Preparation and structure of 3D ordered macroporous alloys by PMMA colloidal crystal templating

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Received (in Irvine, CA, USA) 18th April 2000, Accepted 20th June 2000

Three-dimensionally ordered macroporous (3DOM) metal alloys of Ni_xCo_{1-x} (a solid solution) and Mn_3Co_7 (an intermetallic compound) have been prepared by templated precipitation of mixed metal salts within colloidal crystals of poly(methyl methacrylate) spheres and subsequent chemical conversion of the inorganic precursors.

In the past three years, several chemical preparations of ordered macroporous materials based on colloidal crystal templating have been described. By using close-packed arrays of monodisperse spheres (polystyrene or silica) as templates, three-dimensionally ordered macroporous (3DOM) structures have been fabricated whose compositions include silica,[1–4] metal oxides,[3,5–8] simple metals,[9–11] metal chalcogenides,[12] carbon[13] and polymers.[14–17] Since the pore diameters (typically a few hundred nanometers) are comparable to optical wavelengths, 3DOM dielectric materials can be used to create photonic crystals, which exhibit interesting optical effects based on Bragg diffraction and the formation of optical stopbands.[6,18] In addition, applications including catalysis, sorption, and separations may benefit from the bicontinuous void and wall structures and from the well-defined pore sizes of these materials.

Recent theoretical and experimental studies have suggested that metals with well-ordered porous networks would also exhibit interesting photonic properties,[19] and that 3DOM metals provide relatively large surface areas which are uniformly accessible in electrochemical experiments.[9] Periodic macroporous metals have now been prepared by several methods, including hydrogen reduction of preformed macroporous oxides,[9] decomposition of templated metal oxalates in a non-oxidizing environment,[9] electroless deposition,[10] deposition of colloidal gold particles in colloidal crystals,[11] and infiltration of natural calcium carbonate skeletons with gold paint, followed by annealing.[20] All of these macroporous solids contain a single metal. However, most technological applications of metals employ alloys containing two or more elements, because with alloys it is possible to realize an extensive variety of physical properties by varying the composition of the alloy. Here we report a method of synthesizing 3DOM metal alloys, using a solid solution (Ni_xCo_{1-x}) and an intermetallic compound (Mn_3Co_7) as examples.

Colloidal crystals were prepared from uniformly sized poly(methyl methacrylate) (PMMA) spheres synthesized according to the literature[21] and close-packed by gravity sedimentation or centrifugation. To prepare a 3DOM Ni_xCo_{1-x} alloy, 0.008 mol nickel(II) acetate tetrahydrate and 0.008 mol cobalt(II) acetate tetrahydrate were dissolved in 20 mL methanol at 60 °C. After cooling to room temperature, any undissolved solid was removed by filtration and a clear precursor solution was obtained. Centimeter-scale PMMA colloidal crystals (*ca.* 8 g) were soaked in this solution for 3–5 min. Excess solution was removed from the impregnated colloidal crystals by vacuum filtration. The samples were dried in air at room temperature for 1 h. Then the dried composites were soaked in oxalic acid solution (*ca.* 3.6 g oxalic acid in 30 mL ethanol) for 2 min to form metal oxalate inside the PMMA colloidal crystals. After an additional vacuum filtration and drying step, the samples were processed at 400 °C in flowing H_2 (0.3 L min^{-1} in a 22 mm i.d. quartz tube) for 1 h (heating rate: 2 °C min^{-1}). Carbon (0.52 wt%) and hydrogen (0.19 wt%) analyses of a calcined sample confirmed that most of the PMMA template was removed by this treatment and that the metal oxalates had been fully decomposed.

Fig. 1(a) shows a typical SEM image of the template-free macroporous product. Open voids and interconnected walls form a pore structure that is ordered over a range of tens of unit cells in three dimensions. Average void diameters of 200 nm were obtained with 410 nm PMMA spheres. Some cracks can be observed, which arise mainly from the large volume shrinkage and sintering during the template removal/chemical conversion processes. X-Ray energy dispersive spectroscopy (EDS) covering one ordered colloidal crystal domain indicated a Ni : Co mol ratio in the walls of 0.69,[22] bulk elemental analysis by ICP a Ni:Co ratio of 0.86. The walls are composed of fused grains with typical sizes of 20–50 nm (determined by TEM). The average grain size based on PXRD line widths, calculated by the Scherrer equation, is 33 nm.

The PXRD pattern. [Fig. 2(a)] of the product shows a single phase cubic structure (space group $Fm3m$), which matches the phase determined by selected-area electron diffraction (SAED) of an ordered area in the TEM. The average calculated lattice constant is 3.529(4) Å, which is between that of Ni (3.5238 Å) and Co (3.5447 Å), suggesting that the Ni_xCo_{1-x} alloy is a solid solution.[23] The 3DOM Ni_xCo_{1-x} alloy exhibited a type II nitrogen adsorption isotherm with a BET surface area of 9.9 m^2 g^{-1}, which is attributed to the surface of fused, nonporous Ni_xCo_{1-x} nanocrystallites composing the wall structure. Owing

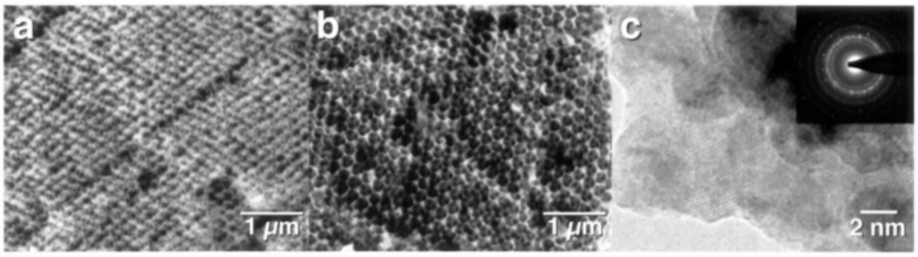

Fig. 1 Scanning electron micrographs (SEM) of (a) 3DOM Ni_xCo_{1-x} and (b) 3DOM Mn_3Co_7. (c) Transmission electron micrograph (TEM) showing a close-up view of the wall and lattice fringes of the Mn_3Co_7 grains. The inset is the SAED pattern of the ordered area including these particles.

