

### Formation of Mesoporous Nickel Particles with Highly Ordered Porous-nanostructure by Electroless Deposition

T. Yokoshima<sup>1)</sup>, Y. Yamauchi<sup>2,4)</sup>, H. Mukaibo<sup>2,4)</sup>,  
M. Tezuka<sup>2,4)</sup>, T. Momma<sup>2,4)</sup>, K. Kuroda<sup>2,3,4)</sup>,  
and T. Osaka<sup>1,2,3)</sup>

<sup>1)</sup>Advanced Research Institute for Science and Engineering,

<sup>2)</sup>Graduate school of Science and Engineering,

<sup>3)</sup>School of Science and Engineering;  
Waseda University.

Okubo 3-4-1, Shinjuku-ku, Tokyo 169-8555, Japan

<sup>4)</sup>CREST, Japan Science and Technology Corporation.

Mesoporous materials, which have high specific surface areas and well-ordered porous-nanostructures with a diameter of few nanometers, have interest for nano-structured materials as nano-sized reactors for various chemical reactions. Mesoporous materials of oxide ceramics have been studied by many researchers, where lyotropic liquid crystalline medium are used as a template for the synthesis of those materials [1]. Recently, there have been several reports on mesoporous metallic materials [2]. These materials have interest for electrodes with specific surface area for electrochemical reactions, and are expected to be applied to the microelectrodes for catalysts, fuel cells, and secondary batteries. However, there are no reports on mesoporous metals with high regularity such as those reported for mesoporous ceramics, and a method to form mesoporous metal materials with highly ordered porous structure is required.

In this study, the formation of highly ordered mesoporous metal was investigated by using electroless deposition. The synthesis of such nickel particles was performed by using lyotropic liquid crystalline media as a template.

The plating bath contained nonionic surfactant, Ni ion, reducing agent and water. Firstly, Brij 56 and NaCl<sub>2</sub> with appropriate concentrations were dissolved into water, and aged to form lyotropic liquid crystalline media. Next, the electroless deposition bath was constructed by dissolving a reducing agent into the liquid crystalline media. Here, electroless deposition of Ni particles progressed automatically within the bath. After deposition, the particles were rinsed with ethanol to remove the surfactant. The surface morphology of the deposited particles was observed by FE-SEM, and the structure of the particles was determined by low angle X-ray diffraction and N<sub>2</sub> adsorption isotherm.

First, the deposition behavior using sodium borohydride, SBH or dimethylamineborane, DMAB, as a reducing agent was investigated. Figure 1 shows the SEM images of the Ni particles from SBH bath (a) and DMAB bath (b). From the SBH bath, Ni particles with diameter of less than 100 nm were observed. On the other hand, from the DMAB bath, Ni particles with diameter of 300-800 nm were observed. It was suggested that this difference was due to the difference in the nucleation behavior of Ni between the two reducing agents. The main effect of the oxidization reaction of DMAB was the grain growth at Ni nuclei because here, the electroless deposition reaction occurred autocatalytically. In the SBH bath, the oxidization was an autolytic reaction since the pH was low enough for the SBH reaction. Therefore,

the main reaction was the nucleation of Ni. Figure 2 shows the XRD profiles of the Ni particles from the SBH bath (a) and the DMAB bath (b). No peaks at the low angle were observed for the Ni particles from the SBH bath. On the other hand, a peak at 1.5 degree (2θ), that corresponding to d = 7 nm, was observed for the particles from the DMAB bath. From the analysis of N<sub>2</sub> adsorption isotherm, the formation of mesopores was observed. Oxidization reaction of DMAB was very slow compared with that of SBH, and the electroless deposition reaction may have occurred so that the surfactants were wrapped in the Ni metal matrix. From these results, the successful formation of mesoporous Ni particles was confirmed.

Next, the combination of SBH and DMAB was investigated. The aim of this investigation was to control both the Ni nucleation and grain growth during the electroless deposition. From the bath containing two kinds of the reducing agents, Ni particles with diameter of 300-600 nm were observed by SEM observation. From Fig.2(c), a very clear peak at 1.5 degree was observed in the XRD pattern of the particles. The N<sub>2</sub> adsorption isotherm showed the mesoporosity. From these results, the successful formation of mesoporous Ni particles with highly ordered porous-nanostructure was confirmed. It can be concluded that the selection of reducing agent is very important to form mesoporous Ni particles by electroless deposition.

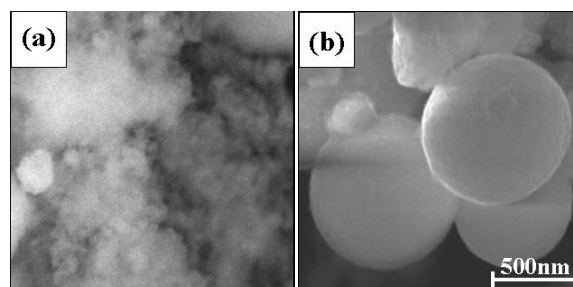


Fig. 1 SEM images of electroless-deposited Ni particles from SBH bath (a) and DMAB bath (b).

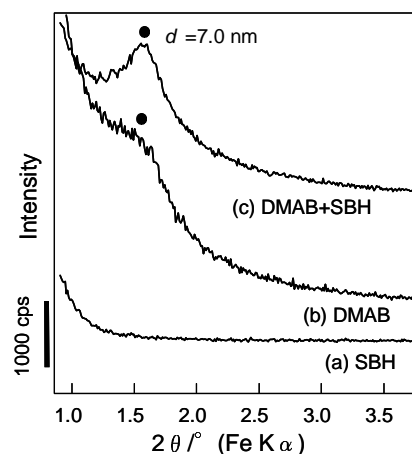


Fig. 2 XRD profiles of electroless-deposited Ni particles from SBH bath (a), DMAB bath (b), SBH and DMAB bath (c).

#### References

1. G.S.Attard, et al., *Nature*, **378**, 366 (1995).
2. G.S.Attard, et al., *Science*, **278**, 838 (1997).

#### Acknowledgement

This work is supported in part by a Grant-in-Aid for Center of Excellence (COE) Research "Molecular Nano-Engineering", and the 21st Century COE Program "Practical Nano-Chemistry" from the Ministry of Education, Culture, Sports, Science and Technology.