ELECTRON-DIFFRACTION STUDY OF AN THE STRUCTURE OF ELECTRO - DEPOSITED METALS.

By G. I. FINCH AND C. H. SUN, PH.D.

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1. Introduction.

A more or less pronounced tendency for the crystals to orientate in accordance with a position of maximum mechanical stability can generally be observed when a crystalline film is formed by the deposition of crystals upon a substrate. For example, in the case of colloidal solution of graphite, the crystals of which are known to be exceedingly thin in the c axial direction but of relatively large cleavage plane dimensions, the particles settle out in such a manner that this plane is parallel to the On the other hand, when the crystals are formed on the substrate. substrate as, for example, by the condensation of vapour or by chemical attack, the substrate may either serve as a virtually inert supporting medium in contact with which the most readily formed external plane of the crystal is developed, or the substrate crystals may themselves govern the orientation of the deposited crystals by determining the type of face first developed on condensation. Many examples are known of the first case which is, in effect, virtually the parallel to that in which already formed crystals take up an orientation imposed by considerations of Thus, Kirchner¹ found that cadmium iodide mechanical stability. formed by the condensation of the vapour on a celluloid film was orientated with the (001) planes parallel to the support, and even more striking was Jenkins' 2 observation that the crystalline oxide scums on molten lead, tin, zinc and bismuth displayed similar orientation effects. amples of the substrate playing the much more active rôle of causing the deposit crystals to adopt the orientation of those of the substrate are less frequent, but well-authenticated cases of crystals being constrained by the substrate into taking up unusual modes of orientation are known. Thomson,³ for example, showed that silver electro-deposited on an etched copper cube face rigidly followed the orientation of the copper;

¹ Kirchner, Ergeb. exakt. Naturw., 1932, 11, 64.

² Jenkins, Proc. Physic. Soc., 1935, **47**, 109. ³ Thomson, Proc. Roy. Soc., 1931, **A133**, 1.

and Finch, Quarrell and Wilman⁴ found that crystals formed by the cathodic sputtering of gold under conditions favourable to the production of a random film exhibited (III) orientation when deposited on platinum of similar orientation, but were randomly disposed when grown on a glass surface. Even more intense are substrate effects such as those giving rise to the phenomenon of pseudomorphism ⁵ and the dissolution of crystalline metal films in the polish layer on metals.⁶

Jenkins 7 and Finch, Quarrell and Wilman 4 have drawn attention to the fact that a film of orientated graphite crystals adheres much more strongly to a substrate than does a similar but unorientated layer, and Finch, Quarrell and Roebuck ⁶ remarked that certain metal films formed by condensation of the vapour are firmly held only by a polished but not by a crystalline metal substrate. On the other hand, as far as we are aware, the effect on the adhesion of a deposit, the crystal orientation of which has been determined by that of the substrate, has not been examined.

Some of the problems hinted at in these introductory remarks have already been the subject of study by X-rays.⁸ The limitations of this method, however, when applied to such cases of surface phenomena are obvious. Thus, our interest centres in the main about the region of contact between substrate and deposit; and a probable change between abnormality in, for example, the orientation in the first deposit layers and a more usual type of orientation possibly reverted to with growing film thickness might well escape detection by X-rays, particularly if the change were at all rapid. On the other hand, the subject is one which appears eminently suitable for study by the method of electron diffraction.

The object of the experiments described below was to study by electron diffraction surface orientation effects and their associated phenomena as exhibited by electro-deposited metal films, not only at grazing incidence but also by transmission. In addition to preparing specimens mounted on massive substrates and therefore only suitable for examination at grazing incidence, we have been able to devise methods for producing robust metal films, by either electrodeposition or chemical displacement, which were sufficiently thin for transmission purposes and consisted, as desired, of the deposit either alone or together with the substrate. We have found, inter alia, that whilst in the case of chemical deposition the change from substrate to deposit is a gradual one of alloying, in electrodeposition the composition change is abrupt, though the substrate orientation nearly always profoundly affects that of the initial deposit layers. In certain cases, characterised by inability of the substrate to impose a definite orientation on the crystals in the deposit, poor adhesion was observed.

2. Preparation of Reflection Specimens.

The metal to be examined was electrodeposited either on to a metal layer previously deposited on a suitable metal disc, such as copper, or directly on to the disc. After plating, the specimen was washed with

- Finch, Quarrell and Wilman, Trans. Faraday Soc., 1935, 31, 1051.
 Finch and Quarrell, Proc. Roy. Soc., 1933, A141, 398.
 Finch, Quarrell and Roebuck, *ibid.*, 1934, A145, 676.

