

AN ELECTRON-DIFFRACTION STUDY OF THE EFFECT OF CODEPOSITION OF FOREIGN MATERIAL ON THE STRUCTURE OF IRON ELECTRODEPOSITS

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Received June 5, 1963

(Communicated by Prof. S. Ramaseshan, F.A.S.C.)

ABSTRACT

An electron-diffraction study has been made of iron electrodeposits on copper (110) and (111) single-crystal faces. A comparison has been made of the orientation of these deposits under two sets of conditions: (a) when they reveal the incorporation of crystalline codeposits, and (b) when inclusions of foreign matter are absent. Ring radii measurements strongly suggest that the codeposit is hexagonal ferrous hydroxide. Further, it has been shown that, in the presence of codeposit, the iron electrodeposits (obtained at a particular current density) have crystal orientations which were normally obtained at higher current densities.

INTRODUCTION

THERE have been several references in literature to the inclusions of foreign material in electrodeposits.^{1, 2} However, there are very few studies of the effect of these inclusions on the structure and orientation of electrodeposits. The present work is concerned with the modifications introduced into the structure of iron electrodeposits by codeposition of foreign material.

The present authors^{3, 4} have carried out a detailed study of the structure and growth of iron electrodeposits on various faces of copper single crystals. The changes in structure of these deposits were investigated at several thicknesses (up to 10000 Å) and current densities.

The results were presented in the form of a diagram, as was first done by Setty and Wilman.⁵ In this diagrammatic representation with current

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density on the x -axis and thickness on the y -axis, a particular point represented a deposit of a particular thickness and a particular current density. The orientation of this deposit was indicated by a symbol written next to the point. This mode of representation enabled curves to be drawn demarcating *isostructure zones*, in each of which the deposits had predominantly the same crystalline orientation.

At a particular thickness, the following sequence of crystal orientations (predominant on the iron deposit surface) was observed with increase of current density: (1) epitaxial orientation, (2) twinning, (3) "random" orientation in which the deposit crystals were either randomly oriented or, if not random, had a very wide range of orientations, and (4) one-degree or preferred orientation.

EXPERIMENTAL DETAILS

Electropolished copper single-crystal faces were taken as substrates. The electroplating bath consisted of 350 gm. per litre of ferrous ammonium sulphate and 2.5 gm. per litre of sulphuric acid. The anode was of mild steel electrodeposited with iron. The single-crystal face was made to touch the surface of the electrolyte, and iron was deposited on to it at a particular current density and at room temperature. The thickness of the electrodeposit was estimated utilising Faraday's Laws and experimentally-determined current efficiencies. Care was taken to minimize atmospheric oxidation after electrodeposition, by flooding the crystal face with distilled water, absolute alcohol and iso-propyl alcohol in rapid succession. The crystal was then quickly transferred to the electron-diffraction camera keeping the crystal surface covered by a film of the high boiling-point alcohol. Electron diffraction examination of the surface structure of the electrodeposit was carried out in the usual way.

RESULTS

An account of the changes in the structure of the iron electrodeposits brought about by changes in thickness, current density and temperature has been described elsewhere.^{3, 4} Attention is here focussed upon the fact that a few of the iron electrodeposits clearly showed (from the electron-diffraction patterns obtained therefrom) the codeposition of foreign matter. For instance, the 10000 Å iron electrodeposit on copper (110) at 12.5 mA/cm.² gave electron-diffraction patterns (Fig. 1) definitely showing that in addition to the iron rings there are extra rings due to a crystalline codeposit which is randomly oriented. In the presence of the latter, the crystals of the iron

deposit are also randomly oriented in the main, though the greater intensity of the iron 222 ring in the plane of incidence suggests a trace of one-degree (111)-orientation. On the other hand, in the absence of this inclusion of foreign matter, 10000 Å iron electrodeposits (prepared under the same conditions of current density and temperature) normally show (Fig. 2) a small extent of two-degree (211)-orientation with {211}-twinning, amidst a pronounced "asymmetrical directed disorientation" of the epitaxially oriented iron crystals (the latter phenomenon has been discussed in detail by us^{3, 4}).

Again, the 1000 Å iron electrodeposits at 10 mA/cm.² obtained with a randomly oriented codeposit are partly epitaxial (211)-orientation and partly with a wide range of orientations (Fig. 3), while the deposits obtained without codeposition have a purely epitaxial structure, *i.e.*, (211)-orientation (Fig. 4).

Similarly, on the copper (111) face a 5000 Å iron deposit prepared at 15 mA cm.⁻² contains extra rings (Fig. 5) due to randomly-oriented codeposited material, in the presence of which the iron electrodeposit had random orientation. When there is no codeposition, however, a deposit of the same thickness and prepared at the same current density and temperature, contained on its surface iron crystals which were partly in epitaxial orientation and partly in a wide range of orientation (Fig. 6).

