

Electron Microscopic Investigations on the Structure and Topography of Electrodeposited Nickel

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As a result of successful application of electron waves in revealing many structural details of electrodeposited metal surfaces (1-6), the mechanism of growth of cathodic deposits is becoming better understood. It has become evident that a detailed knowledge of surface conditions of the initial cathode surface (based on chemical, electrochemical, and metallurgical studies) is necessary before one can arrive at a valid conclusion as to the factors determining not only the cathodic growth processes but also many of the physical and mechanical properties of the electrodeposits (2, 3, 7, 8). Experimental evidences in favor of the dislocation theory of crystal growth processes are overwhelming, but very few attempts have been made, to the authors' knowledge, to explain many structural details that develop on the surfaces of electrodeposited metals on the basis of this theory. In our electron microscopic investigations of the topography of such surfaces, we have observed not only the formation of substructures but also striations or steps and dendritic type of growth during initial stages of deposition and microcavities resembling etch pits at an advanced stage of deposition. These finer structures formed on a growing cathode surface, stress the importance of the various structural imperfections and the thermal energies involved in the growth of electrodeposited metals (2, 7, 8).

Experimental

Our experiments mainly consist of an electron microscopic study of the structures and topography of Ni at various stages of electrodeposition on reagent grade Cu, Ag, Au, Ni, and Pt cathode surfaces.

Results for Ni, electrodeposited on two types of Cu cathodes are presented in particular detail. Carbon replicas of surfaces preshadowed with Pt at angles varying from 15° to 25° generally were used for electron microscopic investigations. The Ni was electrodeposited at a current density of 10 ma/cm² and at a bath temperature of 25°C from a purified sulfate-chloride bath adjusted to different pH conditions (2.1, 3.2, 5.1). Deposition times generally ranged from about 1 min to about 120 min. The procedures involved in the preparation, purification, and pH adjustments of the reagent grade plating solutions have been given elsewhere (1, 2). The thickness of the Cu and Ag foils was adjusted to about one mil by etching them slowly in dilute acid solutions, followed by washing in distilled water. Slow etching generally helps in revealing grain boundaries in greater detail. The Au foils, originally of 0.4 mil thickness, were further thinned to reveal grain boundaries by slow etching in dilute aqua regia. Figure 1 is a typical electron micrograph revealing the small grained structures of the Ag foil. Foils of Au, Cu, Ni, and Pt possess similar structure. Details of the preparation of the carbon replicas and the method of their separation from the metal surfaces have been published previously (2). Two types of Cu surfaces were used as the cathodes for electrodeposition: (A) Two mil thick copper foils were etched in moderately dilute HNO₃ to adjust the ultimate thickness to about one mil followed by a dip in concentrated HCl and a rinse in distilled water (2). (B) This surface was prepared by electrodepositing Cu for 15 min on a type (A) surface of Cu

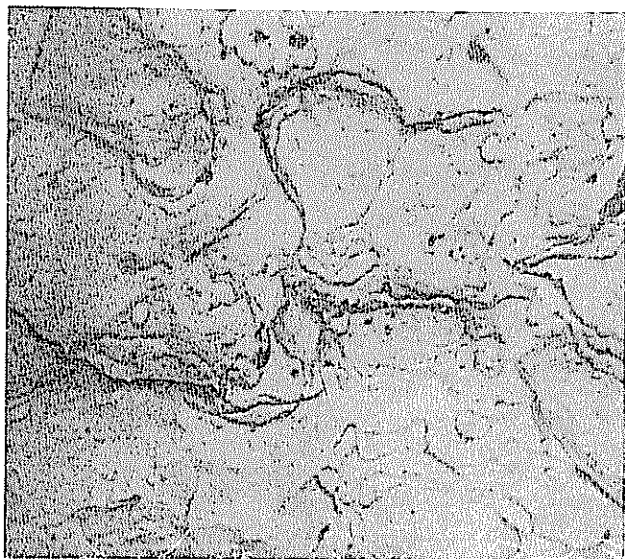


Fig. 1. Electron micrograph of the surface of the Ag cathode obtained by etching in moderately dilute HNO_3 (5500X).

foil from a complex Cu-glycine bath of pH 2.5 maintained at 25°C and a current density of $10\text{ma}/\text{cm}^2$. The deposits mostly consist of grains with well-developed boundaries and $(10\bar{1}0) + (211)$ preferred orientations (2).