⁷ Jenkins, Phil. Mag., 1934, 17, 457. ⁸ Frolich, etc., Trans. Am. Electrochem. Soc., 1926, 49, 369; Wood, Proc. Physic. Soc., 1931, 43, 138.

distilled water and rapidly dried by evacuation in the electron-diffraction camera. The deposition conditions are given in Table I.

| Metal. | Bath Composition (g./l). | Current Density A/dm ² . | Bath Temperature °C. |
|---------------------|--|---|----------------------------|
| Cu | Cu(C ₂ H ₃ O ₂) ₂ . H ₂ O, 25 g. ; Na ₂ SO ₃ . H ₂ O, 50 g. ; | | |
| | KCN, 35 g.; Na_2CO_3 , 10 g. | 0.3 | 20 |
| Au | AuCl ₃ . NaCl, 2 g.; KCN, 15 g. | 0.1 | 50 |
| Ag | AgCN, 36 g.; KCN, 52 g.; K_2CO_3 , 38 g. | 1.0 | 20 |
| Fe | $FeSO_4 . (NH_4)_2SO_4 . 6H_2O, 350 g. ; H_2SO_4, 2.5 g.$ | 1.0 | 20 |
| Co | $CoSO_4$. $(NH_4)_2SO_4$. $6H_2O$, 175 g.; NaCl, 17 g.; | | 1 |
| | $H_{3}BO_{3}$, 50 g. | 1.0 | 20 |
| N1 | $N_1SO_4 \cdot 7H_2O_7, 50 \text{ g.}; Na_3C_6H_5O_7, 20 \text{ g.}$ | 0.5 | 50 |
| Sn | $SnCl_2 \cdot 2H_2O, 11.5g.$; KOH, 62g.; KCN, 13.5g. | 0.2 | 50 |
| As | As ${}_{2}O_{3}$, 50 g.; KCN, 50 g.; Na ${}_{4}P_{2}O_{7}$. H ${}_{2}O$, 20 g. | 7.0 | 80 |
| Sb (amorphous) | SbCl ₃ , 200 g.; HCl, 300 c.c. | 8.0 | 80 |
| Sb (crystalline) | Schlippe's salt, 50 g.; Na_2CO_8 , 10 g. | 0.2 | 70 |
| Bi | $B_{1_2}O_3$, CO_3 , H_2O , 47 g.; H_2CIO_4 , 19 g. | 0.2 | 50 |
| Cr | CrO_3 , 250 g.; H_2SO_4 , 2.5 g. | 13.2 | 20 |
| a-Brass | $Cu(C_2H_3O_2)_2H_2O, 12.5 g.; KCN, 23 g.;$ $Zn(C_2H_3O_2)_2 H_2O, 16.2 g.; Na_2CO_3, 10 g.;$ | | |
| Pt | Na2SO3 . H2O, 50 g. H2PtCl6 . 6H2O, 13·3 g. ; (NH4)2HPO4, 45 g. ; | 0.2 | 20 |
| | Na ₂ HPO ₄ . 12H ₂ O, 240 g. | 0.4 | 70 |
| Cd (as basis metal) | CdO, 32 g. ; NaCN, 75 g. | 1-1.5 | 20 |
| Zn (as basis metal) | ZnSO ₄ . 7H ₂ O, 240 g. ; NH ₄ Cl, 15 g. ; | | |
| | Al ₂ (SO ₄) ₃ . 18H ₂ O, 30 g. | 5-10 | 20 |

TABLE I.

3. Orientation in the Absence of Substrate Effects.

Preliminary experiments were carried out with the main object of determining the normal type of crystal orientation assumed in the various metal films formed under the electrodeposition conditions outlined in Table I. Amorphous or polished metal substrates were used in order to preclude as far as possible any specific orientating influence such as might possibly be exerted by the crystalline substrate. The results obtained are summarised in Table II., and typical patterns illustrating some of the more striking orientation effects are produced in Figs. 1, 2 and 3. As previously,⁴ we continue to define the direction of orientation in terms of the indices of planes parallel to the substrate surface or specimen film.

