

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

Part 2 (011) and (111) faces

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Experiments on the chemical deposition of Co-P alloys on (011) and (111) faces of Cu and Ni single crystals have shown that the crystal growth occurs corresponding to the growth on (001) faces. Three ranges of crystal growth may be identified. For thin deposits, no pseudomorphism has been detected, moreover martensitically transformed hcp Co is observed from the first layers on (111) faces. For medium thick deposits, twinning on {10.1} composition planes has been confirmed; this anomalous twinning has been attributed to the high density of growth faults and is also observed in the case of electrodeposition. At high thickness, oriented regions are observed and the bath orientation predominates. The occurrence of these orientations has been related to the competing role in the adsorbed layer of Co-hydrolyzed species and hypophosphite ions.

1. Introduction

The investigation of epitaxial growth by deposition from aqueous solutions has attracted only a few researchers in past years. Recently, the need for further studies in this field and the possibility of considerable use of this technique have been stressed [1]. Co-P films, their structure and morphology are of particular interest because of their magnetic characteristics.

In a previous study [2] the crystal growth of chemically deposited Co-P on (001) faces of copper and nickel single crystals, was examined in the thickness range 10 Å to 12 μm. The bath used for chemical deposition gave <11.0> textured deposits on amorphous and polycrystalline substrates, which corresponds to the case of freest outgrowth. Accordingly the most relevant features are: (1) the occurrence of the martensitic transformation of cubic β-Co from the early chemically deposited layers; (2) the obtainment of two-degree preferred orientations at medium thickness, related to the martensitically transformed α-Co

by rhombohedral twinning with composition planes {10.1}; (3) the transformation of the preferred orientations towards that given by the bath, with small zones two-degree oriented.

In parallel investigations on depositing Co-P on (011) and (111) faces of copper and nickel single crystals in the same thickness range, we have examined the influence of the orientation of the base on the crystallographic structure and morphology of chemically deposited Co-P. In this case also, electrodeposition has been examined for comparison at medium thickness.

Experimental methods were described in the previous paper [2], to which we also refer for a review of the existing literature.

As yet, the published results on the crystal growth of cobalt deposited on the (011) and (111) faces of metallic single crystals are limited, and are concerned with electrodeposited cobalt only [3–6]. Wright [6] has reported the occurrence of a twinned structure after a phase transformation at 350 Å on a (011) copper substrate.

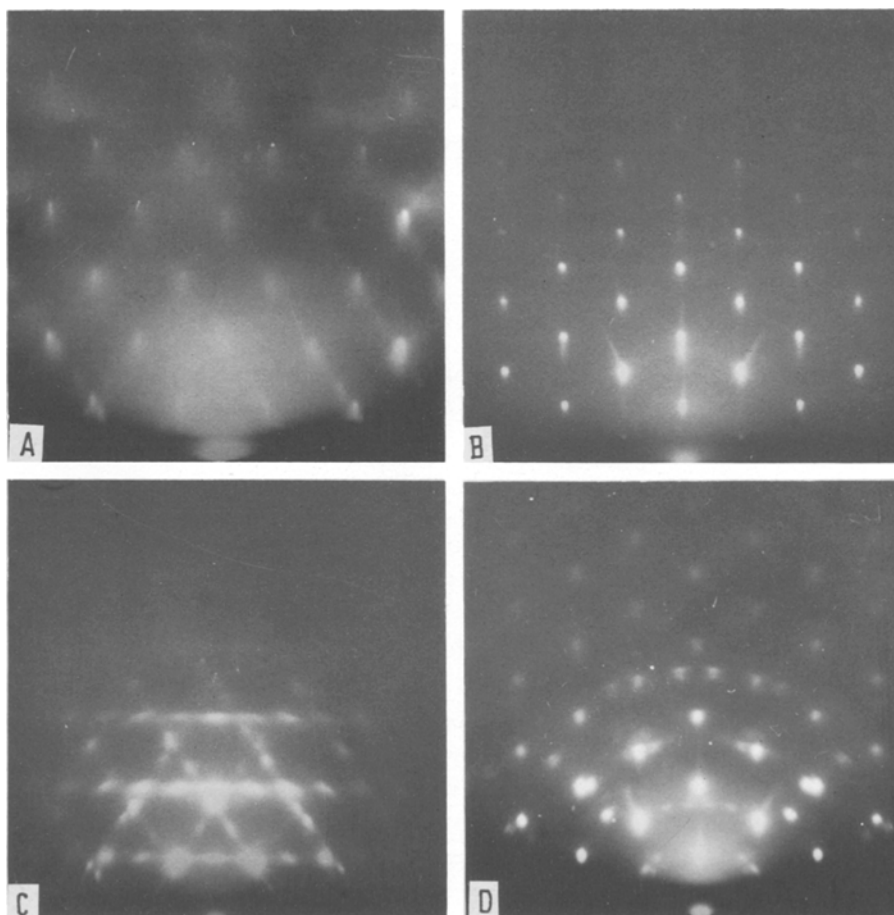


Figure 1 RHEED patterns of Co-P chemical deposits on (011) faces. (A) 10 Å on Ni, beam along $[0 \bar{1} 1]$; (B) 310 Å on Cu, beam along $[0 \bar{1} 1]$; (C) 310 Å on Cu, beam along $[1 0 0]$; (D) 8000 Å on Cu, beam along $[1 0 0]$; (E) 4.2 μm on Cu, beam along $[1 0 0]$; (F) 4.2 μm on Cu, beam along $[0 \bar{1} 1]$; (G) 7.8 μm on Ni, beam along $[1 0 0]$; (H) 7.8 μm on Ni, beam along $[0 \bar{1} 1]$.

