RAPID COMMUNICATIONS

Magnetophoretic deposition of nanocomposites

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This communication reports the novel idea of using a magnetic field gradient to hold magnetic nanoparticles at desired densities in a fixed location (e.g., on an electrode surface), while metal atoms are deposited electrochemically in the interstices between them. Using it, nanocomposites consisting of γ–Fe_2O_3 nanoparticles (with a mean size of about 40 nm) in a copper metal matrix were reproducibly fabricated, with particle volume fractions ranging from 0.2% to 50%. These nanocomposites, ceramic magnetic particles in a conductive metal matrix, are expected to have unusual or enhanced mechanical, electrical, and magnetic properties.

Nanostructured materials display a wide variety of unusual, and often enhanced, physical properties.[1–4] One example is a nanoparticulate composite composed of a matrix in which are embedded nanoparticles. Various deposition techniques have been used to produce such nanocomposites. For example, physical vapor deposition often is used to fabricate ceramic films in which metal particles are dispersed.[5–7] Electrochemical deposition has been employed to produce metal films with embedded ceramic particles.[8–11] In this electrochemical deposition technique, ceramic nanoparticles are suspended in the electrolyte and a few become embedded in the growing metal film during deposition. However, the concentration of particles embedded typically is less than 5 vol% (although there is one report of a film with 18% volume fraction).[9] Furthermore, control of the particle volume fraction is poor.

A schematic diagram of this magnetophoretic process is shown in Fig. 1. Mechanical stirring of the electrolyte solution causes shear forces at the electrode surface in addition to maintaining the dispersion of particles in the host medium. By adjusting the magnitude of the field gradient and by adjusting the stirring speed, the volume fraction of nanoparticles embedded in the matrix material can be varied and very sensitively controlled. The experimental setup is shown in Fig. 2. It consists of a beaker, an anode, a cathode, and a magnet. A Pyrex glass double-walled beaker (5 cm inner diameter, 8 cm high) is used as the deposition bath; temperature is controlled by circulating water through its jacket. The anode is a rectangular piece of 99.9% pure copper, 0.065 cm thick, 2 cm wide, and 6 cm long. The cathode substrate is a 1×1 cm square of the same purity copper, whose surface was polished using a series of silicon carbide polishing papers (down to 1200 grade), resulting in a mirror surface onto which the film is deposited. The substrate is glued onto a piece of glass and a thin wire is used to connect it to the power supply. Before being submerged into the bath, the substrate is etched in 2.5-M nitric acid for 20 s and then rinsed thoroughly with de-ionized water.

The electrolyte is a 0.6-M copper sulfate, 0.5-M sulfuric acid, aqueous solution in which γ–Fe_2O_3 nanoparticles are dispersed, at concentrations of 1.0 to 8.0 g/l. The dispersion is placed in an ultrasonic bath for 5 min to break up agglomerates. The nanoparticles were synthesized using a counterflow diffusion flame reactor[12] and have a mean size of about 40 nm. Deposition of the copper occurs by applying a constant voltage (voltages of 0.5 to 4 V are used) across the two electrodes. The volt-

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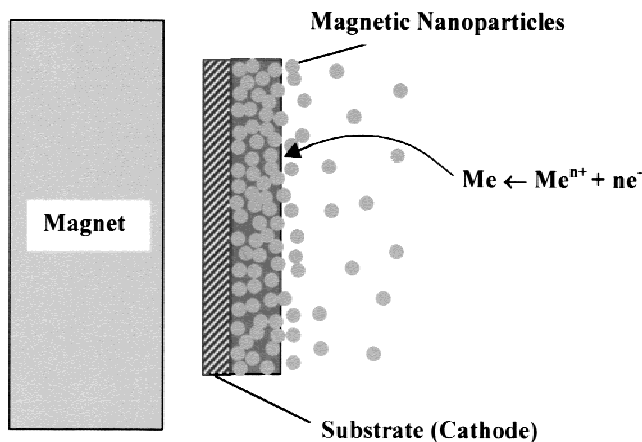e-mail: JLK@jhu.edu

FIG. 1. Schematic of the fabrication of nanocomposite films. Magnetic nanoparticles are held against a substrate by magnetic force while metal atoms, "Me," deposit in the interstices between these particles.
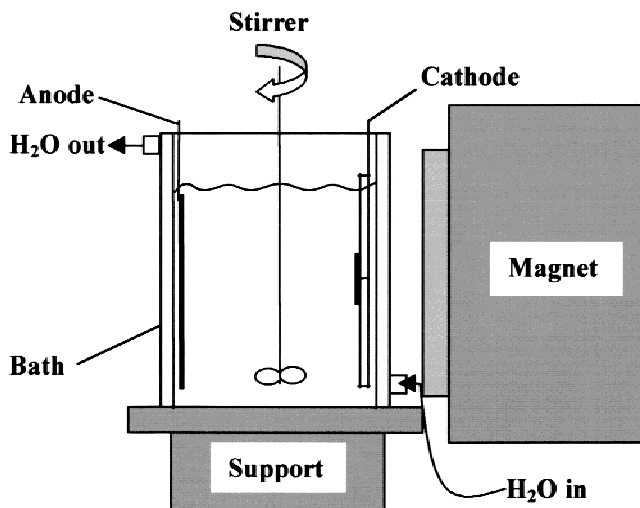

