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Submicron particles of Co, Ni and Co–Ni alloys

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Abstract. Magnetic sub-micron sized particles (with diameters in the range 100–600 nm) of Co, Ni and Co–Ni alloys, protected with polyvinylpyrrolidone have been prepared in gram quantities using the polyol process. Experiments carried out with different metal precursors and starting compositions have yielded reliable routes to produce particles of the desired diameters in the 100–600 nm range. The particles were characterized with X-ray diffraction, scanning electron microscopy, energy dispersive X-ray analysis, thermogravimetric analysis and magnetic measurements. The particles are found to be stable under ambient conditions indefinitely. The coercivity values of the Co and Ni particles are ~ 50% higher compared to the corresponding bulk values. The alloy particles follow a trend similar to the bulk alloys.

Keywords. Submicron particles; Co; Ni; Co–Ni alloys.

1. Introduction

Metal particles with size in the range of few nanometers to several microns occupy the central place in catalysis, surface coating, microelectronics and magnetic storage and allied fields (Ferrier *et al* 1985; Zenia 1986). The geometric effect of increased surface to volume ratio imparts such attributes to the particle system that its various properties undergo major changes at some critical sizes (Edwards *et al* 2000). Thus, metal to nonmetal transition is seen in metal particles with diameters < 2–3 nm (Vinod *et al* 1998), while a change in the magnetic property is often seen at larger sizes, say several microns (Cullity 1972). Moreover, the properties of a tiny particle are affected by the ligand or the surfactant shell protecting it (Bradley 1994; Osuna *et al* 1996), an issue which, so far has not been understood in great detail.

Large-scale synthesis of metal particles is invariably carried out using chemical routes. Of the many procedures, the polyol process (Fievet *et al* 1989; Seshadri and Rao 1994; Ayyappan *et al* 1996), involving the reduction of metal salts with polyols such as ethylene glycol, diethylene glycol, has been in wide use to obtain metal particles, especially of large diameters (10 nm–1 micron). Thus, particles of Co, Ni, Ag, Au and Pd (Ganapathi *et al* 1987; Silvert and Tekaia-Elhsissen 1995; Ayyappan and Rao 1996; Ayyappan *et al* 1996, 1997; Tekaia-Elhsissen *et al* 1999) and of alloys, Pd–Ni, Fe–Ni (Viau *et al* 1996a), Co–Ni (Viau *et al* 1996b) have been synthesized. Uniform, spherical non-agglomerated particles with bulk structures were obtained in the above cases. The magnetic nanoparticles Co, Ni, Co–Ni, Co–Fe have been a focus of attention due to their microwave absorption properties (Viau *et al* 1994) and their potential uses as radiation shields (electromagnetic absorbers).

We considered that a polymer coating such as with polyvinylpyrrolidone (PVP) may improve the stability of particles with respect to atmospheric oxygen and facilitate easy handling of metal powders and accordingly, prepared particles of Co, Ni and their alloys in the sub-micron range. The particles were characterized using scanning electron microscopy (SEM), energy dispersive X-ray analysis (EDAX), powder X-ray diffraction (XRD) and thermogravimetry (TGA). The magnetic properties of the particles were examined using a vibrating sample magnetometer (VSM). It may be noted that Co and Ni form a solid solution in the bulk, $\mathrm{Co}_x\mathrm{Ni}_{1-x}$. For $x < 0{\cdot}75$, the alloy exists in hcp structure, while for $x > 0{\cdot}7$, the alloy has a fcc structure, with a mixed regime in the intermediate compositions. The atomic moments in Co–Ni alloys increase linearly with Ni content (Tebble and Craik 1969). We have found a similar trend with our work on sub-micron sized alloy particles. Thus, the ligand shell that dramatically alters the properties of small particles (Bradley 1994; Osuna *et al* 1996), has few undesirable effects in the case of sub-micron sized alloy particles.

