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LETTER TO THE EDITOR

Small Nickel Metal Particles in Ni–Al_2O_3 Metal–Ceramic Composites[1]

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Magnetic measurements have been used in combination with transmission electron microscopy to investigate small nickel metal particles in metal–ceramic composites. Estimates of the average number of atoms in the particles are given for nonmagnetic samples with low Ni content. © 1987 Academic Press, Inc.

There has been much interest in the study of small metal particles (divided metals) in the last few years (*1*), an important objective of such investigations being, "How many atoms make a metal?" With this in mind, colloidal metals and a variety of other metal particulate systems are being studied. We investigated this problem by examining small metal particles dispersed in the matrix of a ceramic oxide such as Al_2O_3 or SiO_2, having prepared the composite by the sol–gel technique (*2*). After characterizing the metal particles by X-ray diffraction, transmission electron microscopy, and scanning electron microscopy, we employed magnetic measurements to probe the nature of the metal particles. In this letter we provide a preliminary report of our studies on nickel particles in the Ni–Al_2O_3 metal–ceramic composite produced by the sol–gel technique.

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Ni–Al_2O_3 composites with different proportions of Ni (0.05–30 wt%) were prepared by incorporating the required quantities of nickel nitrate in the gel. The gels were prepared by dissolving appropriate mixtures of aluminum nitrate and nickel nitrate in water and slowly adding excess ammonia to the solution while stirring. Dried xerogels, after reduction in a stream of H_2 (below 1275 K), contained crystalline metal particles distributed in an amorphous alumina matrix. While very small metal particles ($\leq$10 Å) cannot be seen in such micrographs, the distribution of larger particles can readily be seen (Figs. 1 and 2). The average size of such particles seen in the transmission electron micrographs varies with the Ni content. Thus, composites with 0.1, 0.25, 0.5, and 1.0 wt% of Ni showed average particle sizes of 25, 45, 50, and 75 Å, respectively (Fig. 1). The number of Ni atoms in such particles can be estimated from the average diameter of the particles by assuming a spherical shape (with 70%

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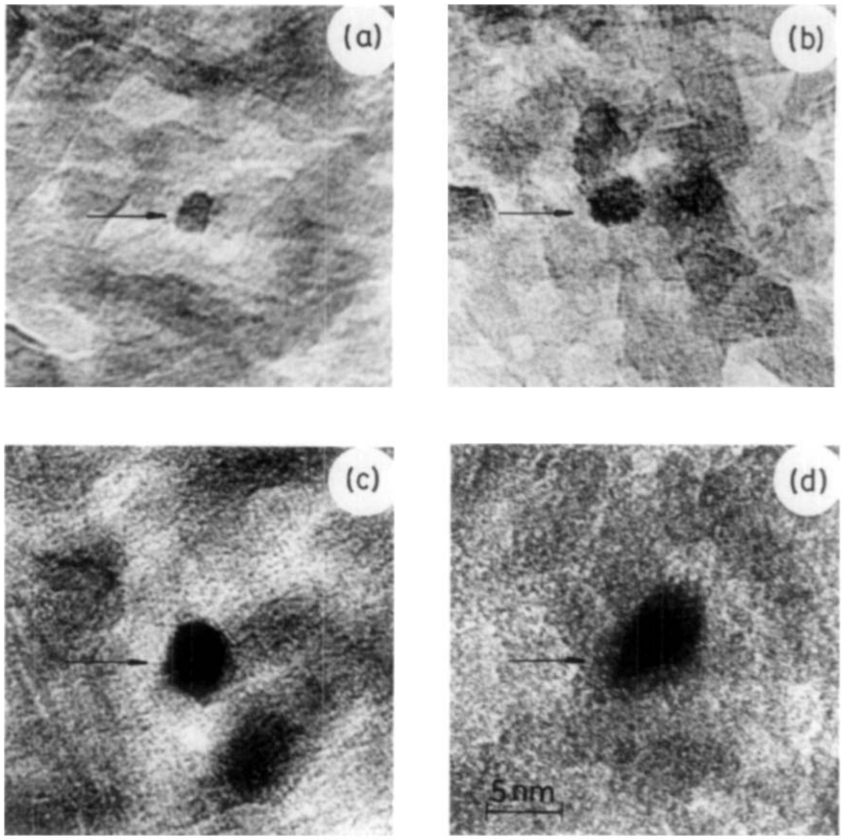