He has interpreted this structure as the generation of an hcp structure on the fcc $\{111\}$ planes, followed by a twin process on a $\{11\bar{1}\}$ plane, and has extended this interpretation to previous results [4] on cobalt electrodeposited at high pH on (001) copper surfaces. Results are, however, lacking, especially at high thickness.

2. Results

2.1. Chemical deposits on (011) faces

The structures which develop on copper and nickel bases appear to be very similar and only obvious differences will be mentioned here. The interpretation of the different preferred orientations in terms of epitaxial relationships of the deposit with the substrate, is summarized in Table I, where we also give the labelling of the different struc-

TABLE I Preferred orientations of Co-P chemical deposits on (011) faces of Cu and Ni single crystals

	Orientations	Thickness range
A	$(011) [0 \bar{1} 1]_{\text{Co}} // (011) [0 \bar{1} 1]_{\text{sub}}$	$\leq 2000 \text{ \AA}$
B	$(00.1) \langle 11.0 \rangle_{\text{Co}} // \{111\} \langle 110 \rangle_{\text{sub}}$	$\leq 2000 \text{ \AA}$
C	$(10.0) [00.1]_{\text{Co}} // (011) [100]_{\text{sub}}$	$\geq 100 \text{ \AA}$
D	$(11.0) [00.1]_{\text{Co}} // (011) [1\bar{1}1]_{\text{sub}}$	$\geq 2000 \text{ \AA}$
E	$(11.0) [1\bar{1}0]_{\text{Co}} // (011) [1\bar{1}1]_{\text{sub}}$	$\geq 1 \text{ \mu m}$
F	$(11.0) [00.1]_{\text{Co}} // (011) [0\bar{1}1]_{\text{sub}}$	$\geq 1 \text{ \mu m}$
G	$(11.0) [00.1]_{\text{Co}} // (011) [100]_{\text{sub}}$	$\geq 1 \text{ \mu m}$
H	$(11.0) [1\bar{1}.1]_{\text{Co}} // (011) [0\bar{1}1]_{\text{sub}}$	$\geq 1 \text{ \mu m}$

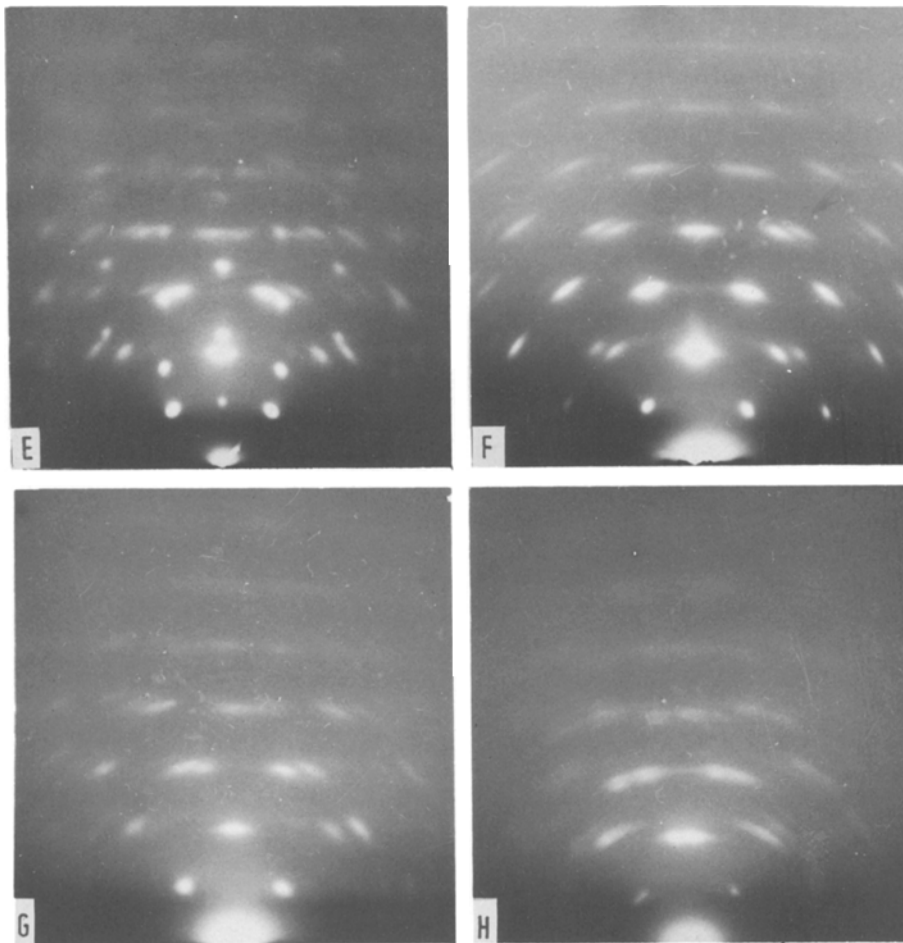


Figure 1 continued.

tures used in the text. The Miller–Bravais indexing is adopted for hcp cobalt.

Fig. 1 shows RHEED (reflection high energy electron diffraction) patterns of deposits of increasing thickness whilst the interpretation of these patterns is given in Fig. 2 and the related morphology revealed by TEM or SEM (transmission or scanning electron microscopy) techniques in Fig. 3. From the beginning, martensitically transformed hcp cobalt of orientation B is observed, together with the fcc structure parallel to the substrate of orientation A (see Fig. 1A and B).

