Crystal growth of chemical Co-P and electrodeposited Co on Ni and Cu single crystals

Part 1 *(001) faces*

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The crystal growth of Co–P alloys chemically reduced with hypophosphites from aqueous solutions on the (0 0 1) faces of Ni and Cu single crystals has been studied in a wide range of thicknesses: 10 Å to 12 μm. Smooth deposits of β–Co and martensitically transformed α–Co are first obtained. Upon increasing the thickness, outgrowth is observed and the mechanism of formation is attributed to an anomalous (1 0 . 1) twinning mode. At high thickness, outgrowing basal planes become perpendicular to the base, transform towards the growth mode imposed by the bath and form regions of equi-oriented planes. Electrodeposition of Co films at medium thickness yields similar results.

1. Introduction

The nucleation and crystal growth of cobalt on ionic and metallic substrates has received special attention in recent years owing to the magnetic characteristics of thin cobalt films and, from a metallurgical point of view, because of the occurrence of a martensitic transformation for pure cobalt. The deposition on single crystal appears especially useful in investigating the crystallographic relations between deposit and substrate, and to elucidate how the morphology and the structure develop.

Cobalt has been deposited by vacuum evaporation on ionic [1–11], semiconducting [12] and metallic [13–20] single crystals. The general features of nucleation and growth for thin films obtained by this method have been shown. Other methods for depositing cobalt on single crystals have also been studied, although to a lesser extent. Cobalt films have been electrodeposited onto Cu single crystals [21–26], but no definite conclusions have been drawn from the results, especially with respect to the morphology of electrodeposits.

Chemical reduction of cobalt ions by means of hypophosphites gives Co–P deposits which have interesting magnetic properties and are of wide use to the electronic industry. Although many authors have underlined the dependence of magnetic properties on the crystallographic and morphological structure of the films, only very few studies have been dedicated to the fundamental aspects of the cobalt crystal growth by chemical reduction. A review of the literature shows that several papers are devoted to the nucleation and the obtaining of preferred orientations of Co–P deposits on amorphous or polycrystalline substrates [27–41]. Only a preliminary investigation by Jones and Aspland [42] deals with the chemical deposition of Co–P on a Cu single crystal of (0 0 1) orientation. They refer to a twinned f c c epitaxial structure for the Co–P deposit, together with the polycrystalline h c p form.

In this work we have examined the crystal growth of Co on (0 0 1) planes of Cu and Ni single crystals; specifically we have considered f c c metals with lattice parameter very close to that of f c c Co (β–Co). Jesser and Matthews [13–14] examined the pseudomorphic growth of vacuum evaporated cobalt on these two metals. They underlined the different sign of the elastic strain (tension in copper and compression on nickel) of the pseudomorphic deposit, and the

appearance of stacking faults of different natures.

Our investigation is directed towards observation of the crystal growth of Co—P by chemical deposition over a range of thickness (10 Å to 12 μm). We have studied the joint influence of substrate and solution on orientation, morphology and martensitic transformation of the deposited cobalt films.

The bath for chemical plating was chosen to give well-textured structures of α—Co. We used a bath that gave deposits with a strong $\langle 1\,1\,.0 \rangle$ preferred orientation parallel to the base on amorphous or polycrystalline substrates. With this orientation the closest packing direction $[1\,1\,.0]$ is perpendicular to the surface and this fibre texture was related [29] to a decreased interaction with the surface of Co hydrolysed species. Sulphamate anions were used, because sulphamate baths give deposits with very low internal stresses and better structures than, for instance, baths based on sulphates.

Chemical plating has been compared with the electrochemical method; to this purpose we have examined, in the range of thickness 1 to 3 μm, the structure of electrodeposits obtained from cobalt sulphamate baths, which also in this case gave $\langle 1\,1\,.0 \rangle$ preferred orientation. In this range the crystallographic and morphological structure depend on the substrate as well as on the orienting properties of the solution.

2. Experimental
2.1. Cu and Ni single-crystal substrates
The substrates were cut from 4 N pure Cu and Ni single crystals grown by a modified Bridgman technique and were oriented to the desired crystal orientations within 2°. The techniques of single crystal preparation, cutting and surface orientation have been described elsewhere [43]. The crystal surfaces were ground on SiC paper with abrasive grain size decreasing from 35 to 14 μm. They were then roughly polished on nylon-covered polishing wheels loaded with diamond lapping sprays containing abrasive grains having a diameter of 6 and 3 μm, respectively. The Cu crystals were finally electropolished for 7 to 10 min in a 50 to 60% H_3PO_4 electrolyte at the optimum point of Jacquet. Fine polishing of the Ni crystals was chemically performed for 30 to 40 sec in a bath containing concentrated acids CH_3COOH, HNO_3, H_2SO_4 and H_3PO_4 in the volume ratio 5:3:1:1. The best

polish was obtained at a temperature of about 80° C. After each experiment the crystals were repolished.

When prepared, the crystals were immediately rinsed thoroughly in a 0.1 M H_3PO_4, flushed with distilled water, and then quickly transferred to the deposition bath. When subjected to electron diffraction, such prepared surfaces produced bright Kikuchi lines and rather weak spots elongated towards the shade edge.

