Fractal Dimension of Gas-Evaporated Co Aggregates: Role of Magnetic Coupling

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Aggregated Co particles were produced by inert-gas evaporation in Ar. A fractal dimension D_f was extracted from electron micrographs; it was strongly dependent on the mean particle radius $\bar{R}$. We found $1.9 \lesssim D_f \lesssim 2.05$ at $\bar{R} \lesssim 8$ nm and $1.35 \lesssim D_f \lesssim 1.6$ at $\bar{R} \gtrsim 8$ nm. The low D_f can be understood as an effect of magnetic dipole interaction, leading to chainlike aggregates when the critical size for ferromagnetism in Co particles is exceeded. The experimental values are in good agreement with recent computer simulations.

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Aggregation processes leading to fractal structures have recently attracted much interest,[1-4] and computer simulations have yielded insight into details of the growth of real aggregates. Earlier work[5,6] on gas-evaporated samples composed of nonmagnetic particles could be understood in terms of cluster-cluster aggregation.[7,8] Thus the individual particles, produced by a cooling of the metal vapor, form clusters in the gas, and subsequently the clusters collide and create larger aggregates. The main purpose of this paper is to elucidate the role of a *magnetic* interaction among the particles, and to demonstrate that aggregates with a reasonably well-defined fractal dimension D_f, lower than the one pertinent to nonmagnetic particles, are found. Specifically, we work with gas-evaporated Co specimens. Individual Co particles are expected to be ferromagnetic for $R > R_M$ and superparamagnetic for $R < R_M$, where R denotes the radius and[9] $R_M \approx 4$ nm. Our value of D_f for ferromagnetic Co samples agrees with recent computer simulation of cluster-cluster aggregation with dipolar interactions by Mors, Botet, and Jullien.[10]

Ultrafine Co particles were produced by inert-gas evaporation[11] from a heated tungsten spiral in a conventional bell-jar system. Evaporation took place in an Ar atmosphere, whose pressure lay in the range $0.25 \lesssim p_{Ar} \lesssim 10$ Torr. Sootlike deposits were collected on carbon-covered Cu grids for transmission electron microscopy and also on glass slides. The average thickness of the deposits was 10 to 200 μm, as determined by optical microscopy. The mass per unit area of the deposits was found by weighing. The volume fraction occupied by the Co particles was estimated to be in the interval 10^{-4} to 10^{-2}.

Transmission electron microscopy was carried out on the Co deposits. Figures 1(a)-1(c) show bright-field images for samples produced with p_{Ar} being 0.25, 3, and 10

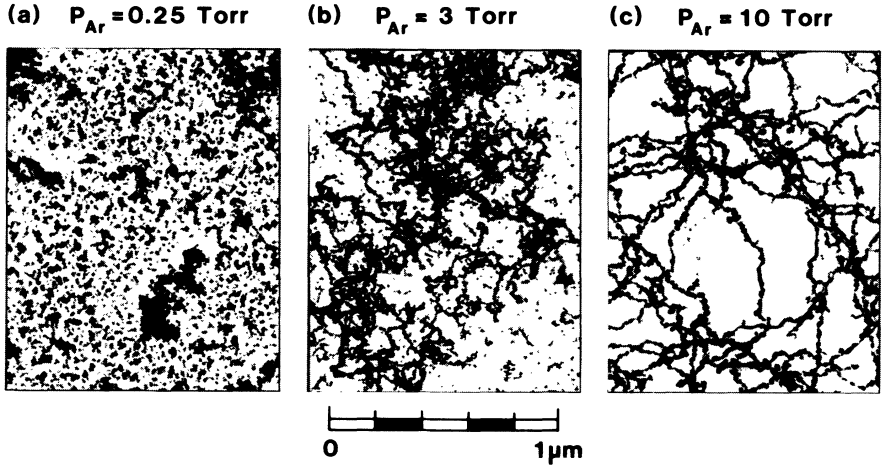

FIG. 1. Transmission electron micrographs for Co particles produced by evaporation in Ar having the shown pressures p_{Ar}. We used a Philips model EM300 electron microscope operated at 100 keV.

