

STUDY OF METAL FILM ON GLASS SURFACE

by B. K. BANERJEE, *I.C.I. Research Fellow, N.I.S.I., Indian Association for the Cultivation of Science, Jadavpur, Calcutta 32*

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INTRODUCTION

The problem of deposition of metal film at the glass surface has a great technical importance. The electrodeposition of metal on metal is known for a long time and in this case some interesting observations have been made such as lattice distortion, selective orientation, etc., of the deposited metal. Although glass is non-metal, yet numerous methods are known such as metal sputtering process, chemical reduction process, pyrolysis of organometallic compounds, etc., whereby an adherent metal film can be deposited at the glass surface. It is known that the surface structure of glass plays a leading rôle in the process of formation of metal film at the glass surface.

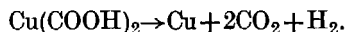
Recently a large amount of work has been done on the structure of glass surface. Weyl (1945, 1948), K. Nakanishi (1933), and a few other workers are responsible for a considerable advancement in that direction. It is quite evident from their works that the structure of glass surface is quite different from that of the bulk. As a matter of fact, by contact with liquids containing metallic cations the glass surface modifies its structure by ion-exchange of the Na ions of the glass surface with the metallic cations of the liquid. H. Devaux and H. Aubel (1927) demonstrated the validity of ion-exchange mechanism on the glass surface with the dilute CaSO_4 solution. Weyl and Williams (1945) made a successful application of ion-exchange process in the preparation of red Cu-glass. In the case of silvering of the glass by the chemical process ion-exchange mechanism is also a potent factor. It is worthwhile to mention here that the ion-exchange mechanism itself produces no colour change at the glass surface; the colour is due to the reduction of the metallic cations to the elemental state by the reducing agent already present in the glass and then the aggregation of metal to the crystal or colloidal size.

In view of the above facts it will be interesting to make an investigation of: (1) the change in the structure of glass undergone by keeping it in contact with the solution of noble metals, (2) the nature of the metal film deposited on the glass surface by the chemical reduction process as well as by the pyrolysis of the organometallic compounds and (3) the effect of temperature on the metal film deposited on the glass surface.

EXPERIMENTAL

Prior to the deposition of the metal film on the glass surface of high alkali content (17% Na_2O), glass specimen was thoroughly cleaned and then heated to about 500–550°C. for half an hour whereby the concentration of Na ions increases at the glass surface. In some cases the glass specimen was treated with a solution of SnCl_2 and due to that operation, some Na ions at the glass surface are exchanged for Sn^{++} ions. After the above preliminary treatment of the glass specimens, metal films of Au, Cu and Ag were deposited on the surface in the following way.

Cu films were deposited on the glass surface by two distinct processes (1) pyrolysis of organometallic salt of Cu and (2) chemical reduction process. By rapidly heating copper formate in a thin test tube at about 150°–200°C, a bright mirror of Cu is deposited at the inner glass surface of the test tube due to the decomposition of copper formate in the following way:—



