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Nickel nanofibers and nanowires: Elaboration by reduction in polyol medium assisted by external magnetic field

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ABSTRACT

Nickel nanowires, with diameter 250 nm and a length of several microns, were prepared by the polyol process (chemical reduction) while an external magnetic field of 1.4 T has been applied during preparation. This combination has allowed the elaboration of Ni nanowires with a yield of over 90%. X-ray diffraction (XRD) showed that these nanowires crystallize with the face-centered-cubic structure. Magnetic static measurements showed the effect on the nanoparticles' morphology of the external magnetic field applied during the synthesis. They also allowed studying the effect of the external magnetic field on the magnetic properties of nanowires as a function of their orientation. When nanowires are aligned parallel with magnetic field, the hysteresis loop obtained is very open with a coercivity field (Hc) value of 385 Oe and a high remanence to saturation ratio Mr/Ms of 0.85.

1. Introduction

Up to now two main chemical methods have been developed to synthesize anisotropic ferromagnetic nanoparticles. The first method consists of conducting chemical or electrochemical reduction in the pores of inorganic or organic templates such as alumina, polycarbonate membranes [1–3], mesoporous silica (5–40 nm in diameter) [4] or carbon nanotubes [5].

The second method consists of reduction in solution without the presence of a template agent. This method is more difficult to conduct because of the high surface tension of metals, which leads generally to spherical particles. Among these approaches, one can find the organometallic route which consists of the reduction by hydrogen gas of organometallic complexes in the presence of a surfactant [6]. Another recent approach is to use a strong reducing agent such as hydrazine in aqueous or polyols media with the application of an external magnetic field. This method allows to obtain a coalescence of anisotropic nanoparticles bonded to each other forming aligned chains [7,8]

All these techniques can produce anisotropic nanoparticles with quite remarkable features. However, it necessitates the use of a matrix (mineral, organic) and surface-active agents which must be removed subsequently resulting in additional study on the physico-chemical properties. In addition, using a strong reducing agent such as hydrazine or hydrogen makes manipulation very difficult and dangerous especially for a possible application to the industrial scale.

A survey of the literature shows that the polyol process presents an alternative to partly overcome these difficulties. This process belongs to the soft chemistry methods. It takes benefit from the properties of polyol as solvent, complexing and reducing agents to produce a great variety of inorganic materials (oxides, metals, layered hydroxysalts) [9,10]. Furthermore it provides high yield and can easily be scaled-up to produce large quantities of nanoparticles. More, polyols allow forming highly crystalline particles [11,12]. Recently, it has been possible by adjusting the speed of nucleation and growth to produce Co or Co–Ni nanowires in a polyol medium [13]. However this method cannot be extended to the synthesis of pure nickel nanorods or nanowires. Indeed only isotropic particles or platelets of nickel have been prepared according to this process [14].

This work reports on a simple and friendly environmental approach for the fabrication of Ni nanofibers and nanowires in the absence of any template, substrate, surfactant, or strong reducing agent such as hydrazine. Nickel nanofibers and nanowires were prepared by combining chemical reduction by a polyol along with the application of an external magnetic field. We show that parallel assemblies of these nano-objects present enhanced magnetic properties in comparison with nickel nanoparticles and nickel bulk material.

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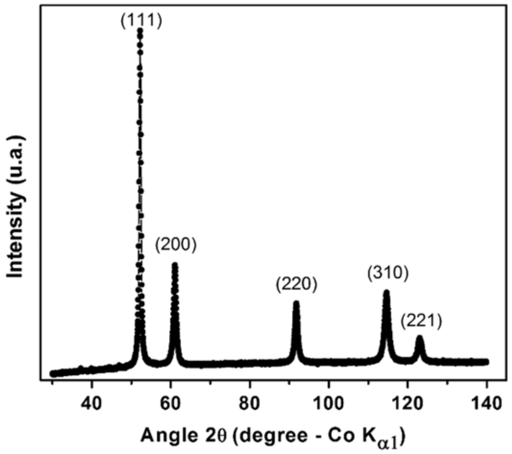

Fig. 1. Typical XRD pattern of Ni powders prepared by reduction in polyol medium of nickel acetate in the presence of a magnetic field of 1.4 T.