In the case of zinc, evidence was obtained of the layers first deposited going into solution in the polished copper surface. Thus, in order to obtain a zinc layer sufficiently thick to afford a pattern recognisable as characteristic of a crystalline structure, it was necessary to deposit from the cyanide bath at 0.08 A./dm.^2 and 20° C. during at least 3 minutes on to a polished copper substrate, whilst 30 seconds sufficed with a crystalline copper substrate, other conditions being the same. In view of the results obtained by Finch, Quarrell and Roebuck ⁶ in their study of the surface action of the Beilby layer it is quite probable that a similar preliminary solution of deposit in substrate occurred to a greater or lesser extent in the majority of the cases of deposition on polished substrates set forth in Table II. The fact that even the thin deposits on arsenic were for the most part well orientated supports this view and suggests further that the electrodeposited arsenic substrate was not in fact amorphous but consisted rather of exceedingly small crystals.

The types of orientation set forth in Table II. and exhibited by thin

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layers on arsenic and by all the thick deposits may be taken as normal and representative of the plating conditions outlined in Table I. In some cases, for example, α -brass and gold, where in the same specimen some crystals exhibited one and others another direction of orientation, the second type of orientation has been traced to bath concentration changes occurring during deposition. Thus, a fresh gold bath always led to a mixture of (111) and (100) orientated crystals, whilst a partially used bath in which the gold contents had been enriched from the anode yielded crystals of (111) (Fig. 2) orientation alone.

| TADLE II.—SUBSTRATE ORIENTATION EFFECTS ON AMORPHOUS SURFAC. | TABLE | II.—Substrate | ORIENTATION | Effects | ON | Amorphous | SURFACES |
|--|-------|---------------|-------------|---------|----|-----------|----------|
|--|-------|---------------|-------------|---------|----|-----------|----------|

| Substrate. | Substrate Structure. | Deposit. | Orientation in Thin Deposit. | Orientation in Thick Deposit. |
|--------------|----------------------|---|--|--|
| Cu, polished | Amorphous | Cu Au Ni Fe α-Brass Pt Sn Bi Zn | Random Random Random (111) Random Random Random (Fig. 3) Random | (110) (111) (Fig. 2) (110) (111) (Fig. 1) (111) and (311) (111) (231) No definite pattern No definite |
| Ni, polished | Amorphous | Ni | Random | (110) |
| | - | Au | Random | (111) |
| Au, polished | Amorphous | Au | Random | (111) |
| | (Amorphous (?), | ſ Au | (100) | (111) and (100) |
| | or very | Cu weak | (110) | (110) |
| As, electro- | | { Ni | (110) | (110) |
| deposited | crystals | Fe | (111) | (111) (Fig. 1) |
| | l | C-Brass | (111) | (111) and (311) |

4. Substrate Orientation Effects.

In these experiments a basis metal was electrodeposited on to a polished copper disc either in the form of a thin layer exhibiting random crystal array, or to a thickness such that it showed well the normal type of orientation as set forth in Table II., and the specimen metal was in turn deposited on this basis as substrate, the plating conditions being as given in Table I.

When the substrate consisted of fairly large (50-100 A) crystals in random array, it was found that thin films of iron on copper and of gold or copper on nickel were unorientated, but displayed their normal characteristic orientations with sufficient thickening of the deposits. Thus, thick iron, gold and copper exhibited (111), (111) and (110) orientations respec-These results suggested a strong substrate orientating influence tively. on the first deposit layers, because otherwise we would have expected to find similar orientations in both thick and thin deposits. This view was strikingly confirmed by results obtained with deposits on electrodeposited substrates the crystals of which were well orientated. The results are set forth in Table III. and representative patterns illustrating some of the more unusual modes of orientation observed and due to substrate effect are reproduced in Figs. 4, 5 and 6. The outstanding feature of these results is that the crystal orientations

The outstanding feature of these results is that the crystal orientations of the thin deposits were abnormal except in those few cases where the substrate orientation followed that of the normal type as taken up by the deposit under the conditions outlined in Tables I. and II., or when either copper or nickel were deposited on iron of normal orientation. Further,

the crystal orientation of a thin face-centred cubic metal layer formed on a substrate of similar structure, but of an orientation not normally assumed by the deposited metal, followed that of the substrate, though sometimes some differently orientated crystals were also formed, as in the case of copper (Fig. 6) and nickel on gold in (111) and copper on platinum, likewise in (111) orientation. With increasing thickness of the deposits the orientation in general tended to become less pronounced, and in the cases of nickel and copper on gold in (111) orientation, where the progressive changes could readily be followed, it was observed that this loss in orientation went so

