

SOME FACTORS INFLUENCING THE ADHESION OF FILMS PRODUCED BY VACUUM EVAPORATION

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Sommaire. — De nombreux facteurs interviennent dans la préparation des couches par évaporation, parmi lesquels on peut citer les suivants :

- le vide réalisé;
- le liquide utilisé dans les pompes et les dispositifs employés comme pièges;
- la méthode de nettoyage des surfaces traitées;
- la température des sources et, par suite, l'intensité du jet moléculaire.

Un travail est en cours pour déterminer la part jouée par quelques-uns de ces facteurs en contrôlant la dureté et l'adhésion des couches évaporées dans le vide. L'auteur indique quelques résultats préliminaires obtenus avec l'aluminium. Il étudie également les propriétés des couches d'aluminium déposées sur un support de chrome évaporé.

Introduction. — In view of the rapidly increasing application of vacuum evaporation methods, an investigation has been made to try to assess the relative importance of the many factors which affect the adhesion of metal films produced by this process. This report contains some preliminary results of the investigation, in which films of silver, aluminium and chromium have been studied.

It is known that the adhesion of aluminium to glass is improved by the prior deposition of a thin layer of chromium. The dependence of the adhesion of aluminium, and also of silver, films on the thickness of the chromium layer has been examined. A simple method is described for measuring the thickness of a transparent metal film without removing the film from the vacuum.

remove the metal, deformation of the film occurred but without appreciable removal of the metal.

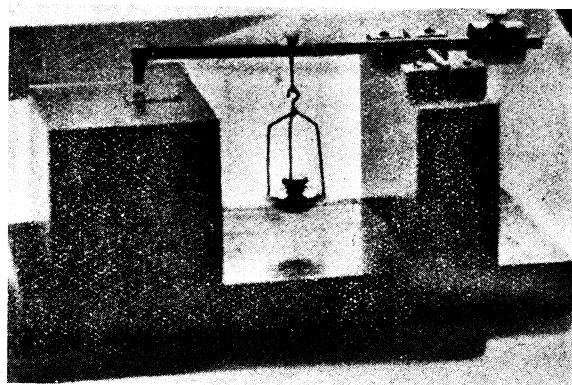


Fig. 1. — Apparatus for testing the adhesion of metal films.

Method of testing the adhesion of films. —

The measurement of the true adhesion between a film and the substrate presents considerable difficulty. The so-called « Scotch Tape » test, in which an adhesive tape is applied to the film and then stripped off, is of little use as a quantitative test. The method employed in this work is to measure the load on a chromium-steel point necessary to remove the film from the substrate. The point has a smooth contour, the radius at the tip being about 0.03 mm, and is drawn across the surface at a definite rate. The apparatus is shown in figure 1. In testing the adhesion of single metal films, gradually increasing loads were applied until the film was removed completely. It was found that for loads smaller than that necessary to

This suggests that the coherence in the film is greater than its adherence to the substrate. In the work on the effect of chromium layers on silver and aluminium deposits, reference plates with no chromium substrate were prepared at the same time as the test plates and the differences in the figures obtained were taken to be a measure of the improvement in adhesion of the superposed film.

Degree of vacuum. — The nature of films of substances produced by evaporation varies considerably with the pressure in the evaporation

chamber. Films can be produced, on targets a few cm from the source, at pressures as high as 10^{-2} – 10^{-1} mm mercury but such films are generally powdery and consist of aggregates of the order of colloidal dimensions. At about 10^{-4} mm mirror-like films are produced on, e. g. a glass substrate, such films showing reasonably good coherence. Their adherence to glass is usually poor. At a pressure of about 10^{-5} mm, the adhesion of the film to the substrate improves. There is some evidence that films prepared at pressures below 10^{-6} mm in all-glass vacuum systems show much greater adherence and coherence than those deposited at 10^{-5} mm. No quantitative measurements have been made on these films.

In vacuum systems containing large masses of metal which cannot readily be outgassed, very low pressures cannot be expected. The work to be described has been done with such a system, the pressure being in the region of 10^{-5} mm.

Pumping fluid and trapping arrangements.

— When a mercury diffusion pump is used, efficient trapping is obligatory if stable films, possessing good coherence and adherence are to be produced. Aluminium films are particularly sensitive to mercury contamination. Cooling by solid carbon-dioxide-acetone mixture (-80°C) has been found to be insufficient to prevent instability in evaporated aluminium films although silver films appear to be satisfactory with this coolant.