2.2. Chemicals and solutions
Cobalt sulphamate solution was prepared from cobalt carbonate and recrystallized sulphamic acid. The solution was purified by treatment with charcoal and pre-electrolysis at different current densities for 24 h [44]. The solutions used for chemical reduction were of the following composition: $Co(NH_2SO_3)_2$, 0.3 M; $C_6H_6O_7(NH_4)_2$, 0.3 M; NaH_2PO_2, 1.2 M, with a pH-value usually adjusted to 10.5 at 25° C by addition of NaOH.

Electrodeposition was carried out from a solution composed of: $Co(NH_2SO_3)_2$, 1.35 M; H_3BO_3, 0.5 M, with a pH value adjusted to 4.5 at 25° C with NH_2SO_3H, and the electrolyte purified as described above.

All solutions were prepared from analytical reagents (Carlo Erba) with doubly demineralized and distilled water.

2.3. Procedure
Depositions by chemical reduction were performed at 80 ± 1° C, and the specimens were immersed into the solution with a pair of Co-coated Ni-tongs. The crystal surface was completely covered with a Co-film within a few seconds. The growth rates were found to be in good agreement with previous determinations [37].

Electrodeposition was carried out at 50 ± 1° C. The electrolytic cell was of the type previously described [43] with a uniform current distribution and separation of the cathode from the anode compartment.

The thickness of the deposits was measured by selected-area anodic dissolution of the films. The thickness of the electrodeposits calculated by assuming 100% cathodic current efficiency [45] and the thickness of chemical deposits obtained by weight increase, corrected for P content, were found to be in agreement, within 5%, with the results obtained by anodic dissolution. The sensi-

tivity of the method was better than 5 Å in the range 0 to 500 Å; the sensitivity slowly decreased to a value of 0.05 μm at 10 μm.

2.4. Microscopic investigation
The morphology of the deposits was examined by SEM (Jeol JSM − U 3) and the study of the thinnest films was supplemented with TEM (Siemens Elmiskop 1 A) of surface replicas. These were two-stage plastic carbon replicas of the type developed by Bradley. Contrast was enhanced by 45° shadowing of the plastic replicas with Cr or Pd before evaporation of C.

The specimens were etched for 5 sec in 0.1 M H_3PO_4 before microscopic examination, to eliminate possible oxidation. The treatment did not alterate the morphology of the deposits. RHEED was performed in a 50 kV electron beam of a Trüb Taüber electron diffractometer; a slight etching in 0.1 M H_3PO_4 was found useful.

To accurately determine the unit meshes of the observed structures, the specimens were in some cases dipped in a dispersion of fine MgO powder in absolute alcohol. The sample was adjusted so that the electron beam, although always nearly parallel to the surface, grazed along only the furthest 1 to 3 mm of the surface. This method resulted in weak but sharp MgO ring patterns superimposed on the cobalt structure pattern from which the camera constant and thus the unit meshes of the structures have been determined.

3. Results
3.1. Chemical deposits
The examined thickness range was 10 Å to 12 μm. The pH was usually adjusted to 10.5; only a few experiments have been performed at higher pH values.

The structures which develop on Cu and Ni substrates were found to be similar. Distinction between deposition on Cu and Ni is, therefore, only referred to when pertinent.

The interpretation of the different crystallographic structures in terms of epitaxial relationships between substrate and deposit are summarized in Table I and are referred to by the letters denoting them. The Miller−Bravais indexing is adopted for h c p Co.

Fig. 1 shows RHEED patterns of deposits of increasing thickness on the (0 0 1) face of Cu single crystals. Initially, Co deposits have mainly

TABLE I Preferred orientations of chemical Co−P deposits on (0 0 1) faces of Ni and Cu single crystals

	Orientation	Thickness
A	(0 0 1) [1 0 0]$_{Co}$//(0 0 1) [1 0 0]$_{sub}$	$\leqslant$ 2000 Å
B	{0 0 .1}⟨1 1 .0⟩$_{Co}$//{1 1 1}⟨1 1 0⟩$_{sub}$	$\leqslant$ 2000 Å
C	(1 $\bar{1}$ .0) [0 0 .1]$_{Co}$//(0 0 1) [1 1 0] or [1 $\bar{1}$ 0]$_{sub}$	$\leqslant$ 1 μm
D a	(0 0 .1) [1 1 .0]$_{Co}$//(1 0 0) [0 1 1] or [0 $\bar{1}$ 1]$_{sub}$	$\leqslant$ 5 μm
D b	(0 0 .1) [1 1 .0]$_{Co}$//(0 1 0) [1 0 1] or [$\bar{1}$ 0 1]$_{sub}$	
E	(1 1 .0) [0 0 .1]//(0 0 1) [1 0 0] or [0 1 0]$_{sub}$	$\geqslant$ 2000 Å
F	(1 2 .0) [0 0 .1]//(0 0 1) [1 0 0] or [0 1 0]$_{sub}$	$\geqslant$ 5 μm

an f c c structure parallel to the substrate (orientation A), but, even at 20 Å, h c p Co is observed with orientation B, which is the usual epitaxial relation in the martensitic transformation of Co. Long streaks due to {1 1 1} stacking faults are observed; Kikuchi lines, of decreasing intensity with deposition time, and very faint reflections attributed to a ⟨1 1 .0⟩ texture are present in the patterns from very thin deposits.