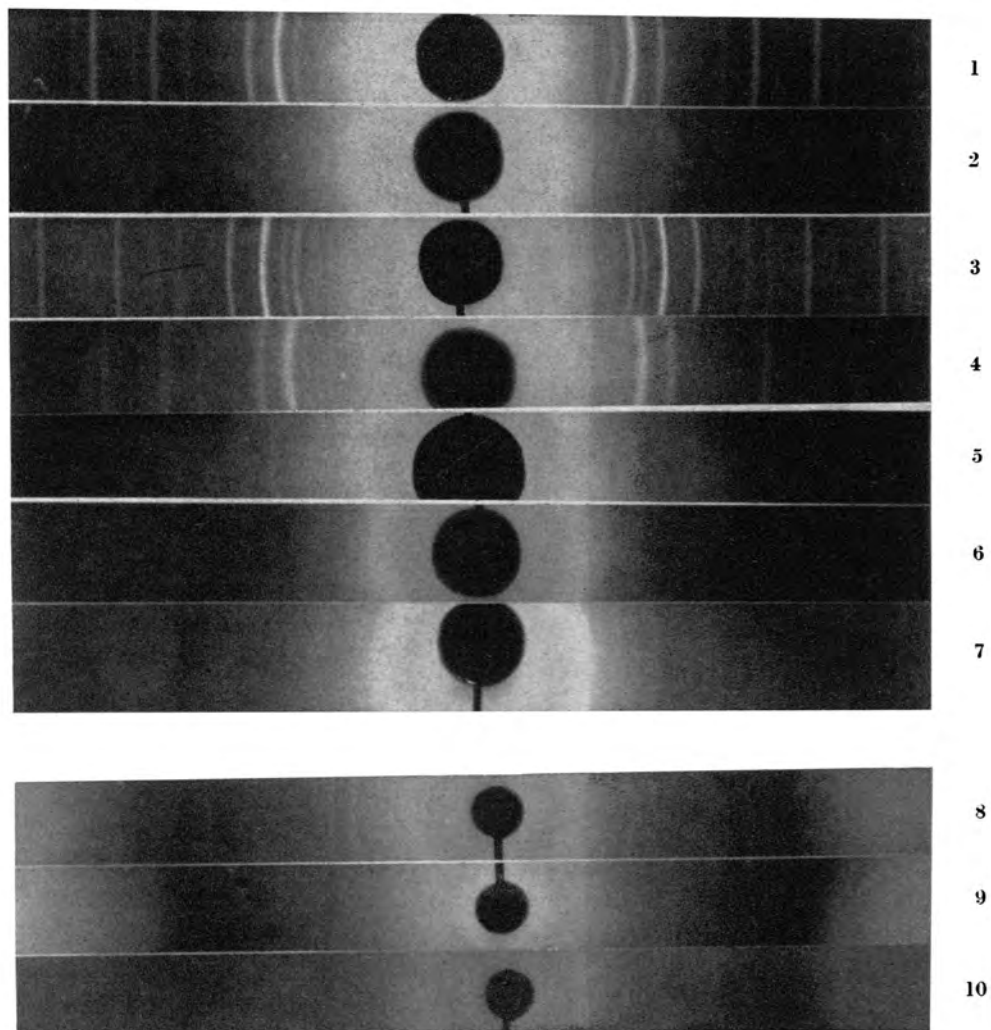
Similarly a film of Cu is also deposited at the glass surface by the reduction of alkaline cupric tartrate solution by formaldehyde solution. Silver is deposited at the glass surface from the ammoniacal silver nitrate solution by formaldehyde reduction process as well as by Brashear's process. Methods adopted for the film deposition of copper and silver are quite well known and the metal is usually supplied in the form of complex ions. In the case of gold, a slight departure was made from the usual process. A thin film of gold was deposited at the glass surface by keeping 7.5 per cent Auric chloride solution in contact with the glass surface for a long time. Similar result was obtained by keeping of 5 per cent AuCl_3 solution and 40 per cent formaldehyde solution in the volume ratio of 1 : 3 for a few days. In the case of gold, the above two processes are very slow. Platinum was deposited on the glass surface by Prof. Bottger's method (vide *The Scientific America Cyclopaedia for Formula*, Vol. I, p. 499).

The thickness of the metal film can be controlled by the manipulation of the experimental condition. Each process has its own limitation and within a certain range the thickness of the metal film can be varied. Generally the thickness of the film is of the order of colloidal dimension. In some cases the film is almost transparent or translucent in transmitted light. Again in some cases the thickness is such that it is almost opaque in transmitted light. But in every case there is a metallic reflexion in the reflected light.

Use has been made of X-ray diffraction method for the determination of the nature of the film as well as for the estimation of the size of the constituents of the metal film. The investigation is confined to the specimens of appreciable thickness, otherwise if the thickness of metal film is very small, no useful result is obtained from the X-ray diffraction study, although in those cases the electron diffraction study is quite helpful. The usual Hadding type of the X-ray apparatus has been used for that purpose and the tube was run at 60 KVP copper anti-cathode with 20 milliamperes tube current. The diffraction photographs of some representative specimens have been shown in Plate VIII. The X-ray pictures of those specimens reveal the presence of both band and lines. Band is due to the glass base and broad lines are due to the metal film. The data of spacing are given in the following table.

TABLE I

Gold			Silver		
Spacing	Intensity	Plane	Spacing	Intensity	Plane
2.35 Å	s	(111)	2.36 Å	s	(111)
2.03 Å	ms	(200)	2.04 Å	ms	(200)
1.439 Å	m	(220)	1.445 Å	m	(220)
1.227 Å	m	(311)	1.232 Å	ms	(311)
1.173 Å	mw	(222)	1.179 Å	mw	(222)
1.019 Å	w	(400)	1.022 Å	w	(400)



1. Silver (Brashear's process).
2. Cu (Alkaline Cupric tartrate process).
3. Cu (Pyrolysis process).
4. Gold (Formaldehyde process).
5. Platinum (Böttger's process).
6. Platinum (After heat-treatment).
7. Cu (After heat-treatment) (Camera radius 3.9 cm.).
8. Silver (Formaldehyde process).
9. Gold (AuCl₃ Solution process).
10. Gold (After heat-treatment) (Camera radius 2.975 cm.).