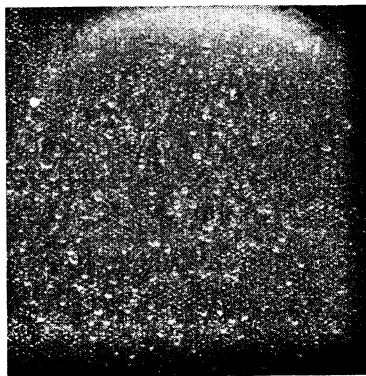


Fig. 2. — « Blisters » observed on evaporated aluminium film (Magnification $\times 40$).

Tests have been made with a system using silicone oil as pumping fluid (a) with no cooling, (b) using solid CO_2 -acetone mixture and (c) using liquid air. In the last mentioned case no defective films have been observed. When no cooling is used and the evaporation is done within a short time of pumping down, the films are good. When, however, the system is left pumping for several hours before

the evaporation, films of aluminium sometimes show minute raised « blisters » (fig. 2) as though tiny droplets (~ 0.05 mm) were present on the glass. This has been observed on plates maintained at room temperature and also at temperatures of 200 – 300°C . The possibility that this trouble is due to contamination by silicone vapour makes it desirable that some coolant be used. With solid CO_2 -acetone cooling, hard films of silver and aluminium result, although the adhesion is not quite so strong as that obtained with liquid air trapping.

Preparation of target surface. — Following normal chemical cleaning, the plate is subjected to a glow discharge at a pressure below 0.1 mm for several minutes. The use of aluminium for the glow discharge electrode avoids sputtering.

A series of tests was made to investigate the effect of prolonged heating of the target (glass) on the adhesion of evaporated aluminium films. Plates were heated to temperatures of up to 390°C for periods of up to 44 h. Two general conclusions arise from these tests :

(a) The adhesion of films to plates which have been subject to glow discharge is better than that for plates which have been pre-heated only.

(b) No significant improvement in adhesion results from prolonged heating of the target after the glow discharge has been used.

The influence of chromium on the adhesion of silver and aluminium to glass. — The adhesion of chromium to glass has been found to be considerably better than that of silver or aluminium. The use of a chromium substrate for improving the adhesion of aluminium for the production of mirrors has long been known. Two possible mechanisms for this process are (1) a « sensitisation » phenomenon similar to that observed by Ditchburn [1] in connection with cadmium or (2) a process in which a crystalline deposit of chromium induces orientation of the superposed aluminium.

Ditchburn has found that when a beam of cadmium atoms whose intensity is of the order 10^{17} atoms : cm^2 : s is allowed to impinge on a glass surface at room temperature, no deposit is obtained. If the glass target is cooled with liquid air, condensation of the cadmium atoms occurs and a visible deposit forms rapidly. Under this condition practically all the impinging cadmium atoms remain on the surface of the glass. When the target at liquid air temperature is exposed to a feeble beam of cadmium atoms for a short time, so that an amount of cadmium corresponding to 10^{-3} – 10^{-2} of a molecular layer is deposited and is then exposed at room temperature, a visible

deposit of cadmium forms. The name "sensitisation" phenomenon is given to this effect.

Experiments were made to determine whether any improvement in the adhesion of aluminium films resulted from the prior deposition of chromium films of the order of 1 molecular layer in thickness. No effect was observed.

If the mechanism (2) above were to operate, films of chromium considerably in excess of a

that part of the target received chromium only part received chromium and aluminium and part.

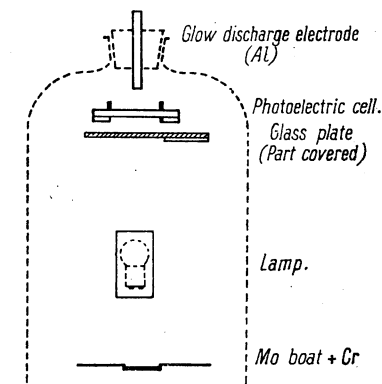


Fig. 3. — Arrangement of apparatus for depositing chromium films and measuring their transmission.