Torr, respectively. Qualitative differences for the aggregation of the Co particles are apparent, with the sample produced at $p_{Ar} \approx 10$ Torr having conspicuous chainlike aggregates. The mean particle radius $\bar{R}$ increases with increasing p_{Ar}. Electron diffractograms showed rings consistent with hcp Co. No traces of oxide pellicles were detected.

The most striking feature of the micrographs is the occurrence of chainlike aggregates at the largest p_{Ar}. From studied of samples produced under diverse conditions it was found that the distinctive property of the chains is that $\bar{R} \gtrsim 8$ nm. We interpret the chains as a manifestation of magnetic dipole coupling among sets of adjacent particles. The fact that $\bar{R} > R_M$ can be ascribed to the presence of a wide distribution in particle radius. Co colloids show results[12] which are consistent with our data on gas-evaporated samples.

A quantitative structural characterization, with ensuing determination of D_f, was accomplished by our first evaluating the pair correlation function. To this end the center coordinates of the particles seen on the micrographs were entered into a computer via a graphics tablet, and the number of particles within a distance r from a chosen origin was calculated. An averaged number of particles $N(r)$ was obtained by our taking each particle in turn as the origin. The pair correlation function $g_2(r)$ was obtained from

$$g_2(r) \sim N(r)/\pi r^2. \quad (1)$$

For a fractal structure, the pair correlation function is expected to vary as[13]

$$g_2(r) \sim r^{D_f - 2}, \quad r < \xi, \quad (2)$$

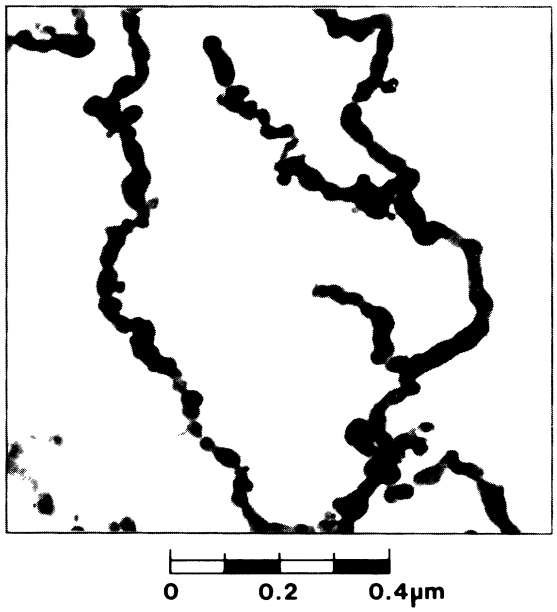

FIG. 2. High-magnification transmission electron micrograph for Co particles produced by evaporation at $p_{Ar} = 8$ Torr.

in a two-dimensional image, where ξ denotes a correlation length. To test this relation we also evaluated an effective dimension $D_{eff}(r)$ from

$$D_{eff}(r) = 2 + d[\log g_2(r)]/d(\log r). \quad (3)$$

Our technique yields the fractal dimension pertinent to a projection of a three-dimensional structure onto a plane. It is known[14] that such a projection of an ideal fractal structure does not alter the value of D_f when $D_f < 2$. For $D_f > 2$, the dimension of the projection equals 2. The occurrence of a limited ξ, as well as a shadowing of particles on the micrographs, makes it necessary to invoke corrections[15,16] on the evaluated fractal dimension in order to derive the correct magnitude of D_f, as we return to shortly.

