

SILICA COATING OF COBALT NANOPARTICLES INCREASES THEIR MAGNETIC AND CHEMICAL STABILITY FOR BIOMEDICAL APPLICATIONS

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INTRODUCTION: Cobalt-based magnetic fluids designed for possible use in medical applications have been synthesized. The magnetic properties of silica-coated and non-silica-coated cobalt particles are compared and used to probe the chemical nature of the particles. Measurement of the magnetic properties of frozen ferrofluids gives insight into the chemical stability and structure of their particles and enables comparisons of the properties of magnetic fluids prepared by different methods.

METHODS: The magnetic fluids studied consist of a suspension of metallic cobalt nanoparticles in polydimethylsiloxane (PDMS) carrier fluid¹. In two of the magnetic fluids, the particles are stabilised against aggregation by a triblock copolymer: poly[dimethylsiloxane-b-(3-cyanopropyl)methylsiloxane-b-dimethylsiloxane] (15kPDMS-2kPCPMS-15kPDMS). The central polymer block binds to the cobalt particles through CN-Co coordination and the two outer blocks act as tails to increase stability. The remaining two magnetic fluids were prepared in PDMS fluids using a pentablock copolymer: 15k PDMS-2kPMTEOS-2kPCPMS-2kPMTEOS-15kPDMS². Following the cobalt nanoparticle formation, the additional PMTEOS blocks were condensed to form a silica coating at the nanoparticle surface. In both methods, the cobalt particles are prepared through thermal decomposition of $\text{Co}_2(\text{Co})_8$ in copolymer micelles using toluene as the solvent fluid. The particles are then transferred to a PDMS carrier fluid. After production, one sample produced by each method was exposed to air for the duration of the experiments and another sealed under an argon atmosphere. The differences in production are summarised in Table 1.

Magnetic measurements were performed using a magnetic susceptometer incorporating a superconducting quantum interference device sensor (MPMS-7, Quantum Design). The freezing point of the fluids was approximately 222 K and initially magnetic fields were not applied above this temperature so the particles would not be exposed to field gradients which may cause aggregation of

the particles in the fluid. Magnetisation in a 100 Oe field was measured from 5-220 K after the fluids had been cooled from 220 K (i) in zero field and (ii) in a 70 kOe field.

Table 1. Production method, exposure to atmosphere after production, and final composition of each fluid.

Fluid Label	Production Method	Exposure	% cobalt
A	no coating	air	1.9
B	no coating	argon	1.6
E	silica coating	air	2.0
F	silica coating	argon	2.0

Cobalt specific magnetization (σ) vs. applied field (H) behaviour of the fluids was measured from -70 kOe to 70 kOe at 5 K. The σ vs H responses were measured both after cooling from 220 K in a zero field and a 70 kOe field.

The σ vs H behaviour at 5 K was studied over time for all samples to measure the chemical stability of the particles. After this series of measurements, σ vs H behaviour at fields up to 1 kOe at 298 K was measured. Particle size was studied with electron microscopy.

RESULTS: The zero-field-cooled and field-cooled temperature dependent cobalt specific magnetisations in 100 Oe are shown in Figure 1. The two families of particles have different peak zero-field cooled magnetisation temperatures, the temperatures of the peaks representing a characteristic magnetic blocking temperature for the sample. The silica-coated particles have lower characteristic blocking temperatures than the non-silica-coated particles. The characteristic blocking temperatures of the non-silica-coated particles appear to be above the freezing points of their fluids. Measurement of the temperature dependent magnetisation of the fluid above this point provides no further information about the size

distribution of the particles as they rapidly rotate into the field direction.

There is a second clear peak at 15 K in the curves of the silica-coated particles. This is not evident in the curves for the non-silica-coated particles. For the non-silica-coated particle dispersions, A and B, the bifurcation temperature of the field-cooled and zero-field-cooled magnetization in 100 Oe is above the melting temperature. The bifurcation temperature for samples E and F is 160 K.