2. Experiments

The experimental protocol adopted to elaborate the nickel nanowires can be summarized as follows: Nickel acetate (Ni concentration of 0.08 M) and sodium hydroxide (0.08–0.25 M) were dissolved in 1, 2-butanediol (BEG). A small amount of ruthenium chloride ($RuCl_3$) is added. The Ru will be reduced before and will serve as seeds during the growth of nanoparticles (heterogeneous nucleation). According to previous works, the Ru/Ni molar ratio was set equal to 2.5% [13,14]. In some of our experiments we have tripled this ratio (7.5%) without any significant change neither in the length nor in the diameter of the obtained nanowires. The reactor containing the mixture is placed in an oil bath preheated to 170 °C and a magnetic field was immediately applied. After 1.30 h of reaction at 170 °C the reduction was completed and the solution 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.

X-ray diffraction (XRD) patterns were recorded using an INEL diffractometer with a cobalt anticathode ($\lambda = 1.7809$ Å) over the range $10° < 2\theta < 100°$, with a step size of 0.04°. The transmission electron microscopy images were taken by a microscope JEOL-2011 TEM, operating at an accelerating voltage of 200 kV. A standard superconducting quantum interference device (SQUID) magnetometer was used to measure the magnetic properties at 140 K.

3. Results and discussion

3.1. Structural properties and morphology

According to the work of Soumare et al. [13b], the concentration of nickel salt was taken equal to 0.08 M and 1, 2 butanediol was used as solvent and reducing agent. Indeed, it was demonstrated that such conditions allowed the synthesis of anisotropic nanoparticles of cobalt and cobalt–nickel $Co_{80}Ni_{20}$. Two main parameters have been varied in the present work: the strength of the applied field and the concentration of the sodium hydroxide. The concentration of sodium hydroxide has been varied in the range 0.08–0.25 M. The magnetic field was varied up to 1.4 T the highest limit allowed by our equipment.

All the conducted experiments led to the formation of pure nickel. The typical X-ray diffraction (XRD) pattern is shown in Fig. 1. Indeed all XRD patterns can be indexed in the face-centred cubic system with a cell parameter characteristic of pure nickel compound: $a = 3.524$ Å (JCPDS file No. 04-0850).

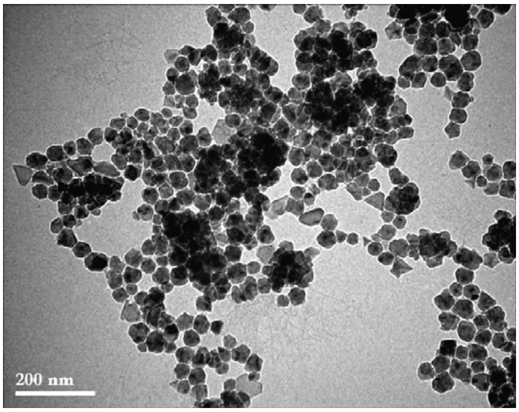

Fig. 2. TEM image of Ni nanoparticles prepared in the absence of an external magnetic field.

First, we conducted experiments in the absence of an applied magnetic field. In this case the sodium hydroxide concentration hardly influences the morphology and size of the particles. TEM characterization of the produced powder (Fig. 2) shows spherical and platelets like Ni nanoparticles with 30–50 nm in diameter whatever the sodium hydroxide concentration.

In a second step, we conducted experiments under the highest applied field allowed by our equipment (1.4 T). In this case, the morphology appears to be dependent on the amount of sodium hydroxide. When this amount is low namely 0.08 M, the obtained particles appear as micrometric fibers with 200 nm in diameter and 3 μm in length. They are aggregated, not well defined and growing from a metallic heart with 5 μm in diameter (Fig. 3(a)). For the highest value of sodium hydroxide amount (0.25 M), the anisotropic morphology is no longer observed. Indeed, TEM observations reveal that the obtained particles in this case are spherical with diameters in the nanometric range (Fig. 3(b)).

