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In-situ coated nanomagnets

Johanna Forsman [a,*], Pirjo Koskela [a], Ari Auvinen [a], Unto Tapper [a],
Sebastiaan van Dijken [b], Jorma Jokiniemi [a,c]

[a] Fine Particles, VTT Technical Research Centre of Finland, P.O. Box 1000, FI-02044 VTT, Finland
[b] NanoSpin, Department of Applied Physics, Aalto University School of Science, P.O. Box 15100, FI-00076 Aalto, Finland
[c] Department of Environmental Science, University of Eastern Finland, P.O. Box 1627, FI-70211 Kuopio, Finland

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ABSTRACT

Nanomagnets with controlled size distribution are produced by continuous hydrogen reduction technique and coated in situ by carbon or copper. The copper layer can be oxidised ex situ. The coated nanomagnets are well-protected against oxidation occurring over time or in elevated temperatures. The optical and electrical properties of the magnets are controlled by coating. The coating can also be functionalised. The saturation magnetization of all nanomagnets is close to that of bulk, Co, indicating a highly crystallised structure and the avoidance of oxidation. Copper coating increased the measured magnetic hysteresis.

1. Introduction

The variety of magnetic nanoparticle applications covers high-frequency RF devices [1] magnetic separation [2], ferrofluids [3], microwave absorption [4] and various catalytic effects [5,6]. Applications for soft ferromagnetic materials include recording heads and magnetic shielding [7]. High-density magnetic recording [8] is an example of hard ferromagnetic material applications. Most applications benefit from coating of the magnetic particle to prevent oxidation and degradation, to avoid magnetic interaction between the particles or enabling dispersion in liquids and surface modifications. Electric properties such as conductivity may also be affected by surface coating.

Magnetic nanoparticles are also widely used in nanobiotechnology. For diagnostic uses, specific and generic recognition of nucleic acids are developed [9,10]. Phosphopeptides were selectively trapped using niobium-oxide-coated magnetic nanoparticles by Lin et al. [11]. Cellular separation is studied by Roveimiab et al. [12].

Copper is widely used as core material in core–shell particles, but rarely as the shell layer. However, in addition to merely protecting the cobalt core and affecting its magnetic properties, the copper oxide applications, such as antimicrobial [13] and water splitting [14] would greatly benefit from a magnetic core to facilitate their handling or verify their location. Theoretical work on Co + Cu nanoalloys is summarized by Ferrando et al. [15]. The only experimental work the authors are aware of is a liquid-phase study by Subramanian et al. [5] of catalysts for higher alcohol synthesis from syngas. Giant magnetoresistance was observed for copper–cobalt granules [16]. Also cobalt particles in copper matrix have been produced for magnetic anomalies [17]. Copper oxide nanoparticles are produced, e.g. by flame spray pyrolysis [14] and have been found to be semiconducting [18].

Much research has been conducted on carbon-coated metal nanoparticles by aerosol methods. Gas phase methods cover flame, arc plasma, thermal decomposition, chemical vapour condensation and pyrolysis [19–26]. Thermal decomposition typically leads to the formation of carbides in addition to graphitic C. Arc-plasma technique may lead to the formation of cobalt oxide or carbide. Liquid techniques have been employed and similar sizes were obtained by [27]. The magnetic properties of carbon-coated cobalt particles have been studied e.g. by Sun et al. [28]. The ethene decomposition method for carbon coating is also described in [29]. In batch manner ethene decomposition has been used by Narkiewicz et al. [30].

The authors present here an economic, continuous production route to in-situ coated nanomagnets by chemical vapour synthesis. Two coating techniques are presented, enabling control of size distribution and magnetic field response. The conductive properties of the shell can be varied between conductive (copper coating), semi-conducting (copper oxide coating) or graphitic (conductive along surface, semiconducting perpendicular to surface). The method is characterised by high yield and narrow size distribution [31].

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[*] Corresponding author.
E-mail address: johanna.forsman@vtt.fi (J. Forsman).

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Table 1
Overview of experiments. In all experiments, hydrogen concentration was 13.8 mol% and reaction temperature 950 °C.

	Precursors	Ethene fraction of reaction flow	Cu fraction of metal	Evaporation temperature	Oxidation	Number average diameter
		mol%	wt.%	°C		nm
Co	$CoCl_2$	0	0	800	No	84
Co + C	$CoCl_2$, C_2H_4	0.04–9.2	0	800	No	17–63
Co + Cu	$CoCl_2$, CuCl	0	31–90	800–850	No	54–84
Co + Cu + O	$CoCl_2$, CuCl	0	31–90	800–850	"Light" or "heavy"	n/a

2. Experimental

The magnetic core was produced by continuous gas-phase hydrogen reduction of cobalt chloride (97 wt.%, Sigma-Aldrich) as presented earlier [1,31]. The precursor was fed by powder feeder to heated evaporation stack. The stack temperature was 800 °C for carbon-coated particles and 800 or 850 °C for copper-coated particles. Nitrogen flow carried the evaporated precursor to the reaction zone where it was mixed with hydrogen gas (13.8 mol% of total reaction flow) at 950 °C. The flow was then quenched with room temperature nitrogen gas. Particles were collected on PTFE filter bags. An overview of the experiments is given in Table 1.

