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Dipentaerythritol: a novel additive for the precipitation of dispersed Ni particles in polyols

Angshuman Pal,[a] Igor Sevonkaev,[a] Brandon Bartling,[b] Job Rijssenbeek[b] and Dan V. Goia*[a]

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Highly dispersed uniform Ni particles ranging in size from 0.1 to 1.2 μm were synthesized by reducing nickel carbonate in polyols in the presence of dipentaerythritol (DPE) and noble metal salts. DPE was essential in preventing the aggregation of nickel particles, while the noble metal ('seeding' approach) effectively tailored their size. Ferromagnetic particles with a cubic closed packed (ccp) crystal habit were obtained using short reduction times at temperatures below 200 °C. Non-magnetic particles with hexagonal closed packed (hcp) structure were obtained after extended heating times (>16 hours) at temperatures above 220 °C. The temperature of the reduction and heat-treatment process was adjusted by using polyols with different boiling points.

Introduction

Dispersed nickel particles are widely used in conducting[1] and magnetic inks,[2] ferrofluids,[3,4] as well as in the manufacturing of optical,[5] catalytic,[6] and electronic devices.[7] In these applications a precise tuning of powder properties is critical for optimum performance. Developing methods that offer the ability to tailor the size, dispersion, and structure of particles is a challenging task, particularly when attempting to prepare powders at industrial scale. Hydrothermal growth,[8,9] ethanol–water extraction,[10] electrochemical,[11,12] sol–gel,[13,14] microwave-assisted,[15] and polyol reduction[16,17] are some of the techniques used to produce such particles. Among these methods, liquid phase precipitation *via* polyol reduction stands out as a versatile, environmentally friendly, and cost effective approach well-suited to industrial scale manufacturing.

Since the pioneering work of Fievet *et al.*[18] on the polyol system, extensive research has been carried out to obtain finely dispersed metal powders with controlled properties.[19–22] The nature and concentration of metal salt, the chemical structure of the polyol, and the reduction temperature have been found to play important roles in the particle formation. Additionally, the use of dispersing agents to keep the metallic particles dispersed at high metal concentration has been extensively investigated. Since high molecular weight organic compounds are often detrimental, low molecular weight dispersants similar in structure to the polyols have been considered. Prior studies have shown that sorbitol (a small linear polyalcohol molecule) has a beneficial effect on the dispersion and uniformity of precipitated metallic particles.[23] Goia *et al.*[24] showed that pentaerythritol (a branched polyalcohol) effectively prevents the aggregation of nickel particles at high nickel concentration. In this work, we report that larger branched polyol molecules, such as dipentaerythritol, are even more effective in maintaining the nickel particles dispersed at very high metal concentrations (>15 wt% nickel).

This study also reveals that at these high concentrations, the size of highly dispersed nickel particles can be readily adjusted in the 0.1 to 1.2 μm range by using noble metal salts as 'seeding' agents. Finally, processing conditions that convert magnetic cubic closed packed (ccp) Ni particles (typically formed in the conventional polyol system) to nonmagnetic hexagonal closed packed (hcp) particles are described. The ability to obtain highly dispersed uniform Ni particles with controlled size and magnetic properties using a concentrated, easily scalable, and cost effective precipitation process is of significant importance for many practical applications.

Experimental

Reagents

Nickel basic carbonate (~54% Ni) was purchased from Sheppard Chemical Co. 1,2-Propylene glycol was obtained from Pharmco-aaper (Brookfield, CT). Tetraethylene glycol was purchased from Sigma-Aldrich. Pentaerythritol (PE) and dipentaerythritol (DPE) were received from Alfa Aesar. Hexachloroplatinic acid (H_2PtCl_6, 33.57 wt% platinum) and palladium chloride ($PdCl_2$, 24.29 wt% palladium) solutions were supplied by Umicore (South Plainfield, NJ, USA). All reactants were used as received.