A small angular deviation of the (011) plane of the deposited fcc cobalt from perfect parallel orientation with respect to the surface, causes the occurrence of satellite spots. They can be reduced to the usual fcc spots by a small tilting around the [100] axis, in the way reported by Otsuka and Wayman [7], and as we have reported for de-

position on (001) bases [2].

It is possible to observe diffraction from orientation C at thicknesses of more than 100 Å, this orientation prevails at approximately 300 Å for the copper base and 500 Å for the nickel base. Very thin deposits are bright and the diffraction patterns show typical features of smooth surfaces, i.e. spots elongated towards the edge of the shade, and Kikuchi lines. As the thickness increases these features disappear.

TEM replicas (see Fig. 3A) show that parallel striations already exist at 135 Å, with a medium distance of 200 Å apart. By increasing the thickness, outgrowing basal planes of structure C with the close-packed direction parallel to $[0\bar{1}1]$ of the base become evident (see Fig. 3B to D). At approximately 2000 Å, basal planes with a close-packed direction perpendicular to the base may be observed. The planes may be initially slightly tilted (see Fig. 1), but straighten very quickly as shown

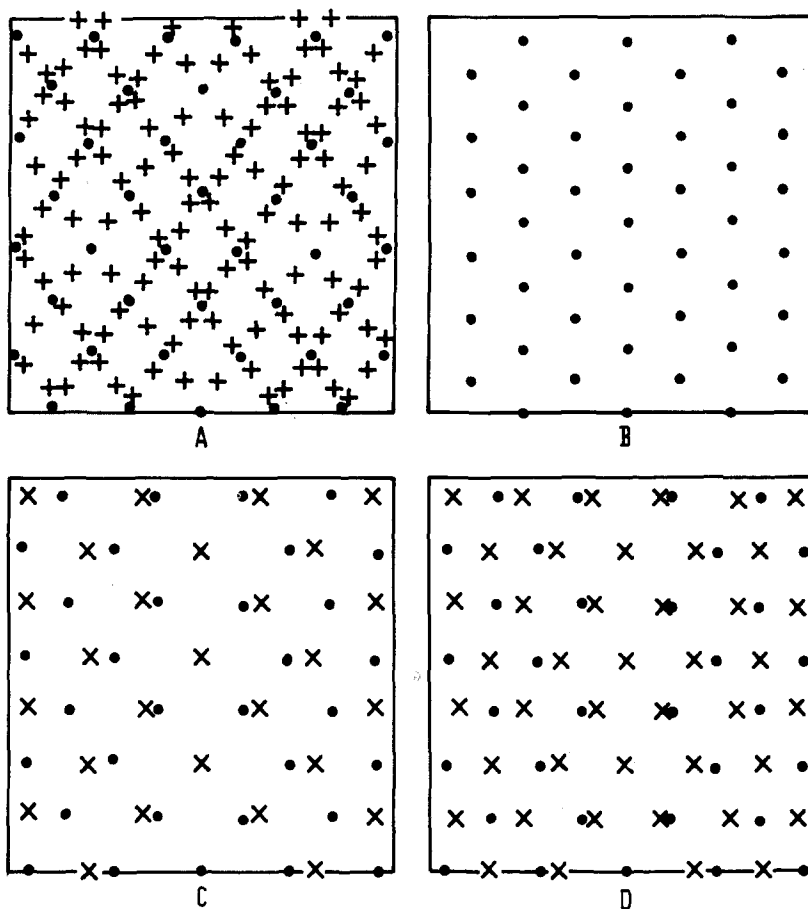


Figure 2 Interpretation of typical diffraction patterns of Co deposits on (0 1 1) faces. (A) Thin deposits orientation A • and B ×, beam along $[0 \bar{1} 1]$; (B) medium thick deposits; orientation C, beam along $[1 0 0]$; (C) thick deposits, orientation D • and H ×, beam along $[1 0 0]$; (D) thick deposits; orientation D • and H ×, beam along $[0 \bar{1} 1]$.

in Fig. 1E to H. They grow mainly with $[1 \bar{1} 0]$ approximately along the $\langle 1 1 1 \rangle$ and $\langle 1 1 2 \rangle$ directions of the substrate surface (orientations D and E).

Crystallites of orientations F and G are also observed, having basal planes with $[1 \bar{1} 0]$ parallel to the $[1 0 0]$ and $[0 \bar{1} 1]$ directions of the base, especially on copper single crystals. With increasing thickness, basal planes with $[1 \bar{1} 0]$ at 45° to the base along the $[1 0 0]$ direction are also observed (orientation H). Orientation D is usually the predominate structure, together with orientation H at the highest thicknesses.

The micrographs show the outgrowth of the basal planes (see Fig. 3E and F) which tend to align, forming zones of equi-oriented crystals with increasing thickness. At higher thicknesses, fine parallel cracks are observed, which are closer on copper than on nickel. Where zones of different crystal orientation contact each other the structure becomes more random.

2.2. Chemical deposits on (1 1 1) faces

Many of the growth characteristics for deposition on (0 0 1) and (0 1 1) bases are found here too and differences are only referred to when pertinent. Table II summarizes the interpretation of the developing orientations in terms of epitaxial relationships between substrate and deposit;

TABLE II Preferred orientations of Co-P chemical deposits on (1 1 1) faces of Cu and Ni single crystals.