monolayer would be required. It has been shown that evaporated layers a few atoms thick are amorphous. The effect of chromium films of thickness up to some 500 \AA was therefore studied. It is necessary that the thickness of the deposited chromium films be measured in vacuum so that the aluminium layer may be deposited without admitting air to the system, as this would involve the possible complication of the adsorption of a layer of air on the chromium surface. The following simple method proved satisfactory. The relation between thickness of chromium and its transmissibility was first obtained, the transmission measurements being made by mounting a photoelectric cell and lamp in the vacuum chamber. Part of the glass plate was covered with a razor blade so that the chromium film formed a well-defined step on the glass (*fig. 3*). An opaque deposit of silver was then evaporated on to the plate, the razor blade having been removed. The method of Tolansky [2] using multiple-beam Fizeau fringes produced between a heavily silvered optical flat and the test plate enabled the thickness of the chromium layer to be found. Typical fringe steps are shown in figure 4. The relation between transmission and thickness is shown in figure 5. The lamp was covered by a magnetically-operated shutter during the evaporation of the chromium so that errors due to the deposition of scattered chromium atoms on the bulb were avoided.

In the tests on aluminium films it was arranged

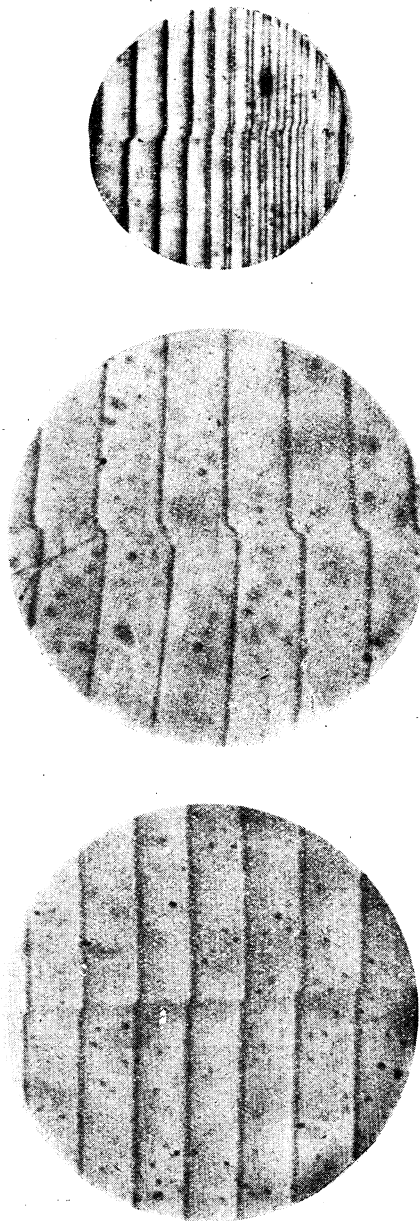


Fig. 4. — Multiple-beam Fizeau fringes used in the determination of the thickness of chromium specimens.

received aluminium only (*fig. 6*). The hardness of the chromium films was used as an indication that no interfering conditions attended. One plate on which the chromium deposit did not adhere well was rejected. Aluminium was deposited until the film on the clear part of the target just became opaque, this corresponding to about 1000 \AA thick-

ness. The adhesion of the aluminium was tested using the scratch test described above and the results are shown in figure 7. It appears that

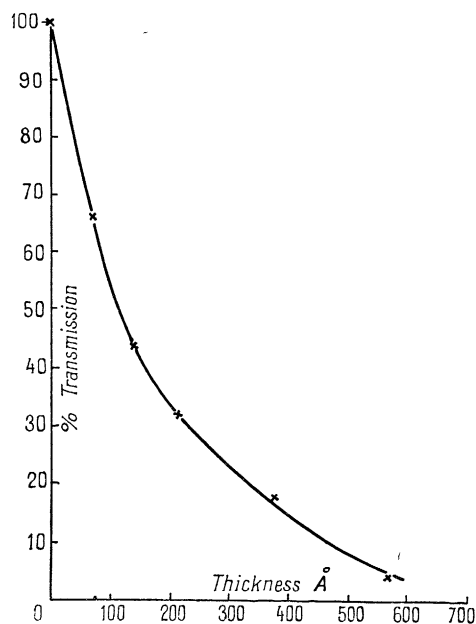


Fig. 5. — Relation between transmission and thickness for evaporated chromium films.

below a thickness of chromium substrate of about 300 Å, a negligible improvement of adhesion results.

