Morphology and Permeability of Nickel Electrodeposits

By Wolfgang Paatsch

Field-oriented, fiber-textured nickel electrodeposited in a Watts nickel bath with direct or pulsed current changed from [100] to [21 O] preferred orientation with increasing current density. Hydrogen diffusion through nickel-plated steel and electroformed Ni foil increased with increasing crystal defects associated with higher current densities. Annealing at temperatures greater than 600° C reduced hydrogen permeation. Increasing the annealing temperature from 700 to 800° C recrystallized the deposits.

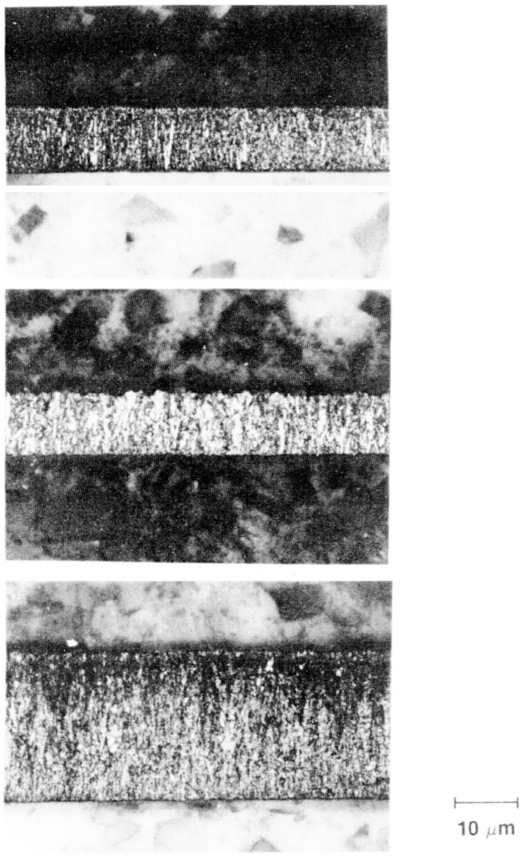

Fig. 1—SEMs showing microstructure of Watts-type nickel plated at 0.35,2. and 13 A/dm^2 (top, center and bottom, respectively) with direct current.

The relationship between the orientation of electrodeposited metals and the plating conditions has been the subject of several studies. With a given solution, texture depends mainly on the cathodic overpotential and the temperature and pH of the bath.[1] On the other hand, the composition and structure of the deposits strongly affect hydrogen permeation, which is important to consider in order to avoid hydrogen embrittlement when high-strength steel parts are plated.

The morphology of nickel deposits from Watts nickel baths and the effects of anneailng on recrystallization and grain growth are discussed in this paper. Also, the relationship between microhardness and hydrogen permeation through the nickel is examined.

Experimental Procedure

Steel samples (AISI 1017) with dimensions of 4x4 cm and a thickness of 50 µm were abraded before cleaning. The mechanically agitated Watts nickel bath contained 300 g/L of $NiSO_4 \cdot 7H_20$, 35 g/L $NiCl_2.6H_2O$, and 40 g/L of boric acid. The solution pH was adjusted to 1.0 or 2.6 and the temperature was maintained at 50° C. Current density with

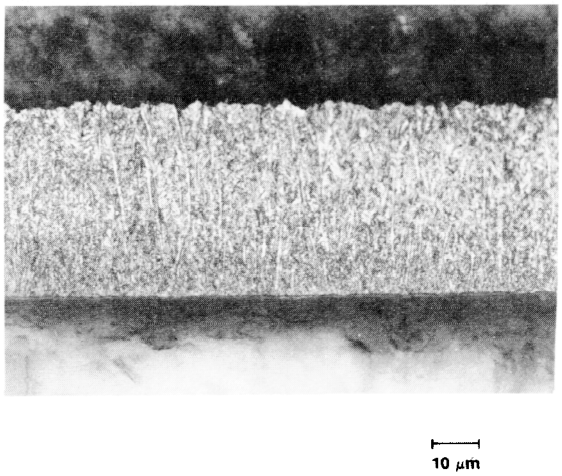

Fig. 2—SEM showing the microstructure of Watts-type nickel pulse plated at 25.3 A/dm^2 with an on-time of 1 msec and an off-time of 10 msec; the average current density was 2.3 A/dm^2.

direct or pulsed current ranged from 0.35 to 25.3 A/dm^2. Nickel foils 30 to 100 µm thick were obtained by using a passivated stainless steel substrate.

Scanning electron microscopy (SEM) was used to examine the surface morphology of nickel. The structure was analyzed by using optical microscopy and X-ray diffractometry. Samples were heat treated for 1 hr at 200 to 900° c.

