Letters

A Transmission Electron Microscope Study of the Structure of Electrolytic Nickel

The structure of electrodeposited nickel has been investigated by one of the authors [1] using quantitative X-ray diffraction methods. The results showed that the average domain size and strains in samples electrolysed from acid sulphate solutions vary strongly with the pH of the solution and a possible later heat treatment of the sample. Furthermore, an observable density of twin stacking faults was found under certain conditions.

In the present work, the structure of nickel samples electrolysed under the same conditions as in [1] was studied by transmission electron microscopy. Similar studies of structures electrolysed from Watt's solution ($NiSO_4 + NiCl_2$ electrolyte) have been recently made by Maurin and Froment [2], whereas Crossley *et al* [3] and Dennis and Fuggle [4] investigated the effect of addition agents on the structure.

Electrolysed samples of a few tenths of a millimetre were prepared under the same conditions as explained in [1], table I. The pH values used in the electrolysis were 1.6, 3.0, 4.0, and 6.0. Specimens for transmission electron microscopy were made from the samples by conventional thinning techniques. (Some of the samples were given one-hour heat treatment before the specimen was made.) The specimens were investigated in a Siemens electron microscope using a beam voltage 100 kV.

Fig. 1 shows the structure typical of a sample electrolysed at pH = 6. A part of the sample is strongly twinned. The average thickness of the twins is of the order 10^3Å. The structure inside an individual twin lamella is rather free of faults. Some thin twins in otherwise faultless crystals can be found (fig. 2). At the lower right corner of fig. 1 is seen an area with much smaller grains, the detailed structure of which is not resolved in the picture. This type of structure becomes more prevalent at somewhat lower pH (fig. 3; pH = 4). Many thin twins are observed in the larger grains. The structure at pH = 3 consists almost entirely of very small grains, but a sample electrolysed at pH = 1.6 shows on the average a considerably larger grain size (fig. 4). Twins are relatively few, and some of them are quite large (fig. 5).

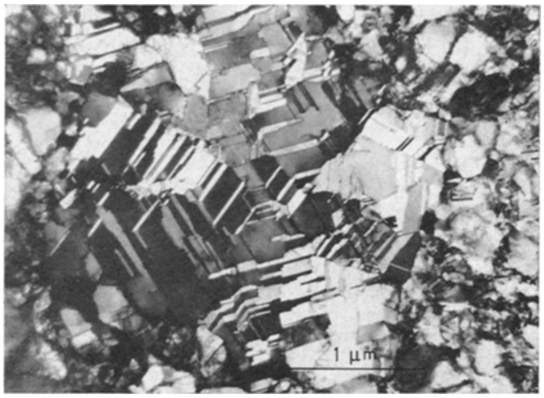

Figure 1 pH=6.0; as-electrolysed.

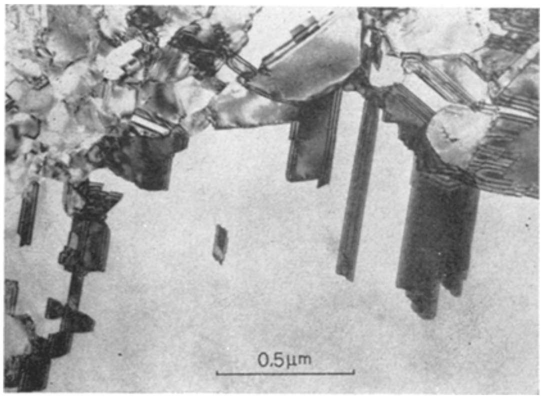

Figure 2 pH=6.0; as-electrolysed.

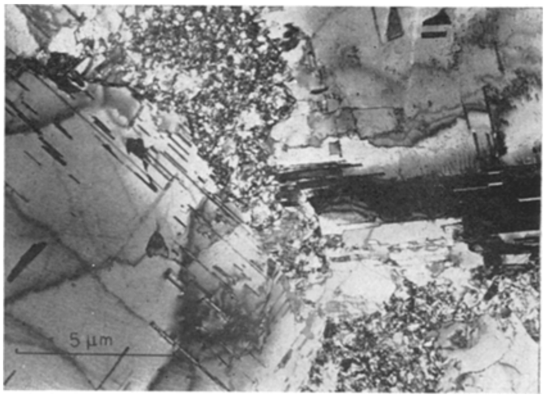

Figure 3 pH=4.0; as-electrolysed.

No preferred orientation of the *small* grains could be found in any of the samples, whereas a very strong texture with the [100] direction perpendicular to the surface of the cathode is typical of the *larger* grains at pH = 4. The size

Figure 4 pH = 1.6; as-electrolysed.

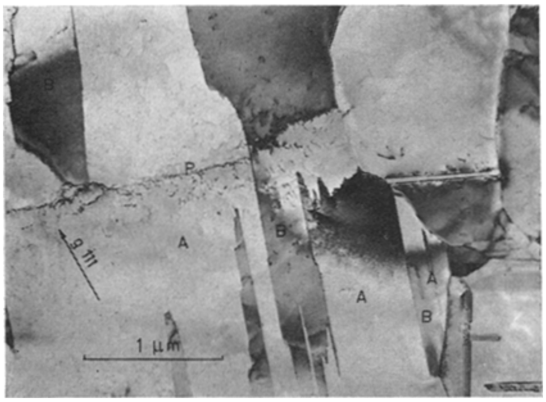

Figure 5 pH = 1.6; as-electrolysed.

of the "small" and "large" type of grains is very different: the "small" grains rarely exceed 0.1 μm diameter whereas the "large" grains extend from roughly 1 μm (at pH = 3) to more than 10 μm (pH = 4 to 6). A third type of grain is the strongly twinned grain (pH = 6) of about 1 μm in diameter.