Characterization

The size and shape of nickel particles were determined by field emission scanning electron microscopy (FESEM JEOL-7400).

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[a] *Center for Advanced Materials Processing, Clarkson University, Potsdam, NY 13699-5814, USA. E-mail: goiadanv@clarkson.edu*
[b] *GE Global Research, One Research Circle, Niskayuna, NY 12309, USA*

Their crystal structure was assessed by X-ray powder diffraction (XRD) with a Bruker-AXS D8 Focus X-ray diffractometer. The data was processed through Rietveld refinement (TOPAZ Academic) and the crystallite size of the final particles was determined using the Scherrer equation.[25] The magnetic properties were measured by a vibrating sample magnetometer (Quantum Design VersaLab) using a 20 kOe magnetic field. The particles were immobilized in wax before the measurements. Particle size distributions were obtained by laser diffraction analysis using a Malvern Mastersizer 2000e. The tapped density of the dried and sieved powders was measured with an AUTOTAP Quantachrome instrument and the thermogravimetric analysis (TGA) was performed using a PerkinElmer Pyris 1 analyzer.

Synthesis of ccp nickel particles

A volume of 500 mL of propylene glycol was introduced in a 4-neck 1.0 L spherical flask placed in an electrically heated mantle. A propeller was inserted through the center neck to provide effective stirring. A Kjeldahl trap connected to a Claisen take-off adapter and a condenser were placed in two of the side necks and a digital thermocouple in the fourth. The propylene glycol was heated to 80 °C and an amount of dipentaerythritol representing 5 to 25% of the final reduced nickel weight was added to the flask. After ~5 minutes of vigorous stirring, the basic nickel carbonate powder was slowly fed into the polyol–dispersant mixture.

The amount of nickel salt added in a typical experiment was 150 g (~80 g of Ni) which translated to a concentration of ~16% metal in the final dispersion. Next, the reaction mixture was heated to the boiling point of the polyol (~188 °C) at 5 °C min^{-1} rate, and maintained there until the metal was completely reduced. The dispersion was then cooled to 60 °C and poured into a 1.0 L beaker to allow the metal to settle. The nickel particles were washed 4–5 times with deionized water and twice with ethanol before being filtered and dried at 100 °C. In the 'seeding' experiments, the metal salt ($PdCl_2$, H_2PtCl_6) was added into the flask prior to nickel carbonate addition.

Preparation of hcp nickel particles

The large scale conversion of ccp Ni particles to an hcp structure was achieved by replacing the propylene glycol at the end of the reduction with a higher boiling point polyols (tetraethylene glycol or diethylene–tetraethylene glycols mixture), re-heating the metal dispersion above 220 °C, and maintaining it there for several hours under the same vigorous stirring. The details of the conversion process are given elsewhere.[26]

Results and discussion

Selection of nickel precursor and dispersing agent

While any nickel salt can be in principle used in the polyol process, the carbonate is the most suitable for generating dispersed metal particles. Most common inorganic anions (Cl^-, SO_4^{2-}, NO_3^-) are stable at the boiling point of the polyol and generate a high ionic strength that drastically reduces the range of stabilizing repulsive forces between metallic particles. In contrast, in the same conditions the carbonate ion decomposes to volatile carbon dioxide yielding a low ionic strength solution in which the electrostatic stabilization mechanism is still effective. Coupled with the intrinsic ability of polyols to prevent particle aggregation, the use of carbonate makes possible the preparation of dispersed Ni particles at higher metal concentrations without using dedicated dispersants. Using this strategy, well dispersed nickel particles can be precipitated at nickel concentrations approaching 1 wt%. At even higher metal concentrations dispersing agents are necessary to prevent particle aggregation.