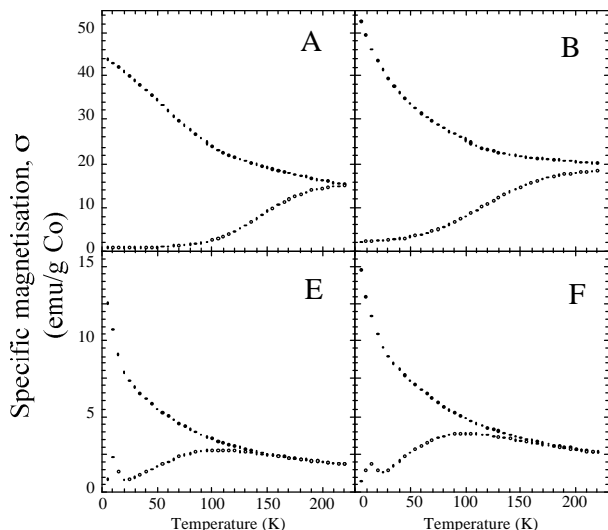


Fig. 1: Temperature dependent specific magnetisation of cobalt particles. Filled dots are field-cooled measurements, empty dots are zero-field cooled measurements. The letters on the plots refer to the sample measured

The zero-field-cooled and field-cooled magnetic hysteresis behaviour of samples at 5 K is shown in Figure 2. The centres of the field-cooled magnetic hysteresis loops at 5 K are shifted to negative fields for all samples. Sample B is almost magnetically saturated at 70 kOe and has a smaller negative bias field than sample A. The silica-coated samples (samples E and F) have loop shifts which are similar to that of the argon-sealed non-silica-coated sample (B). However, the maximum specific magnetisation is much less than that of sample B.

It is clear from the hysteresis loops that the samples have not reached magnetic saturation at 70 kOe. The behaviour of the magnetization at high fields has been modelled by fitting the sum of a Brillouin function (representing magnetization of paramagnetic species) and a constant (representing the expected saturated magnetization of metallic cobalt particles, $\sigma_{s\text{-met}}$) to the magnetisation for fields greater than 30 kOe. The constant, $\sigma_{s\text{-met}}$, and the atomic angular momentum quantum number J were allowed to vary freely during the fitting procedure. The value of J from the fit ranged from 0.35 to 0.84.

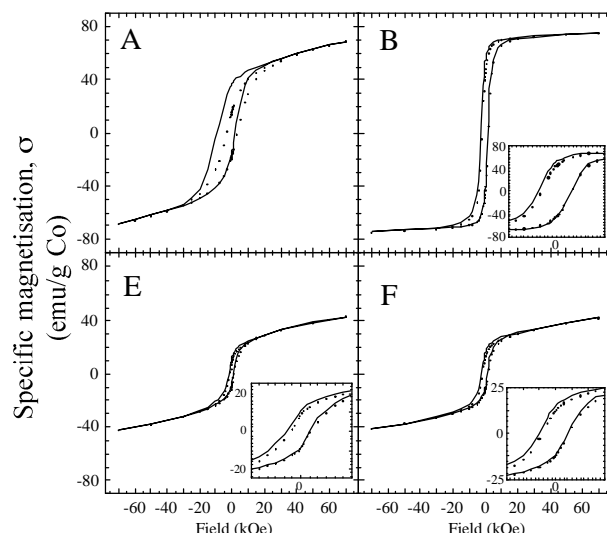


Fig. 2: Magnetic hysteresis loops of cobalt particles measured at 5K after cooling in zero field (closed circles) and in 70 kOe field (line). The letters on the plots refer to the sample measured. The inset plots are from -6 kOe to 6 kOe.

The magnetisation loss per day is calculated from a linear fit to $\sigma_{s\text{-met}}$ against time (Figure 3). The non-silica-coated particles exposed to air (sample A) clearly lose more specific magnetisation per day than the other particles. A linear fit to the $\sigma_{s\text{-met}}$ vs time data using a Levenberg-Marquardt algorithm yields the uncertainties on the rates of saturation magnetisation decay (shown as error bars in Figure 3).