2. Experimental

Particles of Co and Ni were prepared by refluxing an ethylene glycol solution of their acetates or sulphates containing a desired amount of PVP (MW–40,000 gmol^{-1}). In a

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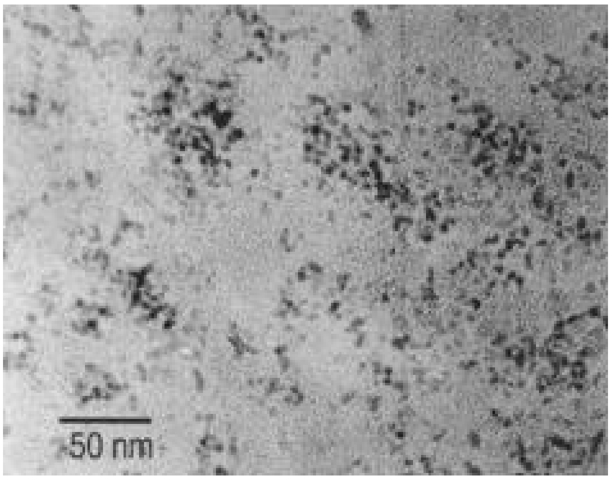

Figure 1. Transmission electron micrograph of small PVP covered Ni particles produced by reduction of Ni(SO_4).

typical reduction, 2 g of PVP, 0·5 g of the metal precursor were dispersed in 50 ml of ethylene glycol and the resulting solution refluxed at 198°C for 10 h. In the case of Ni, the pH was adjusted to 9–11 by addition of NaOH prior to reduction. In all cases, the solution turned black within a few minutes of reaching 198°C. The particles were studied by scanning electron microscopy (SEM) and transmission electron microscopy (TEM).

By varying the Ni^{2+} : ethylene glycol mole ratio from 0·008 : 1 to 0·0045 : 1, the mean diameter of the particles could be varied from 520 nm to 750 nm. Similarly, in the case of Co, a change in the Co^{2+} : ethylene glycol ratio from 0·005 to 0·0022 resulted in a change of the particle diameters from 410 nm to 550 nm. A variation in the metal : PVP weight ratios in the range 1 : 4–1 : 20 however, produced no change in the obtained particle diameters. When Ni(SO_4) was used instead of Ni(*ac*)$_2$, very