| Electro- deposited Substrate. | Substrate Crystal Orientation. | Deposit. | Orientation in Thin Deposit. | Orientation in Thick Deposit. |
|-------------------------------------|-----------------------------------|---------------------------------|---|---|
| Cu | (110) | Au Ni α-Brass Fe Bi | (110)* (110) (110)* (100)* Random* | (111) (110) (111) and (113) (111) ? |
| Ni | (110) | Cu Au Fe | (110) (110)* (100)* (Fig. 4) | (IIO) (III) (III) |
| Au | (110)‡ | (Bi Fe (Cu | Random* (100)* (111)* and (100)* (Fig. 6) | (111) |
| Au | (111) | N1 Ag Pt | (III)* and (I00)* (III) (III) (III) | (110) (111) (111) |
| Cu | (111) and (100)‡ | Fe Sn Fe Sn | (110)* (110, 5) (110)* (110)* (110)* | (111) (231) (111) (231) |
| Ni | (111) and (100)§ | Fe Sn Cu | (110)* Random* (110) | (111) (231) (110) |
| Fe | (111) | Ni Bi | (110) Random* | (110) |
| Pt Sn | (111) (231) | Cu Ni | (111)* and (100)* Random* | (110) |

TABLE III.—SUBSTRATE ORIENTATION EFFECTS OF THICK ELECTRODEPOSITS.

* Unusual types of orientations for the electrodeposition conditions used are asterisked.

† Gold in (110) orientation was obtained by deposition on a (110) nickel substrate.

[‡] Obtained by depositing a thin layer of copper on a (111) gold substrate.

§ Obtained by depositing a thin layer of nickel on a (111) gold substrate.

 $\|$ No pattern could be obtained without interfering with and destroying the surface structure by scratching, etc.

far that the patterns became almost characteristic of a random crystal array. With still further thickening, however, crystal orientation once more became pronounced but was now of the normal type. Estimates based on the deposition conditions showed that the effect of the substrate on the crystal orientation in the deposit could still be detected up to a thickness which depended upon the nature of the metal, but was generally of the order of 1,000 A., and that the normal type of orientation did not as a rule appear strongly until the deposit had become considerably thicker. The persistence of the substrate influence was most marked with nickel and was somewhat affected by the nature of the substrate, being greatest in the case of gold and decreasing with tin, α -brass and copper. Even on

gold, however, the substrate effect was completely lost when the nickel deposit thickness was of the order of 2,000 A.

No substrate orientating influence could be detected with copper or nickel on iron; thus at a thickness estimated at only 50 A. the normal (110) orientation appeared in both cases.

Unlike the face-centred cubic deposits on face-centred cubic substrates, the body-centred cubic metal, iron, did not follow the substrate orientation, but exhibited nevertheless a strong substrate influence in that the crystal orientation in thin layers was abnormal; in general this was such that the atom population density in the orientation plane of the deposit crystals approached to that of the substrate. This was also the case with tin on gold or copper.

We have examined the adhesion of the deposits enumerated in Table III. by comparing their resistance to abrasion by rubbing between dry fingers. All showed by this rough test good powers of adhesion with the exception of nickel on tin, and bismuth on iron, nickel or copper, all of which rubbed off easily. Thus it would seem that ability to orientate, even in the thin initial layers of an electro-deposit, is of advantage in securing good adhesion.

5. The Preparation of Transmission Specimens.

As in the case of the experiments outlined above, the electron diffraction examination of the orientating effects of crystalline substrates have hitherto always been carried out with the beam at grazing incidence on specimens mounted on massive substrates. Certain disadvantages are inherent in Thus there is some degree of uncertainty as to the effective this method. camera length, and the error involved might well tend to obscure any lattice distortion effect produced by the substrate. A further inaccuracy is liable to be introduced by the small height to which the crystals project over the shadow-throwing surface; for it is now a matter of experience that, compared with transmission, "reflection" patterns are often inferior from the point of view of ring sharpness, and in many cases the difference in definition is largely to be ascribed to the relaxation of the Laue diffraction condition corresponding to the direction normal to grazed specimen surface. It was chiefly for these reasons that in continuing this study of substrate effects we turned to the use of transmission specimens.

Two methods for preparing this type of specimen by electro-deposition have been developed and previously described,⁴ but have since been considerably improved. In the one, commercial metal leaf floating on the plating bath served as cathode under the conditions outlined in Table I. and was removed from the resulting deposit by submersion in a suitable etching bath. The second method, of more general utility, led to the production of robust transmission specimens which were remarkably uniform in thickness and yielded good diffraction patterns throughout their whole area. In general, the procedure consisted in plating a polished stainless steel disc with a thick layer of some suitable "basis" metal under the conditions outline in Table I. After washing, the disc was further plated with the metal required for examination. The composite basis and specimen metal film was then stripped off the disc and immersed in a reagent to dissolve away the basis metal whilst leaving the specimen metal intact.

