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Electron Microscopic Investigations of Pyramidal Structures formed on the Surfaces of Electrodeposited Nickel

IN a previous communication[1], we reported the development of various structures on the growing surfaces of electrodeposited nickel, using electron microscopy. The deposits examined were obtained by electrodepositing nickel, mainly on polycrystalline copper foils, at a current density of 10 m.amp/cm^2 from a Watt's type of bath at a temperature of 25° C. Deposition times of about 1 and 120 min were used for most of the work. The presence of growth features, such as sub-grain structures formed at an early stage and microcavities formed at an advanced stage of deposition, led us to believe that internal stresses associated with dislocations and other structural defects play an important part in the growth of cathodic crystals. Recently, we have observed by electron microscopy the development of pyramidal structures at intermediate times of deposition from the same baths and at the same deposition conditions as used previously. In this communication, results on the development of these structures are d.presente

Purified sulphate–chloride baths of pH 5·1, having compositions as described in the previous work[1-3], were used. Deposition was carried out on 1-mil-thick platinum foils, which were previously etched in dilute aqua regia. The electron micrograph of the platinum surface is shown in Fig. 1. Replicas of the electrodeposited nickel surfaces for electron microscopic investigations were prepared as previously described[1,2].

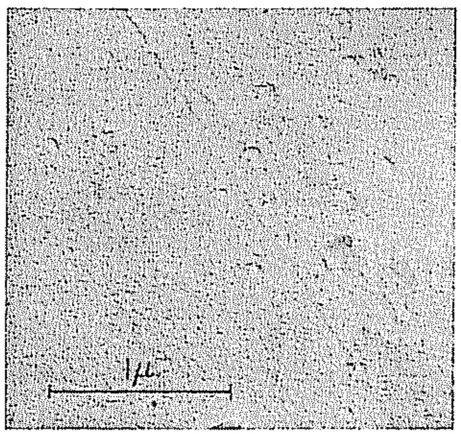

Fig. 1. Electron micrograph showing the polycrystalline structure of the etched platinum cathode

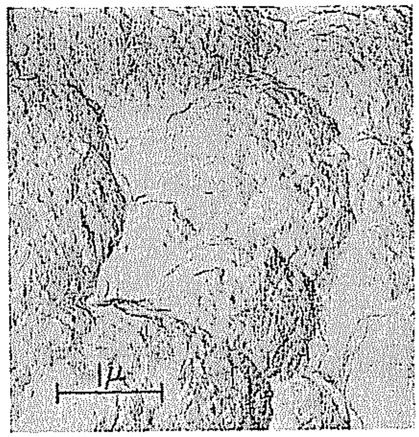

Fig. 2. Electron micrograph revealing the formation of crystal grains during electrodeposition of nickel from a sulphate–chloride bath, of pH 5·1, at 25° C, and a current density of 10 m.amp/cm^2, for 5 min

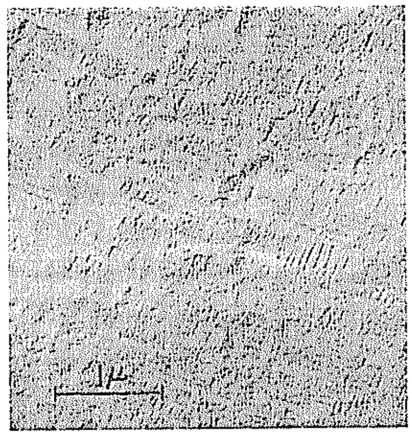

Fig. 3. Electron micrograph showing the development of parallel lines as well as steps during the electrodeposition of nickel using the same bath conditions as in Fig. 2, but for a deposition time of 10 min