Results and Discussion

Nickel was deposited on Cu surface (A) for 1 min from baths having a pH of either 2.1 or 5.1. An electron micrograph of this Ni surface (Fig. 2) shows that the Ni deposits reproduced the particle size and texture of the Cu substrate. Similar results also were found for Ni deposits formed from the same bath on substrates of Ag, Au, Ni, or Pt.

On the other hand, if electrodeposition of Ni is conducted for 1 min from a bath having a pH of 3.2, different results are obtained. When deposition occurs on Cu substrate (A), an elongated type of subgrain structure develops [Fig. 3a to 3c]. These sub-

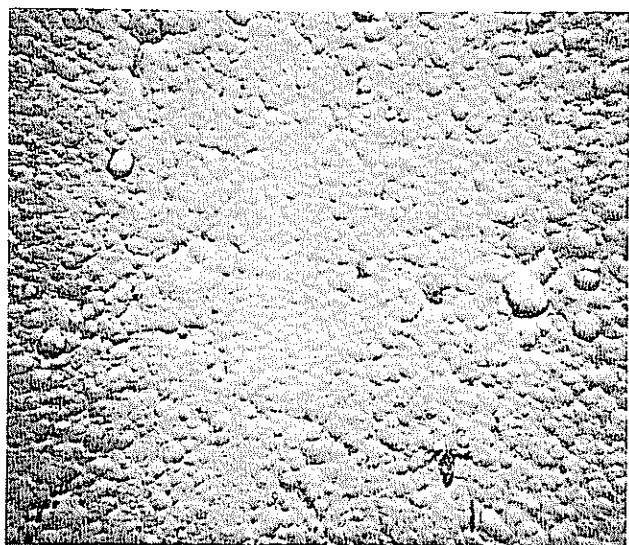


Fig. 2. Electron micrograph of the surface of Ni obtained by electrodepositing Ni from a sulphate-chloride bath at 25°C and at a current density of $10\text{ma}/\text{cm}^2$ on Cu cathode (A) for 1 min at a pH of either 2.1 or 5.1. (2400X).