In the case of silver films a definite improvement in

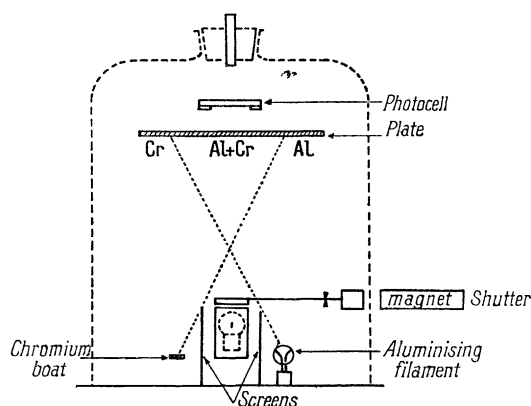


Fig. 6. — Arrangement of apparatus for chromium + aluminium deposition.

adhesion was found for chromium layers up to 300 Å but a much larger increase in adhesion was found

with thicknesses in excess of about 300 Å (fig. 8).

A study of the crystal structures of chromium, aluminium and silver yields the following results.

The (110) planes of the chromium lattice contain atoms lying in a face-centred rectangular array, the dimensions of the rectangle being 4.070 Å by 2.878 Å. The (110) planes of aluminium consist of a rectangular array in which the spacings are 4.041 Å and 2.858 Å. In the case of silver,

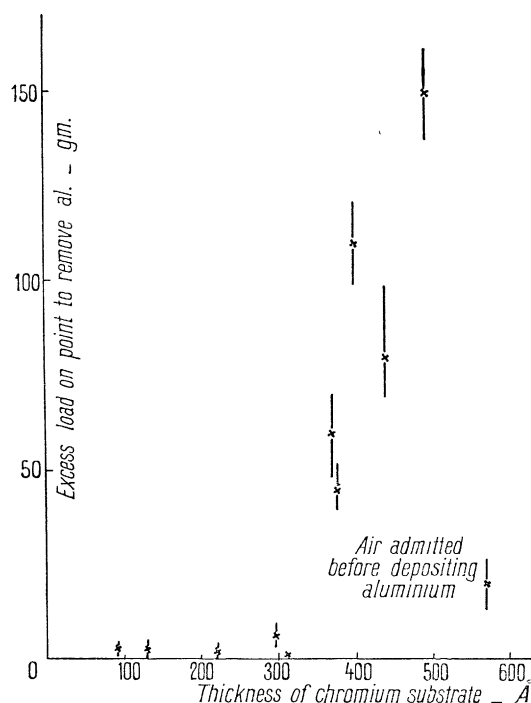


Fig. 7. — Results of adhesion tests on aluminium with chromium substrate.

which has a structure similar to that of aluminium, the inter-atomic distances in the (110) plane are 4.078 Å and 2.884 Å. The aluminium and silver spacings are well within 1 per cent of those of the chromium spacings, so that the possibility of induced crystallisation of the aluminium or silver at the interface with the chromium layer is strong.

Many examples of this type of crystallisation have been found by electron diffraction methods. Finch [3] has shown that when aluminium is deposited on a platinum substrate, the aluminium atoms form tetragonal crystals, their separations in the plane parallel to the interface being shortened by the influence of the underlying platinum lattice. The difference in spacings in this case is 3.2 per cent. Wilman [4] finds that PbS crystals will grow on a rock-salt crystal following the NaCl orientation although the difference in spacing is about 5 per cent.

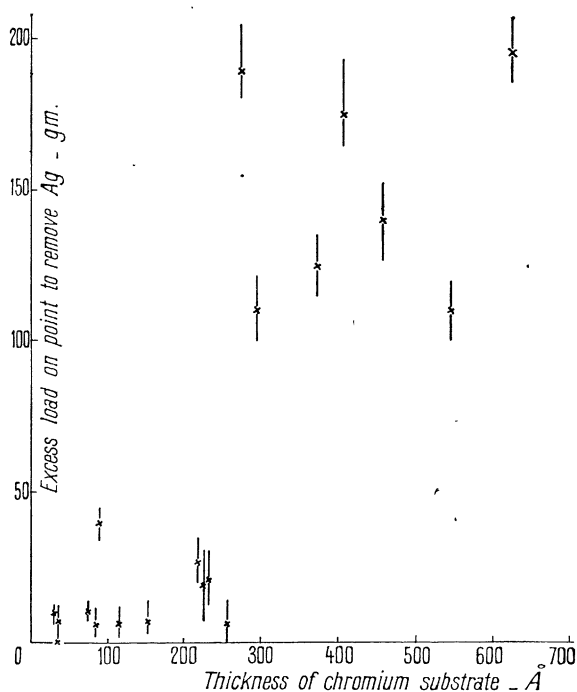


Fig. 8. — Results of adhesion tests on silver with chromium substrate.

