

MAGNETIC NANOPARTICLE FORMATION BY FERRIC ACETYLACETONATE DECOMPOSITION IN SUPERCRITICAL CARBON DIOXIDE

Silvia De Dea[†], David R. Miller^{†,*} and Robert E. Continetti[‡]

[†]*Dept. of Mechanical and Aerospace Engineering*

[‡]*Dept. of Chemistry and Biochemistry*

University of California, San Diego

9500 Gilman Drive, La Jolla, CA 92093-0001

**dmiller@ucsd.edu, fax: 858-534-5355*

ABSTRACT

We have recently reported that iron oxide magnetic nanoparticle films can be formed near room temperature when a supercritical solution of Ferric acetylacetonate $\text{Fe}(\text{acac})_3$ in CO_2 is decompressed by the Rapid Expansion of a Supercritical Solution (RESS process) onto a cold Si substrate [1]. We have now used the same supercritical solution and grown magnetically ordered thin cluster films in a batch process. The resulting cluster films have particles in the range 13 nm to 700 nm and show magnetic order. Structural and magnetic have been obtained by SQUID and SEM measurements and compared as a function of several experimental variables (P, T, geometry, substrate conditions, and growth time). The values of coercivity obtained are in the range 35-55 Oe, which are smaller than the bulk values for $\alpha\text{-Fe}_2\text{O}_3$, $\gamma\text{-Fe}_2\text{O}_3$ or Fe_3O_4 , a result which is consistent with the formation of magnetic nanoparticles. While we have found no substantial evidence of solute clusters in the RESS expansion, it is clear that large clusters precipitate in the fluid phase in the batch process prior to film formation. In fact, such precipitation is the basis for cloud point solubility measurements which we have previously reported [1,2]. The new results for the batch process suggest that the initial decomposition to magnetic order takes place in the supercritical fluid phase without influence of the substrate. The mechanism for the decomposition and restructuring of $\text{Fe}(\text{acac})_3$ in the fluid phase is not understood nor easily conjectured at this point.

INTRODUCTION

New synthetic routes for the preparation of magnetic nanoparticles and thin films are under constant investigation. Ferric acetylacetonate $\text{Fe}(\text{acac})_3$ is known to undergo thermal decomposition to form either Fe_3O_4 or $\alpha\text{-Fe}_2\text{O}_3$ magnetically ordered materials when heated above 180 °C. We have recently reported that iron oxide magnetic nanoparticle films can be formed near room temperature when a supercritical solution of Ferric acetylacetonate $\text{Fe}(\text{acac})_3$ in CO_2 is decompressed by the Rapid Expansion of a Supercritical Solution (RESS) onto a cold Si substrate [1]. We report here that similar films can be grown by the depressurization of the saturated supercritical mixture in a fixed volume batch process. We compare the physical and magnetic properties of the films grown by these two processes which have dramatically different rates of decompression of the initial supercritical solution, RESS (μsec scale) and batch (sec scale).

A batch process has some advantages over a continuous RESS process. Often requiring a smaller amount of solvent, a batch process is easier to operate, many samples can be grown at the same time, and a larger area can be coated. Therefore a batch process might be more suitable to scale up to an industrial process for thin film growth. There are many examples of batch processes utilizing supercritical fluids [3, 4]. A batch process which is particularly important to mention, given the similarity with the batch process studied here, is Chemical Fluid Deposition (CFD) [5, 6]. In the sections below we briefly describe the batch process and the SEM structural and SQUID magnetic data for the resulting thin nanoparticle films. Surprisingly, we again find magnetically ordered cluster films at low temperatures.

EXPERIMENTAL APPARATUS AND PROCEDURES

Batch experiments were performed using the solubility UV-Vis cell, previously described [1, 2], and used for cloud point measurements of the solute solubility. For a typical experiment, a known amount of solute and a substrate are placed in the solubility cell, pressurized, allowed to reach equilibrium and depressurized by opening a vent valve. The batch apparatus, whose schematic is shown in Figure 1, includes a CO₂ siphon-tube gas cylinder, an ISCO syringe pump, and the UV-Vis solubility cell.