Our previous investigations[24] have shown that pentaerythritol can improve the dispersion of metallic particles precipitated in polyols. This is illustrated in Fig. 1, which shows SEM images of nickel particles formed in the absence and respectively the presence of pentaerythritol at a metal concentration of 5 wt%. Having a larger molecular weight, dipentaerythritol is expected to be more effective in screening the attractive forces between metal particles and allow the preparation of highly dispersed particles at even higher metal concentrations (15–20 wt%). Its elevated boiling point (356 °C) also makes this compound suitable for high temperature polyol-mediated synthesis. The effectiveness of DPE in preventing the aggregation of nickel particles is illustrated in Fig. 2 and 3. The FESEM images (Fig. 2) clearly reveal a marked improvement in the uniformity and dispersion of nickel particles as compared to the ones obtained with pentaerythritol. The much tighter particle size distribution and higher tapped density (Fig. 3) of the former further confirm the improved particles dispersion and packing efficiency.

Particle size control

Obtaining uniform, highly dispersed nickel particles with controllable size at high metal concentrations is of critical importance for large scale powder manufacturing. It requires a good understanding and appropriate adjustments of the key

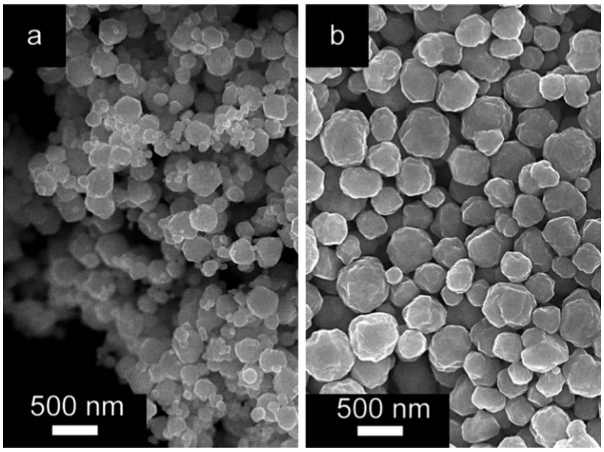

Fig. 1 FESEM images of Ni particles obtained at intermediate metal concentrations (<5 wt% Ni) (a) without dispersant; and (b) in the presence of pentaerythritol.[24]

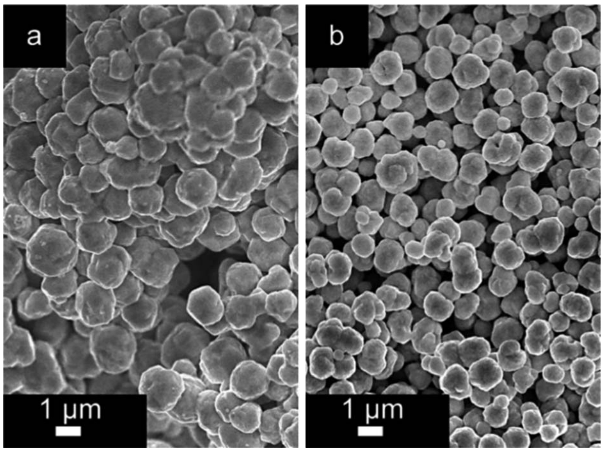

Fig. 2 FESEM images of ccp Ni particles with PE (a) and DPE (b) at a Ni concentration of 16 wt%.

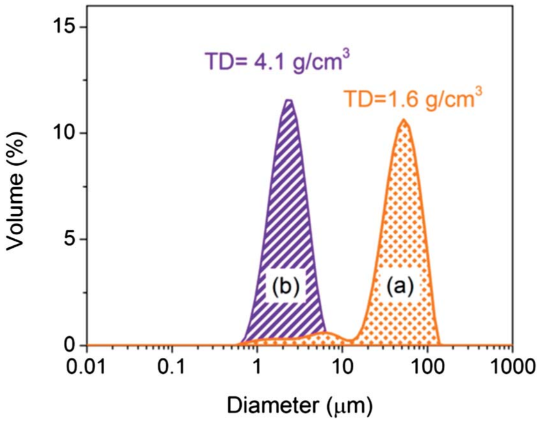

Fig. 3 The particle size distribution and TD (tapped density) of Ni particles prepared in the presence of (a) PE and (b) DPE at a Ni concentration of 16 wt%.