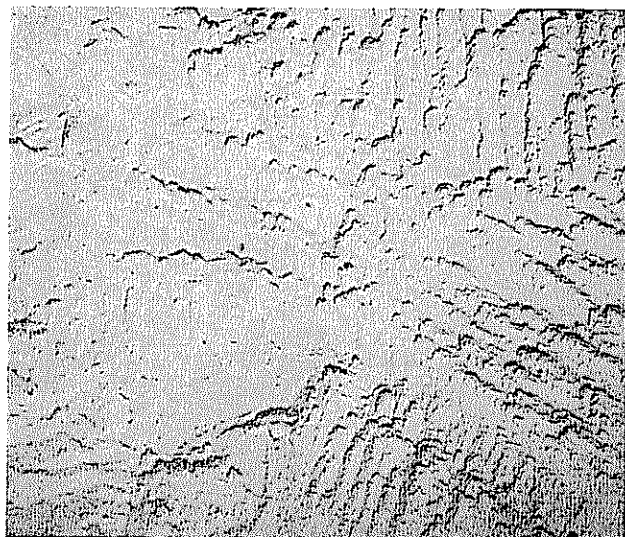
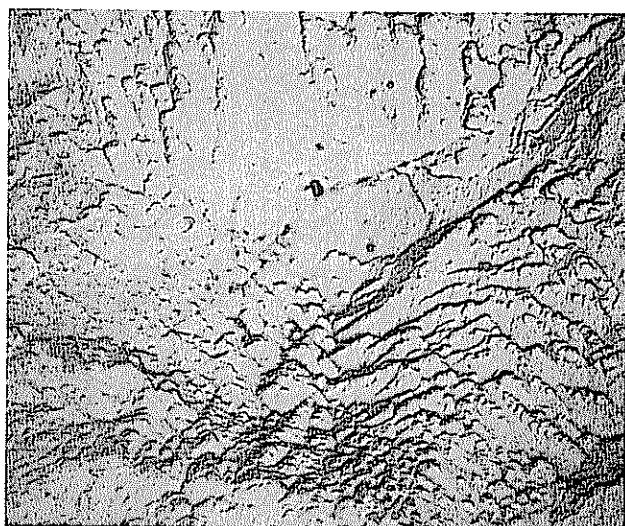
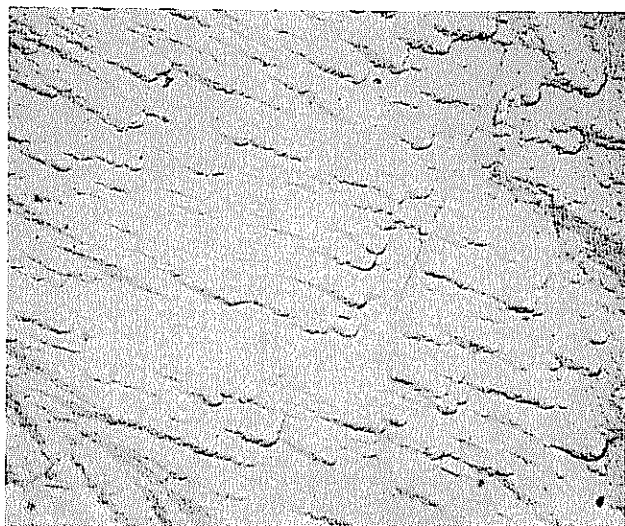


Fig. 3a-c. Electron micrographs of subgrain structures formed on Cu cathode (A) when Ni is electrodeposited from a sulphate-chloride bath of pH 3.2, at 25°C and at a current density of $10\text{ma}/\text{cm}^2$ for a deposition time of 1 min. (2400X).

structures are oriented parallel to each other within a grain, but considerable difference in grain orientation is noted. When deposition occurs on the Ag or Au substrates, a similar type of substructure also is

observed. Analogous substructures were obtained by Deslisle (9) who heated a polycrystalline Cu foil near its melting point for more than 1 hr and then etched the surface of the annealed copper in a suitable reagent. When deposition occurs on Cu substrate (B), large (111) facets containing a dendritic type of structure (Fig. 4) and striations or steps (Fig. 5) are observed. Figure 4 is very similar to the photomicrograph of the surface dendrites obtained by Laukonis and Coleman (10) in the case of γ -phase Fe formed on Fe whisker surfaces that were annealed in H_2 for 2 hr at 1200°C.

No such substructures, dendritic type of growth, and striations or steps were found for Ni electrodeposited on the surface of Pt or Ni at any of the above pH conditions.

The development of subgrains on metal surfaces generally is thought to be a thermally activated process. Subgrains have been obtained by various workers (11-13) by annealing a slightly deformed high-purity metal near its melting point, followed by an etch in a suitable solution. Dislocations require sufficient mobility in order to arrange themselves in dislocation walls to produce this effect. There is evidence, such as that put forward by Lambot (14), that deformation itself is able to produce subgrains without the requirement of substantial thermal energy. In this connection, it has been found that electrodeposits develop large amounts of internal stresses (7, 8, 15) which vary in magnitude with deposition conditions.