Conclusions. — The conditions necessary for the production by evaporation in vacuum of hard metal films with good adherence to the substrate may be summarised as follows :

(1) The pressure in the system should be not greater than 10^{-5} mm Hg.

(2) With mercury as the pumping fluid, trapping with liquid air is required.

(3) With silicone oil as the pumping fluid, trapping with solid CO_2 -acetone is desirable.

(4) Subjecting the target to a glow discharge at below 0.1 mm for several minutes is very effective in cleaning the surface. No advantage results from prolonged heating of the target at a pressure of 10^{-5} mm.

The thickness of chromium films necessary to produce an improvement in adhesion of aluminium and silver films has been found to be about 300 Å. Films of this order of thickness are known to be crystalline from electron diffraction observations [3]. It is suggested that the close similarity of interatomic distances in the chromium, aluminium and silver lattices induces oriented crystalline regions in the superposed films, and thus produces strong binding between the two layers.

REFERENCES.

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- [2] TOLANSKY. — Multiple Beam Interferometry, 147, Oxford 1948.
- [3] FINCH, QUARREL and WILMAN. — *Trans. Farad. Soc.*, 1935, **31**, 1051.
- [4] ELLEMAN and WILMAN. — *Proc. Phys. Soc.*, 1948, **61**, 164.

Intervention de M. Kuhn.

The influence of the residual gas on the properties of the metal films is presumably produced by the occlusion of foreign gas atoms into the structure of the metal. If this is true, the ratio of the rates of bombardment of the target by gas atoms to that by metal atoms should be the decisive factor. To

test this view, we carried out several aluminium depositions with different distances of the target from the source, thus varying the speed of deposition at constant gas pressure. We found markedly higher values of reflectivity for smaller distances, which appears to support the assumption made.

Intervention de M. Arnulf.

L'expérience nous a montré qu'il y a le plus grand intérêt à effectuer les essais d'adhérence des couches immédiatement à la sortie des échantillons de la cloche à vide. Une couche bien adhérente dans ces

conditions offrira ultérieurement la meilleure résistance possible aux actions mécaniques, chimiques et atmosphériques.

Intervention de M. W. Scott.

Before a glass mirror form is placed in the coating tank it is cleaned with aerosol and concentrated chromic acid cleaning solution. The thoroughly rinsed form is carefully dried with a soft oil-free cotton cloth—well laundered diaper cloth has proved satisfactory.

The chemically cleaned form, which is subsequently subjected to the cleaning action of a d. c. glow discharge, is placed in the coating tank.

The pressure in the tank is reduced to about 5×10^{-5} mm Hg; the high vacuum valve is closed, and air is admitted through a needle valve until the pressure is high enough so that a potential of 5 000 V d. c. will cause a current of approximately 15 mA to flow (These figures are for a 40 cm diameter tank). After the glow discharge has continued for about ten minutes the high vacuum valve is opened and the chamber is again evacuated to a pressure of about 5×10^{-5} mm Hg. The aluminium coating is applied while the mirror form is still warm.

The electrode for the glow discharge is a thick annular ring of aluminium placed parallel and as close to the bottom of the tank as practicable. It is made negative with respect to the baseplate which is at ground potential. It is important that the discharge heat the mirror form hotter than any other part of the coating chamber otherwise volatile materials may evaporate from the heated portions and condense on the mirror form resulting in poor adherence of coatings.

When large curved surfaces are to be coated it is advisable to use a cathode having a curved surface approximately paralleling the surface to be bombarded.

When a glass coating tank is used a heat-conducting cylindrical metal shield is placed inside the bell-jar. This shield prevents accumulation of heat at undesired places and prevents the bell-jar from becoming coated.