	Orientations	Thickness range
A'	$(0 0 \cdot 1) [1 1 \cdot 0]_{\text{Co}} / (1 1 1) [1 1 0]_{\text{sub}}$	$\leq 5000 \text{ \AA}$
B'	$(1 0 \cdot 1) [0 1 \cdot \bar{2}]_{\text{Co}} / (1 1 1) \langle 1 1 2 \rangle_{\text{sub}}$	$2000 \text{ \AA} - 1 \mu\text{m}$
C'	$(1 0 \cdot 0) [0 0 \cdot 1]_{\text{Co}} / (1 1 1) \langle 1 1 2 \rangle_{\text{sub}}$	$5000 \text{ \AA} - 4 \mu\text{m}$
D'	$(8 3 \cdot 0) [0 0 \cdot 1]_{\text{Co}} / (1 1 1) \langle 1 1 2 \rangle$ or $\langle 1 1 0 \rangle_{\text{sub}}$	$\geq 4 \mu\text{m}$
E'	$(2 1 \cdot 0) [0 0 \cdot 1]_{\text{Co}} / (1 1 1) \langle 1 1 2 \rangle$ or $\langle 1 1 0 \rangle_{\text{sub}}$	$\geq 4 \mu\text{m}$
F'	$(1 1 \cdot 0) [0 0 \cdot 1]_{\text{Co}} / (1 1 1) \langle 1 1 2 \rangle$ or $\langle 1 1 0 \rangle_{\text{sub}}$	$\geq 4 \mu\text{m}$

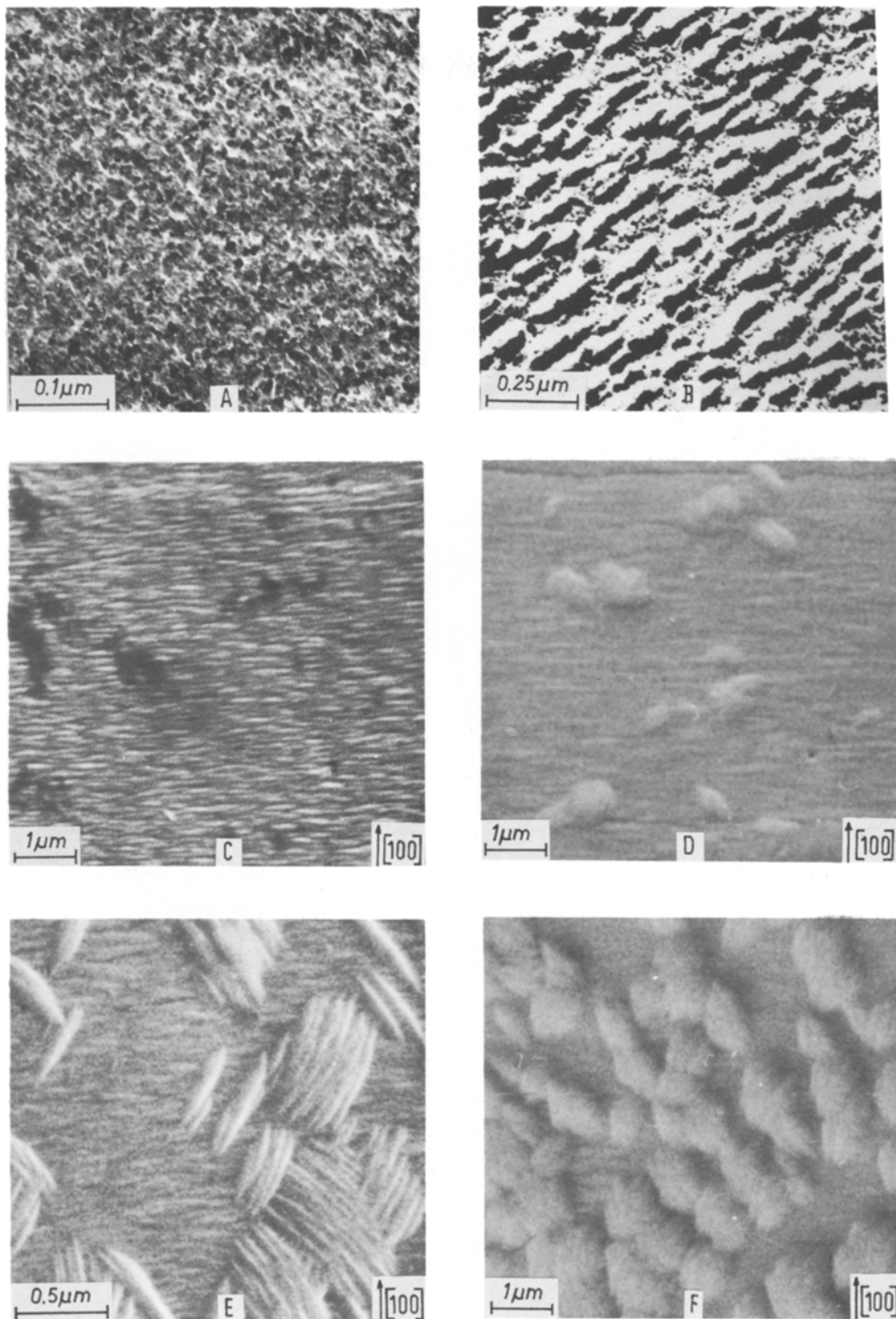


Figure 3 Micrographs of Co-P chemical deposits on (0 1 1) faces. (A) TEM on Cu, 125 Å; (B) TEM on Cu, 2000 Å; (C) SEM on Ni, 1.6 μm; (D) SEM on Cu, 4.2 μm; (E) SEM on Cu, 4.2 μm; (F) SEM on Ni, 7.8 μm.