Electrodeposited Ni generally develops (210), (100), and $(10\bar{1}0) + (211)$ preferred orientations at the deposition conditions used in these experiments at pH conditions of 2.1, 3.2, and 5.1, respectively (1, 2). Another interesting feature of our results, then, is the development of microcavities, which resemble etch pits, on parts of the (210) and (100) surfaces of Ni, when the deposit thickness exceeds

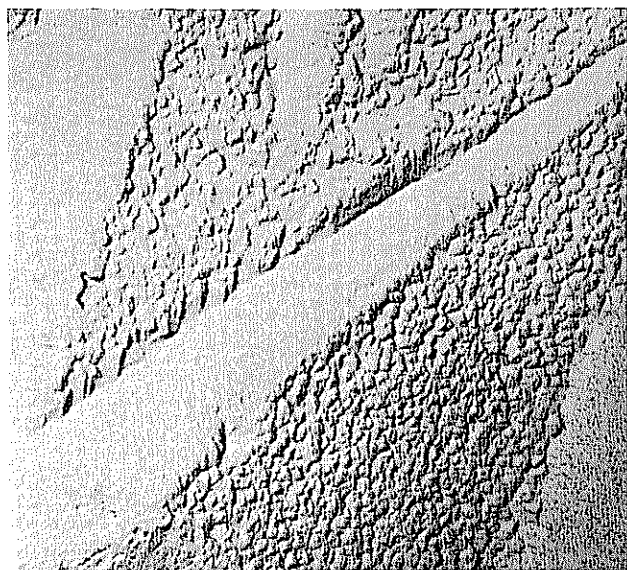


Fig. 4. Electron micrograph showing the tendency of Ni deposits to form a dendritic type of growth on a (111) facet of Ni when Ni is electrodeposited on Cu cathode (B) from a sulphate-chloride bath, of pH 3.2, at 25°C, and at a current density of 10ma/cm² for 1 min. (7100X).



Fig. 5. Electron micrograph showing striations or steps formed on parts of the Ni surface under deposition conditions similar to those in Fig. 4. (7100X).

20 μ . The development of these microcavities is found to be independent of the original cathode material used. They are often found to be either square or rectangular in cross section, the shape depending on the crystal symmetry of the surface on which they are formed. Figures 6 and 7 show microcavities formed on (210) and (100) Ni surfaces, respectively. No cavities were found on surfaces at thicknesses below 20 μ . For example, Fig. 8 is an electron micrograph for either the (210) or (100) nickel surface at a deposit thickness of about 12 μ .

Many structural features of our results at the advanced stages of deposition can probably be explained on the basis of a "Bunching Mechanism" of cathodic crystal growth, proposed recently by the Birmingham School (3, 4). They suggest that kinks or structural inhomogeneities present on the surface of the original cathode may become extended and

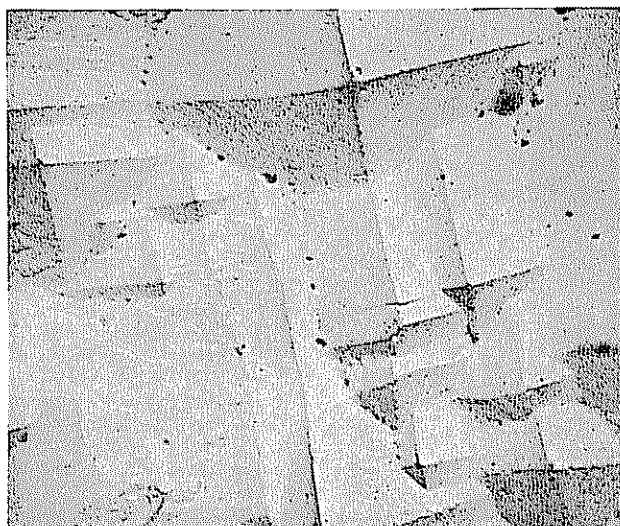


Fig. 6. Electron micrograph showing microcavities formed on the (210) surface of Ni electrodeposited for 120 min on cathode surfaces from the sulphate-chloride bath of pH 2.1, at 25°C, and at a current density of 10ma/cm². (2400X).