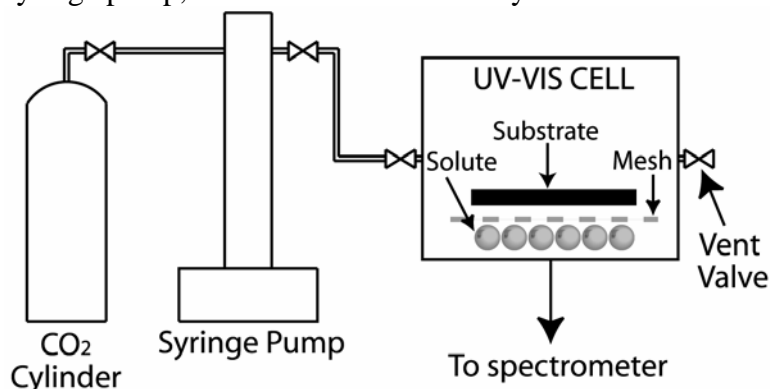


Figure 1 BATCH experimental apparatus

The experimental procedure is as follow: approximately 20 mg of Fe(acac)₃ powder are loaded into the cell, sufficient to fully saturate the solution. A wire mesh is placed above the powder to isolate Fe(acac)₃ from the substrate (a 7x4 mm silicon wafer) which is placed above the mesh. Usually three substrates are loaded at one time to insure reproducibility of the magnetic measurements. The cell is then heated to 40-45 °C, purged with 2 bar of CO₂, pressurized to 140 bar and isolated from the pump. The system is then left at 140 bar for approximately 3 hours to nearly approach a saturated solution and subsequently depressurized by opening a vent valve. Typically the cell pressure was reduced to about 50 bar, well below the cloud point so that solute readily precipitates out of solution and onto the film substrate. The substrate is then removed and the deposited nanoparticle films analyzed with a FEI Quanta 600 Scanning Electron Microscope (SEM), and a Quantum Design MPMS-XL5AC superconducting quantum interference device (SQUID) based magnetometer.

We have studied the effect of venting time, a slow depressurization (60 second time) and a fast depressurization (2 second time), as well as substrate material, collecting particles on both silicon and gold (99.9% purity) substrates; the latter to ascertain if any chemical role of solute-surface interaction was prevalent. Since it was found that the solute did not stick to gold flat substrates, we modified the experimental procedure by collecting the particles that precipitate out of solution in a gold cup. For this purpose we appended an additional volume

to the UV-Vis cell, loaded $\text{Fe}(\text{acac})_3$ starting material only in the cell to avoid direct contact between the powder and the gold cup, and placed the gold cup in the appended volume. Once the system was vented, the particles were collected from the gold cup with adhesive tape and their magnetic properties analyzed with the SQUID based magnetometer.

RESULTS AND DISCUSSION

A. Structural Properties of Batch Nanoparticle Films

We present only a brief summary of our batch results here; more detailed results will be presented elsewhere [2].

Under slow depressurization we find two different types of cluster film growth materials. In one arrangement particles of the order of 20-75 nm appear to self organize in elongated chain-like structures. In the other arrangement particles are fused together to form filaments several micrometers long and approximately 70 nm wide. It was not possible to resolve particles < 20 nm with our SEM but it is clear that there are many such smaller particles.

The main features of nanoparticle films formed under fast depressurization consist of a very thin coating and spherical nanoparticles. These particles can be classified in three distributions. The larger particles have a minimum size of 150 nm, maximum size of 350 nm, mean size of 200 nm and standard deviation of 73 nm. As found in particles grown with a slow depressurization these nanoparticles consist of smaller units self-organized into spherical assemblies. The second size distribution is characterized by the spherical particles with a minimum size of 60 nm, maximum size of 100 nm, mean size of 80 nm and standard deviation of 13 nm. The third morphology of particles was given by very small spherical particles distributed over the substrate and not organized into larger structures with a minimum size of 16 nm, maximum size of 46 nm, mean size of 28 nm and standard deviation of 10 nm. Particle morphology appears more uniform for the rapid depressurization and the long filaments observed on the thin film using a slow depressurization are not present.