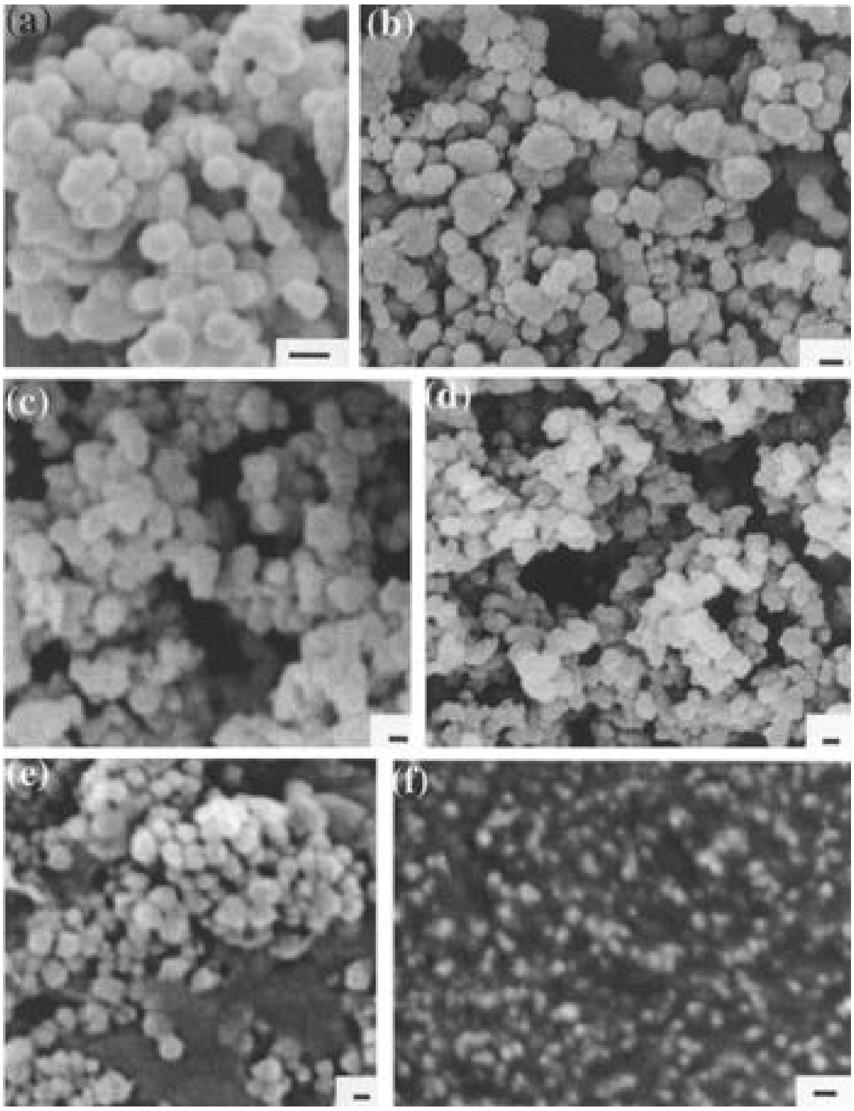

Figure 2. Typical SEM micrographs of Co, Ni and Co–Ni alloy particles. (**a**)–(**b**) Co particles; (**c**)–(**d**) Ni particles; alloy particles of the composition (**e**) $Co_{0·50}Ni_{0·50}$ and (**f**) $Co_{0·90}Ni_{0·10}$. The scale bars on the images correspond to 500 nm.

small Ni particles in the 10 nm size range were obtained (see TEM image in figure 1).

The Co–Ni alloy particles were obtained by co-reducing the metal precursors in the desired molar ratios with a fixed metal : PVP weight ratio of 1·0 : 4·5. The total metal ion concentration was held constant at 0·1 M for all the preparations. Thus, to obtain alloy particles of the composition $Co_{0\cdot 9}Ni_{0\cdot 1}$, 1·12 g of $Co(ac)_2\cdot 4H_2O$ and 0·124 g of $Ni(ac)_2\cdot 4H_2O$ were dissolved in 50 ml of ethylene glycol and were refluxed at 198°C overnight.

In all the above cases, the particles could be precipitated from the solution by adding excess water or acetone and were isolated by centrifugation. The particles were then washed with water several times to remove excess PVP, and unreduced matter if any. Finally, the obtained black precipitate was dried in vacuum to obtain waxy solids.