We now discuss the fractal dimension of Co particles prepared at different values of p_{Ar}. At $p_{Ar} \lesssim 0.6$ Torr [exemplified by Fig. 1(a)], the deposits comprise almost randomly distributed small aggregates together with a few interdispersed large and dense aggregates. Evaluation of $g_2(r)$ from electron micrographs and use of Eq. (2) yields $D_f = 2$ to a good accuracy. Thus the fractal dimension of these aggregates is larger than 2. It is also possible that the structure is nonfractal. For intermediate pressures, $0.9 \lesssim p_{Ar} \lesssim 8$ Torr, the structure is markedly different [cf. Fig. 1(b)]. We found $1.75 \lesssim D_f \lesssim 1.9$, which is consistent with earlier work on gas-evaporated samples.[5,6] At $8 \lesssim p_{Ar} \lesssim 10$ Torr, finally, we have chainlike aggregates [cf. Fig. 1(c)]. An evaluation of D_f requires some consideration for this case, and the outcome may be influenced by a crossover between well-defined chains at short length scales and a two-dimensional network at large length scales. However, a relevant measure of D_f can be obtained by analysis of thin portions of the samples, for which chains with little cross linking are apparent. An example of such a specimen is depicted in Fig. 2. Its pair correlation function is given in Fig. 3. The almost linear slope yields $D_f \approx 1.4$. The decrease at small r depends on the finite size of the

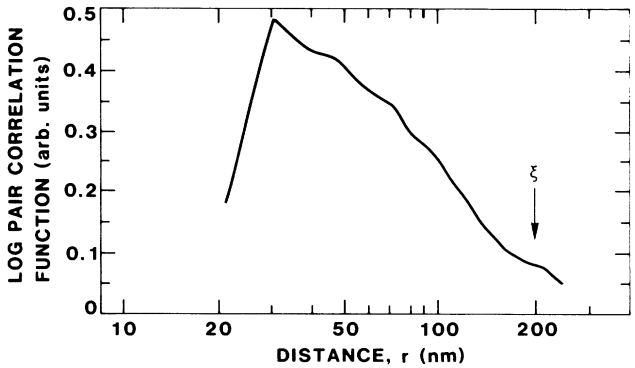

FIG. 3. Log-log plot of the pair correlation function vs distance for the aggregated Co particles depicted in Fig. 2. Arrow marks the correlation length ξ.

individual particle, and the flattening of the curve at $r \approx 200$ nm can be associated with the correlation length. The distance-dependent effective dimension $D_{\text{eff}}(r)$, introduced in Eq. (3), is illustrated by the filled circles in Fig. 4.

It has been shown[15] that an analysis of D_f from projected images with Eq. (2) in most cases yields an underestimation of the fractal dimension because of the finite correlation length. In order to correct for this effect, as well as for the fact that particles may shadow one another, we performed extensive calculations[16] on a model structure taken to be fractal for $r < \xi$ and having average density for $r > \xi$. The solid curve in Fig. 4 shows the result of such a calculation with $D_f = 1.41$ and $\xi = 210$ nm. The estimated uncertainty in D_f is ± 0.1. Analyses of several samples yielded

$$1.35 \lesssim D_f \lesssim 1.6,$$

when chainlike aggregation was manifest. The lowest D_f's tended to occur in the samples with largest particles. Samples without chains, corresponding to intermediate p_{Ar}'s and $\bar{R} < 8$ nm, had corrected fractal dimensions in the range $1.9 < D_f < 2.05$.

The physical implications of our results are considered next. At $p_{\text{Ar}} < 0.6$ Torr, mostly small clusters are formed. Cluster-cluster collisions are not very frequent and hence there is not time enough to grow large aggregates before deposition onto the substrate.

The structures formed at $0.9 \lesssim p_{\text{Ar}} \lesssim 8$ Torr and with $\bar{R} \lesssim 8$ nm are probably caused by cluster-cluster aggregation in the gas phase. The evaluated fractal dimension is consistent with—or slightly higher than—the value calculated for cluster-cluster aggregation with linear trajectories.[3,17,18] It should be remarked that, for example, structure readjustments[19] can lead to an increase of D_f for cluster-cluster aggregation. Linear trajectories are physically realistic for gas evaporation since the mean free path in the gas is much larger than typical aggregate sizes.

