INVERSE POROUS NICKEL NANOSTRUCTURES FROM OPAL MEMBRANE TEMPLATES

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Currently there is a strong interest in fabricating nanoporous metal arrays using various template methods.[1-3] Porous opal membranes of close-packed silica beads, for example, have a unique template structure due to their tetrahedral and octahedral interstices. Such structures can be infiltrated with a variety of materials, especially metals, to form continuous inverse networks. Interest in these forms comes from their potential application in a variety of areas including photonics, magnetics, catalysis, and thermoelectrics. In this paper, we present electron microscopy characterization of inverse nickel photonic materials prepared by electrodeposition method.

Electrodes were formed from opal pieces (typically 7 x 10 x 1.5 mm with silica spheres about 300 nm) by first depositing about 0.5 micron thick copper films on one side of the piece with magnetron sputtering. A length of wire was then attached to the copper backing with silver paste. Electrodeposition of nickel was carried out by a constant current method over 36 hours. To remove the silica matrix, metal-opal pieces were soaked in 2% HF solution for 24 hours. This resulted in a dark metal membrane for SEM and TEM observations. To check the deposition thickness and fine structure of the nickel in the interstices, cross-sectional TEM samples were also prepared by gluing a silicon pallet on the copper film side, then grinding, polishing and ion milling to electron transparency.

Figure 1 is an SEM image of well-ordered nickel (001) nanoporous frame after etching away the colloidal silica. The framework consists of cubes that arise from filling the octahedral sites in the closed-packed opal. Each cube is connected to eight other cubes through its vertices via tetrahedra. Since the silica spheres are about 300 nm, one would expect tetrahedra and octahedra with diameters of approximately 70 and 120 nm, respectively, and this is observed. Figure 2 is cross-sectional SEM image presenting the interface structure of the deposited copper layer and the opal. The bright cube dots are electrodeposited nickel in the interstices, which were also confirmed by EDS analysis.

In order to determine the exact thickness of electrodeposited nickel, TEM was employed to observe the cross-sectional sample as shown in Figure 3. The deposition thickness was about 160 µm. (001) monolayer and multiple colloidal silica layers were also observed as shown in Figure 4. Nickel cubes (black contrast) can be observed in the interstices of opal. By gluing a small piece of the inverse nickel on a TEM grid, the two dimensional projection of nickel network can be also seen as shown in Figure 5. On close examination of a single cube, microtwins were found as shown in the left inset, which can be also determined from the <011> SADP from the right inset. This indicates that the nickel octahedra or tetrahedra are single nanocrystals, but with some defects, such as microtwins and stacking faults. On examination of a larger area containing many of the nickel cubes, the SADP showed polycrystalline features with homogeneous diffraction rings implying that the deposited nickel octahedra and tetrahedra have no preferential growth orientation. The authors gratefully acknowledge support from the DARPA MDA972-97-1-0003 and DAA-96-J-036.

References
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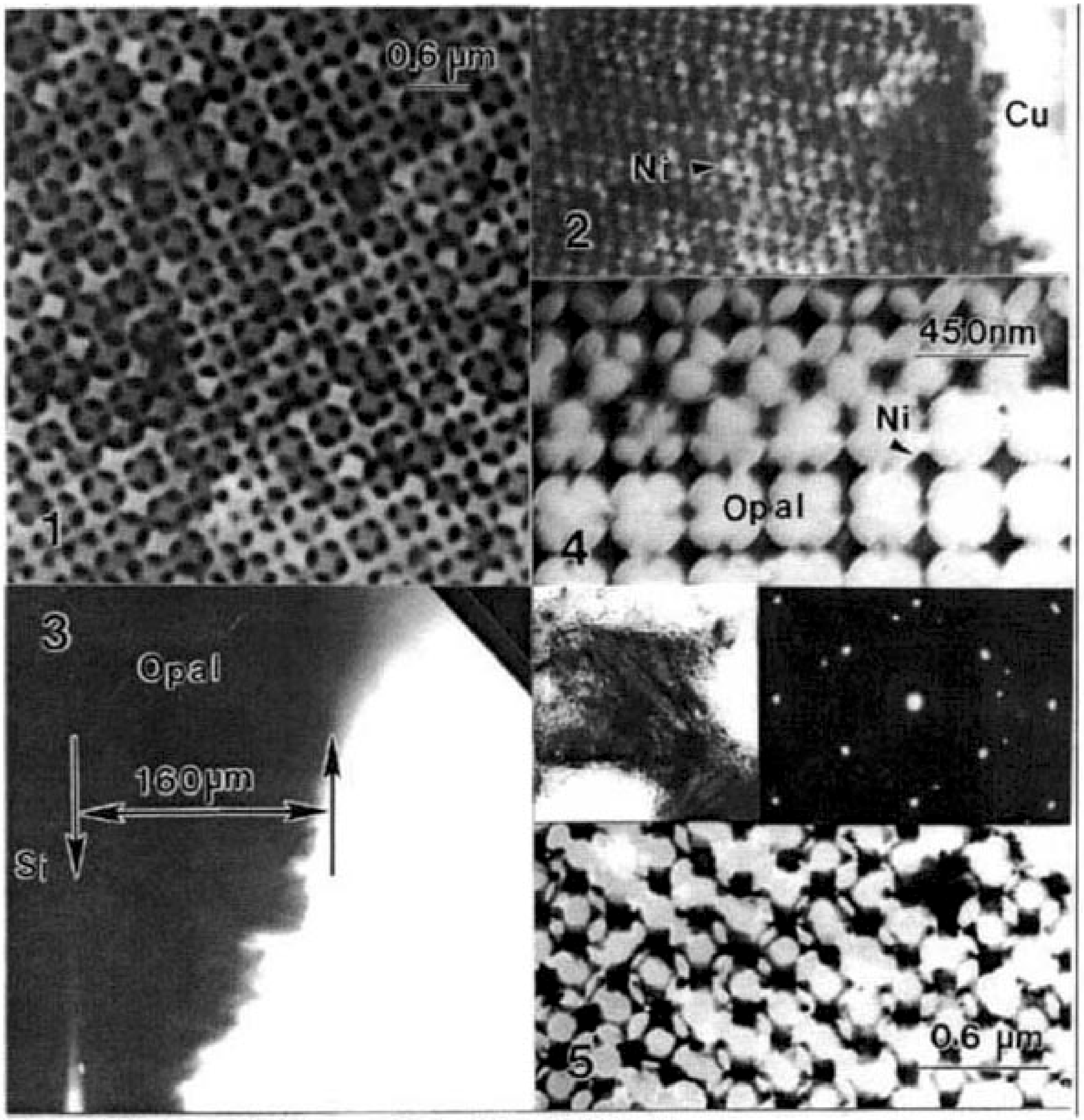

Figure 1 SEM micrograph of inverse nickel opal along [001] direction.
Figure 2 Cross-sectional SEM micrograph presenting interface of Cu layer and opal with deposited Ni.
Figure 3 Cross-sectional TEM image showing the deposited nickel thickness.
Figure 4 TEM image of monolayer and multilayer silica colloids with Ni cubes.
Figure 5 TEM image showing Ni nanoporous. The insets are microtwin and <011> SADP of one cube.