The carbon coating (Co + C particles) is attained by adding ethene to the reaction flow either mixed with hydrogen or with the metal chloride–nitrogen mixture. The formed metallic nanoparticles catalyse ethene decomposition to carbon and hydrogen. The ethene concentration was varied by 0.04–9.2 mol% of the total reaction flow to see the effect of the ethene to chloride vapour molar ratio on particle size distribution and carbon content. For copper coating (Co + Cu particles), copper chloride (97 wt.%, Sigma-Aldrich) was mixed with the cobalt chloride and the mixture was fed to the evaporation stack. This copper layer was oxidised (Co + Cu + O particles) by placing the powder collected in filter bags into a furnace in a flow of 2 mol% oxygen in nitrogen. The furnace temperature was 130 °C with an oxidation duration of 30 min for "heavy oxidation" and 100 °C with a duration of 10 min for "light oxidation". Uncoated cobalt particles (Co particles) were produced as a reference for magnetic measurements. The procedure is the same as for carbon-coated particles except that no ethene is fed to the reactor. The diameter of the uncoated particle can be varied by changing the mass concentration of the precursor [31].

The gas-phase was analysed with Fourier-transform infrared spectroscopy (FTIR, Gasmet Dx4000) for HCl, H_2O, CO_2, CH_4, C_2H_4 and C_2H_6. HCl concentration, a product from metal chloride decomposition, is a direct measure of production rate of particles. H_2O and CO_2 concentrations reveal the purity of the carrier gas. CH_4, C_2H_4 and C_2H_6 concentrations indicate fraction of elemental carbon in ethene decomposition products. Ultramat 23 (Siemens) was used to analyse oxygen concentration for safety purposes. This enabled on-line information on the precursor concentrations and fraction of reacted ethene. The gas flow was directed through alkaline water tanks for removal of HCl before the exhaust duct. Gravimetric analysis of mass concentration was conducted by taking samples with 47 mm analysis filters (Millipore 0.2 μm FG Fluoropore, flow rate 0.38 Nlpm) for 1 min. These samples were also used for transmission electron microscopy (FE-TEM, Philips CM-200 FEG equipped with EDS analyser) to determine composition and particle size distribution characteristics. In addition, crystal structure of the particles was studied with selected area electron diffraction (SAED). The number average diameter was determined by measuring the diameter of 150–500 particles from the micrographs. Sample standard deviation and specific surface area (SSA) were determined directly from these data points. The batch-to-batch variation of the size distribution characteristics was previously found to be 5% [1]. The SSA was also measured directly using BET method (ASAP2020, Micromeritics Instruments Co.). For the Co + Cu particles, in addition to core–shell diameter, the diameter of the Co core was measured from the TEM micrographs. The uncertainty of the core diameter measurement is significantly larger than the uncertainty of the core–shell diameter measurement. These core diameters are only used as estimates for proper analysis of the magnetic measurements.

The structure was also studied with X-ray diffraction (XRD, Philips X'pert MPD X-ray diffractometer) and elemental composition with X-ray fluorescence (XRF, Philips PW2404 X-ray spectrometer with SemiQ). The XRF method does not directly see carbon and thus cannot be used to determine small carbon concentrations. For copper coated particles, XRD was conducted both prior to and after controlled oxidation of copper. The oxidation behaviour of particles was analysed with thermogravimetric analysis (TGA, Mettler TGA 851e). The sample was heated at 5 °C/min with a 50 ml/min air flow from 25 to 500 °C. Assuming full oxidation to Co_3O_4 or CuO, the analysis was also used to estimate the carbon content of the carbon-coated particles.

The magnetic properties (saturation magnetization M_s, coercive field H_S and remanent magnetization M_r) of the particles, were measured using Quantum Design SQUID magnetometer with a 7 T superconducting magnet. Measurements were conducted at room temperature (300 K) within 1 day after production of Co + C particles

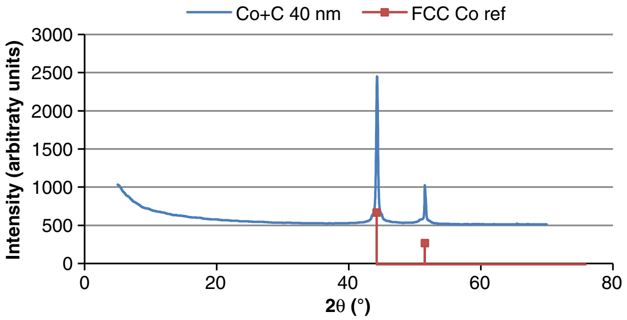

Fig. 1. XRD graph of Co + C particles with 40 nm number average diameter. Cubic (FCC) Co is the only material observed. The crystal size is 35 ± 2 nm. The results were similar for other Co + C samples. The reference peaks illustrate XRD signal from pure FCC bulk cobalt.

Table 2
TGA results for Co + C particles with three number average particle diameters (NAD). The table shows the initiation temperatures for surface oxidation and complete oxidation and calculated carbon content. Surface oxidation temperature indicates the temperature where slow oxidation mass gain begins (weight gain of the sample less than 1% until initiation of complete oxidation). Temperature of complete oxidations indicates the beginning of fast oxidation of all metal in the particles, typically ~30% weight gain within the next 30 °C temperature increase. The carbon concentration is calculated assuming oxidation of all Co to Co_3O_4.

Ethene concentration in reaction flow	NAD	Surface oxidation	Complete oxidation	Carbon content of particles
mol%	nm	°C	°C	wt.%
0	84	165	200	0
0.15	40	185	227	3.0
9.2	17	202	229	6.2