FIG. 2. Experimental setup for the fabrication of nanocomposite copper films with embedded γ–Fe_2O_3 nanoparticles.
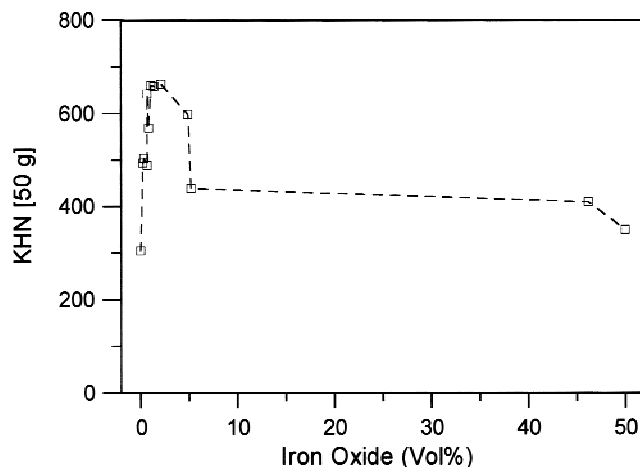

FIG. 3. KHN of the copper nanocomposite films containing different volume fractions of γ–Fe_2O_3 nanoparticles.

age drives the copper ions through the tortuous path created by the oxide particles (after depletion by electrochemical deposition of those ions in closest to the cathode). Both the voltage and the current are monitored, and the duration of the deposition process is chosen such that approximately 10-μm-thick films are produced.

A variety of Cu–Fe_2O_3 nanocomposite films were synthesized. Scanning electron microscope images show that the nanocomposite films are continuous. Particle volume fractions of γ–Fe_2O_3 particles ranged from 0.2% to 50%, as measured by energy dispersion x-ray spectroscopy using an integration area of 0.01 mm^2. Magnetic hysteresis loops were measured for these films using a vibrating sample magnetometer (Digital Measurement Systems, Model 1600). All were ferromagnetic with coercivities of about 210 Oe, slightly decreasing with increasing Fe_2O_3 volume fraction.

Knoop microhardness measurements were made on several films. Figure 3 shows the microhardness as a function of nanoparticle volume fraction. The hardness of a copper film deposited without particles in the electrolyte under the same conditions was found to be 305 Knoop hardness number (KHN; see Fig. 3). The microhardness of the nanocomposite films initially increased as the volume fraction of particles was increased, reaching a maximum at a volume fraction of 3%. The maximum hardness enhancement of over 100% at a volume fraction of 3% is similar to that previously obtained in electrodeposited nanocomposites of nickel containing approximately 2% volume fraction of Al_2O_3.[11] As the particle volume fraction was increased beyond 3%, the hardness enhancement strongly decreased, and eventually reached a value close to that of pure copper. The reason for this behavior is not completely clear, but may reflect agglomeration of the particles. Detailed microstructure studies are currently being conducted to investigate this in more detail.

In summary, a novel magnetophoresis technique was used to produce nanocomposite films of up to 50% (by volume) of γ–Fe_2O_3 nanoparticles embedded into copper. Although this technique requires that the nanoparticles be magnetic, this is not a severe restriction because one can coat a magnetic layer onto nonmagnetic materials (and vice versa), or produce multicomponents particles with one component being magnetic, in a manner similar to those used to make Al_2O_3–TiO_2 composite particles.[13]

ACKNOWLEDGMENTS

REFERENCES

1. *From Instrumentation to Nanotechnology,* edited by J.W. Gardner and H.T. Hingle (Gordon and Breach, Philadelphia, 1991).
2. *Nanostructures and Mesoscopic Systems,* edited by W.P. Kirk and M.A. Reed (Academic, New York, 1992).
3. *Nanostructured Materials: Synthesis, Properties and Applications,* edited by G.C. Hadjipanaynis and R.W. Siegel (Kluwer, Dordrecht, 1994).
4. *Nanomaterials: Synthesis, Properties, and Applications,* edited by A.S. Edelstein and R.C. Cammarata (IOP, Bristol, 1996).
5. B. Abeles, P. Sheng, M.D. Coutts, and Y. Arie, Adv. Phys. **24,** 407 (1975).
6. B. Abeles, in *Applied Solid State Science: Advances in Materials and Device Research*, edited by R. Wolfe (Academic, New York, 1976), p. 1.
7. C.L. Chien, in *Recent Advances in Magnetism and Magnetic Material*, edited by H.L. Huang and P.C. Kuo (World Scientific, Singapore, 1990), p. 296.
8. J.P. Celis and J.R. Roos, J. Electrochem. Soc. **124,** 1508 (1977).
9. H. Hayashi, S. Izumi, and I. Tari, J. Electrochem. Soc. **140,** 362 (1993).
10. P.C. Searson and T.P. Moffat, Crit. Rev. Surf. Chem. **3,** 171 (1994).
11. R.R. Oberle, M.R. Scanlon, R.C. Cammarata, and P.C. Searson, Appl. Phys. Lett. **66,** 19 (1995).
12. S.L. Chung and J.L. Katz, Combust. Flame **61,** 271 (1985).
13. C-H. Hung, P.F. Miquel, and J.L. Katz, J. Mater. Res. **7,** 1870 (1992).