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Highly crystalline cobalt nanowires with high coercivity prepared by soft chemistry

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Cobalt nanorods and wires were prepared by reduction of a cobalt salt in a liquid polyol. These particles crystallize with the hcp structure and the growth axis is parallel to the crystallographic *c*-axis. The kinetic control of the growth allows to vary the mean diameter of the rods and their aspect ratio. Dumbbell like shape particles consisting of a central rod with two conical tips were also obtained. Magnetization curves of oriented wires present very high coercivity (up to 9 kOe) resulting from both a high shape anisotropy and the high magnetocrystalline anisotropy of the hcp cobalt. Micromagnetic simulations showed that the magnetization reversal is shape dependent. The conical tips of the dumbbell particles strongly contribute to the coercivity decrease and must be precluded for permanent magnet applications.

1 Introduction Magnetic nanowires and nanorods present several interests in the field of high density magnetic recording [1], spintronics and microwave applications [2] and can be new building blocks for permanent magnets [3]. Several ways have been developed for the preparation of such objects: the most studied consists in the electrochemical deposition using porous polycarbonate membranes or anodic aluminium oxide as template [4]. Liquid phase syntheses like organometallic chemistry or reduction in a polar solvent are an alternative way presenting several advantages. They provide high yield and can easily be scaled-up to produce large quantities of nanoparticles. More they have the interest to form highly crystalline particles. In this paper we present results on the synthesis of magnetic rods and wires by the polyol process. We show that parallel assemblies of these nano-objects present hard magnetic properties. Micromagnetic simulations are also very useful to optimize the particle shape in order to improve the magnetic properties.

2 Co-based nanowires synthesis

2.1 Experimental The reduction of a cobalt carboxylate in sodium hydroxide solution in 1,2 butanediol leads to cobalt metal particles presenting a great variety of shape depending on the growth conditions [1]. The experimental protocol is very simple: the cobalt precursor is dissolved in a sodium hydroxide solution of polyol (cobalt concentration of 0.08 M). A small amount of ruthenium chloride ($RuCl_3$) is added to seed the medium (the Ru/Co molar ratio is fixed equal to 2.5%). The mixture is then heated to 170 °C with a controlled temperature ramp. The solution turns to black progressively when the reduction occurs. After 30 min at 170 °C the reduction is complete and the solution is cooled down. The magnetic powder is recovered by centrifugation, washed with absolute ethanol and dried under vacuum. In order to preserve the particles from oxidation they are kept in the polyol solution. The same procedure is also used to synthesize bimetallic cobalt-nickel particles. In that case a mixture of cobalt and nickel carboxylates in the desired proportion is reduced in the liquid polyol. The cobalt/nickel ratio measured by EDX in the final metal particles is very close to the ratio in the starting medium.

Various metal carboxylates $M(C_nH_{2n+1}CO_2)_2$ can be used as metal precursor, from the simplest acetate ($n = 1$) to long chain carboxylate like laurate ($n = 11$) or palmitate ($n = 15$). The basicity, the carboxylate chain length and the slope of the temperature ramp have a strong influence on the reaction rate on which it is possible to act in order to modify the metal particle shape.