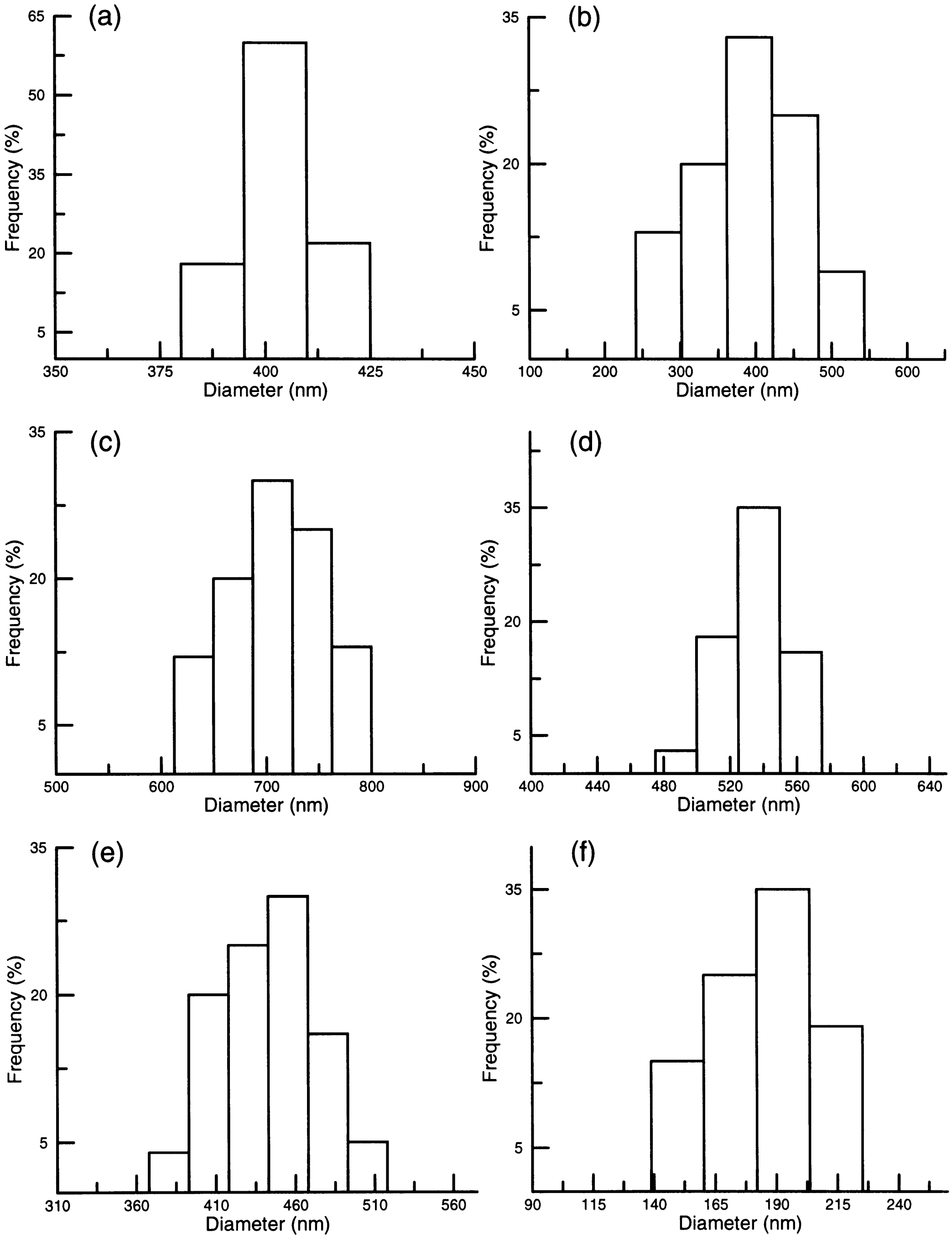

Figure 3. Histograms showing the size distribution of the Co, Ni and Co–Ni alloy particles. (a) and (b) Co particles; (c) and (d) Ni particles; alloy particles of the composition (e) $Co_{0\cdot 50}Ni_{0\cdot 50}$ and (f) $Co_{0\cdot 90}Ni_{0\cdot 10}$.

SEM and energy dispersive X-ray analysis (EDAX) were performed with a Leica S-440i instrument. Samples were prepared by depositing a drop of the toluene sol on an aluminum stub. Thermogravimetric measurements (TGA) were carried out with a Mettler–Toledo instrument in the temperature range 100–900°C under a N_2 or O_2 atmosphere at a heating rate of 5°C/min using typically 25 mg of the solid in a porcelain boat. X-ray diffraction (XRD) data were collected using a Seifert 3000 instrument employing the Co–Kα radiation for pure Co and alloy samples and Cu–K$_\alpha$ for the Ni samples. The magnetic measurements were carried out employing a vibrating sample magnetometer (VSM 7300, Lakeshore) equipped with a 10 kOe magnet using typically 20 mg of the dried sols. The metal content estimated from TG measurements was used to calculate the magnetization in terms of emu/g.

3. Results and discussion

Typical SEM images of the Co, Ni and Co–Ni alloy particles are shown in figure 2. The images reveal that the particles are generally spherical with a uniform diameter. In some portions of the images, we see agglomerated particles perhaps due to their magnetic nature. By picking out over 100 particles in each case, histograms of the particle diameter were obtained. Typical histograms are shown in figure 3. The particles of various compositions were monodisperse with s ~ 15–20%.

XRD measurements confirmed the crystalline nature of the nanoparticles. All the Ni particles were found to exhibit a fcc structure, similar to bulk Ni. The Co nanoparticles on the other hand, exhibited a hcp structure. The alloy nanoparticles, rich in Co exhibited both fcc and hcp peaks, while those with higher Ni content exhibited only fcc peaks. However, owing to the small difference in the lattice spacings of Ni and Co (Co = 0·35477 nm, Ni = 0·35238 nm), the peaks could not be definitively assigned to a solid solution of Co and Ni. These results are similar to the ones with uncoated Co–Ni alloy nanoparticles obtained by other workers (Viau *et al* 1996b). The diameter of the nanocrystals could be estimated from the width of the X-ray peaks, according to the

Table 1. Analysis of Co–Ni alloy particles.