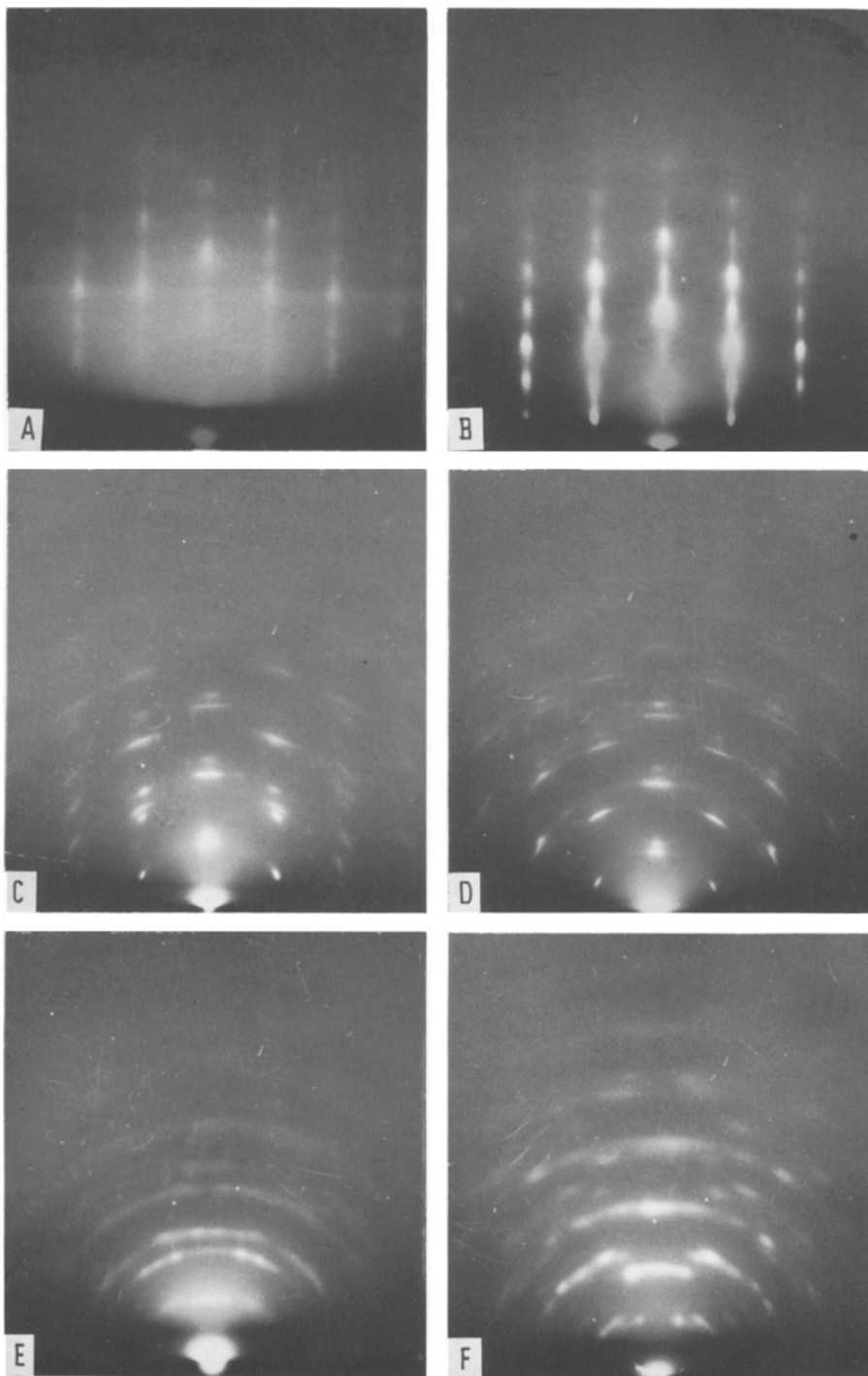


Figure 4 RHEED patterns of Co-P chemical deposits on (111) faces. (A) 45 Å on Cu, beam along $[1\bar{1}0]$; (B) 2000 Å on Ni, beam along $[1\bar{1}0]$; (C) 0.8 μm on Cu, beam along $[1\bar{1}0]$; (D) 0.8 μm on Cu, beam along $[1\bar{1}2]$; (E) 4.1 μm on Cu, beam along $[1\bar{1}0]$; (F) 11.6 μm on Cu, beam along $[1\bar{1}0]$.

where we also give the labelling which is used in the text to denote the different structures.

Fig. 4 shows the experimental RHEED patterns, Fig. 5 their interpretation and Fig. 6 SEM

and TEM micrographs of the deposits. From the first observations thin Co-P deposits have an hcp structure, with close-packed planes parallel to the surface (orientation A'). The deposits remain