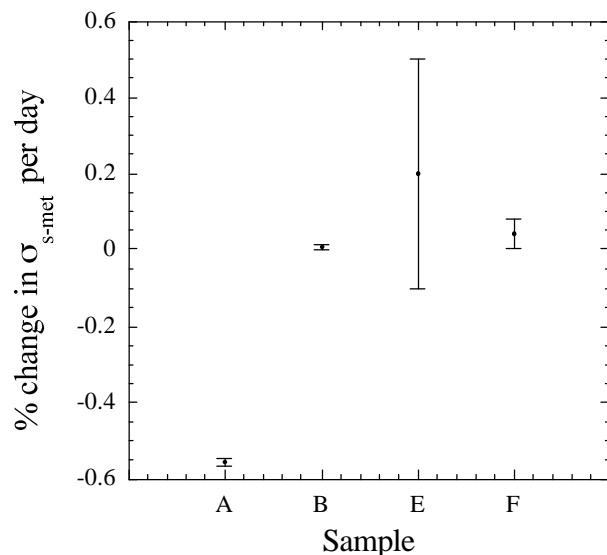


Fig. 3: Change in $S_{s\text{-met}}$ per day for all samples.

All fluids show non-hysteretic σ vs H behaviour at 298 K. There is no remanent magnetisation observable and the particles do not reach saturation at the fields studied. Electron microscopy images show the non-silica-coated particles cluster into

groups of 2-4, while the silica-coated particles do not appear to cluster. The silica-coated particles are smaller than the non-silica-coated particles.

DISCUSSION & CONCLUSIONS: The peak in the zero-field-cooled temperature dependent magnetisation of an ensemble of particles gives an indication of the average size of the magnetic core of the particles³. The temperature of bifurcation of the zero-field and field-cooled curves is related to the volume of the largest particles in the ensemble. The lower temperature of peak magnetisation and bifurcation for the silica-coated particles indicates a smaller average magnetic core size of the particles. The smaller overall size of the particles as observed by electron microscopy supports this. Particle size differences alone may not entirely account for the much higher temperature of the peak in the zero-field-cooled magnetisation of the non-silica-coated samples. The electron microscopy images of the particles clearly show clustering of the non-silica-coated particles into groups of 3-5. This clustering will have a demagnetising effect on each of the particles in a cluster. The energy needed to align the magnetization of each particle with the magnetic field will be greater for particles in a cluster than for an isolated particle. This means that in the case of clustered particles the temperature of the maximum in the zero-field-cooled peak may not be simply related to particle size. Although the non-silica-coated particles have both a characteristic blocking temperature and a bifurcation temperature above the measurement range this does not necessarily mean there will be a remanent magnetisation at room temperature. It is unclear whether the clustering observed by electron microscopy is present when the particles are in the fluid state. Nevertheless, the time for rotation of a cluster of particles is still less than the measurement time. From the 298 K σ vs H measurements, the measured remanence of Samples A and B above the freezing point of the liquid is zero.

The significant loss of specific saturation magnetisation σ_{s-met} with time for the air-exposed non-silica-coated particles (A) indicates a chemical change in the particles over time. This observation strongly suggests that the particles are steadily oxidizing. This sample also has a larger shift of the centre of its field-cooled magnetic hysteresis loop than any other samples. Field-cooled magnetic hysteresis loops can exhibit a shift in the centre of the loop when antiferromagnetic surface states on the particle are coupled to the core⁴. The susceptibility of cobalt to oxidation is well known so the shell is most likely cobalt oxide. As neither a

significant loss of saturation magnetisation nor a large field-cooled hysteresis loop shift are evident in the argon-sealed non-silica-coated sample (B), an oxidation effect is the most likely explanation for these observations rather than particle-particle interaction effects.