Metal salts feed ratio	Composition of the particles by EDAX	Phases as seen by XRD	Diameter	
			SEM (nm)	XRD (nm)
$Co_{0·10}Ni_{0·90}$	$Co_{0·13}Ni_{0·87}$	fcc	200	190
$Co_{0·30}Ni_{0·70}$	$Co_{0·31}Ni_{0·69}$	fcc	350	342
$Co_{0·50}Ni_{0·50}$	$Co_{0·53}Ni_{0·47}$	fcc	450	440
$Co_{0·70}Ni_{0·30}$	$Co_{0·69}Ni_{0·31}$	fcc + hcp	–	–
$Co_{0·90}Ni_{0·10}$	$Co_{0·88}Ni_{0·12}$	fcc + hcp	190	170

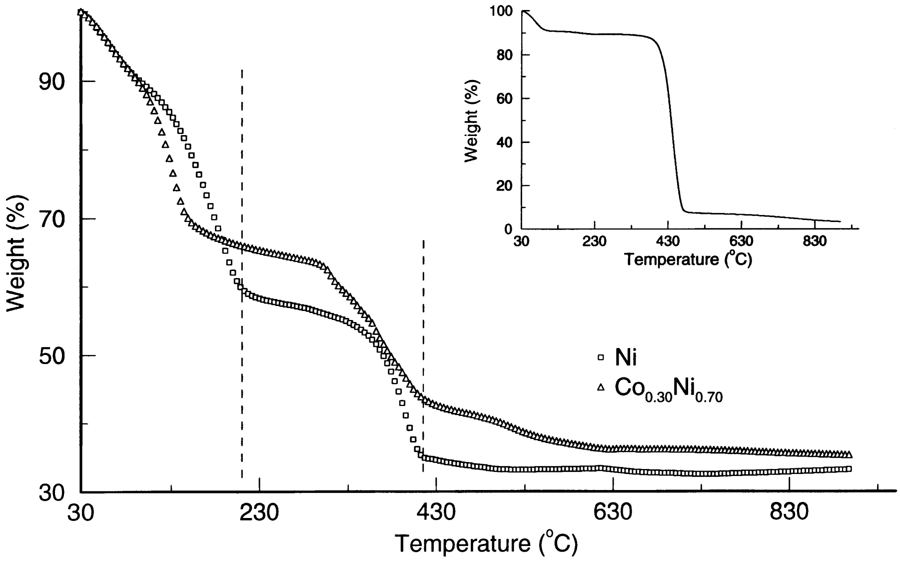

Figure 4. TG curves of Ni and $Co_{0·30}Ni_{0·70}$ alloy particles. The vertical lines demarcate the regions of weight loss corresponding to the solvent at ~ 200°C and PVP and ~ 410°C. Inset shows the TGA curve of PVP.