The hydrogen diffusion coefficients of both foils and nickel-plated steel sheet were determined at room temperature by electrochemical permeation measurements in an electrolytic cell[2] based on the design of Devanathan and Stachurski.[3] Hydrogen permeation under steady-state conditions was analyzed.

Results and Discussion

All deposits from the Watts nickel bath were of the field-oriented type with a fiber-like texture. Figure 1 shows cross sections of layers deposited at 0.35, 2.3, and 13 A/dm^2. Increasing the solution temperature coarsened the texture. With direct current, surface roughening could be detected when the current density was increased. Pulsing the current at the same average current density refined grain size (Fig. 2). Figure 3 shows the surface morphology of nickel plated with direct current; Fig. 4 is a scanning electron micrograph (SEM) of the surface of a pulse-plated nickel electrodeposit. Deposits produced with pulsed current were brighter, due to changes in nucleation and crystal growth.[4]

X-ray diffractometry showed a change in orientation from [100] to [210] as either direct or pulsed current density was increased. Our results agree with those presented in a previously published diagram’ reproduced in Fig. 5; the diagram shows the textures of different nickel deposits as a function of current density and solution PH.

Figure 6 shows calculated hydrogen diffusion coefficients as a function of current density. The coefficients were calculated from data on hydrogen permeation for 50-µm-thick steel samples plated with 6µm of nickel in the Watts bath. The diffusion coefficients increased parabolically with increasing current density. This trend would be expected because hydrogen diffusion is known to increase as the number of crystal defects increases, and the number of defects generally increases with increasing current density.

Figure 7 illustrates the influence of annealing on the hydrogen-diffusion behavior of 100-µm-thick electroformed nickel foils produced at 2.3 A/dm^2. Figure 7 also shows microhardness values that decreased more or less continuously as the annealing temperature was increased. On the other hand, hydrogen diffusion coefficients did not change appreciably when foils were annealed at tem-

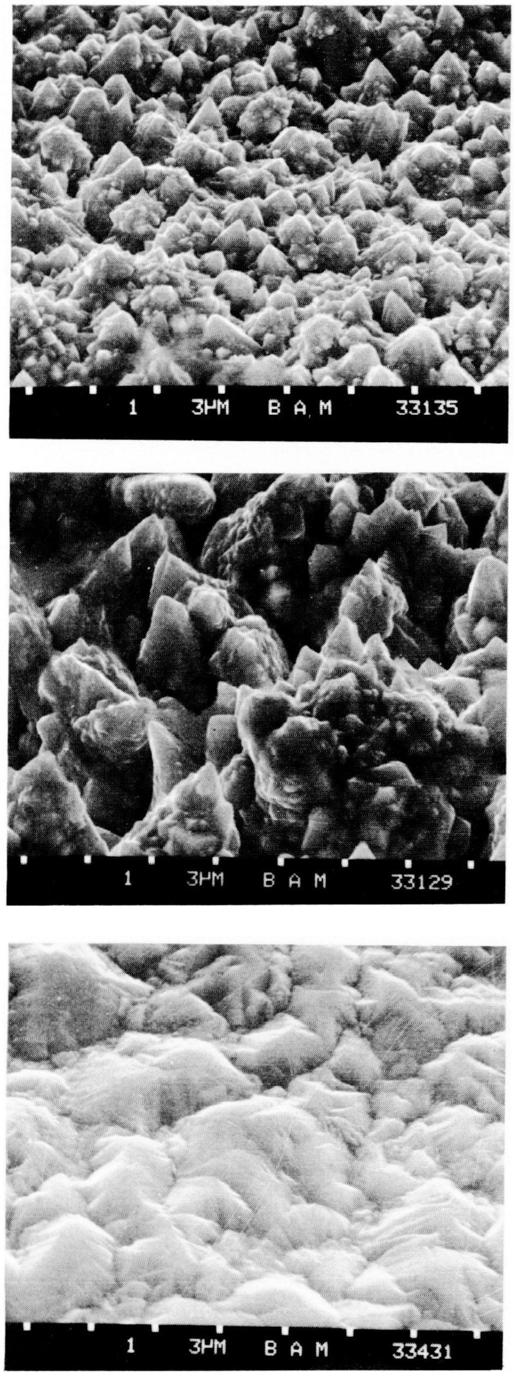

Fig. 3—SEMs showing the surface morphology of Watts-type nickel plated at 0.35, 2.3 and 13 A/dm^2 (top, center and bottom, respectively) with direct current.