Although strong twinning was found in many of the samples, no individual stacking faults, either extrinsic or intrinsic, could be found. However, it should be borne in mind that only the larger grains were accessible to a reliable study. The existence of individual faults in the very small grains is still possible,

A heat treatment of 1 h at 300° C after the electrolysis was not found to have any clearly detectable effect on the structure as revealed by the transmission pictures. After heating at 400° C (fig. 6), the average size of the "small" grains has grown somewhat, but numerous twins can still be seen. After heating at 600° C (fig. 7), the "small" grains have grown considerably. Twins can still be seen in the structure.

Figure 6 pH = 4.0; heat treatment: 1h, 400° C.

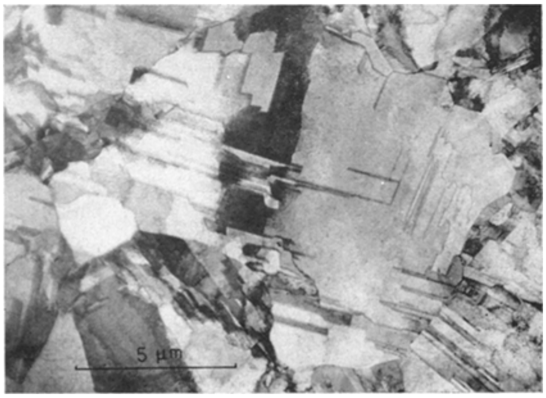

Figure 7 pH = 4.0; heat treatment: 1h, 600° C.

The "large" grains correspond, with respect to both their size and orientation, roughly to the structure found by Maurin and Froment [2] at high current densities. The "small" randomly oriented grains were not found by Maurin and Froment, but Crossley *et al* [3] and Dennis and Fuggle [4] found similar structures in samples electrolysed from solutions containing various organic additives. Since the "small" grains were found in this work in the pH region in which the presence of a colloidal film of $Ni(OH)_2$ at the cathode is to be expected ([1], p. 45), it can be concluded that this film is probably responsible for them. It is especially interesting that the typical "small" grain structure is not found at pH = 1.6, which is probably below the limit of the existence of such films.

The coexistence of areas with "small" and "large" grains in the same structure can be understood, assuming that the hydroxide film covers only parts of the cathode. The exposed areas exhibit the "large" grain size similar to that found by [2], in which case the inhibitive effect was eliminated by the Cl^- ions in the electrolyte ([5], p. 114).

Although frequent twinning was seen in the "large" grains in many samples, the densities of twin faults found in earlier work [1] cannot be confirmed because no individual faults could be observed. The twin fault densities computed from the densities of the observed "ordinary" twin boundaries are rather low. However, the overall densities can be essentially raised by possible twinning in the "small" grains, predominant in structures in which measurable fault densities were reported in [1]. In fact, observations by Zieler ([3], p. 1155) support twinning in small grains of samples electrolysed from solution containing additives.

On the other hand, numerous "stacking faults" rather than twins were reported in "large" grains in structures electrolysed from Watts solution by Maurin and Froment ([2], p. 107). However, the evidence for their presence in transmission pictures is not given, and it is not certain whether the faults mentioned are really individual stacking faults.

Although it is difficult to make a good estimate of the average grain size from the pictures exhibiting the dual grain morphology, the results of the X-ray measurements of the average particle sizes in [1] are roughly in agreement with qualitative estimates.

The roughly isotropic grain size of the "small" grains is in agreement with the X-ray results.

Conclusions

In conclusion, during the electrolysis of nickel from acid sulphate solutions, the coverage of the cathode by a possible colloidal film of nickel hydroxide is the decisive factor. In its presence, the cathode exhibits a very fine-grained, randomly oriented structure. If the film is removed, the structure consists at these current densities of relatively large grains with a very strong texture [100] perpendicular to cathode. The large grains are often twinned, but no individual stacking faults are found.

The inhibitive action of the hydroxide film can be eliminated by chloride ions [2], or it can be replaced by an organic additive [3].

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References

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Preparation of Gold Films with Low Dislocation Densities

The growth of single-crystal films on single-crystal substrates usually begins with the generation of three-dimensional nuclei [1] and proceeds with the growth and coalescence of these nuclei. Complete films that grow in this way contain about 10^{10} dislocation lines per cm^2 [2-5]. They may also contain wide stacking faults and numerous microtwins. Studies of the generation of dislocations, stacking faults and twins have shown that most of them result from the presence of three dimensional nuclei whose lattices are either rotated relative to one another or are displaced from one another by non-lattice vectors [4, 6-8]. It is clear that the defect content of complete films would be reduced if the initial deposit did not contain nuclei that were either misaligned or displaced from one another. One of the ways of eliminating these nuclei is to ensure firstly that there is little or no