Finally an intermediate sodium hydroxide amount (0.15 M) appears to be the more appropriate amount to obtain nickel anisotropic nanoparticles. TEM micrographs (Fig. 4) show that the powder consists of two morphology types. The major part of the powder is formed of nanofibers with 250 nm in diameter and a length varying in a large range from a few to ten micrometers (Fig. 4(a)). It is interesting to note that these nanofibers are in fact constituted of nanoparticles of 250 nm in diameter. As revealed by TEM observations, these fibers most likely grew by the coalescence of the isotropic nanoparticles (Fig. 4(a) insert). This morphology and growth type has been recently reported for nickel elaborated by reduction in aqueous solution under an applied field [15] and for cobalt nanofibers [8]. Another morphology type is also observed. It consists of nanorods with 100 nm in diameter and a few microns to about 5 μ in length and showing a smooth surface (Fig. 4(b)). As can be shown in the HRTEM image (Fig. 4(b) insert), the measured spacing 0.25 nm is slightly higher than that corresponding to the (111) planes of the face-centered cubic (fcc) structure of Ni. It is close to that corresponding to the (010) planes of the hexagonal close compacted (hcp) structure of Ni (JCPDS file No. 45-1027.). This suggests that the nanorods belong to this latter structure type. It should however be noted that the amount of nanorods with a hcp structure remains very low (not exceeding 5%) since X-ray diffraction analysis only reveals nickel with a fcc structure as discussed above.

In order to further investigate if obtaining the nickel nanowires is related to the presence of the magnetic field, a sample has been prepared under similar conditions (sodium hydroxide amount equal to 0.15 M) but changing the value of the applied magnetic field to 0.7 T. The nanowires are no longer observed, only less structured and poorly defined nanofibers are obtained (Fig. 5). One

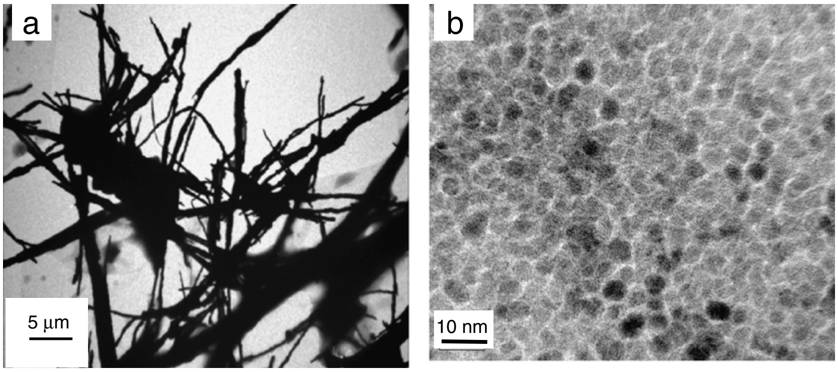

Fig. 3. TEM image of Ni nanoparticles obtained in 1, 2-butanediol in the presence of a magnetic field of 1.4 T: (a) in 0.08 M of NaOH solution; (b) in 0.25 M of NaOH solution.

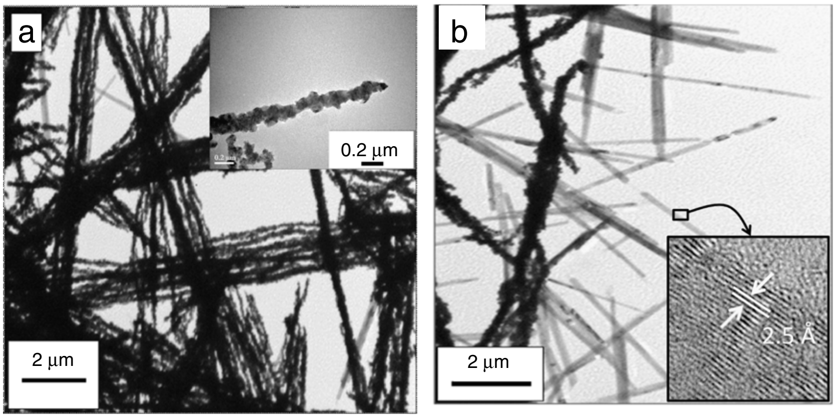

Fig. 4. TEM image of Ni nanowires obtained in 0.15 M NaOH solution in 1, 2-butanediol in the presence of a magnetic field of 1.4 T: (a) diameter of 250 nm (insert: coalescent mechanism growth); (b) diameter of 100 nm (insert: HRTEM image).

