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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.

In thin films diffusion coefficient can be determined by measuring the time required for one film to be completely penetrated by atoms of the other metal. This is done by measuring the variation of reflectivity with time.

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 θ Al-Mg) has previously been observed by the present author in a precipitated phase during the ageing of Al-Mg alloys.

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Experimental

Metal films were evaporated on to carefully cleaned glass microscope slides placed on a jig about 20 c.m. above the evaporating heaters in a vacuum evaporation chamber under a Vacuum of the order of $2-5 \times 10^{-5}$ Torr. The jig could be rotated so that the slides were brought vertically above each heater in turn, thus ensuring uniformity of film thickness. 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. Thickness of the metal films was determined by measuring the width of the Fizeau fringes by multiple beam interferometry.

Magnesium was evaporated first, followed on top by aluminium, using highly pure metals in both cases.

The slides were aged in a thermostatically controlled hot air oven at different temperatures. Reflectivity measurements were made at regular intervals by comparing the intensity of light reflected by the slide 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 and the aluminium surface.

(a) Reflectivity changes at the magnesium surface

A study of the graphs of change of reflectivity with ageing time on the magnesium surface, in films 400 to 1600 Å thick, annealed at 200°C, shows that the curves coincide at the beginning and the end but their shapes differ even when they are adjusted to a normalized time scale. The reflectivity drops from about 85% to 60%, which cannot be explained on the basis of the low solid solubility of aluminium in magnesium at the temperature of study. The length of the initial graph showing no change in reflectivity

(initial plateau) increases with increases in thickness.

According to Schopper's theory of a progressive change in surface composition, the curves of reflectivity in samples with different thicknesses of magnesium should coincide when plotted against time as related to the total time in which maximum fall in reflectivity occurs. This was not so in the present case. The abrupt and sharp change in reflectivity observed, would suggest that a sharply defined phase boundary is advancing towards the surface at a certain rate (the diffusion rate). 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 earlier workers that D' does not vary with 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 activation energy was calculated by using the formula

$\log_{10} t_{70} = K + E/2.3 RT$ where K is a constant, t_{70} , the time for the reflectivity to drop to 70%, E the activation energy of diffusion in cal/mole, R the universal gas constant and T is the temperature in the Kelvin scale. Plotting $\log_{10} t_{70}$ against $1/T$ gave a straight line graph from the gradient of which the activation energy for the diffusion of aluminium into magnesium has been calculated to be 23.7 KCal/mole.

(b) Reflectivity changes at the Aluminium surface:

Reflectivity changes were similarly measured at the aluminium surface in several films having different thickness over the substrate magnesium films, as well as at different temperatures in films having the same thicknesses of aluminium and magnesium. From the graph of $\log_{10} t_{70}$ plotted against the reciprocal of T , the activation energy of diffusion of magnesium into aluminium 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 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 consisting of aluminium rings mixed with another cubic phase ($a_0 = 4.70 \text{ \AA}$). In the process the reflectivity had dropped by 28% and no further change in reflectivity took place. This indicates that reflectivity changes are associated with compound formation.

Discussion

The shape of the experimental curves clearly shows that the changes in reflectivity occurring at both the magnesium and the 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. The phase observed on the aluminium surface was the β Al-Mg (or Al_3Mg_2) intermetallic compound. Some traces of γ Al-Mg (Al_2Mg_3) may also have been formed but it could not be detected by electron diffraction.

The mechanism of diffusion in thin films appears to be the same as in bulk materials - viz vacancy diffusion. The initial precipitation of the intermetallic phase occurs due to the diffusion of one metal atoms into the other at the interface to fill up the vacancies (of the order of 1-2%) generally associated with evaporated films. 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 it ~~phase~~ due to the presence of vacant lattice sites near the interfaces. Thin films formed by evaporation are known to have a large number of dislocations which can act as ideal sinks for vacancies. Thus the vacancy mechanism which causes diffusion in bulk metals, may be taken to hold in thin film diffusion also.
