancies necessary for the occurrence of vacancy diffusion (Van Bueren, 1960).¹⁷ The same mechanism may be taken to hold in thin film diffusion in view of the existence of excessive vacancies due to the large number of dislocations present in thin films.

Acknowledgements

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9 Electron diffraction pattern showing a new phase mixed with aluminium rings

sity of Strathclyde, Glasgow, for suggesting the problem, providing facilities in his laboratory for this work during the tenure of author's Colombo Plan Fellowship and for his guidance in the work.

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Discussions

Mr L. J. Balasundaram (N.M.L.) : Has Kirkendall effect been observed in thin films of aluminium-magnesium ?

Dr Y. N. Trehan (Author) : We did not look for Kirkendall effect during our present studies. We studied only the change in reflectivity of the surface films.

Mr G. P. Tiwari (Bhabha Atomic Research Centre, Bombay) : In reply to the question asked by Mr Balasundaram I may add that the Kirkendall effect has been observed in thin films of gold and nickel. The reason why it has not been observed in Al-Mg system is that the mobilities of aluminium and magnesium are nearly the same.

Dr Trehan has suggested in his paper that the diffusion coefficient could be evaluated by estimating the total amount of solute which has diffused as well as by following the movement of the interface. This is not correct. The former method is applicable only

in systems where complete solubility exists and there is no sudden change of concentration across the interface. Since in the present case, diffusion leads to the formation of an intermetallic and at the boundary of such phase, there occurs a sudden change in concentration and diffusivity (owing to the existence of new phase), the estimation of D' from the amount of total solute is incorrect.

In the paper, the reported D' values have been obtained by considering the movement of only one of the phase boundaries of the intermetallic compound formed. It is evident that the total mass transfer will be greatly influenced by the diffusion rates within the compound as well as the other boundary of the phase.

Dr Y. N. Trehan (Author) : The procedure adopted during the present study has previously been followed by Weaver and co-workers (already referred to in the main paper). The method has been found to be fairly reliable in obtaining values for diffusion coefficient D' .