The above-results and others of a similar nature indicate that the structures of iron electrodeposits in the presence of foreign matter inclusions were those structures, which were normally observed at a much higher current density in the absence of codepositing material. Thus codeposition has the effect of shifting the iso-structure zones towards lower current density regions.

In order to identify the codeposited material the radii of the rings due to the codeposit were measured (Table I). The iron rings were identified and indexed from the known net-plane spacings. The diffraction rings from the codeposited material were thus shown to be due to a hexagonal substance. Using the iron 211 ring for the purpose of calibration, the net-plane spacings corresponding to the *hk0* rings of the codeposit, were calculated, and thereby the lattice constant '*a*'. The '*a*' values thus obtained were found to be constant to within 0.36%.

The three observed rings of *hkl* type, however, are faint and rather diffuse thus introducing errors into ring radii measurements. Together with the sharp *hk0* ring, they indicated a *c/a* axial ratio of about 2.5 as estimated from the charts giving the variation of net-plane spacing of the various planes with the axial ratio of hexagonal materials.⁶

TABLE I
Identification of codeposit

Ring Radii (mm.)	Intensity *	Iron (<i>hkl</i>)	Codeposit		
			<i>hkl</i>	<i>d</i> (Å)	<i>a</i> (Å)
8.23	M		100	2.655	3.060
8.80	W		101		
10.82	W	110			
14.29	S		110	1.529	3.058
14.52	VW		104		
15.29	W	200			
16.53	M		200	1.322	3.053
19.05	M	211			
21.93	M		210	0.997†	3.047
25.78	M		117		
28.66	M		220	0.763†	3.054
29.83	M		310	0.733†	3.054
33.20	W		400	0.658†	3.041

* S = Strong; M = Medium; W = Weak; VW = Very weak.

† *d* (in Å) is calculated from $d = \lambda L/R$ (λ = wavelength, *L* = camera length, *R* = ring radius) except for the values (†) where the more accurate formula $d = \lambda L/R (1 - \delta)$, where the correction factor $\delta = 3/8 (R^2/L^2)$ is used.

Wyckoff⁷ lists Fe(OH)₂ as hexagonal with '*a*' = 3.24 Å and *c/a* = 1.38, and with a CdI₂ type of structure. Finch and Wilman,⁸ however, showed in 1936 that CdI₂ can sometimes show twice its normal axial ratio probably due to stacking faults of the (0001) planes sequence. The present codeposit appears to have this doubled *c*-axis length, though the '*a*' value (3.052 Å) is rather smaller and the axial ratio is also smaller than the above value.⁷ Thus the codeposit observed in the present experiment is probably hexagonal Fe(OH)₂, the differences in lattice dimensions from those observed previously being possibly due to differences in composition and purity.

Further support for this conclusion may be derived from the fact that the codeposition of hydroxides has been observed in electrodeposition^{1, 2}

and has been attributed to the discharge of hydrogen ions. It is suggested¹ that this increases the pH in the vicinity of the cathode and causes precipitation of hydrous oxides, which render the deposit dark in appearance if they are included in the deposit. In the present experiment also, those deposits which contained inclusions of foreign matter (as shown by the diffraction patterns) were dark and dull in appearance.

CONCLUSION

The present study shows that from the point of view of the diagrammatic representation of results in the form of iso-structure zones, deposition of iron along with the inclusion of foreign matter is equivalent (as far as the resultant surface structure is concerned) to carrying out the electrodeposition at a higher current density. It may be argued, therefore, that the role of codeposited material is to increase the effective current density of deposition. While the exact mechanism by which the foreign material modifies the deposit structure has not been elucidated, it is not unreasonable to presume that the precipitation of codeposit on the surface of the cathode leads to a decrease in the substrate area available for electrodeposition, *i.e.*, to an increase in effective current density; and/or to a diminution of the substrate influence which tends to initiate epitaxial growth. The lessening of the substrate influence leads to a decrease of the value of the critical thickness (as defined by the iso-structure zones) up to which the deposit grows in a purely epitaxial orientation. It has been argued elsewhere⁵ that this critical thickness is closely related to the rate of deposition of atoms, *i.e.*, the current density of electrodeposition. Both these effects of precipitation of codeposit would result in a similar type of modification of the deposit orientation, as has been observed.

ACKNOWLEDGEMENTS

One of us (A. K. N. Reddy) is extremely grateful to the Ministry of Education, Government of India, for the award of a scholarship during the tenure of which this work was carried out.