Diffractograms show characteristic satellite spots in place of the usual reflections of a parallel f c c phase. Patterns with the beam along [1 1 0] of the base show doubling of f c c spots along [0 0 1]; in the [1 0 0] azimuth there is separation of the f c c {0 k l} reflections along ⟨1 1 0⟩ giving four satellite spots, and these points correspond well to the projection of ⟨1 1 1⟩ streaks intersection with the Ewald sphere (Figs. 1b and c, 2a). By small tilting (1 to 2°) around the [0 1 0] or [1 0 0] axes it is possible to decrease the distances between the satellite spots and to obtain the usual f c c spots, in the same way as Otsuka and Wayman [6]. The occurrence of satellite spots may be related to small angular deviations of the (0 0 1) plane of the deposited β-Co from perfect parallel orientation with respect to the surface.

It is also possible to observe faint spots of increasing intensity with thickness, which may be attributed to C and D orientations: the first orientation is tilted about 20° with respect to the normal of the surface with rotation around the ⟨1 1 0⟩ axis of the base, the second orientation has basal planes (0 0 .1) perpendicular to the base, in some cases slightly rotated (1°) around the [0 0 .1] axis (corresponding to (5 2 .0)$_{Co}$//
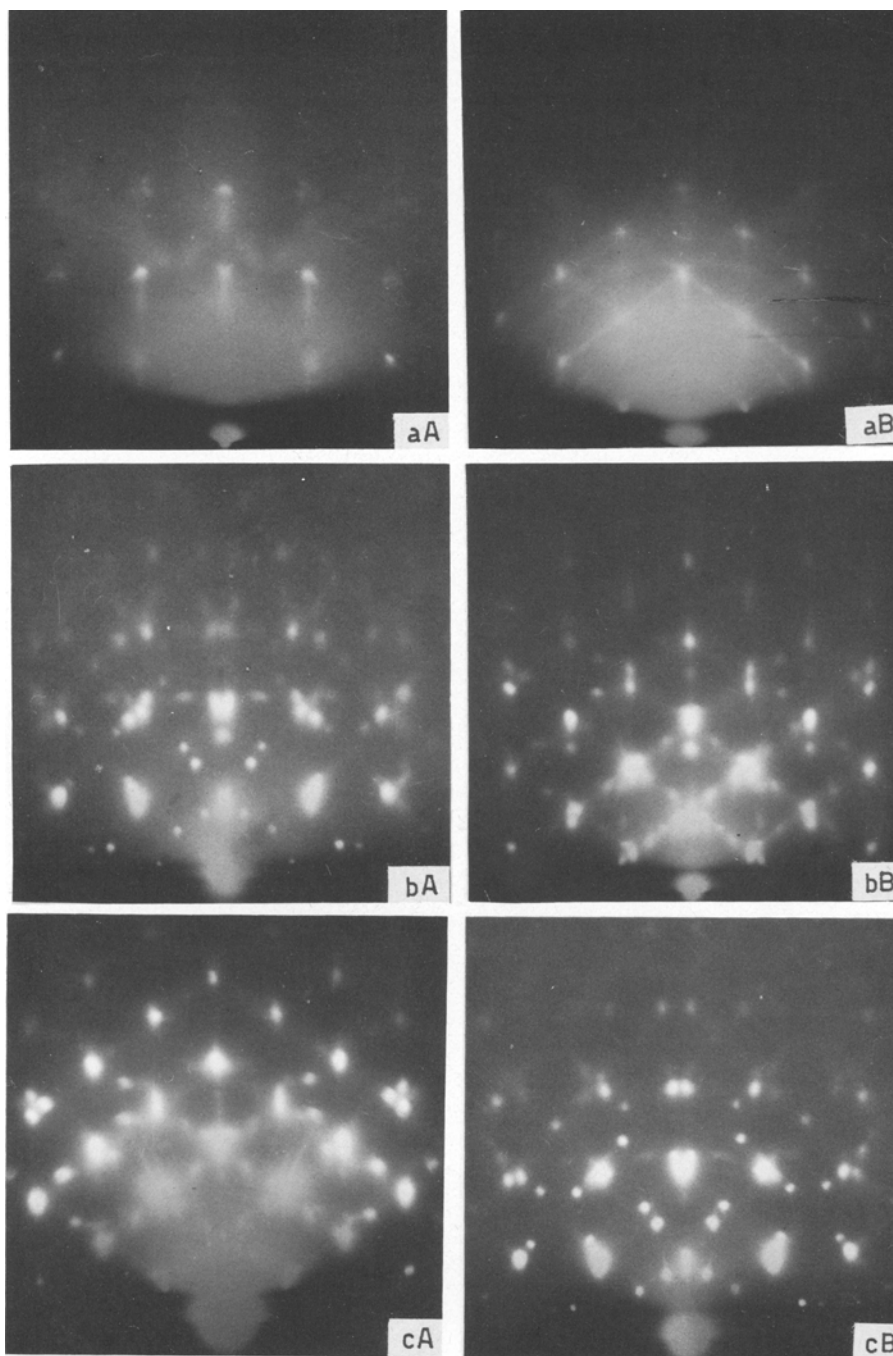
Figure 1 RHEED patterns of Co–P chemical deposits on (0 0 1) faces of Cu single crystals. Deposit thickness: (a) 20 Å; (b) 280 Å; (c) 910 Å; (d) 1600 Å; (e) 0.8 μm; (f) 4.35 μm. Beam along: (A) [1 0 0]; (B) [1 1 0].

$(0\,0\,1)_{sub}$). Fig. 4 represents an interpretation of the diffraction patterns for thin deposits, attributing the most intense spots to orientations A and B.

