

THE STRUCTURE AND GROWTH OF NICKEL ELECTRODEPOSITS ON ELECTROPOLISHED COPPER SINGLE-CRYSTAL SUBSTRATES

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Received September 3, 1964

(Communicated by Dr. S. Ramaseshan, F.A.Sc.)

ABSTRACT

An exploratory study has been made of the orientation and growth of nickel electrodeposits on copper (110) and (111) substrates. The general nature of the variation of deposit structure with current density and thickness has been elucidated, and the results compared with previous work involving a deposit-substrate pair, where both metals belong to the f.c.c. system.

INTRODUCTION

THOUGH some of the first electron diffraction experiments were concerned with electro-deposits, it has only been in the past decade that the structure and growth of these deposits were studied systematically by varying parameters like thickness, current density, temperature, concentration, etc. Setty and Wilman¹ were the first to carry out such an intensive study of cathodic crystal growth. They studied the electrodeposition of silver on silver single-crystal substrates. These authors drew the following conclusions:

1. That there was a minimum critical current density below which deposits grew in parallel orientation (relative to the substrate) up to large thicknesses (of the order 100,000 Å).
2. Deposits prepared at a current density greater than the minimum critical current density showed, with an increase in deposit thickness, the following sequence of changes in surface structure: parallel orientation → twinning → random polycrystalline structure → a preferred one-degree orientation.

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3. The higher the current density, the smaller was the thickness at which parallel orientation of the electrodeposit crystals gave way to octahedral twinning.

Kumar and Wilman² extended these results to the case of copper grown electrolytically on silver single-crystal substrates, and to silver on copper.

These authors also observed a broadly similar pattern of change in surface structure with factors such as current density, thickness and temperature as was observed by Setty and Wilman.¹ However, certain differences in the nature of growth were also observed. For instance, Kumar and Wilman found that when copper grows on a silver (110) face, there is a disorientation of the electrodeposit crystals which adopt a range of orientations about a particular lattice row. This phenomenon was termed *directed disorientation* and it was suggested that it resulted from tensile stresses developed due to the lack of exact fitting of the deposit and substrate lattices. The lattice constant difference in the Cu-Ag deposit-substrate pair was 0.4703 Å.

The present exploratory study was undertaken with two objects in view: (a) to ascertain the general form of dependence of deposit structure on thickness and current density in the case of nickel deposited on copper single-crystal substrates, (b) to study whether the type of directed disorientation (observed by Kumar and Wilman²) generated by the deposit-substrate pair having a relatively large lattice constant difference would also be found in the case of nickel on copper where the lattice constant difference is only 0.0925 Å.

EXPERIMENTAL DETAILS

Electropolished copper single-crystal faces were taken as substrates. The electroplating bath consisted of 240 gpl of $\text{NiSO}_4 \cdot 7 \text{H}_2\text{O}$ and 30 gpl of H_3BO_3 . The anode was a nickel sheet (7 × 5 cm.). The single-crystal face was made to touch the surface of the electrolyte and nickel was deposited on to it at a particular current density and at 20° C. The thickness of the electrodeposit was estimated utilizing 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 isopropyl alcohol in rapid succession. The crystal was then quickly transferred to the electron diffraction camera keeping the crystal face of copper 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. Nickel deposits of different

thicknesses were prepared at different current densities, and their surface structures studied.

RESULTS

Electrodeposition of nickel on the Cu (110) faces

The electron diffraction patterns (Fig. 1) from the 500 Å nickel electrodeposits obtained at 5 mA/cm.² indicate that the nickel has an epitaxial orientation which agrees with that established by Cochrane³ in 1936. He found that Ni (110) was parallel to Cu (110), with all axes of the nickel parallel to all axes of the copper, *i.e.*, the nickel deposit had grown in (110)-parallel orientation to the Cu (110) substrate. The extra spots in the pattern obtained with beam along the copper (110) azimuth are due to octahedral twinning, as shown by Cochrane and discussed in detail by Menzer⁴ and by Goche and Wilman.⁵ Since the twin spots are very faint compared to the main pattern, it can be concluded that the bulk of the crystals on the deposit surface are in parallel orientation, and that there is only a small trace of (111)-twinning. In the above pattern these spots of the centered $\sqrt{2}$ -rectangle pattern show considerable elongation towards the shadow edge. On the other hand, the twin spots are sharper and show little such elongation. This observation can be interpreted to mean that those parts of the deposit surface where twinning of the parallel-oriented crystal occurred were much rougher than those parts where the nickel follows both the orientation and the surface topography of the atomically-smooth, electropolished Cu (110) substrate.