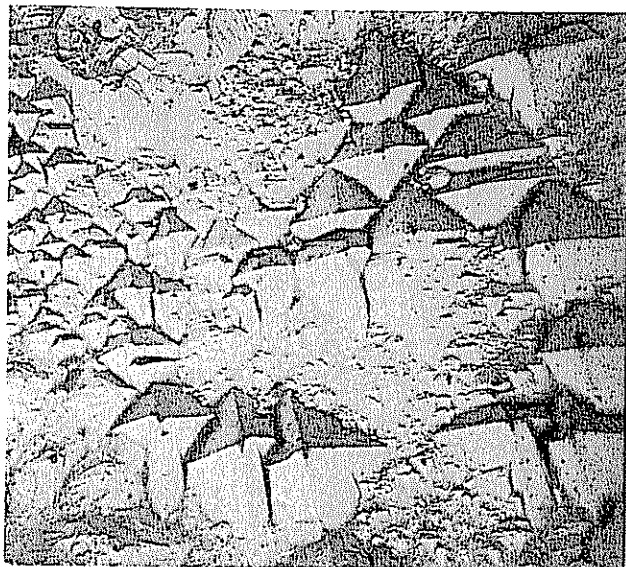


Fig. 7. Electron micrograph showing microcavities formed on the (100) surfaces of Ni at 25°C from the bath of pH 3.2, at a current density of 10ma/cm² when the deposit thickness is about 20μ. (2400X).

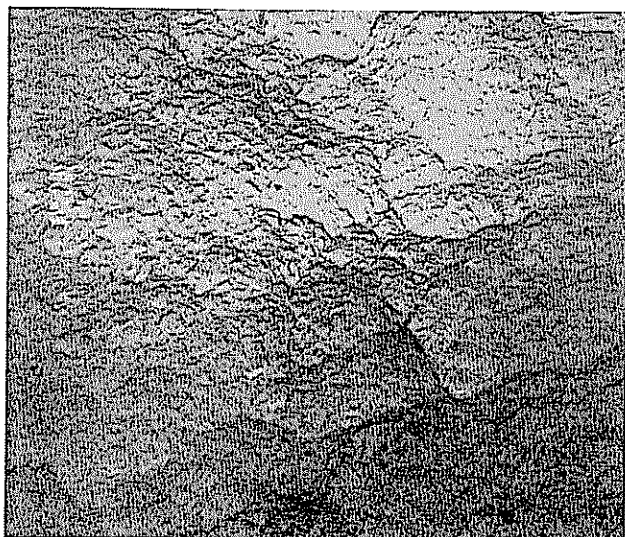


Fig. 8. Electron micrograph of (210) surface of Ni, obtained by electrodeposition of Ni from the bath of pH 2.1, at 25°C and at a current density of 10ma/cm² with a time deposition which favors a thickness of about 12μ. (1300X).

hence magnified on a macroscopic scale as the deposit grows thicker (3). But the development of substructures, the formation of dendritic-type of structures, and steps or striations during the early stages of deposition cannot be understood on the basis of any one of the existing mechanisms for the cathodic crystal growth processes. The importance

of considering some of the parameters involved in the solid-state reactions operative in cathodic crystal growth processes at the various stages of deposition might be helpful in the understanding of this complex phenomena, rather than restricting our ideas wholly to classical mechanisms of crystal growth processes (5, 6). Consideration of the porosity of thinner electrodeposits, the properties of line imperfections in acting as scattering centers for conduction electrons (16), the exothermic nature of the electrodeposition processes (7, 8), and the large deformations of cathode surface layers during various stages of deposition resulting from high magnitudes of internal stresses (7, 8, 15) in the deposits might be particularly helpful in explaining many of the structural anomalies which are often encountered on the surface of a growing deposit during cathodic growth processes.

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