2.2 Shape and structure characterizations Cobalt rods were obtained by reduction of cobalt laurate in basic solution of 1,2 butanediol when the NaOH concentration was in the range 0.02–0.1 M and with a temperature ramp of 5 °C min^{-1}. Electron microscope images of such cobalt nanorods are presented Fig. 1. High resolution transmission electron microscopy (HRTEM) showed that these rods crystallize with the hexagonal structure and that the growth axis is the *c*-axis of the hcp phase (inset Fig. 1a). We proposed recently that the cobalt particle shape was tuned via the kinetic control of the growth step of the hcp phase [5, 6]. The aspect ratio (mean length/mean diameter) can be modified by varying the experimental parameters that control the growth rate: the basicity of the medium, the cobalt precursors and the temperature. When the growth rate is slowed down either by increasing the basicity, by increasing the carboxylate chain length or by decreasing the temperature ramp the growth perpendicular to the *c*-axis is favored. At the opposite when the rate is high enough the growth develops along the *c*-axis. The particle mean diameter (d_m) could be varied in the range 8–35 nm, the mean length (L_m) in the range 100–350 nm and the resulting aspect ratio from 4 to 30. In some cases dumbbell shape and diabolo like particles are formed (Fig. 1c) resulting from a steady decreasing of the growth rate during the reaction. Reduction of mixture of cobalt and nickel acetate with the molar ratio 80/20 allowed also to synthesize bimetallic $Co_{80}Ni_{20}$ nanowires with a small mean diameter (Fig. 1d). These wires present generally two hexagonal heads located at the extremities that are slightly richer in nickel with respect to the global composition [5].

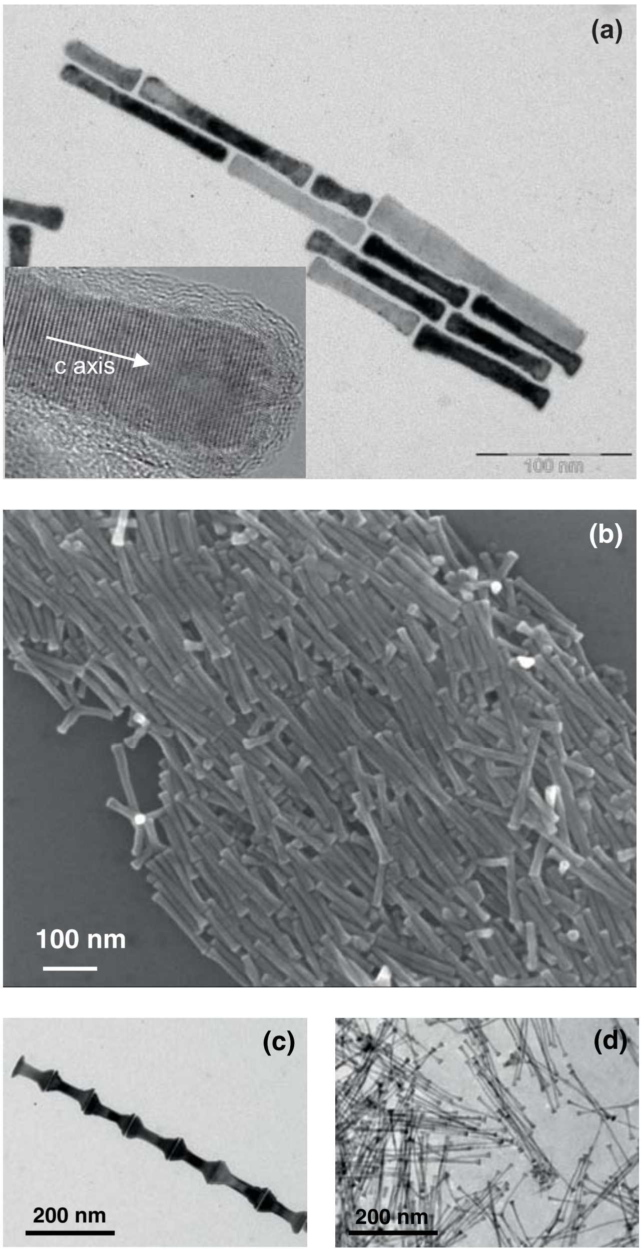

Figure 1 (a) TEM image of cobalt wires prepared by reduction of cobalt laurate in a basic solution of 1,2 butanediol (L_m = 100 nm, d_m = 12.5 nm); *Inset*: high resolution image of a cobalt wire in the $[2\bar{1}\bar{1}0]$ zone axis; (b) SEM image of cobalt wire assembly deposited on Si substrate under a magnetic field; (c) cobalt dumbbell shape particles; (d) $Co_{80}Ni_{20}$ nanowires prepared by reduction of a mixture of cobalt and nickel acetates in a basic solution of 1,2 butanediol (L_m = 250 nm, d_m = 7.5 nm).