Micrographs of thin films (Fig. 3a) show very flat and smooth surfaces with very fine grain size and only few crystallites of greater size. In some cases it is possible to see alignment of the small crystals along ⟨1 0 0⟩ or ⟨1 1 0⟩. As the thickness
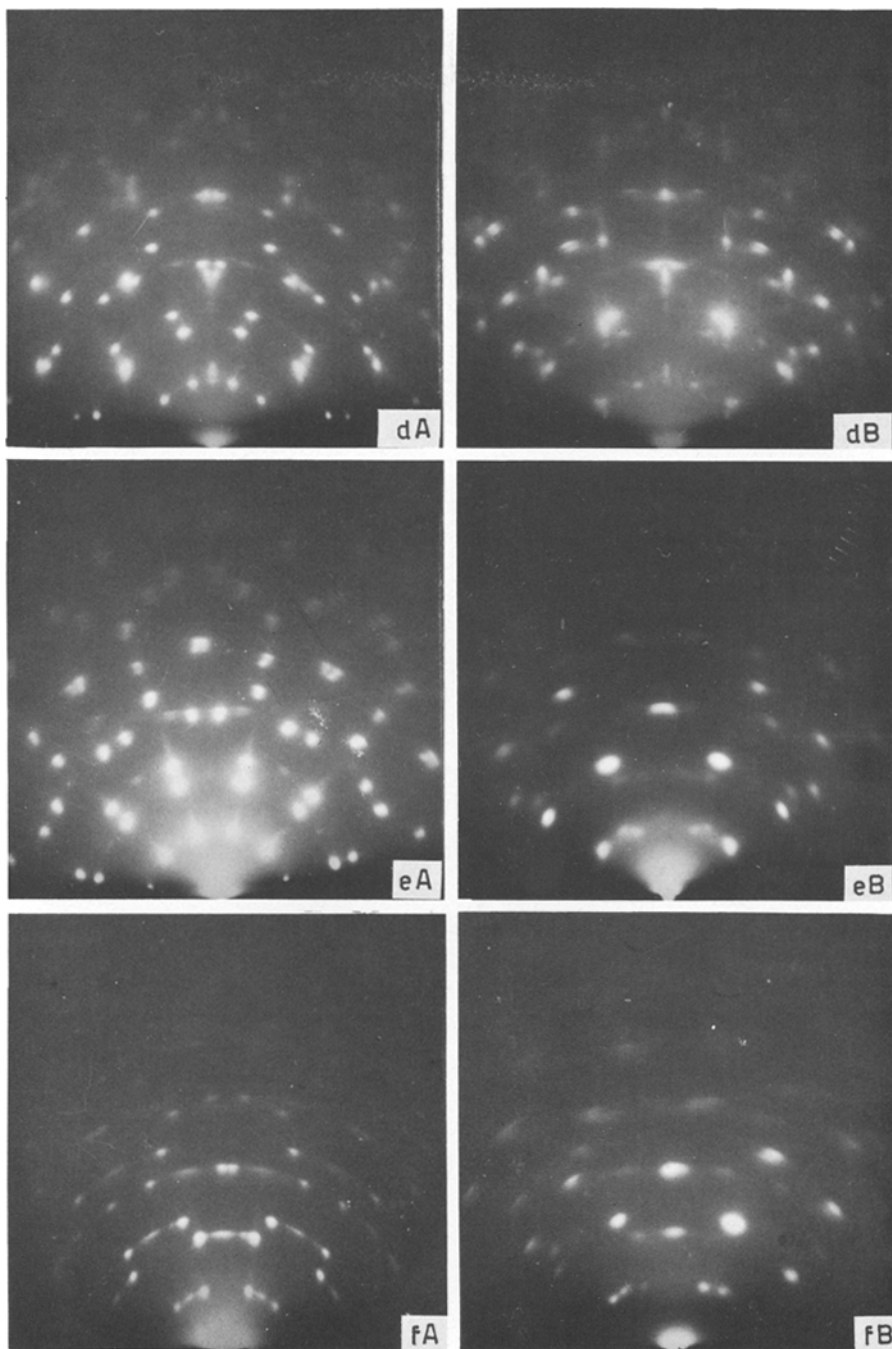
Figure 1 continued

increases, larger crystallites develop, and tend to line up along ⟨1 0 0⟩ and ⟨1 1 0⟩ forming ridges (Fig. 3b).

At about 1000 Å it is possible to see a new structure, related to E type orientation, with basal planes tilted 9 to 10° with respect to the base normal and developing along [1 0 0] and [0 1 0] (Fig. 1d and e).

Fig. 5 shows the usual pattern for deposits of medium thickness, with spots attributed to orientation C and D.

The growth of Co on Ni follows the same outlined general features. The main difference is that structures C and D are observed to develop much faster on Cu than on Ni (cf. Fig. 1c with Fig. 2a). At great thickness the deposits on Ni and Cu have