TABLE I—*contd.*

Copper			Platinum		
Spacing	Intensity	Plane	Spacing	Intensity	Plane
2.08 Å	s	(111)	2.25 Å	s	(111)
1.81 Å	ms	(200)	1.95 Å	ms	(200)
1.277 Å	m	(220)	1.382 Å	ms	(220)
1.089 Å	m	(311)	1.178 Å	m	(311)
1.043 Å	mw	(222)	1.128 Å	w	(222)
0.905 Å	w	(400)			

In each case the composition of the respective metal film consists of metal only with the exception of copper film deposited by the pyrolysis of copper formate where the presence of Cu_2O , denoted by the lines corresponding to the spacing in 3.00 Å (vw), 2.45 Å (mw), 2.12 Å (w), 1.51 Å (w), 1.283 Å (w), are found in the X-ray picture but the amount of Cu(ous) oxide is very very small. It is further observed that by making pyrolysis operation in vacuum, even that trace of Cu(ous) oxide formation can be avoided.

The size of the particle of the film has been determined by the half intensity width method from the following relation of Scherrer:—

$$\beta = \frac{K\lambda}{L \cos \theta} + \mathcal{S}.$$

where β = the breadth of diffraction interference at points of half maximum intensity in radians.

λ = wavelength of X-rays.

θ = the angle of diffraction

L = the edge-length of the crystal considered as cubic.

\mathcal{S} = the mutual breadth of the Debye-Scherrer line which is constant depending upon the particular apparatus, size and absorption of the specimen.

K = a constant, the value of which is 0.90. In the present case an apparent particle size has been determined by ignoring the broadening due to the instrumental factor \mathcal{S} .

TABLE II

Description of the specimen		Apparent Particle size
Metal	Method of Film deposition	
Silver ..	Formaldehyde	35 Å
Silver ..	Brashear's process	44 Å
Gold ..	Formaldehyde and AuCl_3 solution	40 Å
Gold ..	AuCl_3 solution only	100 Å
Copper ..	Pyrolysis of Cu-formate	56 Å
Copper ..	Alkaline cupric tartrate formaldehyde reduction Process	120 Å
Platinum	Böttger's process	48 Å

The size of the particle has been given in Table II and the X-ray pictures of some representative specimens have been shown in Plate VIII.

THE EFFECT OF TEMPERATURE ON THE METAL FILM.

It is well known that the same metal film may show a variety of colours if its physical condition is altered. From that point of view it will be interesting to study the effect of heat treatment of those specimens studied in the present paper. Each specimen was kept at 700°C.–800°C. for 8 hours in a large access of air. The silver specimen turns yellow, copper specimen changes to green, platinum specimen turns slightly greyish and gold specimen turns pink. No doubt the metallic reflection of film also disappeared after heat-treatment. This change is evidently due to the diffusion of the metal either in the ionic state or the elemental state as the case may be, into the interior of the specimen. As a matter of fact the specimen which formerly revealed the presence of lines of moderate intensity in the X-ray diffraction picture, only shows very weak lines of the metal in the X-ray picture after heat-treatment. But in the case of Cu-film, after heat-treatment, the lines of α -cristobalite have been identified. The X-ray picture of that specimen has been shown in Plate VIII and the spacings of those lines are:— 4.04 Å, 3.13 Å, 2.85 Å, 2.48 Å, 2.11 Å. That is apparently due to devitrification of glassy matrix.

ABSTRACT

In the present communication, the nature of the adherent film of different metals such as gold, silver and copper deposited by chemical method as well as by the pyrolysis method, has been studied, and in that connection the size of the metal composing the film has been determined. Further the effect of temperature on the nature of the film has also been investigated. It has been found that the size of the particle composing the film is of colloidal dimension and with temperature treatment, the metallic reflection of the film diminishes considerably and ultimately a transparent glass is formed having a distinct colouration different from the original specimen. The vitreous characteristic of the specimen is retained in the case of Au and Ag after heat-treatment whereas in the case of copper, the partial devitrification of the glassy matrix takes place.

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REFERENCES

- Devaux, H. and Aubel, H. (1927). The adsorption of ions by glasses. *Compt. Rend.*, **184**, 601.
Nakanishi, K. (1933). Effect of gases upon the properties of glass. *J. Soc. Chem. Ind. Japan*, **36**, 595 B, 672 B.
Weyl, W. A. and Marboe, E. C. (1945). Chemical deposition of Copper mirrors on glass. *Glass Ind.*, **26**, 119, 136, 142, 149.
Weyl, W. A. and Williams, H. S. (1945). Surface dealcalization of finished glassware. *Glass Industry*, **26**, 275, 290, 301, 324, 339, 341 and 344.
Weyl, W. A. (1948). The effect of polarized heavy metal ions on the surface properties of glass. *J. Soc. Glass Tech.*, **32**, 247.