3 Magnetic properties

3.1 Magnetization curves The cobalt-based rods and wires are ferromagnetic at room temperature. The saturation magnetization per gram of the dried powders reaches generally between 50% and 70% of the bulk value. These values result from the superficial oxide layer (presence of CoO was inferred from X-ray diffraction and

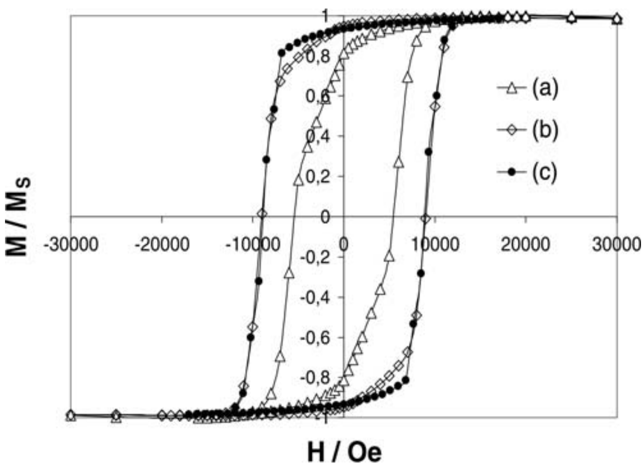

Figure 2 Magnetization curves of cobalt nanorods (L_m = 100 nm; d_m = 12.5 nm), (a) deposited on a flat substrate with an external magnetic field (*T* = 300 K); (b) frozen in toluene under an external magnetic field (*T* = 150 K); (c) simulation of the frozen sample magnetization curve using the Stoner–Wolfarth model for an assembly of non-interacting wires.

HRTEM) and from the presence of organic matter remaining in the powders.

The coercivity and the remanence of the magnetization curves depend on the particle shape and on the orientation of the particles with respect to the magnetic field. Figure 1b illustrates well that the wires can be aligned with an external magnetic field. The magnetization curve of cobalt rods deposited on a flat substrate with an external magnetic field applied during the evaporation of the solvent was measured at 300 K. A coercivity H_c = 5.5 kOe and a remanence to saturation ratio M_r/M_s = 0.81 were obtained (Fig. 2a). Although the orientation of the wires was only partial as revealed by the M_r/M_s ratio, the coercivity value is significantly higher than those reported in the literature for iron or cobalt nanowires grown by electrodeposition in the one dimensional pores of alumina membranes [3]. We think that it is the result of a very good crystallinity of the wires grown by our chemical process. In order to increase the rod orientation, a suspension in toluene was cooled under a magnetic field of 50 kOe and frozen at 140 K. A square-shaped hysteresis with a

Table 1 Coercivity and remanence to saturation ratio of Co rods (L_m = 100 nm; d_m = 12.5 nm) and $Co_{80}Ni_{20}$ wires (L_m = 240 nm; d_m = 7 nm).

	pressed powder (T = 300 K)		frozen suspension (T = 140 K)	
composition	$Co_{80}Ni_{20}$	Co	Co	$Co_{80}Ni_{20}$
Hc(Oe)	3.6	4.5	8.9	6.5
Mr/Ms	0.64	0.57	0.95	0.94