At $8 \lesssim p_{\text{Ar}} \lesssim 10$ Torr and $\bar{R} \gtrsim 8$ nm, finally, the fractal dimension is much lower than for the other structures. In this case we model the Co particles as *magnetic dipoles*. The dipolar interactions bring about that a chainlike structure, with aligned dipole moments, is the most stable configuration, at least for a small number of particles.[20,21] Computer simulations of the aggregation of magnetic particles by random-walk trajectories have recently been reported by Mors, Botet, and Jullien[10] who found that D_f decreases when the magnetic interaction is increased. In the limit of very large dipole moments they obtained $D_f = 1.35$, which is in excellent agreement with the lower limit of fractal dimensions found experimentally by us. In an alternative, but less quantitive, description one can regard the aggregates as being essentially one dimensional over a certain persistence length, defined as the average distance it takes for a chain of particles to make a 90° turn and thus become uncorrelated with itself. The D_f's measured for ferromagnetic Co aggregates would then be related to this persistence length. The latter concept may be useful for the discussion of clustering in systems with different dipole moments. We note, finally, that a recent study of the aggregation of magnetic particles produced by chemical reduction in solution was published by Kim and Brock.[22] Their value of D_f for Co particles was significantly larger than ours, a result which may be due to repulsive electrical double-layer forces in their experiment.

In conclusion, we have demonstrated that inert-gas-evaporated ferromagnetic particles aggregate in a chainlike structure with a fractal dimension significantly lower than the one for similarly prepared superparamagnetic particles. This effect can be understood from magnetic dipole interactions among adjacent particles and is in agreement with recent theoretical work.[10]

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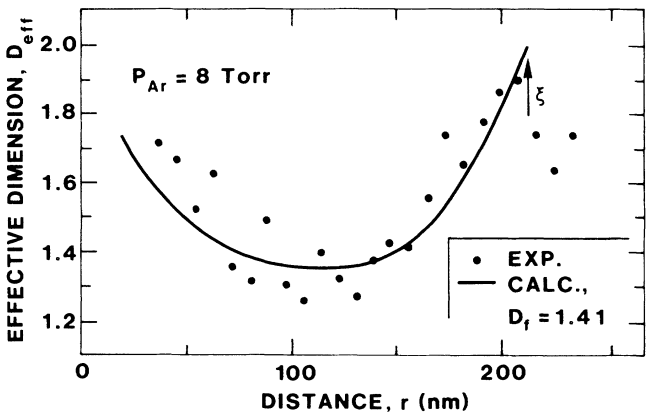
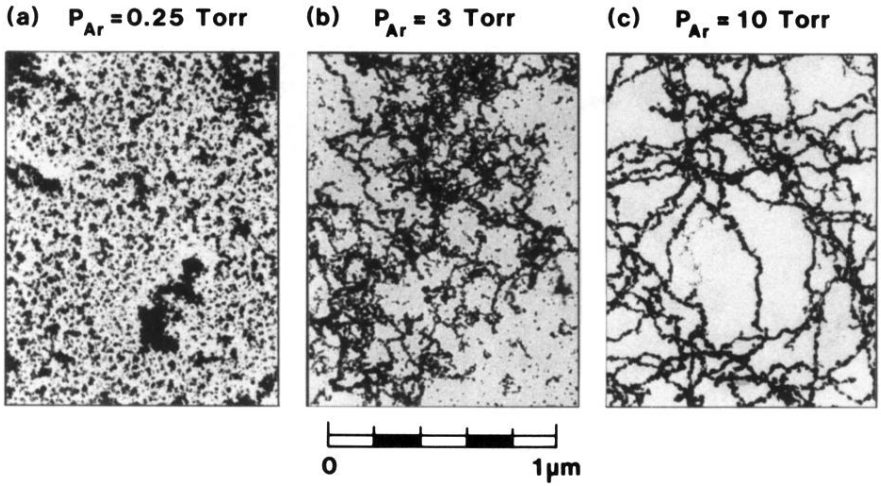


FIG. 4. Effective dimension vs distance for aggregated particles. Circles denote experimental data for the Co particle sample depicted in Fig. 2. Curve shows result of a computer simulation, accounting for the effects of a finite correlation length ξ and shadowing of particles, for the case of $D_f = 1.41$. Arrow marks the magnitude of ξ.