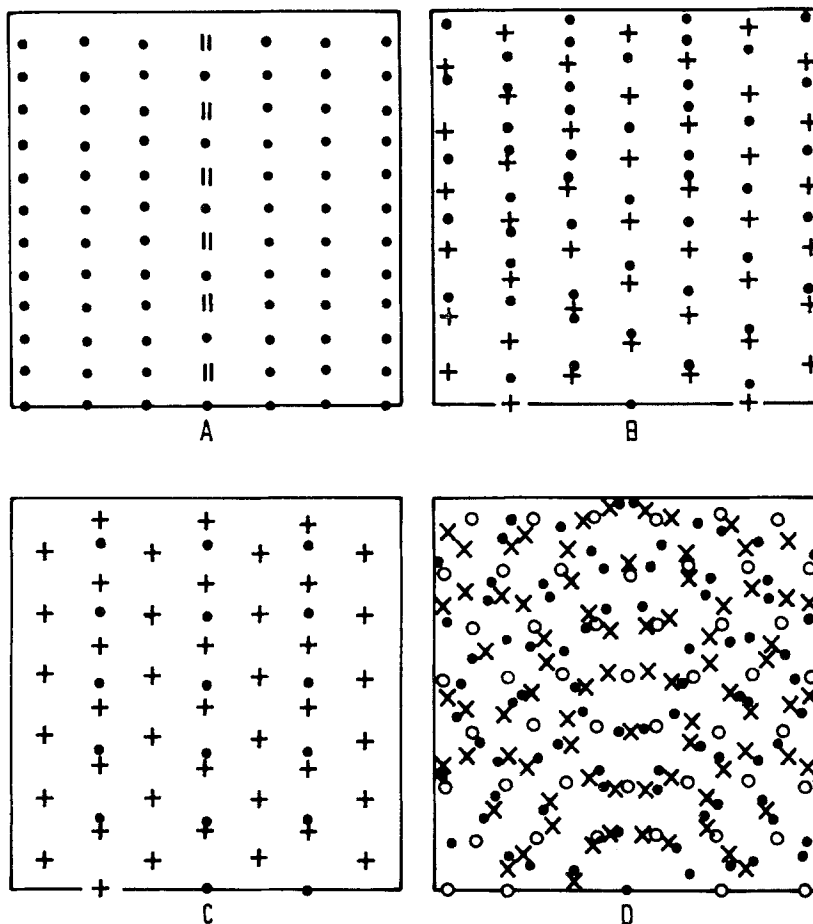


Figure 5 Interpretation of typical diffraction pattern of Co deposits on (111) faces. (A) thin deposits, orientation A', beam along $[1\bar{1}0]$; (B) medium thick deposits; orientation B' • and C' ×, beam along $[1\bar{1}0]$; (C) medium thick deposits; orientation B' • and C' ×, beam along $[1\bar{1}2]$; (D) thick deposits; orientation D' •, E' × and F' ○, beam along $[1\bar{1}0]$ or $[1\bar{1}2]$.

smooth up to medium thicknesses, and RHEED patterns show streaks and Kikuchi lines, as well as double diffraction spots of lower intensity (see Fig. 4A and B, and their interpretation in Fig. 5A). Above approximately 2000 Å, plates tilted with respect to the base in orientation B' are observed (see Fig. 4C and D, and interpretation in Fig. 5B); these plates grow from fine intersecting lines which are present on the whole surface (see Fig. 6A and B).

At increased thicknesses, the basal planes of the deposit growing along the three $\langle 110 \rangle$ directions of the surface contact each other. This promotes rotation of the planes around the $\langle 110 \rangle$ directions, until finally diffraction spots from structure C' appear in the diffractograms (see Fig. 4C and D).

Above approximately 4 μm a great deal of reorientation of the basal planes occurs by ro-

tation along the $[00.1]$ axis with orientations D', E' and F' being successively obtained (see Fig. 4E and F). At high thicknesses, zones of equi-oriented crystallites with $[00.1]$ directions along the six $\langle 110 \rangle$ and $\langle 112 \rangle$ directions of the surface are observed (see Fig. 6C to F). In some cases, especially on the nickel base, one degree $\langle 110 \rangle$ preferred orientation is observed.

2.3. Cobalt electrodeposition

In some preliminary experiments cobalt was electrodeposited at medium thickness from cobalt sulphamate baths, which are known to produce $\langle 110 \rangle$ textures on amorphous and polycrystalline substrates [2]. The same general features of chemical deposits are observed, with the given sequence of preferred orientations. Micrographs show less resolved structures, see Fig. 7, and a