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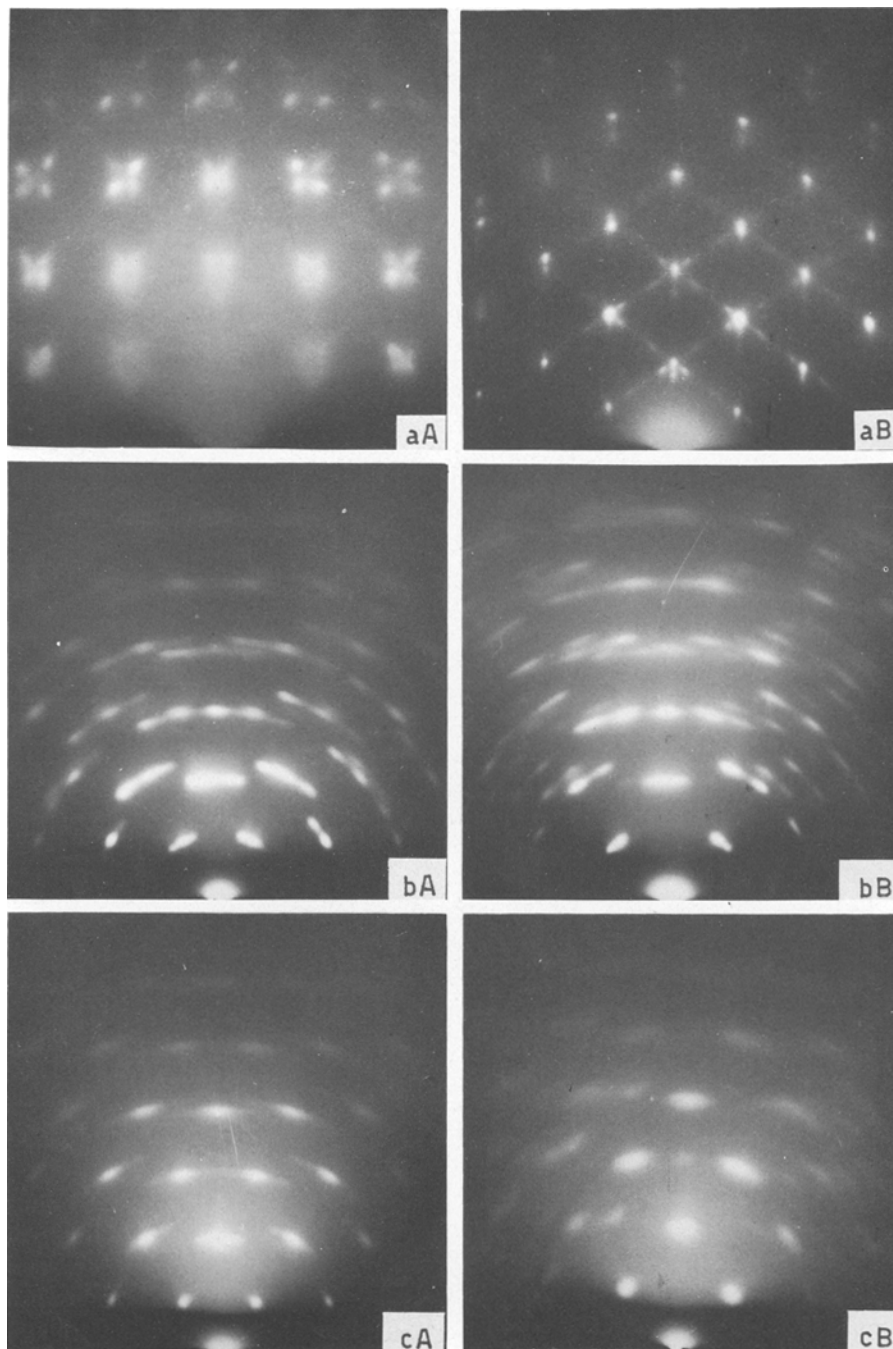
Figure 2 RHEED patterns of Co—P chemical deposits on (0 0 1) faces of Ni single crystals. Deposits thickness: (a) 900 Å; (b) 8 μm; (c) 12 μm. Beam along: (A) [1 0 0]; (B) [1 1 0].

similar structure and morphology.

Micrographs (Fig. 3c) show the presence of plate-like crystallites: some along [1 1 0] and [1 $\bar{1}$ 0] tilted with respect to the normal, attributed to the C structure; others along [1 0 0] and

[0 1 0], for the most part perpendicular to the base and more prominent, owing to a faster growth rate in the direction perpendicular to the base.

At about 1 μm the diffraction spots from structure C disappear (Fig. 1e) and micrographs show