The 500 Å deposits obtained at 10 mA/cm.² give essentially similar electron diffraction patterns (Fig. 2). However, several new features have to be noted. Firstly, the extent of (111)-twinning is considerably greater than in the 5 mA/cm.² deposits. Secondly the diffraction spots have an arrow-head shape, formed by elongation normal to the octahedral planes. This indicates the presence of octahedral facets on the crystals of the deposit. Thirdly the pattern obtained with the electron beam along the copper [001]-azimuth, contains very faint 111 and 222 diffractions in the plane of incidence and also other diffractions forming with these a $\sqrt{8/3}$ rectangular pattern of spots. This suggests that a very small proportion of the deposit crystals have (111) planes parallel to the Cu (110) substrate with Ni [121] parallel to Cu [001].

We shall now consider thicker deposits. 5000 Å deposits prepared at 2.5 mA/cm.² yielded diffraction patterns (Fig. 3), which indicate that in addition to the parallel (110)-orientation, a small proportion of the deposit

crystals are in epitaxial (111)-orientation with (111)-twinning. There is also a suggestion of the formation of octahedral facets. The structure of 5000 Å Ni deposits prepared at 5 mA/cm.² is closely similar to that of 500 Å deposits obtained at 10 mA/cm.² The electrodeposit surface was however, much rougher as indicated by the sharpness of the diffraction spots. Further, facet formation was a little more marked when compared to the 5000 Å deposits prepared at 2.5 mA/cm.²

At 10 mA/cm.² 5000 Å Ni electrodeposits yielded diffraction patterns similar to those from 5 mA/cm.² deposits. One of these 10 mA/cm.² deposits was etched for 30 seconds in an etching solution, consisting of 30 c.c. of a concentrated HCl, 10 g. of ferric chloride and 120 c.c. of distilled water. The copper crystal (with deposit) was quickly washed with distilled water, absolute alcohol and propyl alcohol, and the surface structure examined by electron diffraction. The patterns (Fig. 4) from the etched deposit show several new features. They reveal, firstly, the absence of (111)-oriented nickel, secondly, the smooth nature of the surface (as suggested by the vertical elongation of the spots), thirdly the absence of octahedral facets and finally the presence of a very small extent of twinning. Since the deposit thickness after a 30-second etch must be much less than the original 5000 Å, this experiment shows clearly that the growth of the deposit at 10 mA/cm.² was associated with an increased extent of twinning of the initially parallel-oriented crystals, with a roughening of the deposit surface and also with the formation of facets.

Electrodeposits 5000 Å thick prepared at a still higher current density, 25 mA/cm.², had a predominantly random orientation (Fig. 5). However, the slight variation of intensity along the rings shows that there is a small degree of preferred orientation. The latter is perhaps one-degree (110)-orientation as indicated by the (220) arc in the plane of incidence.

Experiments on the Cu (111)

Using Copper (111) as substrate, electrodeposits of Nickel were obtained at 5 and 20 mA/cm.² The electron diffraction patterns of these deposits are shown in Figs. 6, 7 and 8. The main conclusions to be drawn from these patterns are as follows:

1. The nickel has grown in parallel (111)-orientation with all axes of nickel parallel to all axes of the Cu substrate.
2. With increase of thickness the extent of (111)-twinning increases.
3. There is also the development of random polycrystalline pattern.

DISCUSSION

The above results provide an interesting comparison to those of Kumar and Wilman² who studied in detail the electrodeposition of Cu on silver single-crystal faces and of silver on copper. Both studies concern the electrolytic growth of a f.c.c. metal on single-crystal substrate of another f.c.c. metal. Certain similarities in the results may, therefore, be expected and are found.

For instance, nickel is electrodeposited on the Cu (110) and (111) faces in an orientation which is parallel to that of the copper lattice. Thus Ni (110) parallel to Cu (110) and Ni (111) parallel to Cu (111) have been observed in the present experiment. This result, along with those of Kumar and Wilman shows that *when f.c.c. metals are electrodeposited on single-crystal faces of other f.c.c. metals, the deposit orientation in thin layers and at low current densities is the same as that of the single-crystal substrate surface.* It would be interesting, however, to test whether this conclusion would also hold good for the electrodeposition of lead ($a = 4.950 \text{ \AA}$) on single-crystal faces of Cu ($a = 3.608 \text{ \AA}$), where there is a large lattice constant difference.