factors involved in the formation of metallic particles. As first proposed by Fievet,[18] the precipitation of metal particles in polyols starts with a nucleation burst followed by slow diffusional growth. According to this model, the final particle size is dictated by the number of nuclei generated in the system and the amount of metal deposited in the growth stage. In the system discussed here, nickel carbonate first dissolves in the polyol and releases nickel ions that are subsequently reduced by the solvent molecules. The nucleation rate (and thus the number of nuclei formed) depends on the temperature and the concentration of nickel ions in the dispersion medium. Typically, more nuclei are generated when the temperature of the polyol is raised rapidly. The slow dissolution of the sparingly soluble carbonate maintains the post-nucleation concentration of nickel atoms below the supersaturation level and prevents the formation of new nuclei. It also provides the slow diffusional growth needed for the formation of metal particles with uniform size.

Another effective approach to control the size of the final particles is through heterogeneous nucleation ('seeding'). In this case, a small amount of salt of a more electropositive element (typically noble metals such as Pt or Pd) is added to the polyol before the temperature is brought to the boiling point. Due to its highly positive redox potential (*i.e.*, +1.0 V for the Pd^{2+}/Pd^0 system *vs.* −0.25 V for the Ni^{2+}/Ni^0 pair), the noble metal is reduced at lower temperature and forms nuclei on which nickel is subsequently deposited. Altering the concentration of seeding metal affects the number of nuclei and the final size of the nickel particles. Fig. 4 illustrates the effect of increasing amounts of palladium chloride in the metal/polyol dispersion. While quite large (1.2 μm) nickel particles were obtained in the absence of seeding salt (Fig. 4a), the addition of 0.012 wt% and 0.13 wt% of Pd (as $PdCl_2$) reduces the average particle size to 180 nm and 80 nm, respectively (Fig. 4b and c). The decrease in the particle size is even more pronounced when Pt is used as seeding agent. Since under similar reduction conditions platinum tends to form smaller clusters than palladium,[27] the addition of 0.13 wt% Pt (as H_2PtCl_6) in the polyol generates nickel particles with a size of only ~40 nm (Fig. 4d). The change in the final particle diameter as a function of the amount of noble metal added can be estimated. Assuming that the size of the seeds formed remains essentially the same and only their number increases with the amount of salt added, the final nickel particle size is given by:

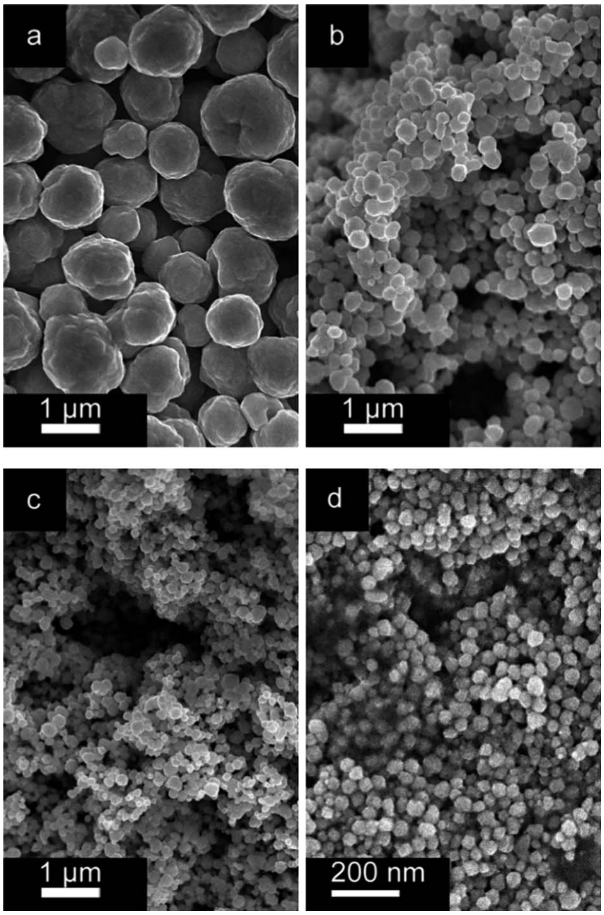

Fig. 4 FESEM images of (a) Ni particles obtained without seeding salt, (b and c) in the presence of increasing amounts of Pd salt, and (d) in the presence of Pt seeds.