In the case of iron, tin, bismuth or arsenic it was found necessary first to plate the steel disc with an exceedingly thin layer of copper or nickel before forming the basis metal film. In this manner iron or tin basis films were deposited on coppered, and bismuth or arsenic on either coppered or nickeled polished stainless steel. The conditions for the electrodeposition of the specimen layer on the basis metal are set forth in sufficient detail in a previous communication 4 and in the further particulars enumerated above in Table I.

After washing to remove the etching reagent, the specimen was picked up on a fine-meshed nickel gauze and transferred whilst still moist to the

camera and rapidly dried by evacuation. The time of deposition varied with the nature of the metal and current density between a few seconds and about r minute. The strength of the specimen film depended largely on the bath temperature and current density and also, though to a lesser extent, on the nature and texture of the basis metal layer. Owing to the low current densities employed, the crystal size increased with, and was determined in the main by, the time of deposition. Composite transmission specimens consisting of two electrodeposited metal layers were also obtained by this method, the second metal being either deposited on the first thin specimen layer prior to stripping, or plated on to a floating and previously suitably thinned leaf acting as cathode.

The preparation of transmission specimens by chemical displacement generally involved the prior formation by electrodeposition and isolation of a thin film of the displacing metal, which was then floated on a suitable salt solution of the metal to be displaced. In some cases a relatively thick film was used, and the excess of metal remaining after partial exchange was removed by the appropriate etching reagent.

6. Orientation in Composite Transmission Films.

In these experiments the specimens consisted of a metal electrodeposited on a commercial leaf which had previously been suitably thinned for transmission purposes. The results are incorporated in Table IV. and illustrated by the patterns, Figs. 7, 8 and 9, which show that the substrates in most cases consisted of more or less well-developed single crystals.

| TABLE | IV.—SUBSTRATE | ORIENTATION | Effects | ON | Electro-Deposits | OF |
|-------|---------------|---------------|------------|-------|------------------|----|
| | Superin | iposed Transi | MISSION SE | PECIN | IENS. | |

| Substrate | Substrate Crystal Orientation. | Deposit. | Orientation in Deposit. | | | |
|-----------------------|--------------------------------------|----------|-------------------------|--|--|--|
| (Commercial Leaf). | | | First Direction. | Second Direction. | | |
| Pt | (110) | Cu | (110) (Fig. 7) | (110) _{Pt} parallel to | | |
| | | Ni | (110) (Fig. 8) | (110) _{Cu} (110) _{Pt} parallel to | | |
| | | Со | (110) | (110) _{Ni} (110) _{Pt} parallel to | | |
| Pd | (100) | Cu | (100) | (110) _{Co} (100) _{Pd} parallel to | | |
| | | Fe | (100) | (100) _{Cu} (110) _{Pd} parallel to | | |
| Au | (100) | Fe | (100) (Fig. 9) | (100) _{Fe} (110) _{Au} parallel to | | |
| | | Co | (100) | (100) _{Fe} (100) _{Au} parallel to | | |
| | | Ni | (100) | (100) _{Co} (110) _{Au} parallel to | | |
| | | | | (100) _{Ni} | | |

These results show that the deposit crystals, like those of the substrate, always exhibited two directions of orientation, at least one of which was common to both substrate and deposit, and the patterns, Figs. 7, 8 and 9, afford convincing evidence of the remarkable degree of faithfulness with which the substrate crystal orientation is followed in these thin films by the deposit. In Figs. 7 and 8, for example, the arcs due to copper and nickel respectively are virtually exact replicas of the corresponding platinum diffractions, even to the reproduction of minute dots due to larger crystals.