These nanoparticle films made with the batch process clearly have a different morphology and particle size distribution than those made with the RESS process [1,2]. If we compare films grown on cold substrates, nanoparticles made with the batch process are generally smaller and have a narrower size distribution. Also the shape of the particles is different for the two processes since orthorhombic particles are grown with the RESS process while spherical particles are formed with the batch process.

B. Magnetic Properties of Batch Nanoparticle Films

Magnetic properties of batch films were analyzed with a SQUID based magnetometer. Initially a blank silicon wafer processed in the batch apparatus with pure CO_2 was analyzed to verify that the only contribution from the substrate material was a diamagnetic signal. All the films grown with the batch process on silicon substrates showed a dominant magnetically ordered signal and some of them a very small paramagnetic contribution.

A batch film grown under fast depressurization showed only a magnetically ordered signal suggesting complete decomposition of $\text{Fe}(\text{acac})_3$ into a magnetically ordered material. The film was characterized by $M_s = 1.86 \times 10^{-6}$ emu, $M_r = 3.91 \times 10^{-7}$ emu and $H_c = 60$ Oe, all results comparable to the magnetically ordered signal of RESS films deposited on cold substrates.

Films grown with the batch process using a slow depressurization showed a dominant magnetically ordered signal and a small paramagnetic contribution. A typical film was characterized by $M_s = 4.27 \times 10^{-5}$ emu, $M_r = 7.45 \times 10^{-6}$ emu and $H_c = 50$ Oe. The principle

difference in magnetic order between the RESS and batch films is that the degree of paramagnetic behavior is much smaller, nearly non-existent, in the batch samples. This result would suggest a higher degree of Fe(acac)₃ decomposition towards an iron oxide structure for the batch processed films.

These results indicate that decomposition of Fe(acac)₃ must then occur either in the supercritical fluid phase itself or as a consequence of interaction with the silicon oxide (SiO₂) layer of the substrate. The reaction of Fe(acac)₃ with the silicon oxide layer has previously been demonstrated to occur in the presence of acidic OH groups on the SiO₂ surface, which initiate the adsorption of acid-sensitive Fe(acac)₃ [7]. However some acetylacetonate ligands in the adsorbed phase remain bonded to Fe³⁺ and Mössbauer analyses of the adsorbed phase indicates the formation of a paramagnetic and non of a magnetically ordered compound [7].

To study the effect of substrate interaction, the silicon substrate was replaced with a gold cup, to collect particles formed by precipitation following fast decompression of the supercritical fluid mixture with T₀ = 45 °C and P₀ = 140bar. Since bulk gold is generally considered to be a chemically inert substrate [8], unlike gold nanoparticles [9], and doesn't have an oxide layer that could react with Fe(acac)₃, we expect to collect particles formed solely in the supercritical fluid phase with subsequent growth in the film. Particles were extracted from the gold cup with adhesive tape to be analyzed with the SQUID based magnetometer; magnetic measurements on a blank tape were performed to verify that the tape did not contribute to the particle magnetic signal. Particles collected on the gold cup are characterized by M_s = 8.6x10⁻⁶ emu, M_r = 2.86x10⁻⁶ emu and H_c = 115 Oe. Again, these values of coercivity are smaller than bulk iron oxide and consistent with the formation of magnetic nanoparticles.

CONCLUSIONS

We find that magnetic nanoparticle films can be grown on cold substrates with a batch process by depressurization of a supercritical mixture of Fe(acac)₃ and CO₂. These nanoparticle thin films were analyzed and compared with those obtained from the RESS process. While cloud point measurements indicate that substantial particle growth occurs in the fluid phase for the batch process, mass spectrometer experiments, presented elsewhere [2], and kinetic modeling [1], suggest negligible or no particle growth in the RESS expansion. These experiments clearly suggest that the initial decomposition and molecular restructuring occurs in the supercritical solution, although additional film growth occurs on the substrate.

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