

### Interaction of Evaporated Carbon Films with Nickel

B. C. BANERJEE AND P. L. WALKER, JR.  
 Mineral Technology Division, The Pennsylvania State University,  
 University Park, Pennsylvania  
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FROM the time that Bradley described a technique for producing thin carbon films by the rapid evaporation of bulk carbon,<sup>1,2</sup> workers have investigated the structure<sup>3,4</sup> and electrical properties<sup>5</sup> of such films before and after heat treatment at elevated temperatures. To the authors' knowledge, no work has been reported, however, on the interaction of evaporated carbon

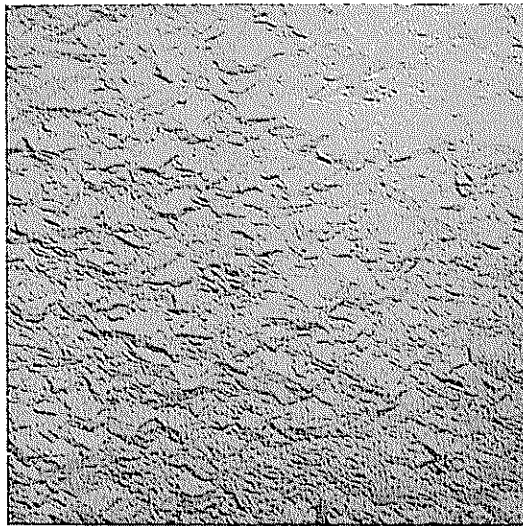


FIG. 1. Electron micrograph of the surface of the carbon film evaporated on the (100) surface of electrolytic nickel (magnification, 1040 X).

films with the substrate material (onto which deposition occurred) upon subsequent heat treatment.

Carbon was evaporated on electrolytic nickel foils having a

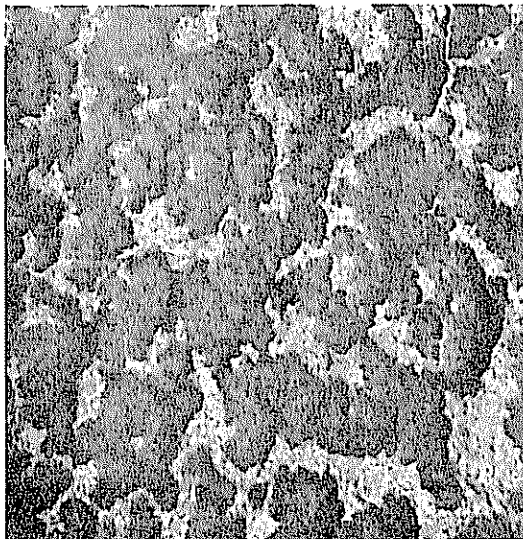
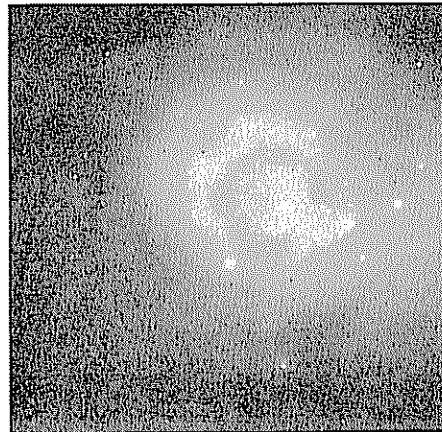
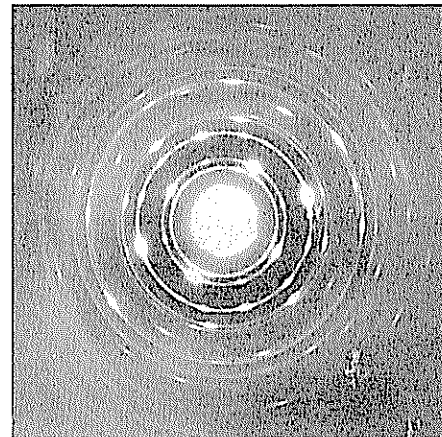


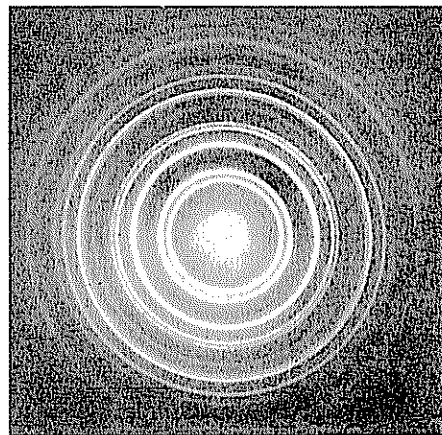
FIG. 2. Electron micrograph of the film obtained by heating the carbon film (Fig. 1) and nickel substrate at 500°C in helium for 15 min (magnification, 4400 X).