Deposits of Ni without twinning were not observed in the few experiments that were performed in the present work. There is sufficient indication, however, that the initial stage is parallel growth. Thus, it has been observed that the extent of octahedral twinning increases with deposit thickness. Again, the experiment in which a 5000 \AA Ni deposit was etched to reveal the nature of the intermediate stages of crystal growth clearly established that at the smaller thicknesses observed after etching, there was hardly any twinning. At 5000 \AA however, the diffraction patterns showed that there was extensive twinning of the deposit crystals on the deposit surface. Apart from this evidence, previous workers have observed some of these initial parallel growths. Thus, it may be concluded that *the initial stage of parallel growth is apparently a general feature of the cathodic crystal growth of a metal on a single-crystal face of a dissimilar metal, when both the deposit and the substrate belong to the f.c.c. system.*

Above a certain current density, the deposits continue in parallel orientation only up to a certain thickness, after which octahedral twinning develops. Twinning is initially negligible, but gradually increases in an extent (as has been shown by the present work) until an increasing proportion of the deposit crystals on the surface are randomly oriented. While Cochrane³ noted that thick deposits showed the presence of twinning, the systematic variation of surface structure with deposit thickness (referred to above) for the case

of dissimilar f.c.c. metals electrodeposited on one another, was first observed by Kumar and Wilman.² However, it was Setty and Wilman,¹ who showed, in the case of silver deposited on silver single-crystal faces, that the twinning corresponded to a definite stage of crystal growth for the deposit-substrate pair studied by them. The present results along with those of Kumar and Wilman, and Setty and Wilman, have thus established *the twinning stage to be an essential intermediate stage between the initial parallel orientation and the random orientation (which gives way to the final one-degree orientation) for the case of f.c.c. metals electrodeposited on single-crystal faces of the same or other f.c.c. metals.*

The lattice constant difference for the Cu-Ag and Ni-Cu deposit-substrate pairs is not, however, the same. Thus there ought to be a difference in the magnitude of epitaxial stresses generated, which would probably reveal themselves in the *absence*, in the present work, of certain phenomena specifically associated with the stresses developed in the deposit lattice. Thus the type of directed disorientation observed by Kumar was not found in Ni electrodeposits on Cu (110), presumably because the lattice misfit is so small.

Finally, the changes in surface topography of the Ni electrodeposits, associated with cathodic crystal growth which have been revealed by the present work are in agreement with the views put forward by Finch, Wilman and co-workers.⁶ Specifically, *even though deposition is commenced on an atomically-smooth electropolished single-crystal substrate, further increase in deposit thickness is accompanied by a roughening of the deposit surface with the development of facets.*