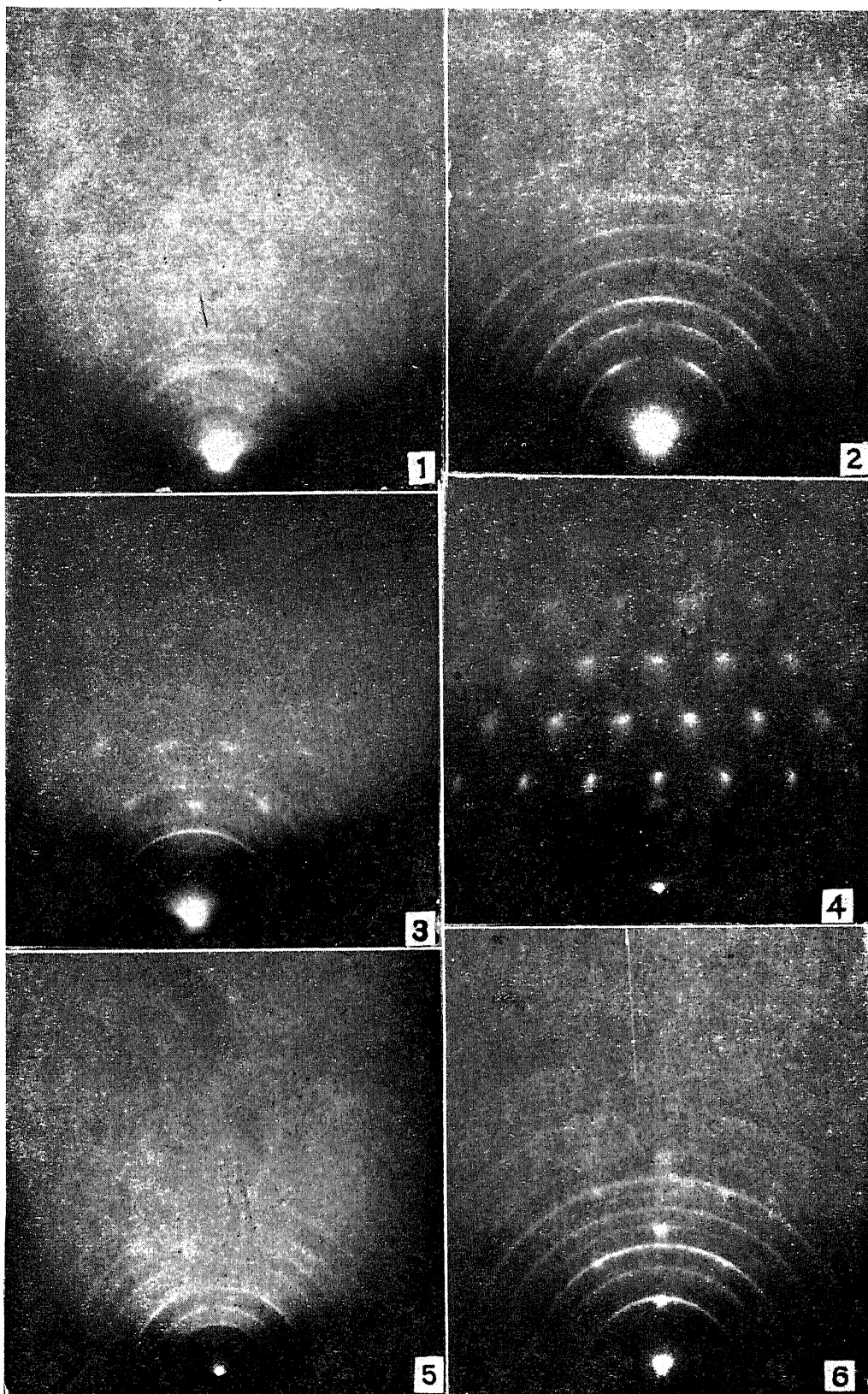
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EXPLANATION OF PLATE IV

- FIG. 1. 10000 Å Iron electrodeposit with codeposit on Cu(110) obtained at 12.5 mA/cm.²
Electron beam along Cu [1 $\bar{1}$ 0] azimuth.
- FIG. 2. Same as Fig. 1, but without codeposit.
- FIG. 3. 1000 Å Iron electrodeposit with codeposit on Cu(110) obtained at 10.0 mA/cm.²
Electron beam along Cu [1 $\bar{1}$ 0] azimuth.
- FIG. 4. Same as Fig. 3, but without codeposit.
- FIG. 5. 5000 Å Iron electrodeposit with codeposit on Cu(111) obtained at 15.0 mA/cm.²
Electron beam along Cu [1 $\bar{1}$ 0] azimuth.
- FIG. 6. Same as Fig. 5, but without codeposit.



FIGS. 1-6