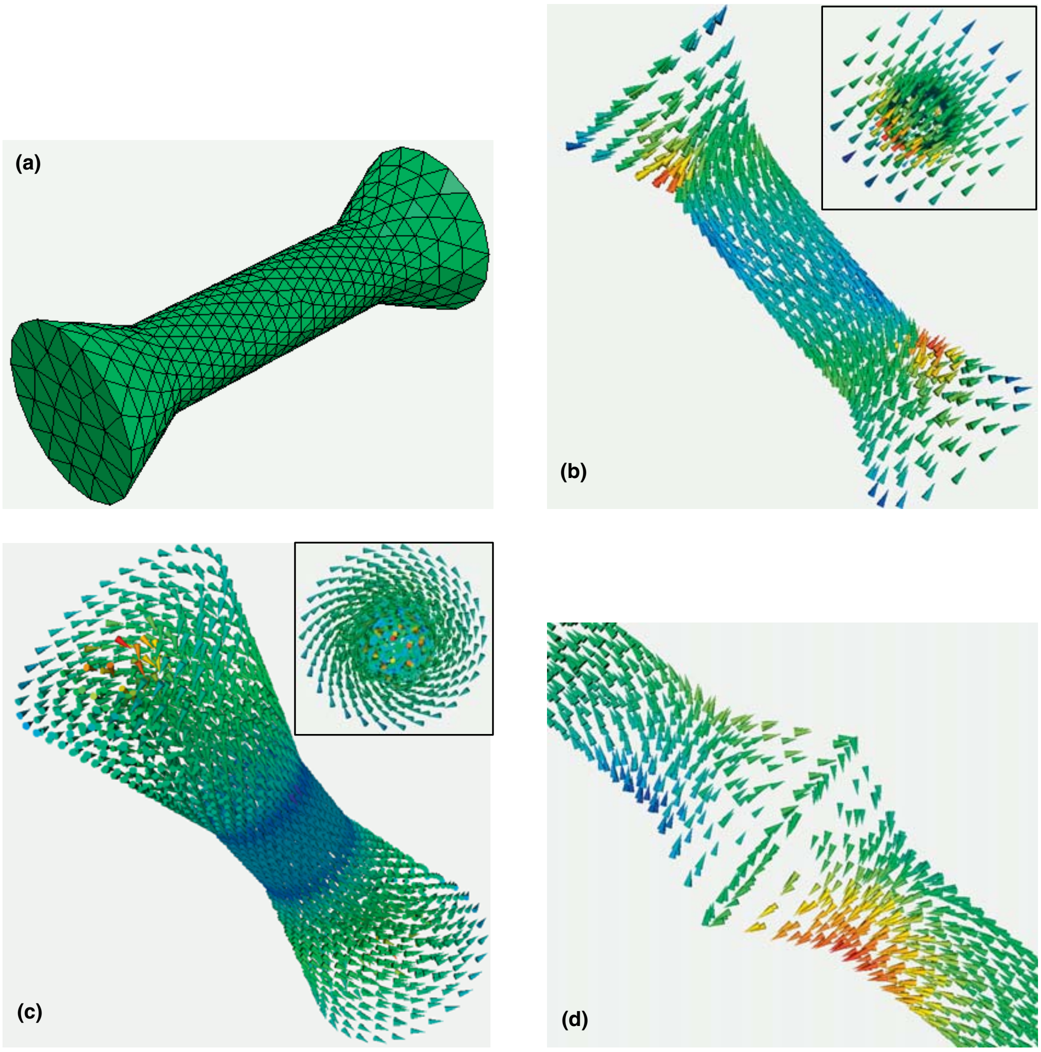

Figure 3 (online colour at: www.pss-a.com) (a) A model of the small Co dumbbells of Fig. 1c. (b) The micromagnetic state just before reversal in a dumbbell like Fig. 1c: a symmetry plane is created breaking the cylindrical symmetry. Inset: view along the rotation axis. (c) Reversal in a dumbbell with tips 1.5 times bigger: a vortex state forms before reversal and the cylindrical symmetry is preserved. (d) The micromagnetic state before reversal for a string of particles (separated by 2 nm). The reduction of the stray field has little effect on the reversal process.

remanence to saturation ratio close to 0.95 was obtained showing a much better wire alignment (Fig. 2b). The increase of coercivity is also very important with the parallel wire orientation reaching 9 kOe. The magnetization curve at 140 K was fitted using the Stoner–Wolfarth model for an assembly of elongated particles presenting both a shape and a magnetocrystalline anisotropy with a dispersion of the particle orientation with respect to the applied magnetic field. More details are given in reference [3]. A standard deviation on the wire orientation $\sigma_\theta = 15°$ (HWHM), a magnetocrystalline anisotropy field $H_{MC} = 4.2$ kOe and a shape anisotropy contribution of $H_{shape} = 4.7$ kOe were deduced from the fit presented Fig. 2c.