Nickel electrodeposited from the sulphate–chloride bath of pH 5·1 at a current density of 10 m.amp/cm^2, and for a deposition time of 5 min, generally developed large crystal grains with well-defined boundaries (Fig. 2). A similar growth for electrodeposited nickel was observed, in some cases, by Weil and Cook[4]. For a deposition time of 10 min, under the foregoing bath conditions, a surface developed which contained mutually parallel lines and steps (Fig. 3). If deposition was carried out at a longer time, say 45 min, simple pyramidal structures bounded by stepped surfaces were formed (Fig. 4). The apexes of a set of pyramids are in general connected by a line,

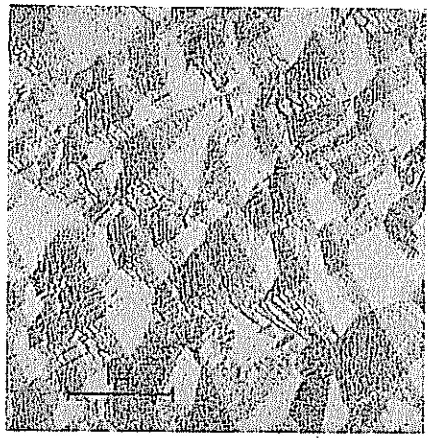

Fig. 4. Electron micrograph revealing the formation of simple pyramidal structures using the same bath conditions as in Fig. 2, but for a deposition time of 45 min

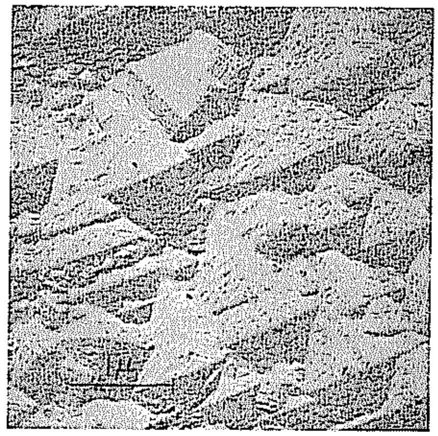

Fig. 5. Electron micrograph of the electrodeposited nickel surface formed under conditions similar to those in Fig. 4, but revealing the formation of pit-like structures on the pyramids

with the lines connecting the different sets of pyramids running parallel to each other. For a still longer time of deposition, say 65 min, pit-like structures appeared at the apexes and on the steps of the surfaces of the pyramids (Fig. 5). The pyramids completely disappeared at sufficiently long times of deposition (120 min), with microcavities, resembling etch pits, forming on the various parts of the cathode surface[1].

No pyramids were formed at comparable thicknesses of electrodeposited nickel from the foregoing baths and deposition conditions at higher current densities of 25 or

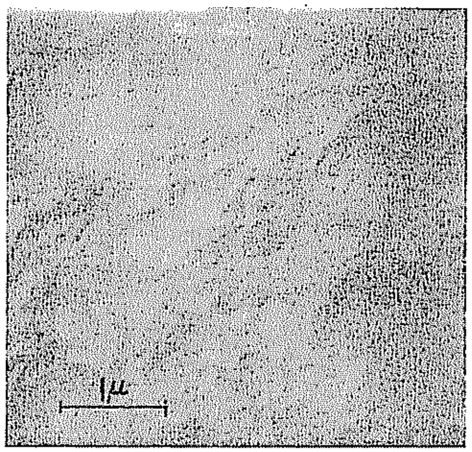

Fig. 6. Electron micrograph of the nickel surface as obtained by electrodeposition from a sulphate–chloride bath of pH 5·1, at 25° C, at a current density of 50 m.amp/cm^2, with a deposition time of 12 min

50 m.amp/cm^2 (Fig. 6). This is in agreement with the finding of Economou, Fischer and Trivich[5], who examined the structure of electrodeposited copper. At low current densities, pyramidal growth predominated; at higher current densities, layer growth predominated. According to these workers, high mobility of dislocations on a growing cathode surface is necessary to account for the development of simple as well as extended pyramidal structures. This high mobility of dislocations could be a consequence of the exothermic character of the electrodeposition process[6] and the fact that newly formed surfaces tend to a configuration which reduces their internal stresses.

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