The manner in which the body-centred cubic structure, iron, orientates on a face-centred cubic metal, such as palladium or gold, is of particular interest in that it differs from that encountered in the case of superimposed face-centred cubic structures. Although substrate and deposit crystas continue to possess in common one degree of orientation in that they have similar, *i.e.*, cube, faces in contact, the respective cube edges in the specimen plane are not parallel but inclined at 45° to each other, with the result that (110) and (100) planes normal to the specimen film in substrate and deposit respectively are parallel to each other. This is clearly a case of a substrate influence complied with by the deposit in such a manner as to lead to as strain-free an arrangement of the atoms in the substrate-deposit interface as possible. Thus, in the pattern, Fig. 9, the gold and iron spacings are such that the 200, 220, etc., gold diffractions coincide with 110, 200, etc., of iron respectively, and it is not until the 11th pattern ring that an iron diffraction, the 123 ring, is obtained free from a gold ring. This means that the cube faces of the iron crystals fit closely on those of the gold substrate when cube corner atoms of iron bisect gold cube edges. When given already one common direction, i.e., (100), of orientation, it is clear that no other arrangement will enable the two structures to fit together so accurately without lattice distortion. It may therefore be concluded that this arrangement of substrate and deposit is also the most strain-free. We have, indeed, observed that iron electrodeposited on a massive gold substrate exhibits exceedingly good adhesion.

In the case of iron electrodeposited on palladium, the two structures fit together in a corresponding manner and, although the fit is not so good as in the case of iron and on gold, it is nevertheless still the best possible under the circumstances.

The remarkable pattern of spots immediately surrounding the undiffracted beam spot in Figs. 7 and 8 is a more or less prominent feature in all the patterns obtained from these composite films in which the substrate produced a pattern approaching to the cross-grating type and therefore practically consisted of a single crystal, or at least of closely packed crystals possessing two well-defined directions of orientation in common.

The origin of this central pattern may be deduced as follows : Owing to the thinness of the composite film, the third Laue condition for diffraction is virtually completely relaxed, and we may regard the specimen as consisting of two superimposed cross-gratings, one of platinum, a = 3.91 A, and the other of copper, a = 3.61 A. Suppose a beam, hkl_{Pt} , from the first crossgrating be diffracted by the underlying copper film, then a complete copper cross-grating pattern should be ascribed about the hklpt diffraction spot. Thus, as in Fig. 10, there will be a ray, A, diffracted radially inwards and another, B, radially outwards from the central spot, the distance of A and B from hklpt being the radius of the hklCu ring. Similarly, other rays, C and D, etc., will be diffracted in various directions from that of the initial hklpt ray. So far we have only considered a single platinum crystal with its underlying layer consisting of a copper single crystal in similar orientation; but the patterns, Figs. 7 and 8, consist of a series of short arcs, and we must therefore consider the effect of rotating the cross-gratings about the primary beam by an angle equal to the angular extent of the arcs of the normal pattern. Quite clearly the effect upon A and B will be to spread the spots over an angle, α , subtended by the normal pattern arcs at the Since A is much nearer the central spot than B, it follows central spot. that the same amount of energy will be concentrated into a much smaller The arc A will therefore be much more intense than area at A than at B. A similar effect will occur for C and D, but in addition there will be В. a two-dimensional spreading and consequent blurring of the C and D arcs, owing to the extent of the primary hklpt arc, and we should therefore hardly expect to observe such diffractions in the patterns.

This view, according to which the central pattern is due to double diffraction, is completely in agreement with the facts. Thus, in Fig. 7.



the pattern close to the central spot corresponds to a facecentred cubic structure, $a_0 = 48.9$ A., in exactly the same orientation as the platinum and copper, the scattering and corresponding angle to each of these inner arcs is the difference between the scattering angles of the corresponding diffractions of the platinum and copper respectively. For example, the radius of the arc ascribed to the III diffraction from the face - centred cubic structure of cube edge 48.9 A. is equal to the difference between the radii of the III platinum and copper diffractions respectively. Again, all three arcs fall on the same radius and

have the same angular extent, and whilst the arcs near the undiffracted beam spot are intense, the corresponding arcs described about, and on the opposite side, of the III platinum diffractions are too weak to be seen in the reproduction, though plainly visible in the original negative.

Similar results obtained with other composite films are set forth in Tables V a, b, c, and d. They completely confirm the above double scattering view.

In addition to those shown in Table Va, three other arcs foreign to either platinum or copper were observed in the pattern. Their origin could be traced to double diffraction. Thus, the arc with radius 1.14 cms. is due to the diffraction of the 222Pt diffraction by $(III)_{Cu}$ (calculated 1.13 cms.); 1.43 cms. arc due to the diffraction of III_{Pt} by $(222)_{Cu}$ (calculated 1.43 cms.); and 1.92 cms. arc due to the diffraction of the 200Pt beams by $(331)_{Cu}$ (calculated 1.92 cms.).