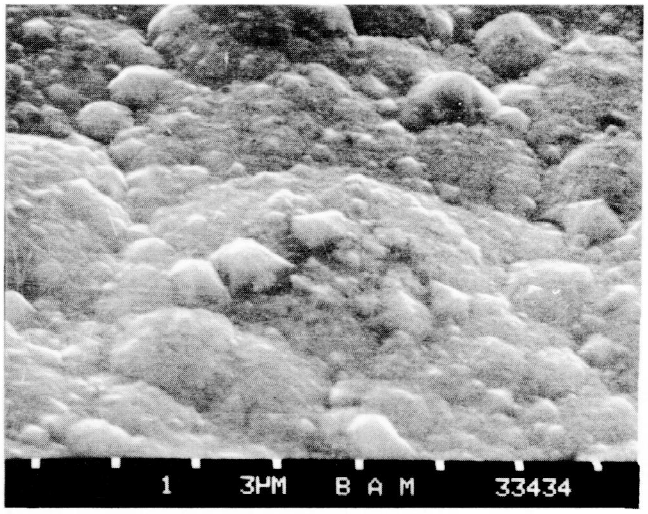

Fig. 4—SEM showing the surface morphology of Watts-type nickel pulse plated at 25.3 A/dm^2 with an on-time of 1 msec and an off-time of 10 msec; the average current density was 2.3 A/dm^2.

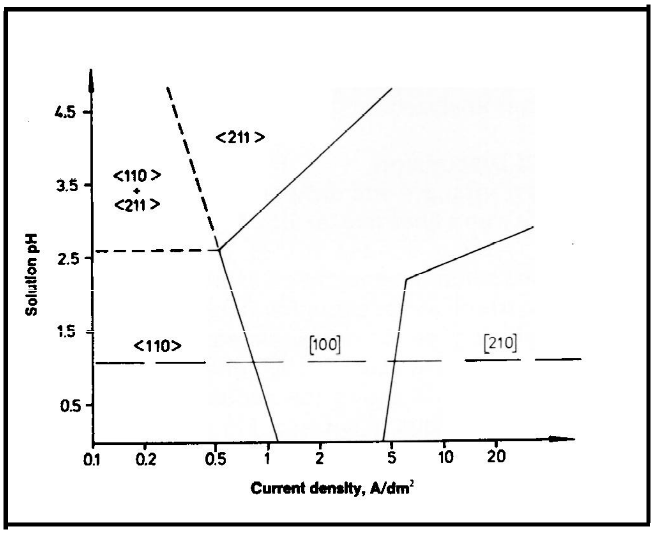

Fig. 5-Orientation of nickel deposits as a function of the current density and pH of Watts-type solutions.[5]

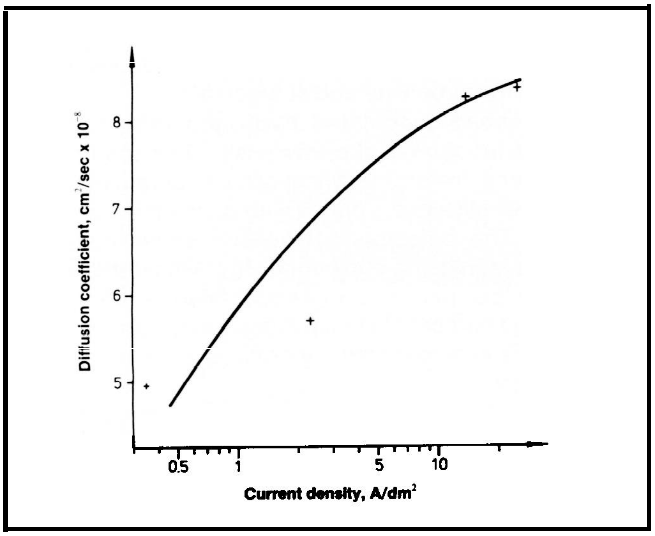

Fig. 6-Hydrogen diffusion coefficient of nickel-plated steel (6 µm of Ni on 50 µm of steel) as a function of current density.

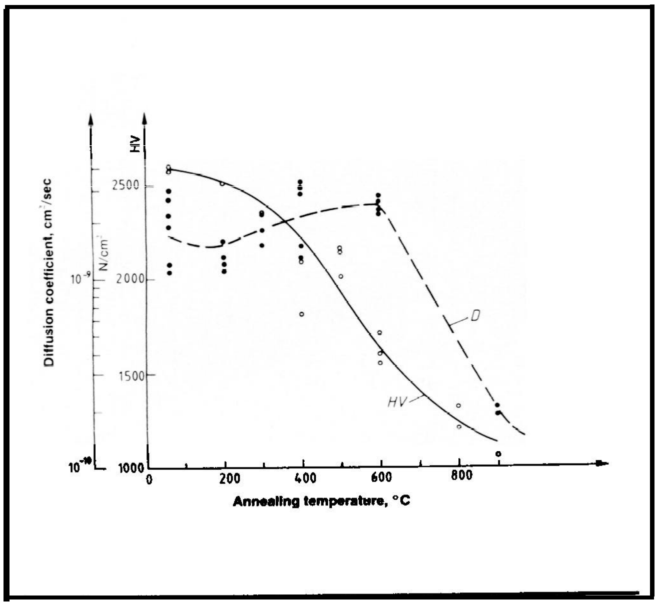

Fig. 7—Hydrogen diffusion coefficient and Vicker's hardness (HV) of electroformed nickel foils (100 µm) as a function of annealing temperature.

peratures to 600° C. However, the coefficient decreased about one order of magnitude to the value for nickel single crystals[6] when the annealing temperature was raised to 900° c.