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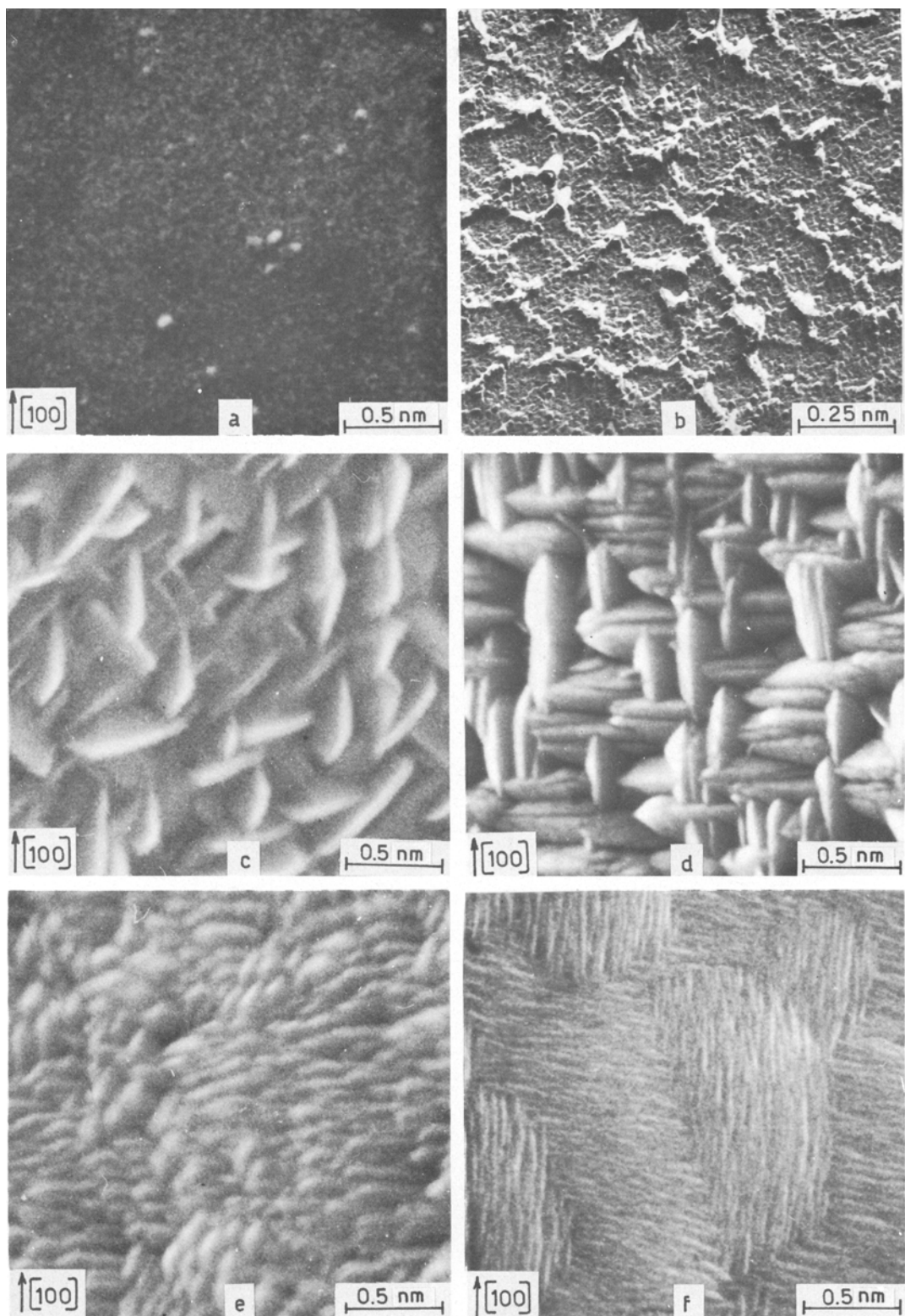
Figure 3 Micrographs of Co–P chemical deposits on (0 0 1) faces. (a) 185 Å, SEM on Ni; (b) 900 Å, TEM on Cu; (c) 7000 Å, SEM on Ni; (d) 1.3 μm, SEM on Ni; (e) 8 μm, SEM on Ni; (f) 12 μm, SEM on Ni.
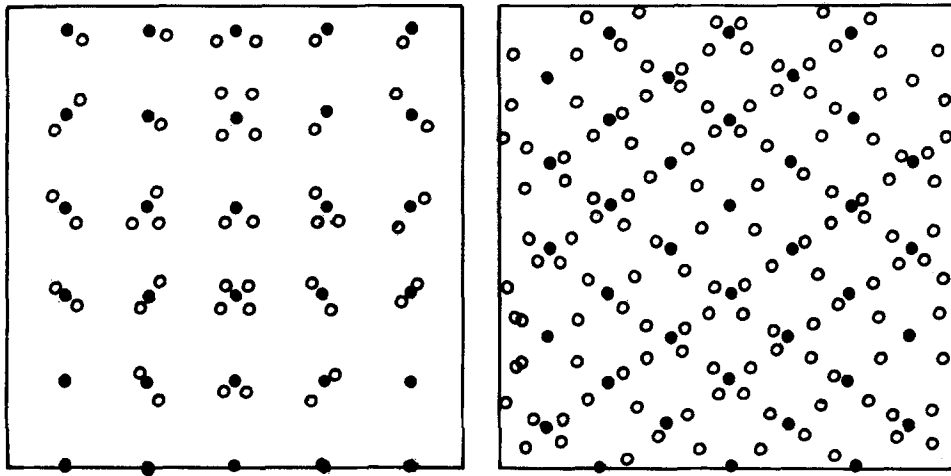
Figure 4 Interpretation of typical diffraction patterns of thin deposit: orientation A, •; orientation B, ○.
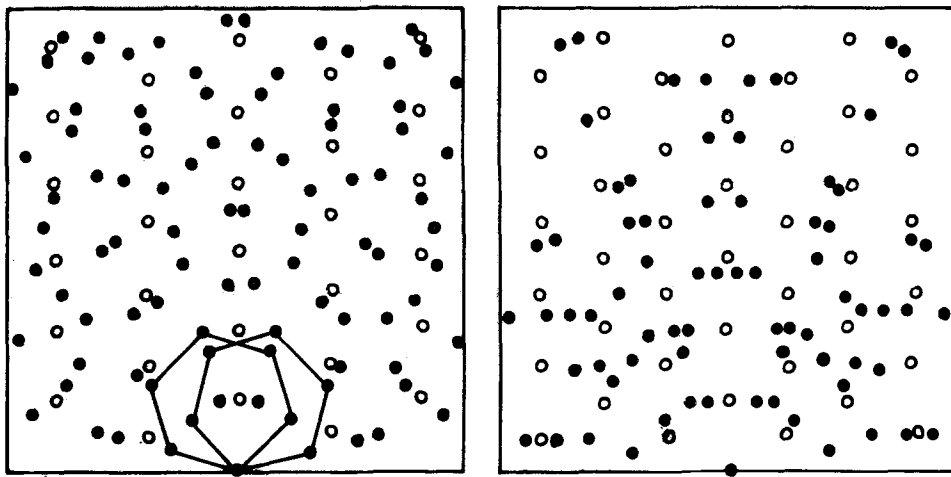