[1]L. M. Sander, Nature (London) **322**, 789 (1986).
[2]T. A. Witten and M. E. Cates, Science **232**, 1607 (1986).
[2]R. Jullien and R. Botet, *Aggregation and Fractal Aggregates* (World Scientific, Singapore, 1987).
[4]P. Meakin, Crit. Rev. Solid State Mater. Sci. **13**, 143 (1987).
[5]S. R. Forrest and T. A. Witten, Jr., J. Phys. A **12**, L109 (1979).
[6]G. A. Niklasson, J. Appl. Phys. **62**, 258 (1987).
[7]P. Meakin, Phys. Rev. Lett. **51**, 1119 (1983).

[8]M. Kolb, R. Botet, and R. Jullien, Phys. Rev. Lett. **51**, 1123 (1983).
[9]B. D. Cullity, *Introduction to Magnetic Materials* (Addison-Wesley, Reading, MA, 1972), p. 410.
[10]P. M. Mors, R. Botet, and R. Jullien, J. Phys. A **20**, L975 (1987).
[11]C. G. Granqvist and R. A. Buhrman, J. Appl. Phys. **47**, 2200 (1976).
[12]J. R. Thomas, J. Appl. Phys. **37**, 2914 (1966).
[13]J. E. Martin, J. Phys. A **18**, L207 (1985).
[14]B. B. Mandelbrot, *The Fractal Geometry of Nature* (Freeman, New York, 1983).
[15]M. Tence, J. P. Chevalier, and R. Jullien, J. Phys. (Paris) **47**, 1989 (1986).
[16]T. Farestam and G. A. Niklasson, to be published.
[17]R. C. Ball and R. Jullien, J. Phys. Lett. **45**, L1031 (1984).
[18]P. Meakin, Phys. Lett. **107A**, 269 (1985).
[19]P. Meakin and R. Jullien, J. Phys. (Paris) **46**, 1543 (1985).
[20]I. S. Jacobs and C. P. Bean, Phys. Rev. **100**, 1060 (1955).
[21]P. C. Scholten, J. Magn. Magn. Mater. **39**, 99 (1983).
[22]S. G. Kim and J. R.Brock, J. Colloid. Interface Sci. **116**, 431 (1987).



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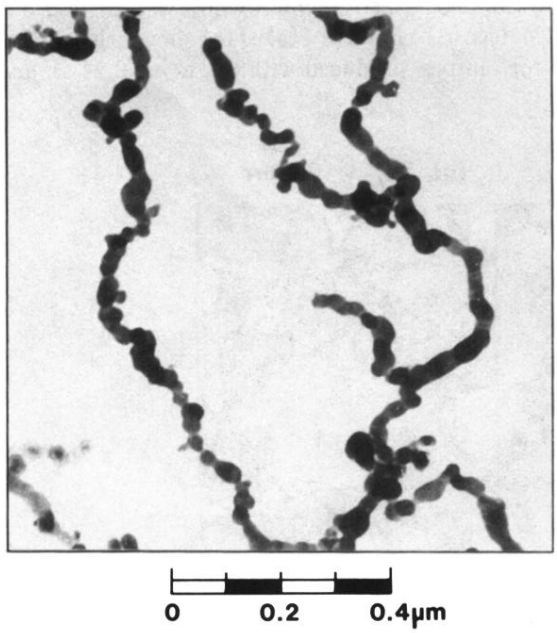

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