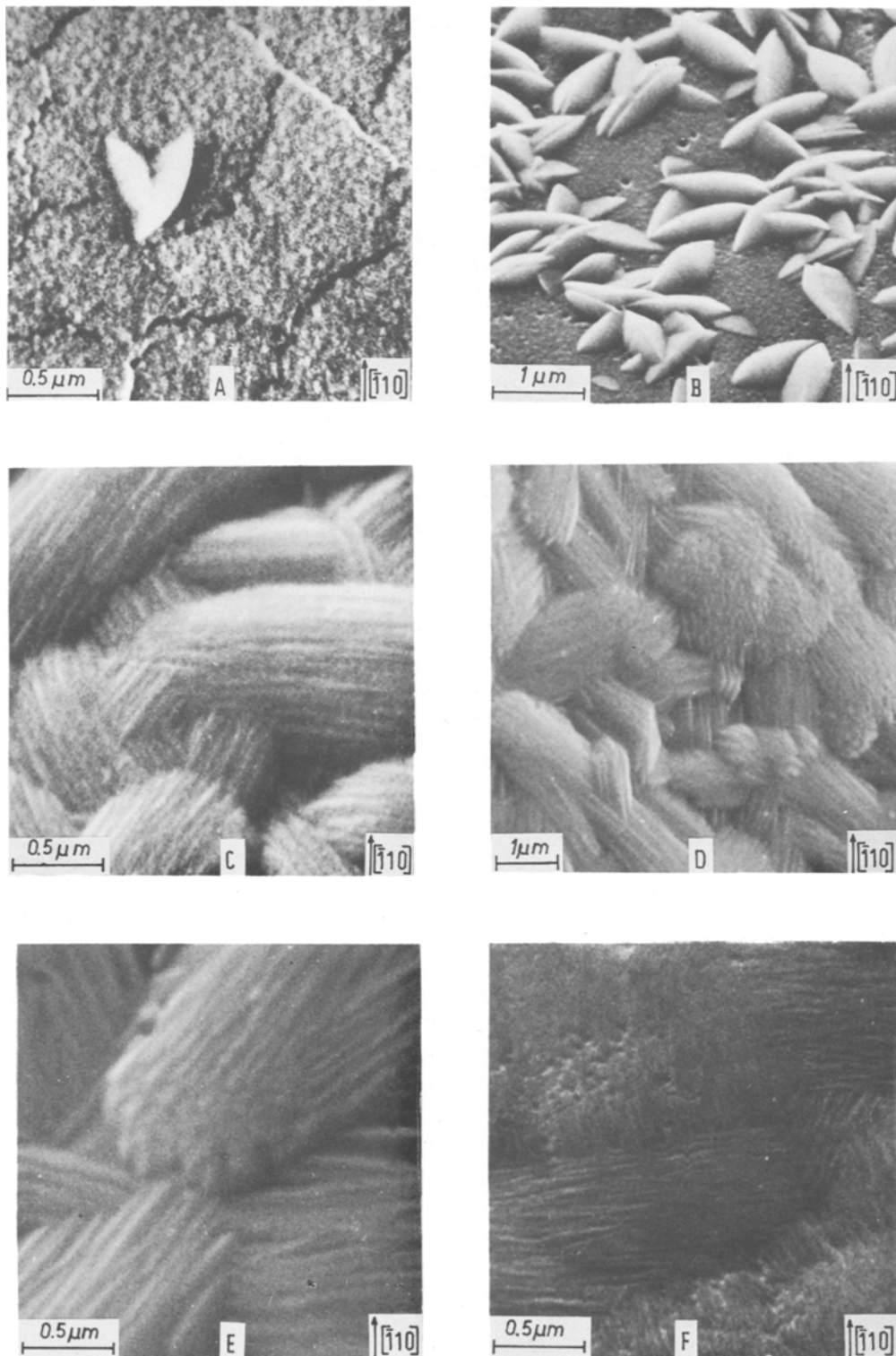


Figure 6 Micrographs of Co-P chemical deposits on (111) faces. (A) SEM on Cu, 2200 Å; (B) SEM on Ni, 1.0 μm; (C) SEM on Cu, 4.1 μm; (D) SEM on Ni, 8.0 μm; (E) SEM on Ni, 8.0 μm; (F) SEM on Cu, 11.5 μm.

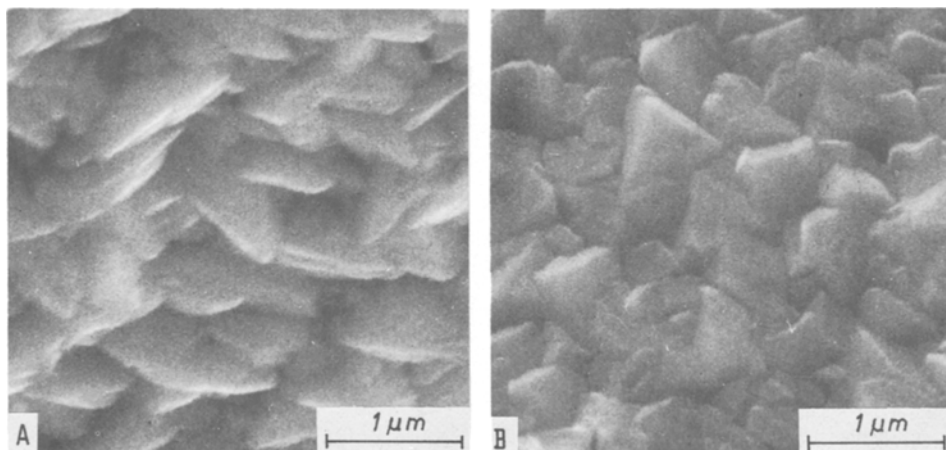


Figure 7 SEM Micrographs of Co electrodeposits of medium thickness. (A) on Cu (1 1 0); (B) on Ni (1 1 1).

more pronounced tendency towards one-degree orientations, according to our experimental conditions.

3. Discussion

Three ranges of crystal growth, according to the thickness of the deposits, can be identified. Thin deposits show the presence of fcc Co and martensitically transformed hcp Co from the first layers formed on the (0 1 1) faces of Ni and Cu single crystals. This range extends up to nearly 2000 Å in the same way as on the (0 0 1) faces. On the (1 1 1) faces, on the other hand, the range of growth of martensitic Co is greater and no fcc Co has been observed.

We were not able to observe pseudomorphism in any of the experiments performed. However, reported observations of pseudomorphic growth are limited to vacuum-evaporated cobalt coatings on metallic single crystal films [8–12]. Chemical deposition is a different process where the reduction occurs from charged species. Moreover, the presence of phosphorus has a stabilizing influence on the formation of the hcp phase [13]; and this may explain the difficulty of obtaining cobalt deposition with the same crystallographic parameter as the substrate.