The air-exposed and argon-sealed silica-coated particles (samples E and F respectively) and the argon-sealed non-silica-coated particles (sample B) all have similar loop shifts. The similar loop shifts for air-exposed and argon-sealed silica-coated particles confirm that the silica coating does protect the cobalt particle from oxidation when the reaction process is complete and the particles are in the carrier fluid. As the production mechanism of silica-coated particles is very similar to that for the non-silica-coated particles, the stability of these particles against oxidation must be attributed to their silica coating. The antiferromagnetic ordering of the surface layer is probably a result of oxidation occurring at some point in the production process. However as yet it is unclear when or why these particles become oxidised.

The measurements give substantial evidence for multiple forms of cobalt in the suspensions. Together, the clear peak at 15 K in the zero-field-cooled magnetisation of the silica-coated particles, the paramagnetic signal in all the 5 K σ vs H measurements and the shift of the centre of all the field-cooled 5 K magnetic hysteresis loops suggest additional non-metallic cobalt species in the fluids. The second species may be a chemically different form of cobalt or a metallic cobalt with a different magnetic ordering. The chemical form of cobalt responsible for this component may be reaction intermediates or fully reacted species which have formed amorphous cobalt compounds instead of metallic cobalt particles. Alternatively, the second species may be surface cobalt with a different magnetic ordering and so different magnetic properties to the cobalt particle core.

The peak at approximately 15 K in the zero-field-cooled curves of the silica-coated particles may indicate a second population of particles with a much smaller core size in these samples. It is possible that clusters of cobalt, which have not formed into larger particles, are producing this peak. It is also possible that the silica coating produces a range of surface states which are not present on the non-silica-coated particles. The surface atoms involved in these states could be weakly magnetically coupled and so be observable as a peak in the zero-field-cooled curve at much

lower temperatures than that associated with the magnetically ordered core. They also may contribute to the paramagnetic signal observed in the σ vs H measurement at 5 K.

The value of J obtained from the Brillouin fit to the σ vs H measurement is lower than expected from theory. The reduced J value suggests that the magnetic moment of the paramagnetic cobalt atoms which contribute to this signal are quenched through interaction with other atoms. The binding of a ligand to a surface is known to quench the magnetic moment of the atoms on the surface. It may be these bound cobalt atoms which are contributing to the paramagnetic signal with a reduced magnetic moment as compared to bulk cobalt. The reduced J value may also be due to a surface spin structure where interactions between the spins prevent the paramagnetic magnetic moment reaching the bulk value. The shifted field-cooled hysteresis loops are usually a result of antiferromagnetic surface states on a particle. Possibly the particles are oxidised at some point in the production process and portions of the surface are antiferromagnetically ordered. The antiferromagnetically ordered states may force other surface atoms into partially antiferromagnetically aligned states, reducing their J value.

It is most likely that there is more than one form of cobalt which contributes to the observed magnetic behaviour. The measurements suggest some effects from the surface of the cobalt particles, as well as the possibility of amorphous paramagnetic cobalt species in the fluids. As yet, the contribution from each form of cobalt cannot be separated.

From this work it is clear that coating the cobalt particles with a polysiloxane based copolymer does not fully prevent oxidation of the particles. A shell of silica surrounding a cobalt core can be used to protect the particles against oxidation. The silica-coated particles have a lower specific saturation magnetisation and magnetic susceptibility, most probably because of an increase in antiferromagnetic or paramagnetic cobalt. The reduced volume of the magnetic core of the silica-coated particles ensures that they are superparamagnetic well below room or body temperature. The increased chemical stability of the silica-coated particles as compared to the non-silica-coated particles makes them more suitable for use in the human body.

REFERENCES: ¹M. Rutnakornpituk, M. S. Thompson, L. A. Harris, et al, (2002) *Polymer* **43**: 2337-2348. ²M. Rutnakornpituk, V.V.

Baranauskas, J.S. Riffle, et.al. (2002) Proc. 4th Int'l Conf. On Scientific and Clinical Applications of Magnetic Carriers. ³M. Hansen, C. Johansson, M. S. Pedersen, et al, (1995) *J. Phys.: Condens. Matter.* **7**: 9267-9277. ⁴J. Nogués and I. K. Schuller, (1999) *J. Magn. Magn. Mater.* **192**: 203-232.