These results are supported by those in a previous report’ on the mechanical properties of nickel deposits. The report showed that annealing at temperatures lower than 600° C had only a slight effect on elongation or yield strength. The elongation of unannealed, 10-µm-thick nickel foil was 4 percent, whereas foil annealed for 2 hr at 400° C had an elongation of 6 percent. Heating for 2 hr at 600° C increased the elongation to 13 percent. Thus, the number of crystal defects in the nickel deposits decreased due to annealing at 600° C.

As a result of recrystallization during heat treatment at higher temperatures, crystal defects were healed to a

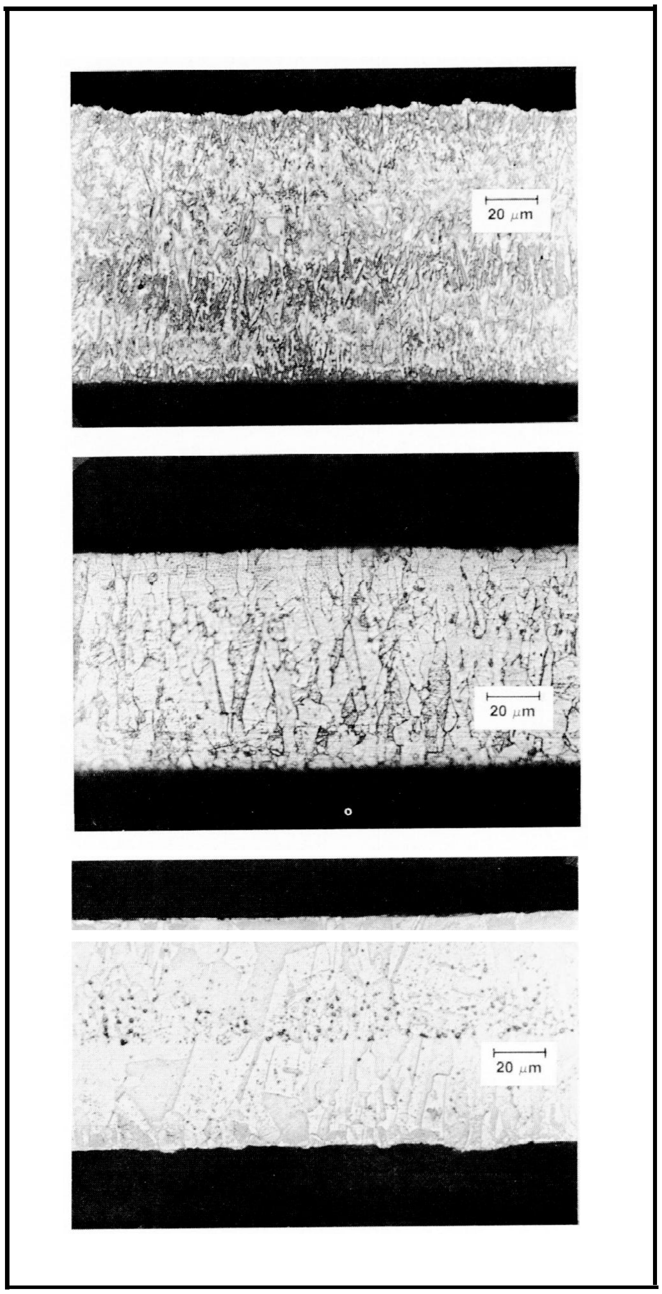

Fig. 8—SEMs showing microstructure of electroformed foils annealed at 600, 700 and 800° C (top, center and bottom, respectively) for 1 hr.

greater extent. Figure 8 shows that the deposit structure was changed abruptly when the annealing temperature was raised from 700 to 800° C. Although the recrystallization behavior of electrodeposited nickel varies with the plating conditions, the results reported in this paper agree with data in another report[8] on recrystallization of electroplated nickel.

Conclusions

Nickel plated on steel and electroformed Ni obtained in a Watts bath at 0.35 to 25.3 A/dm^2 are field oriented and have a fiber-like texture. As current density is increased, crystal orientation changes from [100] to [210], and hydrogen permeation increases. Annealing at temperatures greater than 600” C reduces hydrogen permeation, and, at 800° C, where recrystallization occurs, the hydrogen diffusion coefficient approaches the low value of about 2 x 10-’0, as expected for pure face-centered-cubic metals.

Acknowledgments

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