Three other arcs were also observed in the pattern of Table Vb. The arc with radius 1.03 cms. is due to the diffraction of $222p_t$ by (111)_{Ni} (calculated 1.02 cms.); 1.40 cms. arc due to the diffraction of 111p_t beam by $(222)_{Ni}$ (calculated 1.40 cms.); and the 1.98 cms. arc due to the diffraction of the 311p_t beams by $(440)_{Ni}$ (calculated 1.97 cms.).

The occurrence of this phenomenon of double scattering is of particular importance in connection with the general interpretation of the relative intensities of the diffractions in electron diffraction patterns. In the case of a specimen consisting, for example, of a chaotic aggregation of the same type of crystals, the effect must give rise to an anomalous intensity distribution, in that it will have the tendency to even out the intensity differences between the various diffractions.

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| Indices Diffractio | of ons. | Radii in cm. | Calculated Differences between Radii in cm. | Observed Radii of Inner Secondary Diffractions in cm. | Calculated Sum of Radii in cm. | Observed Radii of Outer Second- ary Diffractions in cm. | | | |
|--------------------------------------|----------------------------------|--|--|---|--------------------------------------|--|--|--|--|
| (a) Cop | (a) Copper on Platinum (Fig. 7). | | | | | | | | |
| 111 111 | Cu | 1·33 1·23 | 0.10 | 0.10 | 2.56 | 2.56 | | | |
| 200 200 | Cu | $\left. \begin{smallmatrix} \mathbf{I} \cdot 5^2 \\ \mathbf{I} \cdot 4\mathbf{I} \end{smallmatrix} \right\}$ | 0.11 | 0.11 | 2.94 | 2.94 | | | |
| 220 220 | Cu Pt | ^{2•17} 2•00 } | 0.12 | 0.12 | 4.17 | — | | | |
| (b) Nicl | (b) Nickel on Platinum (Fig. 8). | | | | | | | | |
| 111 ₁ 111, | Ni | 1·27 1·14 | 0.13 | 0.13 | 2.41 | 2.41 | | | |
| 200 ₁ 200 | Ni | 1·47 } 1·33 } | 0.14 | 0.14 | 2.80 | | | | |
| 220 ₁ 220 | Ni Pt | $\left. \begin{array}{c} 2 \cdot 08 \\ 1 \cdot 87 \end{array} \right\}$ | 0.51 | 0.31 | 3.92 | _ | | | |
| (c) Copper on Palladium. | | | | | | | | | |
| ²²⁰ (²²⁰ 1 | Du Pd | $^{1\cdot55}_{1\cdot45}$ | 0.10 | 0.10 | 3.00 | 3.00 | | | |

TABLE V.—DOUBLE DIFFRACTION BY COMPOSITE FILMS.

(d) Cobalt on Platinum.

Faint, diffuse double diffraction pattern observed near and around the central spot.

In the examples of double scattering set forth above, the relationship between substrate and deposit crystal orientation was so intimate that the specimens could be regarded as being virtually single structures but characterised by an abrupt change of lattice constant occurring at a sharply defined boundary within the structure. We should therefore expect to find similar intensity-levelling double-scattering effects even in the case of single crystal transmissions of the cross-grating type. The effect must occur; otherwise it would be difficult indeed to account for the exceptional intensity of the higher order diffractions which is so characteristic of the electron diffraction cross-grating pattern. Thus, it is by no means unusual to record as many as 15 orders in a mica transmission. Beeching ⁹ has observed a similar effect in the case of the reflection of electrons from a natural diamond face, and other investigators, notably Raether,¹⁰ have recorded similar anomalies. Bethe's 11 dynamical treatment neglects the experimental fact of the co-existence of several strong diffracted beams and their consequent interactions and must therefore be inadequate in its present form as a guide to the quantitative interpretation of intensity distribution. The need for caution at the present time in assigning anything more than a general qualitative significance to intensity measurements of electron diffraction patterns is evident.

> ⁹ Beeching, *Phil. Mag.*, 1931, **20**, 841. ¹⁰ Raether, *Z. Physik.*, 1932, **78**, 527.

¹¹ Bethe, Ann. Physik., 1928, 87, 55.

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7. Orientation Changes Subsequent to Substrate Removal.