$$d_{\mathrm{Ni}} = d_{\mathrm{seed}}\left(1 + \frac{\rho_{\mathrm{seed}}}{\rho_{\mathrm{Ni}}} \times \frac{m_{\mathrm{Ni}}}{m_{\mathrm{seed}}}\right)^{1/3} \tag{1}$$

where d, m, and ρ are the diameter (nm), mass (g), and density (g cm^{-3}) of Ni.

In addition to seeding, the kinetics of polyol oxidation is another factor controlling the final size of nickel particles. Making the oxidation of the polyol more facile results in a greater overall ΔE (reaction redox potential), a faster reduction rate, and smaller particles.[28,29] Drawing from the work of Xia *et al.* on the synthesis of silver nanostructures,[30] Fe(III) ions were added to the polyol to accelerate the nickel reduction. The addition of 1 mL of 0.1 M $FeCl_3$ solution to the polyol/DPE/nickel carbonate solution shortened the time needed for complete reduction to half and decreased the average size of the particles from 1.2 to 0.4 μm (Fig. 5). While Xia *et al.* proposed that Fe(II) ions resulting from the reduction of Fe(III) interact with the surface of the silver and delay crystal growth, we believe that in our case a different mechanism is in play. Previous investigations of the reduction of silver[31] and copper[32] with citrate have shown that Fe(II) ions form with the reductant molecules complex species that more easily release the electrons needed in the reduction. In the system investigated here, the Fe(II) ions resulting from the reduction of Fe(III) interact with the polyol molecules and form complex species that are more prone to oxidation and, thus, more powerful reductants. As a result, in otherwise the same experimental conditions a faster nucleation takes place and smaller nickel particles are formed in the presence of iron.

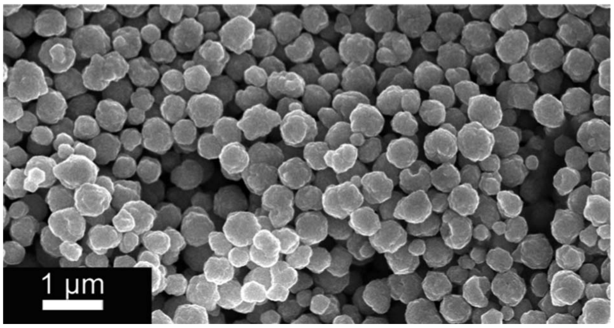

Fig. 5 FESEM image of ccp Ni particles formed in the presence of Fe(III) ions in the conditions used to obtain the Ni particles shown in Fig. 4a.