Rhombohedral twinning of martensitic hcp cobalt on {1 0.1} composition planes satisfactorily explains the occurrence of orientations C and B' on the (0 1 1) and (1 1 1) faces, respectively, in the medium thickness range, as well as the C and D orientations on (0 0 1) faces already reported [2]. The stereographic projection in Fig. 8 shows the twinning operation of the planes parallel to the

base and how this allows the formation of the above-mentioned orientations from martensitic hcp cobalt. Orientation D may also be related to the rhombohedral twinning.

Twinning reflections occur on {1 0.1} composition planes keeping the close-packed direction [1 1.0] parallel to one of the <0 1 1> directions of the substrate. Deformation of cobalt single crystals rarely gives this type of twinning [14, 15]. Holt has related the occurrence of anomalous twinings to the presence of high densities of growth faults, of the same type as those observed by Rashid and Altstetter [16] in Co–Ni alloys. Our findings further confirm this difference. In fact, the occurrence of this rhombohedral twinning can be explained as a consequence of a growth stacking fault.

Thicker deposits show new transformations,

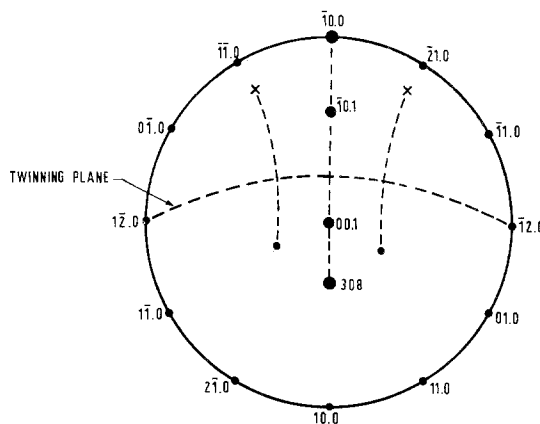


Figure 8 Stereographic (0 0.1) projection showing twinning operations by reflection of planes parallel to the base about the (0 1.1) plane.

which may be interpreted as being due to different growth modes. The observed D' , E' and F' orientations may be explained by rotation along the $[00.1]$ axis of the original structures (B' and C') towards the outgrowth with a close-packed direction perpendicular to the surface.

Orientation D may be obtained by $\{10.1\}$ twinning, as already reported. On the other hand, this twinning cannot explain orientations E , F , G , H , which also have a close-packed direction perpendicular to the substrate. The occurrence of these final orientations can be related to the orienting power of the bath, which promotes the growth of crystallites with basal planes developing according to specific directions of the parent crystal. A relationship between these orientations and internal stresses may be inferred. The initial preparation of the surface has a great influence on the obtainment of two-degree ordered zones at high thicknesses. From this point of view, chemical reduction baths are particularly well suited, as a reducing stage of the more or less oxidized surfaces is effected in the same solution before the start of the autocatalytic cobalt deposition.

Electrodeposition of medium thick deposits shows the same structures as those obtained by chemical reduction. This clearly indicates that phosphorus codeposition by chemical reduction does not affect the general features of the crystal growth from aqueous solution. An inhibiting action has been attributed to phosphorus in chemical deposition [13, 17]. We do not agree with this. In fact, outgrowth modes are easily observed in chemical deposition, and both the morphology and crystal structure of Co-P chemical deposits are remarkably more definite and perfect than those of cobalt electrodeposited by us.

Only preliminary investigations of electrodeposition on the (011) and (111) faces of copper bases have been published. Newman [3] and Goddard and Wright [4] reported the occurrence of orientations B and C of Table I for hcp cobalt electrodeposited on a (011) Cu face in accordance with our results. They have related the production of either orientation to the bath conditions whereas, according to the present work, the developing structures depend both on the bath conditions and on the thickness of the deposit.

According to Wright [6], the transformation to orientation C takes place at about 350 \AA in the film electrodeposited on a (011) copper base, in accordance with our results for chemical deposits.

The interpretation of this as a $\{111\}$ twinning after a martensitic transformation on the $\{111\}$ fcc planes is partially in agreement with our view, although with a different composition plane. On the other hand, the twinning adopted by Wright cannot explain all our results.

Fisher [5] has examined cobalt electrodeposition on a (111) Cu face, and has stressed the possibility of obtaining orientation A' , as named by us in Table II, up to approximately the same thickness observed by us in the case of chemical deposition. Substantial agreement is, therefore, observed for these sporadic results with our general scheme of growth.

Preliminary results with baths of different composition, giving deposits with $\langle 100 \rangle$ texture on amorphous substrates, show the leading role of the orientation of the base on crystal growth for thin and medium thick deposits, where the same $\{10.1\}$ anomalous twinning is always observed. At high thicknesses the bath composition becomes a determining parameter. The importance of the competition between hypophosphite ions and hydrolyzed cobalt species on the development of preferred orientations in Co-P chemical deposits, has been stressed by Cavallotti and Salvago [18]. Experiments with charged nickel hydroxide gels [19], as well as electrochemical measurements [20], indicate that this competition takes place in the layer near the surface, where adsorption occurs. In our case, where outgrowth conditions have been chosen, hypophosphite ions prevail in the layer.

Any parameter change which increases the availability of cobalt hydrolyzed species near the surface, such as a pH increase, a decrease of the hypophosphite concentration, or a decrease of the cobalt complexing agents, favours the formation of deposits with the close-packed directions not perpendicular to the surface; until inhibition conditions are reached, where the surface is mainly covered by hydrolyzed species, close-packed directions of the deposit tend to become parallel to the surface.

Our results are in complete agreement with the theory which we developed previously [21].

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