Experiments were carried out with the object of seeing to what extent. if any, the orientation of the deposit crystals might be affected by the removal of the substrate. That such an effect can and does occur is strikingly demonstrated by the patterns, Figs. 9, 11 and 12. Thus, in Fig. 9, from iron electrodeposited on gold, the arcing shows that both metals were in cube face orientation and with an iron cube face parallel to gold cube-diagonal planes. This specimen was next floated, gold downwards. for a few seconds on a weak cyanide solution and re-examined after washing. The resulting pattern, Fig. 11, shows that much of the gold had gone into solution, and that the arcing of the rings has become much less distinct than previously in Fig. o. After further etching, leaving only a trace of gold, the pattern, Fig. 12, was obtained. The rings are now practically free from arcs, thus showing that with removal of the substrate the second direction of orientation of the iron crystals has been lost. Furthermore, the intensity distribution is now such as to suggest that what slight degree of orientation still remained was (110) rather than (100) parallel to the specimen plane. It is probable that the loss in orientation was due to crinkling of the iron film on removal of the substrate.

We have in other cases observed distinct signs of similar changes due to removal of the substrate influence, but in none were the effects so clearly in evidence as with iron on gold.

8. Substrate Influence on Crystal Size.

An example of the effect of the substrate structure on the crystal size of a deposit has previously been given in the case of chromium electrodeposited on copper, nickel, iron, tin and bismuth substrates.⁴ The size of the deposit crystals appeared to be determined mainly by the crystal size in the substrate, provided the deposition conditions were otherwise the same. Nickel seemed on the whole to be less susceptible than chromium to this specific substrate influence, and generally gave patterns which are remarkable for their clarity and ring definition. Electrodeposited on amorphous arsenic, however, even nickel exhibited a pronounced tendency to form small crystals.

9. Transmission Specimens of Single Metals.

These specimens were prepared in the manner outlined in Table I. and § 5, and had been electrodeposited on basis metals with normal crystal orientations characteristic of the deposition conditions previously outlined. After stripping and removal of the basis metal the films yielded excellent patterns, representative examples of which have previously been reproduced.⁴ It will suffice to recall that it was found that body-centred cubic structures such as iron and chromium tended towards (III), and the face-centred cubic metals towards (IIO) orientation.

10. Metal Films formed by Chemical Displacement.

A copper film, either commercial leaf or electrodeposited, rapidly whitened when floating on a 1 o per cent. acid platinum bi-chloride solution. After immersion in 3N nitric acid to remove any unattacked copper, the film yielded a face-centred cubic pattern. Double-shutter comparison with gold showed that the film formed by displacement had lattice constants intermediate between those of platinum and copper, and this was independently verified by the pattern, Fig. 13, obtained from a similar platinum-displaced-by-copper film superimposed on gold.

Similar results were obtained with platinum, displaced by floating a silver film on the platinum salt solution, followed by washing with a dilute ammonia solution and $1\frac{1}{2}$ hours' treatment in 3N nitric acid to remove

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silver chloride and unattacked silver. A typical double-shutter pattern with gold is shown in Fig. 14, from which it will immediately be evident that the lattice constants of the displaced film lay between those of platinum and silver. This film gave a positive test for silver with p-dimethylaminobenzal-rhodamine, and the two platinum-displaced-by-copper specimens, on testing for copper with sodium-diethyl-dithio-carbamate also yielded a similar result.

The lattice constants of the 20 copper-platinum specimens examined lay between 3.71 and 3.77 A. Similarly, in the case of platinum displaced by silver, the lattice constants were found to vary between 3.97 and 4.05 A, and it was observed that the lattice constant decreased with the time of contact of the silver with the platinum solution. Thus, the chemical and structural evidence both show that copper-platinum and silverplatinum alloys are formed when thin copper and silver films chemically displace platinum, a result which is in sharp contrast to that obtained in the case of electrodeposited single and double films, where no signs of alloying could be detected.

Summary.

The structure of electrodeposited and chemically displaced metal surfaces and films has been studied by the method of electron diffraction.

It has been found that the structure of the substrate upon which a metal is electrodeposited nearly always profoundly affects that of the deposit, in that the orientation of the substrate crystals determines that of the deposit. In those few cases where the effect did not occur the deposit generally exhibited poor powers of adhesion.

Anomalous diffraction effects, shown to be due to secondary elastic scattering, have been obtained, and the bearing of this phenomenon on the interpretation of electron diffraction pattern intensities has been discussed.

It has been shown that, unlike in electrodeposition, chemical displacement of one metal by another leads to the formation of an alloy.

In this communication we have confined ourselves to setting forth the facts brought to light in the course of experiments and to drawing therefrom the outstanding conclusions of fact. We are deferring a more detailed discussion until the completion of further work which is now in hand.

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Imperial College of Science and Technology, London, S.W. 7.