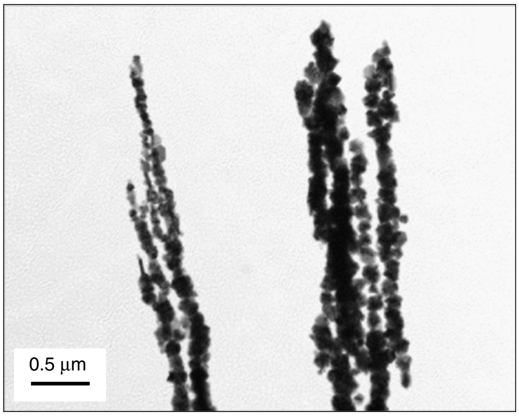

Fig. 5. TEM image of Ni nanowires obtained in 0.15 M NaOH solution in 1, 2-butanediol in the presence of a magnetic field of 0.7 T.

can note that contrary to sample prepared under a higher applied field (1.4 T), here the applied field (0.7 T) is insufficient to induce the coalescence of the nanoparticles, and the fiber appears to be formed by nanoparticles weakly bonded to each other. We also see that the interface between particles is very low; this is in favor of bonding via weak magnetic interactions between particles.

From these results, it can be concluded that the external applied magnetic field is the key factor which controls the morphology of Ni nanoparticles, the anisotropic character depending on the strength of the field. Indeed under a low magnetic field, isotropic particles have been obtained while a strong magnetic field favors the anisotropic morphologies namely nanofiber and nanowire.

Synthesis of Ni nanowires, also passes through a fine control of the basicity of the solution.

Basicity can control the balance between the metallic ionic species in solution and the unreduced intermediate phase [13,14]. Decreasing the basicity promotes the formation of metal ions in solution and therefore the speed of nucleation and rapid growth and thus not well controlled morphology. Increasing the amount of sodium hydroxide causes the displacement of equilibrium towards the formation of the intermediate phase namely hydroxyacetate or alkoxide of the metal ion. This decreases the amount of metal ions in solution and thus allows the nucleation and growth to proceed slowly leading to the formation of platelets and isotropic nanoparticles.

A good compromise to obtain nanowires consists of an intermediate amount of sodium hydroxide. Therefore, a concentration of sodium hydroxide, and applying a high external magnetic field, are two essential conditions for obtaining anisotropic Ni nanowires.

3.2. *Magnetic properties*

Static magnetic properties have been measured on isotropic nanoparticles of Ni (50 nm) obtained by synthesis in the absence of an applied magnetic field (Fig. 6(b)) and on Ni nanowires (Figs. 6(a) and 7) obtained by synthesis under the application of an external field of 1.4 T. Both isotropic and anisotropic samples present a ferromagnetic behavior at low temperatures (behavior at $T = 140$ K is shown in Figs. 6 and 7). Their saturation magnetization (Ms) is qualitatively the same as that of Ni bulk alloy (55 emu/g) in the case of nanowires (50 emu/g) and slightly lower for isotropic nanoparticles. This can be due either to the superficial oxidation of the nanoparticles or to the presence of remaining organic species adsorbed on their surfaces as it has been previously reported on

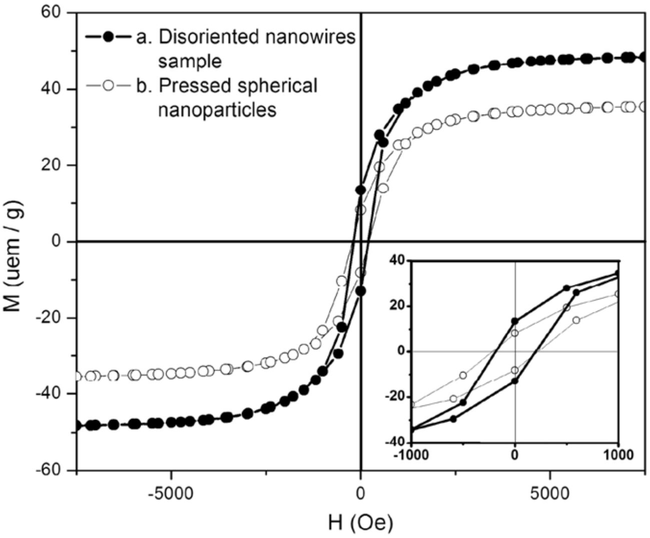

Fig. 6. Magnetization (SQUID) of: (a) Ni disoriented nanowires and (b) Ni nanoparticles.