FIG. 1. Electron micrographs showing Ni particles (indicated by arrows) in Ni–Al_2O_3 composites: (a) 0.1 wt% Ni, (b) 0.25 wt% Ni, (c) 0.5 wt% Ni, and (d) 1.0 wt% Ni.

packing efficiency) for the particles; the number of Ni atoms in the 0.1 and 0.25 wt% Ni samples are approximately 700 and 4100, respectively. Since the micrographs show that the particles are nonspherical platelets, we can also estimate the number of atoms by assuming that the platelets are one atom thick (90.7% packing efficiency). The number of atoms in the 0.1 and 0.25 wt% samples so estimated are 90 and 300, respectively.

High-resolution electron microscopy has enabled us to obtain lattice resolution of the nickel particles. In Fig. 2 we have shown the distribution of the Ni particle in the 5 wt% Ni sample, along with the lattice image of one of the particles. The lattice image clearly shows a spacing of 2.04 Å, the distance corresponding to (111) lattice plane spacings.

We obtained estimates of the average number of atoms in the particles in the samples with low Ni content by using the magnetic susceptibility measurements. It should be noted that samples up to 0.25 wt% Ni are not truly ferromagnetic (unlike bulk nickel), but instead exhibit a field-dependent susceptibility. From low-temperature susceptibility data we can estimate the average number of atoms in the metal particles by assuming that the value of the effective magnetic moment per Ni atom is somewhere between the free spin value and that in bulk (1.0–0.604 μ_B). The average num-

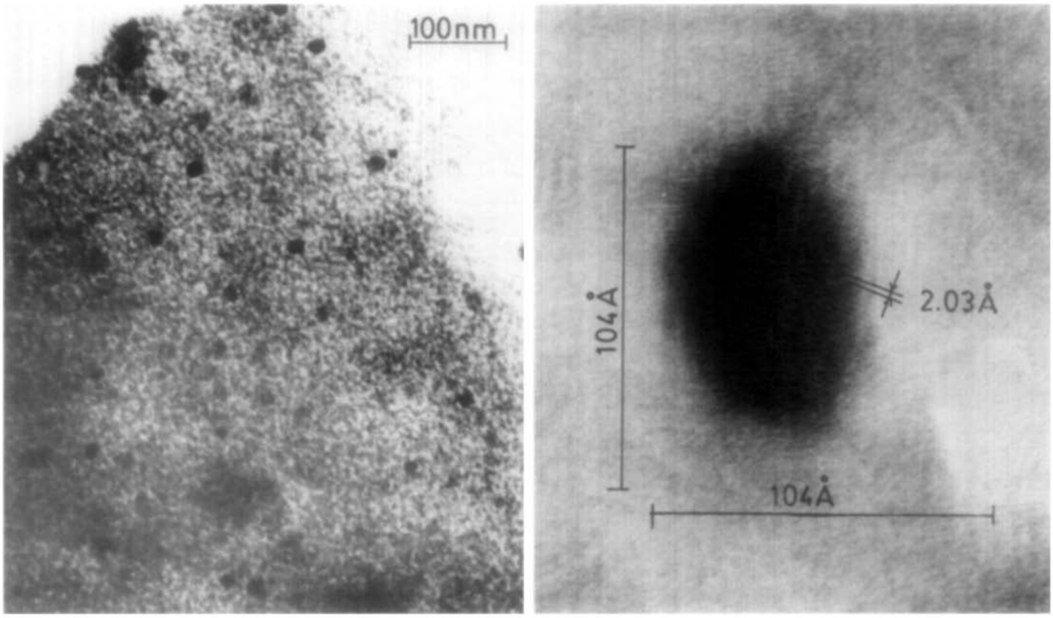

FIG. 2. Electron micrograph showing the distribution of Ni particles (seen as dark spots) in the 5 wt% Ni–Al_2O_3 composite. The lattice resolution of a particle is also shown.

ber is in the range 35–500 for samples with 0.05–0.25 wt% Ni. It is noteworthy that these ranges are not far from those found from transmission electron microscopy. The studies reported in the present letter are relevant to supported metal catalysts which metal particles are dispersed on surfaces of active oxide supports. In the systems we investigated the metal particles are distributed throughout the entire bulk of the oxide matrix.

Detailed magnetic measurements of such metal–ceramic composites are now in progress, and results will be reported in the future.

Acknowledgments

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