DOI: 10.1039/b003147j

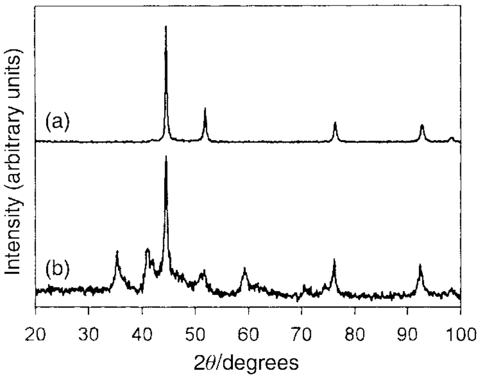

Fig. 2 Powder X-ray diffraction (PXRD) patterns of (a) 3DOM Ni_xCo_{1-x} and (b) 3DOM Mn_3Co_7.

to this large surface area, the fresh products were highly reactive, combusting upon rapid exposure to air even at room temperature. Combustion could be avoided by slow oxidation in a mixture of air (0.2 L min^{-1}) and nitrogen (1.0 L min^{-1}) for 30 min to passivate the sample surface. Passivated samples were air-stable over a period of weeks. Based on the total metals content from ICP analysis, the sample contained at most 4.8 wt% oxygen. However, no metal oxide reflections were observed in the PXRD pattern, indicating that the oxide layers were amorphous or very thin.

As another demonstration of a 3DOM alloy synthesis by the PMMA templating method, we also prepared a Mn_3Co_7 alloy from a stoichiometric mixture of manganese acetate and cobalt acetate precursors, using the same procedure as above. Mn_3Co_7 is an intermetallic compound alloy and has a crystal structure different from both Mn and Co. The PXRD pattern [Fig. 2(b)] shows reflections characteristic of the calcined Mn_3Co_7 alloy in agreement with the standard powder pattern (PDF#18-0407) and with SAED [Fig. 1(c)]. Elemental analysis of the template-free product revealed 1.79 wt% C, 0.20 wt% H and a Mn:Co mol ratio of 0.39 (expected: 0.43). The SEM [Fig. 1(b)] shows that the Mn_3Co_7 alloy has a well-ordered porous structure with average void diameters of 210 nm obtained from 290 nm diameter PMMA spheres. This more ordered structure is probably due to reduced shrinkage and smaller grain sizes [ranging from 15 to 30 nm by TEM, Fig. 1(c)], caused by slower crystal growth kinetics of Mn_3Co_7. The smaller grain size leads to a larger BET surface area of 26.4 m^2 g^{-1}.

It should be noted that the use of PMMA colloidal crystals as templates can significantly improve the periodicity and reduce the remaining carbon content of the resulting macroporous alloys/metals, relative to PS templates. The main reason for the improved performance of PMMA lies in its better thermal degradation character. PMMA decomposes by chain depolymerization, resulting in a gradual reduction in molecular weight and the production of monomer. By this mechanism, the yield of monomer can be as high as 100% in the temperature range 170–300 °C.[24] In comparison, PS degrades to *ca.* 40% of monomer in the temperature range 300–400 °C[24] and leaves a larger amount of carbon after thermal treatment of the product in a non-oxidizing atmosphere (*e.g.* in a macroporous Ni/PS sample, 39 wt% C remained after heating in nitrogen at 450 °C for 10 h, compared to 15 wt% C in a Ni/PMMA sample after 1 h of heating). As a result of the milder conditions required to remove the PMMA template, smaller framework grain sizes and larger surface areas can be obtained. An additional benefit of using PMMA over PS spheres is the better penetration of the precursor solution in the PMMA colloidal crystal owing to increased wettability. Consequently, fewer structural defects are introduced during the composite formation, if a sufficiently concentrated precursor solution is employed.[7]

The PMMA templating method can be used to synthesize 3DOM alloys containing Mn, Fe, Ni, Co and other alloy forming metals whose salt precursors are easily reducible and whose melting points exceed that of the template. Ternary or higher multicomponent alloys may also be formed. For example, we have prepared a Ni/Fe/Co 3DOM alloy by the same procedure. Besides providing a way of structuring metals on a nanometer scale and endowing them with relatively high surface areas, this technique allows one to tailor the physical properties (corrosion resistance, thermal properties, magnetic properties, *etc.*) of the 3DOM structures by changing the metallic composition of the alloy. As a result, the new class of alloys presented here may find applications as high performance catalysts, electrodes, supports and magnetic materials.

We thank 3M, Dupont, the David and Lucile Packard Foundation, the National Science Foundation (DMR-9701507 and the MRSEC Program of the NSF under Award Number DMR-9809364), and the Department of Energy (DOE/DE-FG02-93-ER14384) for support of this research.

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