Figure 5 Interpretation of typical diffraction patterns of medium thickness deposits: orientation C, •; orientation D, ○.
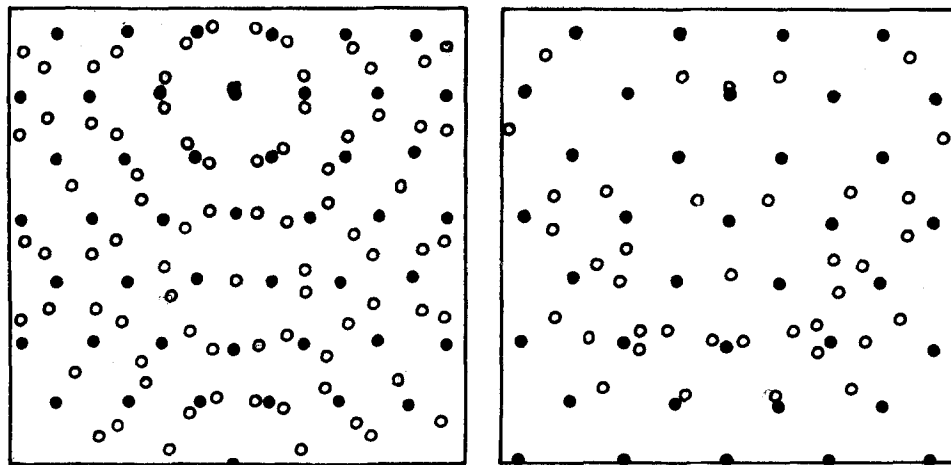

Figure 6 Interpretation of typical diffraction patterns of thick deposits: orientation E, •; orientation F, ○.

very definite crystallites of the D and E structures growing along [1 0 0] and [0 1 0] (Fig. 3d). By increasing further the thickness of the deposit, the growing crystallites come in contact with each other, and produce regions of equi-oriented crystals (Fig. 3e and f). The corresponding diffractograms (Figs. 1f, 2b and c) show that the E structure tends to set upright, while the D structure modifies, rotating around the [0 0 . 1] axis, and gives first (1 2 . 0) planes and subsequently (1 1 . 0) planes parallel to the surface.

Fig. 6 gives an interpretation of the diffraction patterns usually observed in high thickness range, with spots attributed to orientations E and F.

3.2. Growth at higher pH
Additional experiments with baths in the pH range 10.9 to 11.7 which also produce a ⟨1 1 . 0⟩ texture by deposition on amorphous or polycrystalline substrates, showed the same general features of growth. The morphology was, however, less definite than at pH 10.5; structure C developed earlier, and was more evident.

3.3. Electrodeposits
The experiments were also performed at about the same growth rate as in the chemical baths, i.e. at a growth rate of about $35 \, \text{Å sec}^{-1}$. The thickness range examined was 1.5 to $3.0 \, \mu\text{m}$, where characteristic structures are observed in deposits by chemical reduction.

Morphology and crystallographic structure resembles, in nearly every respect, that described
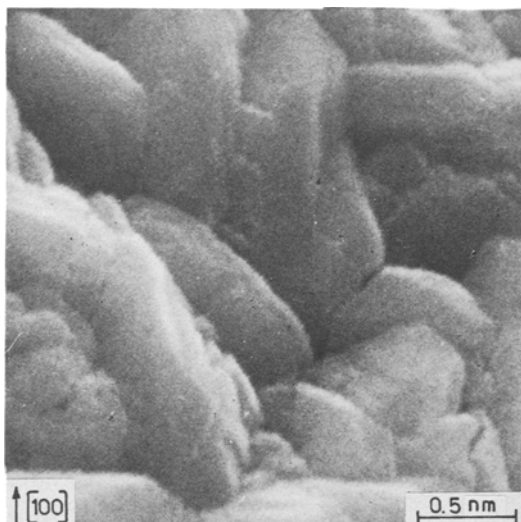

Figure 7 SEM micrograph of an electrodeposit of medium thickness.

for chemical deposits. The morphology, is, however, less sharp (see Fig. 7), and the diffractograms revealed a small arcing of the spots, owing to a less perfect two-degree orientation of the deposits.

3.4. Lattice parameters
The lattice constants of the observed f c c and h c p forms were calculated from the diffractograms with superimposed MgO rings. The parameters were found to be independent of the substrate and thickness of the deposit, and were in agreement with those reported for pure bulk α-and β-Co [46]:

$$a_{fcc} = 3.55 \pm 0.02 \, \text{Å}$$

$$a_{hcp} = 2.52 \pm 0.01 \, \text{Å}$$

$$c_{hcp} = 4.07 \pm 0.08 \, \text{Å}$$

4. Discussion
Jesser and Matthews [13, 14] have shown that evaporated cobalt grows on (0 0 1) faces of Ni and Cu single crystals as continuous layers having an f c c structure; cobalt is strained to fit the crystallographic parameters of the base until misfit dislocations are produced at 30 Å thickness on copper and at 80 Å on nickel. We have not been able to observe pseudomorphism, whilst the diffractograms reveal the presence of martensitic α-Co at very small thickness. The influence of co-deposited phosphorus as a defect promoter must be taken into account.