The effect of the wire orientation was also measured on $Co_{80}Ni_{20}$ nanowires prepared by the polyol process [4]. Nevertheless, the coercivity measured on cobalt-nickel wires was lower, reaching 6.5 kOe at 140 K and 3.6 kOe at 300 K on randomly oriented particles (Table 1). It is noteworthy that the coercivity measured on the bimetallic wires is lower despite a higher aspect ratio. The lower magnetization of the cobalt–nickel alloys could be responsible of this phenomenon. Indeed, the magnetic anisotropy related to the particle shape increases with the saturation magnetization (in the case of long ellipsoids, one would expect an ideal coercive field of $M_s/2$).

3.2 Shape optimization The lower value of coercivity can also be attributed to the particular shape of the CoNi particles that present conical heads. We have used the micromagnetic simulation package "Nsim" [7, 8] to perform 3D micromagnetic simulations of dumbbell cobalt particles with different size of conical tips and different aspect ratio. A model of particle is presented in Fig. 3a.

In the case of dumbbells with dimensions similar to those of Fig. 1c, before reversal, a C-shaped tilt of the magnetization appears in the tips (Fig. 3b). The coercivity resulting from the shape anisotropy is equal to 185 kA/m (2325 Oe). Note that in the simulation we do not take into account any magneto-crystalline anisotropy. If the tips are 1.5 bigger, a full vortex can develop in the tips (Fig. 3c) and the coercivity drops to 155 kA/m. These coercive fields have to be compared with the ones of cylinders (300 kA/m) or ellipsoids (420 kA/m) of equivalent aspect ratio (~5). This proves that the shape of the nanowire tips significantly decreases the coercive field. This tendency is maintained if one increases the aspect ratio from 5 to 20, the coercive field increases from 290 kA/m for dumbbells, to 455 kA/m for wires and 510 kA/m for ellipsoids. Furthermore, as seen on Fig. 1c, particles may form chains. When the particles are attached end to end and form strings simulations show that it does not increase the coercivity significantly. The coercive field increases from 185 kA/m for an isolated particle to 210 kA/m for a string of particles (i.e. only a modest 13% increase). The key effect for high shape coercivity is thus the detailed shape of the particles.

The very high values of coercivity and remanence make the cobalt rods good candidates for the elaboration of permanent magnets. Dense arrays of these particles obtained by compaction may present high $(BH)_{max}$ values. This study shows that shapes such as those showed in Fig. 1c must be precluded in order to get high coercivity. Chemical composition with high magnetization must also be targeted to get both a high remanence and a high coercivity.

4 Conclusion We have showed that it is now possible to synthesize by a liquid phase process cobalt and cobalt–nickel nanowires with various diameter and length. The aspect ratio is varied by acting upon the growth conditions. These wires present a very high coercivity in comparison with nanowires prepared by other routes. A diameter in the nanometer range, a high aspect ratio and a high saturation magnetization are required to get such coercivity. Magnetocrystalline anisotropy of cobalt and cobalt-nickel alloys with hcp structure also contributes to the hard magnetic behaviour. Compaction of such wires to shape dense materials could be a way to get permanent magnets. Some questions are still open. Higher saturation magnetization is expected to increase the coercivity of particles presenting high shape anisotropy. Iron and iron–cobalt alloys would be best candidates as building blocks for permanent magnet application. Nevertheless, the growth of anisotropic nanoparticles with body centered cubic structure by a liquid phase process remains a challenge.

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