(a)



(b)



(c)

FIG. 3. (a)-(c). Transmission electron diffraction patterns of dark particles embedded in the film shown in Fig. 2.

(100) preferred orientation<sup>6</sup> in a vacuum evaporator using spectroscopically pure graphite rods as electrodes. The pressure tended to rise during evaporation owing to outgassing of the electrodes<sup>7</sup> but was usually maintained at about  $5 \times 10^{-4}$  mm Hg. The electrodes were located at a distance of 20 cm from the nickel foil. The rate of deposition was about 50-100 Å/sec. The time of deposition was such that the film thickness deposited was about 500 Å. The nickel foil on which the evaporated carbon film was deposited was then heated, in some cases, to temperatures up to 500°C. (soak time 15 min) in an oxygen-free, flowing helium atmosphere. The film thus obtained was removed from the nickel foil by dissolving the nickel in conc. HCl.

In agreement with the findings of Kakinoki and co-workers,<sup>3</sup> the electron diffraction pattern of the original carbon film showed two diffuse rings, indicating a so-called amorphous carbon structure having a crystallite size of about 10 Å. If subsequent heat treatment was conducted at 400°C, the transmission electron diffraction pattern of the film showed some sharpening of the diffraction halos for carbon, but failed to indicate any diffusion of nickel into the carbon film.

To the contrary, when the nickel foil containing the evaporated carbon was heated at 500°C, considerable interdiffusion occurred. Complete disappearance of carbon from the surface, as shown by reflection electron diffraction which yielded only the (111) preferred orientation of nickel, was found.<sup>8</sup> Upon immersion of this sample in conc. HCl overnight, an insoluble film was recovered. Electron micrographs from representative parts of the film reveal major changes over the original carbon film surface (Figs. 1 and 2), with particles of dark material ranging in size from a fraction of a micron to at least  $10 \mu$  contrasting against a lighter background. Electron diffraction studies by transmission of these dark particles (using a beam width of  $10 \mu$ ) yield results which often show spot patterns, although highly oriented patterns and random polycrystalline rings are not infrequent. Selected patterns are shown in Fig. 3(a)-(c). The  $d$  spacings carefully calculated from

the diffraction patterns identify the dark areas in Fig. 2 as crystalline nickel oxide (NiO).

These results suggest some interesting points for consideration. (1) The oxygen required for the formation of NiO apparently came from the carbon film. Significant contamination of evaporated films with gases during their formation can occur if the rate of impingement of gas molecules onto the film surface is comparable with the rate of incorporation of evaporated atoms into the film. Such is the case in this study. The rate of collision of oxygen molecules with the surface is about  $4 \times 10^{16}$  molecules/cm<sup>2</sup>/sec; the rate of incorporation of new carbon atoms into the film is about  $5 \times 10^{16}$  atoms/cm<sup>2</sup>/sec. The presence of oxygen is known to inhibit the crystallite growth of carbon<sup>9</sup>; this presence could be responsible, in part, for the highly amorphous character of evaporated carbon films formed by us and others.

(2) Nickel oxide is highly soluble in conc. HCl. It is, therefore, interesting to note the insolubility of the NiO dispersed within the carbon-film matrix.

(3) A sample of the electrolytic nickel foil used as the substrate for the evaporated carbon was heated in 1 atm of air at 500°C for 15 min. Reflection electron diffraction only gave the (111) preferred orientation of nickel. This suggests that the rate of formation of NiO upon heating the nickel foil containing the evaporated carbon was substantially more rapid at 500°C than exposure of the nickel to air.

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<sup>8</sup> It is found that the electrolytic nickel of (100) preferred orientation changes to (111) orientation upon heat treatment to 500°C under conditions similar to those used above.

<sup>9</sup> A. E. Austin and W. A. Hedden, Ind. Eng. Chem. **46**, 1520 (1954).