ACKNOWLEDGEMENT

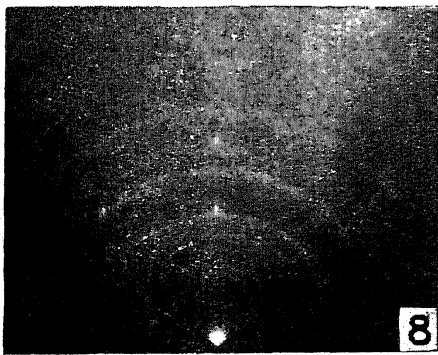
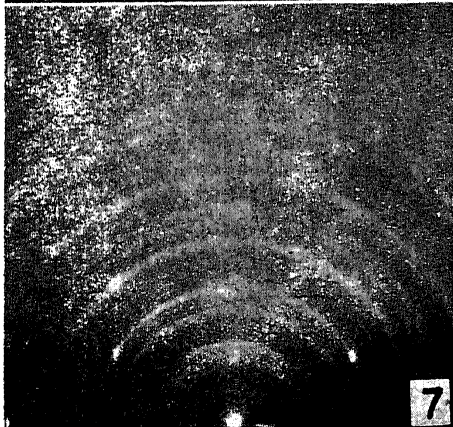
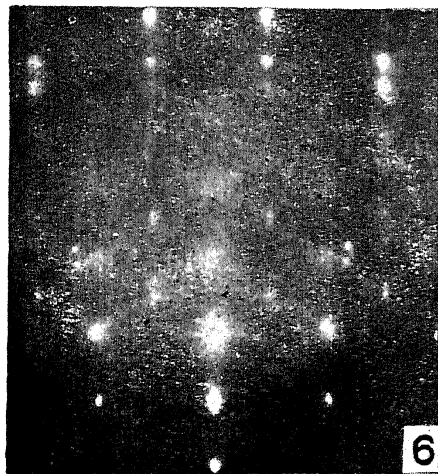
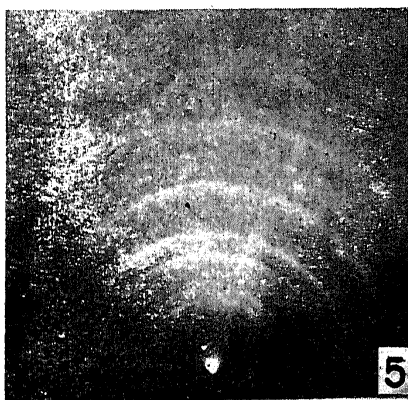
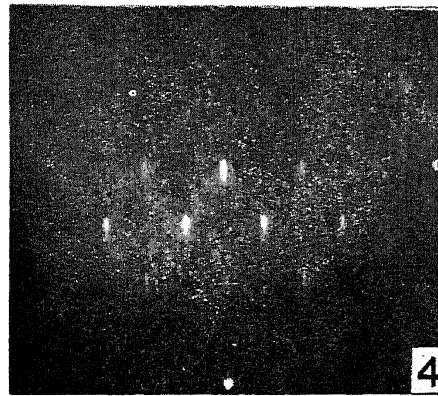
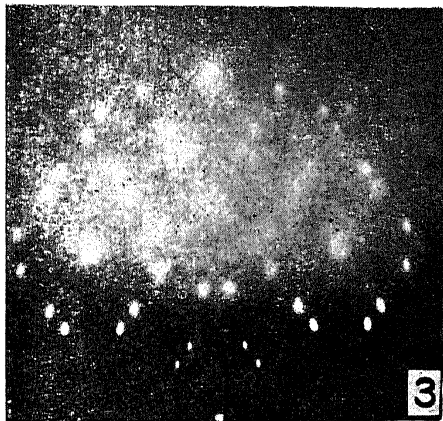
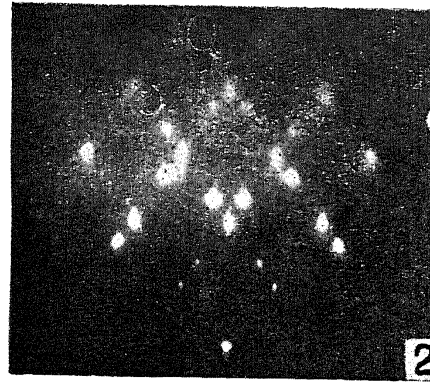
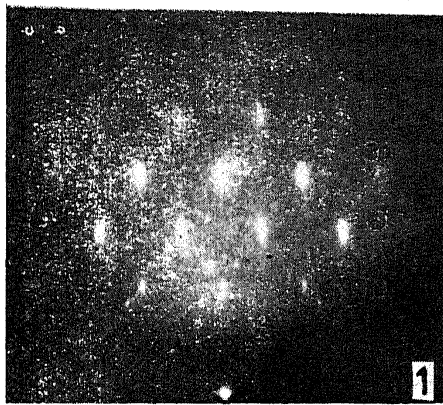
One of us (A. K. N. Reddy) is extremely grateful to the Ministry of Education, Government of India, for the award of a scholarship during the tenure of which this work was carried out.

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EXPLANATION OF PLATE V

- FIG. 1. 500 Å Ni electrodeposited on Cu (110) at 5 mA/cm.² Electron beam along Cu $[\bar{1}\bar{1}0]$ azimuth.
- FIG. 2. 500 Å Ni electrodeposited on Cu (110) at 10 mA/cm.² Electron beam along Cu $[\bar{1}\bar{1}0]$ azimuth.
- FIG. 3. 5000 Å Ni electrodeposited on Cu (110) at 2.5 mA/cm.² Electron beam along Cu $[\bar{1}\bar{1}0]$ azimuth.
- FIG. 4. 5000 Å Ni deposit on Cu (110) obtained at 10 mA/cm.², and then etched for 30 secs. Electron beam along Cu $[\bar{1}\bar{1}0]$ azimuth.
- FIG. 5. 500 Å Ni electrodeposited on Cu (110) at 25.0 mA/cm.² Electron beam along Cu $[\bar{1}\bar{1}0]$ azimuth.
- FIG. 6. 5000 Å Ni electrodeposited on Cu (111) at 5 mA/cm.² Electron beam along $[\bar{1}\bar{2}1]$ azimuth.
- FIG. 7. 5000 Å Ni electrodeposited on Cu (111) at 5 mA/cm.² Electron beam along $[\bar{1}\bar{2}1]$ azimuth.
- FIG. 8. 5000 Å Ni electrodeposited on Cu (111) at 20 mA/cm.² Electron beam along Cu $[\bar{1}\bar{2}1]$ azimuth.



FIGS. 1-8