The tilting of the (0 0 1) planes of β-Co with respect to the surface of the base depends on the imperfections in the cutting and orientation of the single crystals. Greater tilting is related to the obtainment of rotated D orientation, $(5\,2\,.0)_{\text{Co}}//(0\,0\,1)_{\text{sub}}$.

A weak ⟨1 1 . 0⟩ texture is observed only at the very beginning of crystal growth; it is quickly overcome by two-degree oriented structures. The texture is the preferred orientation imposed by the bath, and is probably formed only on small areas not active towards the cobalt chemical reduction. Their presence is probably due to the existence of air oxidized regions, which may only be partly reduced to the metallic state before deposition starts.

The obtainment of orientations C and D may be attributed to a twinning of the martensitic structure in orientation B with composition planes {1 0 . 1}, an anomalous twinning mode for h c p metals. Fig. 8 shows the position of the planes
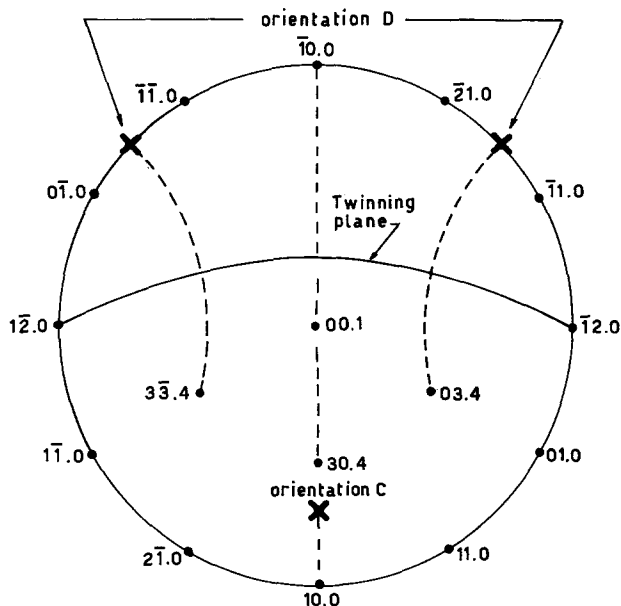
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Figure 8 Sterographic (0 0.1) projection for cobalt, showing twinning operations by reflection about the (0 1.1) plane.

parallel to the surface obtained by a twinning operation of the {3 0.4} planes (parallel to the surface in orientation B) about the (0 1.1) plane. The 20° tilting of the (1 0.0) plane of orientation C with respect to the base is evident; owing to this inclination, D-type orientation grows out faster than C, and predominates at increasing thickness.

The structures C and D grow with [1 1.0]$_{Co}$// $\langle 1\,1\,0 \rangle_{sub}$, i.e. closest-packed directions parallel to that of the substrate and also of the martensitic structure. Therefore, minimum misfit between substrate and deposit is not a valid criterion for explaining the growth mode, as discussed by Patrician and Wayman [8]. As directions seem to play an important role in the cobalt growth, we can acknowledge, in agreement with the Neumann–Curie principle, the important role of linear defects among the causes determining the cobalt crystallization. In fact, we have observed the development of ridges along lines which can be interpreted as dislocations, and, in the same way as the appearance of dislocations [13, 14], twinned C and D structures develop earlier on copper than on nickel.

Our results in the medium thickness range are in accordance with those of Goddard and Wright [25], who examined by RHEED the epitaxial relationships of electrodeposited cobalt on (0 0 1) faces of copper. They interpreted the spots from orientation C as originating from the following structure: (0 0.1) [1 1.0]$_{Co}$//(0 0 1) [1 1 0] or [1 $\bar{1}$ 0]$_{sub}$. We have found no morphological evidence of such a type of growth, with basal planes parallel to the surface. A careful exam-

ination of the electron diffraction patterns shows weak spots of the [0 0.1] zone axis with distances enlarged in the [1 2.0] directions along [1 1 0]$_{sub}$. By increasing the thickness, the basal planes of this structure become perpendicular to the base and the distances decrease towards the right position of the [0 0.1] zone axis.

Structure E, which develops after the C and D structures, is related to the orienting influence of the solution. At greater thickness, crystals of orientation C, D and E begin to come into contact; structure C slowly disappears and structure D rotates about [0 0.1] towards orientation E, the preferred outgrowth structure. Stresses induce fine cracks in the deposit. At very high thickness, $> 10\,\mu m$, two-degree orientation is also observed. Different regions with basal planes perpendicular to the surface, at 90° from each other, are obtained from a spatial organization of the growth.

To our knowledge, only one preliminary investigation has been reported on the epitaxial growth of chemically reduced cobalt on a single crystal substrate [42]. The film was deposited from a bath proposed by Fisher and Chilton [27] on a (0 0 1) face of Cu and examined by TEM and RHEED. Electron diffraction patterns along [0 0 1] azimuth show satellite spots around the f c c reflections and rings from polycrystalline α-Co. The satellites were explained as originated by f c c-twinning on (1 1 1) planes. Also the intervention of a martensitic transformation would have to be taken into account; a diffraction pattern taken along [0 1 1] would have clarified

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the matter. The presence of disordered α-Co may be due to the Pd activation treatment.

Acknowledgements

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