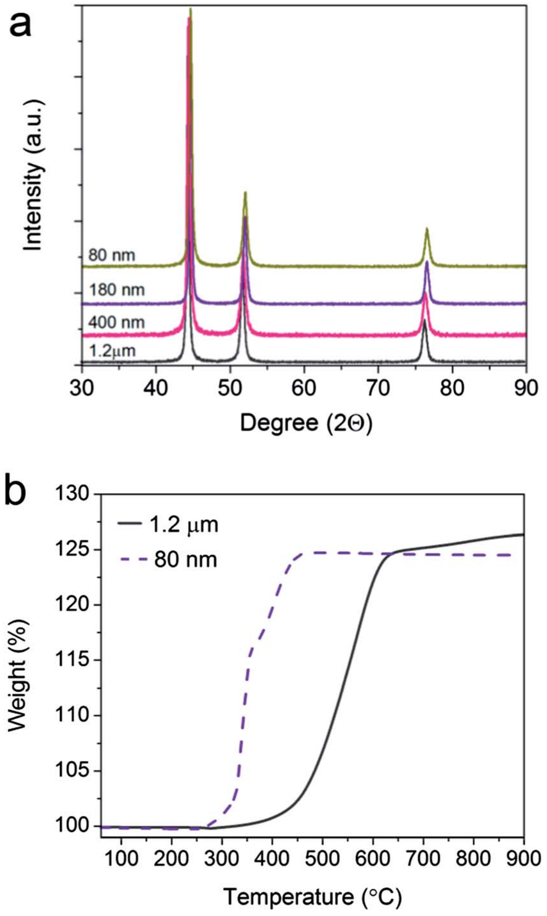

Fig. 6 (a) XRD pattern for ccp Ni particles of different sizes; (b) TGA plots generated for 1.2 μm and 80 nm Ni particles heated in air at 900 °C (10 °C min^{-1} heating rate).

Particle crystallinity and structure

For a given temperature, adjusting the size of the particles through seeding does not have a noticeable impact on their

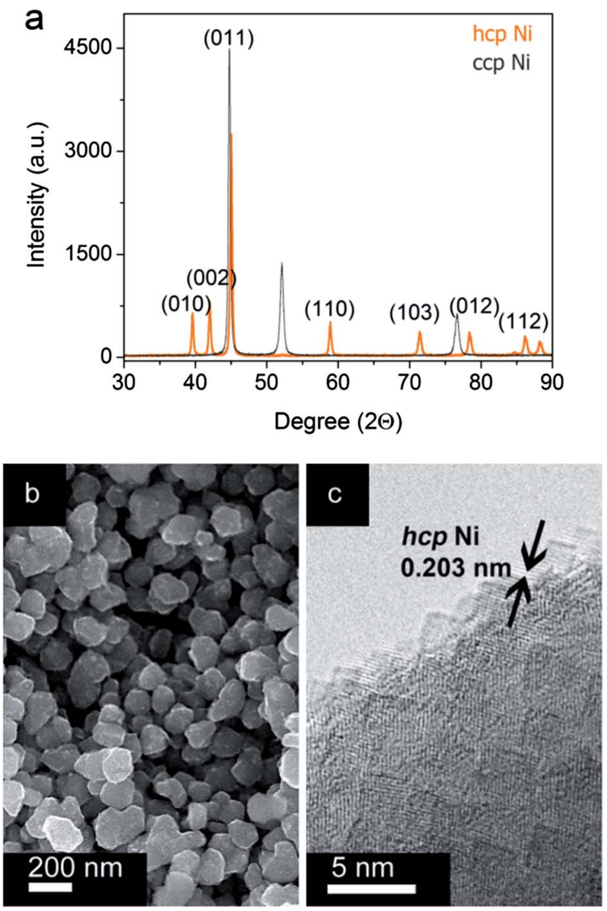

Fig. 7 (a) XRD pattern and (b) FESEM image of hcp Ni particles obtained after heating the ccp particles shown in Fig. 2b in diethylene–tetraethylene glycol mixture at 230 °C for 16 hours,[26] (c) high resolution TEM image of the surface of hcp particles.

crystallinity (crystallite size). This is not surprising considering that the seeds affect only the nucleation stage not the subsequent diffusional growth. Fig. 6a shows the XRD of ccp Ni particles of different sizes obtained at different levels of Pd. The crystallite size calculated by applying the Scherrer equation to the (1 1 1) reflection is in all cases 30 ± 5 nm. On the other hand, changes in particle size (and surface area) can alter significantly the oxidation behavior of nickel particles, with consequences for electronics, catalysis and batteries applications. Indeed, the change in sample weight when heated to 900 °C in air reveals that the oxidation starts at a much higher temperature and the weight increases slower in the case of the large particles (Fig. 6b).