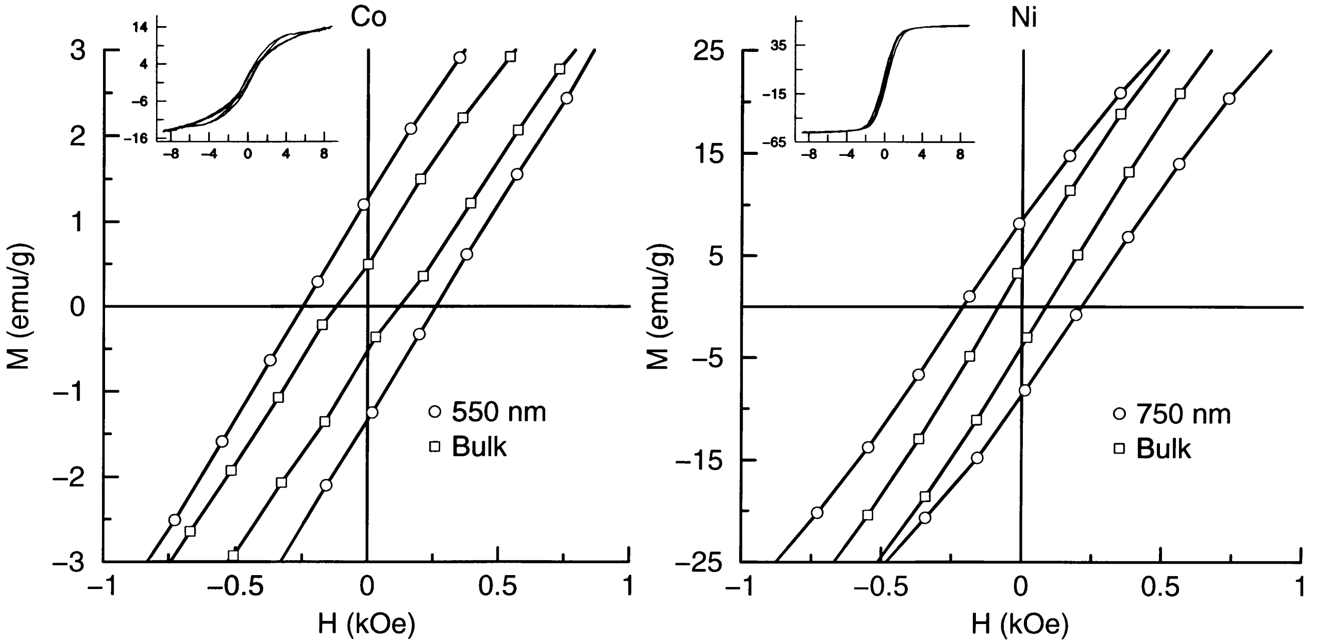

Figure 5. The area around zero field in M vs H sweep, showing the coercive field for Co and Ni particles along with that of the bulk. Inset shows the overlapping hysteresis loops of Co and Ni particles with their bulk analogues.

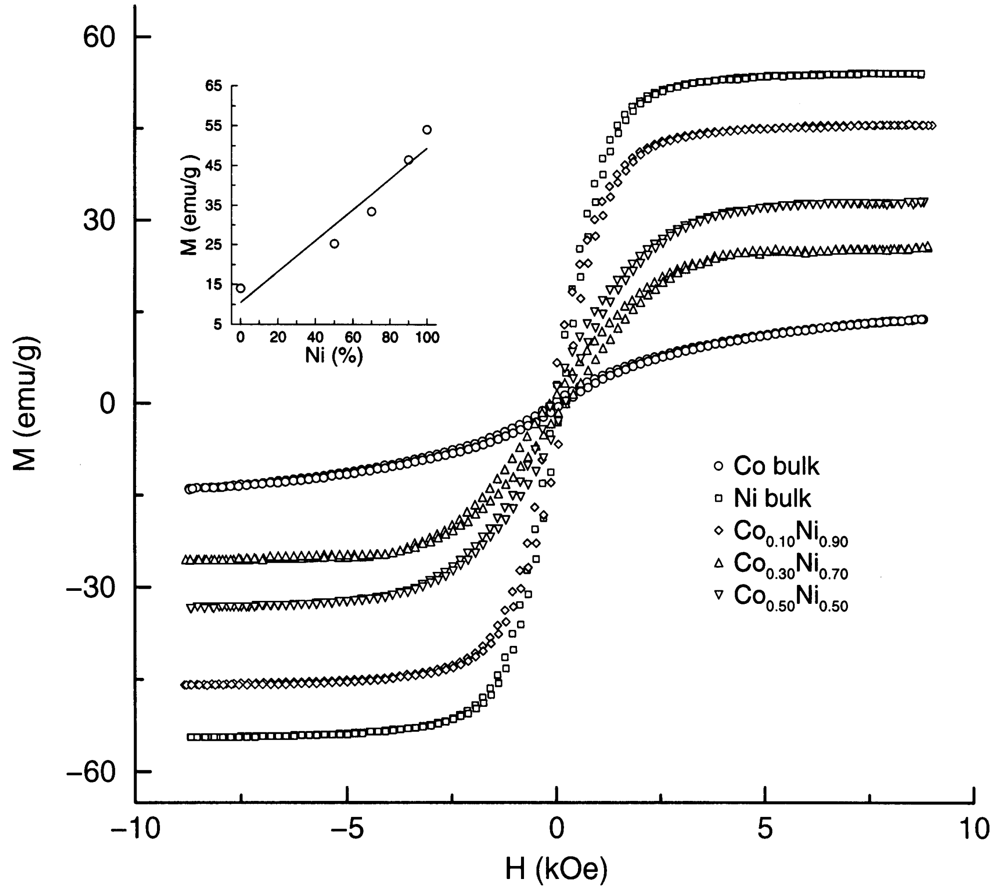

Figure 6. Hysteresis loops of Co–Ni alloy particles along with those obtained with ingots of pure Co and Ni. Inset shows the change in magnetization value at 8·5 kOe field with composition.