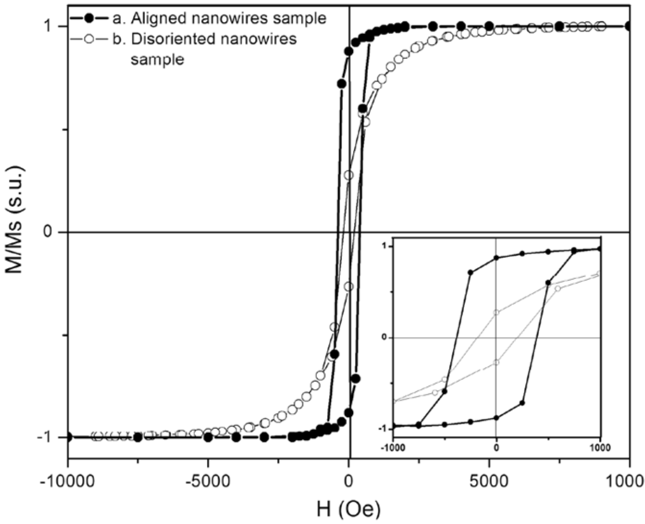

Fig. 7. Magnetization (SQUID) of the Ni nanowires: (a) nanowires aligned by an external magnetic field and subsequently frozen.; (b) disoriented nanowires.

nickel nanoparticles elaborated in a polyol medium [16]. The ferromagnetic behavior of the Ni nanowires shows important differences from that found for the isotropic nanparticles. Indeed the ferromagnetic character of the nanowires depends on their orientation with respect to the magnetic field applied during magnetic measurements. Indeed nanowires randomly orientated (i.e. a 'spaghetti-like system') present remanence and coercivity quite close to that observed for the isotropic nanoparticles (M_r/M_s 0.27 and H_c of 214 Oe) (Fig. 6). Whereas oriented Ni nanowires, frizzed along the field directions in a non-magnetic matrix, have a real enhancement of their magnetic character when their orientation is parallel with the magnetic field applied during the measurements. It is probably important to remind that nanowires are frozen in a non-magnetic solid matrix under the application of a high external field so that they are all parallel with the direction of the magnetic field applied during the solidification. Once the matrix is at 140 K (i.e. solid) magnetic measurements are done as function of the applied magnetic field parallel with the frizzed nanowires direction. Indeed, as shown in Fig. 7, oriented nanowires present a remanence $M_r = 0.85\ M_s$ and a coercivity $H_c = 385$ Oe. The H_c value is in good agreement with that previously reported for Ni nanowires and nano-chains [17,18]. The high remanence confirms a very good orientation of the nanowires in the frozen solution in agreement with previous studies on Ni nanowires arrays grown in porous alumina membranes [19]. The magnetization behavior shows that the magnetic easy axis lies along the wires' longest axis due to the strong shape anisotropy. The coercivity of elongated particles arrays depends on the magnetization reversal mechanism that is related to several parameters like the coherence length with respect to the wire diameter, the presence of crystalline defects and also dipolar interaction. The maximum of coercivity on Ni wires arrays has been observed on 18 nm-diameter nanowires (i.e. $H_c = 950$ Oe) [19]. It has been demonstrated that the coercivity decreases when the nanowire diameter increases. It reaches a value of 200 Oe for a nanowire of 50 nm in diameter. Our measurements confirm such a decrease. However, despite their higher diameter (200 nm) the Ni nanowires described in this paper present a larger coercivity (385 Oe).

4. Conclusion

Ni nanowires have been obtained by a simple synthesis process which does not require the use of host matrix, surfactant or strong reducing agent such as hydrazine or hydrogen. This method combines the effect of reduction and growth in solution of nanoparticles by the polyol process with the application of an external magnetic field during nucleation and growth processes. It also allows the synthesis of large quantities of powder Ni nanowires, with very high yields. The average diameter of the nanowire is between 100 and 300 nm and the length is several micrometers. Obtaining these nanowires is conditioned by a fine control of the concentration of sodium and the value of the magnetic field applied during synthesis. They crystallize in the face-centered cubic (fcc) structure and exhibit enhanced magnetic properties if they are aligned.

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