As previously reported,[26] keeping the ccp Ni particles at ≥220 °C for 16 hours in a polyol containing at least one glycol group converts their structure to an hcp crystal lattice. This is evidenced by the changes in their XRD spectra (Fig. 7a). The phase conversion is accompanied by changes in the surface topography, which presents small but well-defined crystal facets formed by a slow lattice rearrangement (Fig. 7b and c). The need to keep the temperature above 220 °C for extended time limits the choice of polyol to those with high boiling points (diethylene glycol, triethylene glycol, tetraethylene glycol, *etc.*).

Magnetic properties

The magnetic properties of the synthesized ccp nickel powders were investigated at room temperature using a vibrating sample magnetometer. The hysteresis loops for the 1.2 μm and 80 nm nickel particles are shown in Fig. 8a and b. The coercivities at 298 K were 101 Oe for 1.2 μm and 160 Oe for the 80 nm. The saturation magnetization measured above 30 kOe was about 52 emu g^{-1}, which is only slightly lower than that reported for the pure ccp-Ni phase in bulk form (55 emu g^{-1}, at 300 K).[33] As expected,[34] the hcp nickel particles were nonmagnetic. This feature offers important advantages in the post-precipitation processing, the preparation of stable inks/pastes, and in general in all applications involving the assembly of particles into compact packed structures/layers (*i.e.* electronics industry).

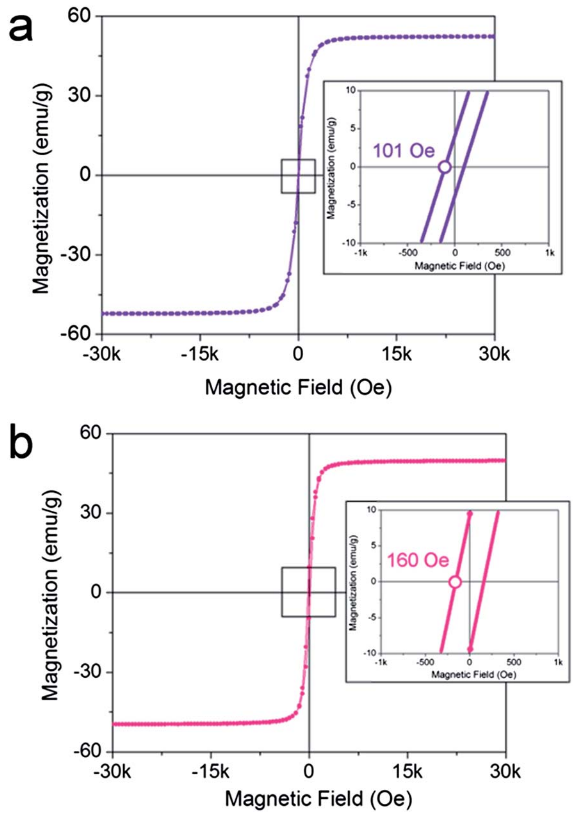

Fig. 8 Magnetization as a function of the applied field measured at 298 K: (a) 1.2 μm and (b) 80 nm Ni particles. The inset is the enlarged magnetization curve.

Conclusions

Highly dispersed Ni powders with improved particle uniformity and packing properties were obtained by a polyol reduction process in the presence of dipentaerythritol. The size of nickel particles could be tailored over a broad range (<0.1 to 1.2 μm) by adding controlled amounts of a precious metal salt ($PdCl_2$ or H_2PtCl_6) or by changing the reducing strength of the polyol with $FeCl_3$. Processing conditions that permit the gradual and controllable conversion of the crystal phase of nickel particles from ccp to hcp were identified and the changes in their magnetic properties were monitored. The highly dispersed crystalline nickel particles obtained are essentially free of bulk and surface NiO and can be used successfully in catalytic and electronic applications, as well as the fabrication of metal hydride batteries.

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