Table 2. Magnetic properties of Co and Ni particles.

Sample	Diameter (nm)	M at 8·5 kOe (emu/g)	Coercivity Oe
Co bulk	–	13·9	235
Co	410	14·5	312
Co	450	13·6	410
Co	550	13·5	512
Ni bulk	–	54·1	176
Ni	520	53·5	280
Ni	690	54·3	378
Ni	750	54·0	426

Scherrer's relation. Ni and Co nanoparticle diameters were estimated based on the widths of the (111) and (011) peaks.

The alloy particles were further analysed by EDAX. Line and spot profile analyses yielded compositions within 2% of the feed ratio of the metal salts. The feed ratios, compositions determined by EDX, the phase, the diameters determined by XRD and the diameters estimated from the SEM micrographs are given by way of summary in table 1. The X-ray diameters are lower than those obtained from SEM as they do not include the PVP shell and correspond only to the diameter of the metal core.

In order to arrive at the actual metal content in polymer covered particles, TGA measurements were done under either nitrogen or oxygen gas flow. The TG curves for both Ni and Co–Ni alloy particles (in N_2 atmosphere) showed a two-step weight-decline pattern with the inflexion points at around 156°C and 372°C (see figure 4), the former corresponding to the desorption of the solvent molecules and the latter, due to degradation of the PVP shell. The thermal decomposition temperature of PVP is ~ 375°C, as seen in an independent measurement. Typically, we have observed weight losses of ~ 30% for the solvent and ~ 40% for the PVP layer. In case of Co, a weight gain of ~ 30% was noticed at ~ 250°C in a O_2 atmosphere. The metal content in this case was estimated, assuming complete oxidation of Co to Co_3O_4. XRD analysis of the heat-treated sample confirmed complete oxidation of Co to Co_3O_4.

Typical curves obtained in a M vs H sweep with sub-micron sized monometal particles, along with the measurement on corresponding bulk ingots are shown in figure 5. The curves tend to saturate in cases of Ni, while in case of Co, saturation was not observed. The saturating magnetic fields were similar to the corresponding bulk metals and showed little dependence on size, in good agreement with studies of similar metal particles obtained by physical methods (Kittle *et al* 1950). The coercivities, however, were different from the bulk, owing to small size of the particles (Cullity 1972) (see table 2). In case of both Co and Ni, a consistent increase in the coercivity value with size is noticed. In the case of Co, the coercivity of 550 nm particle is 512 Oe, significantly higher than the bulk coercivity (235 Oe). Further, it increases from 312 Oe to 512 Oe for a 240 nm change in the average particle diameter. Similarly, in case of Ni, the observed coercivity change is ~ 146 Oe for a change in diameter of 230 nm. The observed increase in coercivity with size indicates that the particles consist of a single magnetic domain (Cullity 1972).

In the case of Co–Ni alloy particles, the Ni rich compositions tend to saturate, while the Co rich compositions display no tendency for saturation (see figure 6). In order to estimate the changes in the magnetic moment with composition, the magnetization at 8·5 kOe were examined (see inset of figure 6). It was found that these values increase progressively to reach bulk Ni value. This trend is similar to the trend exhibited by bulk Co–Ni alloys.

It is noteworthy, that the PVP covered particles are stable in air for extended periods of time (few months) as against the naked Co and Ni particles. This could readily be seen by the fact that the particles are strongly attracted to a magnet, months after the preparation and could be confirmed by X-ray diffraction.

4. Conclusions

Magnetic sub-micron sized Co, Ni and Co–Ni alloy particles (with diameters in the range 100–600 nm) prepared by the method described by us wherein a layer of polyvinylpyrrolidone protects the particles, were found to be stable under ambient conditions, without undergoing oxidation. Further, the PVP coating does not significantly influence the magnetic properties of the Co, Ni and Co–Ni alloy particles.

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