Synthesis and properties of nickel-cobalt-boron nanoparticles

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Abstract. Amorphous cobalt nickel boride nanoparticles were synthesised by chemical reduction synthesis in aqueous solution. Careful control of synthesis conditions and post reaction oxidation enabled the nanoparticles to be converted into a core-shell structure comprising of an amorphous Co-Ni-B core and an outer metal oxide sheet. These particles had interesting magnetic properties including saturation magnetisations and coercivities of the order of 80 emu/g and 170 Oe respectively, making them suitable for a potential use as an exchange-pinned magnetic material.

1. Introduction

Various synthetic routes to amorphous metallic alloys have been pursued over recent years. Thermal decomposition techniques, the utilisation of inverse micelles and the use of surfactants are some of the methods that have been adopted [1-4]. Chemical reduction synthesis (CRS) is a rapid and efficient method of producing amorphous alloys, yielding a large quantity of final product. Amorphous powders are obtained via the reduction of aqueous solutions of metallic salts. Reducing agents such as sodium borohydride or potassium borohydride are used. This reduction route was first reported in 1952 by Schlesinger *et al.* [5] as part of a study into the catalytic effect of certain compounds on the decomposition of sodium borohydride to hydrogen [3]:

$$BH_4^- \; + \; 2H_2O \; \rightarrow \; BO_4^- \; + \; 2H_2 \tag{1}$$

In the case of magnetic alloys, important properties may arise due their structural morphology as well as the particle size. Nanoparticulate materials often exhibit interesting electrical, optical, magnetic and chemical properties, which cannot be achieved by their bulk counterparts. Amorphous metallic alloys can also display core-shell morphology [6,7]. This is especially the case with air passivated particles. The core of the material is metallic (ferromagnetic) and the shell is composed of metal oxides (antiferromagnetic). Interfacial coupling between the core and the shell gives rise to advantageous magnetic properties [7]. This effect is the basis of many of today's sophisticated magnetic devices, such as spin valves for magnetic recording heads.

The aim of the current project is to synthesise core-shell nickel-cobalt-boron nanoparticles that display favourable magnetic properties, and may possibly in the future be laid down as self-assembled magnetic arrays and as thin films.

2. Synthesis and characterisation

Nickel-cobalt-boron nanoparticles were synthesised using CRS. Nickel (II) sulfate and cobalt (II) sulfate salts were dissolved in water or in a mixed water/toluene system using a high speed stirrer. A solution containing the reducing agent sodium borohydride of known concentration was added drop wise over 30 minutes. A black precipitate was formed, and was easily isolated by vacuum filtration. The filtration process was carried out rapidly in order to limit surface oxidation of the powders. The precipitate was extensively washed with water to eliminate residual ions. The slurry was transferred to the antechamber of a glove box and dried in an inert atmosphere (N_2 99.999% for three days). The powder was crushed with a micro-spatula to aid in the slow and controlled passivation of the powders. The samples were extremely air sensitive and pyrophoric in nature. Hence they were stored in an inert atmosphere and small portions were removed from the glove box for analysis.

Samples were characterised by energy dispersive X-ray analysis (EDXA), scanning electron microscopy (SEM), transmission electron microscopy (TEM), differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), X-ray photoelectron spectroscopy (XPS) and inductively coupled plasma mass spectrometry (ICP-MS). Magnetic properties were investigated using vibrating sample magnetometry (VSM) and SQUID magnetometry.

3. Results and discussion

Two sample series were prepared and analysed: (1) in which the water:toluene ratio was varied; and (2) in which the nickel:cobalt ratio was varied.

Electron microscopy was used to measure the sizes of both individual and aggregated nanoparticles. Aggregates ranging between 0.5 to 4 μm in size were seen by SEM, as in Figure 1(a) and 1(b). TEM images revealed individual grains within a clump of nanoparticles, as in Figure 1(c). This image shows evidence of a core-shell morphology wherein the darker areas (the alloy cores) are surrounded by a lighter coating of approximately uniform thickness (the oxide layer). Typical particle sizes observed by TEM were in the range 20 to 60 nm.
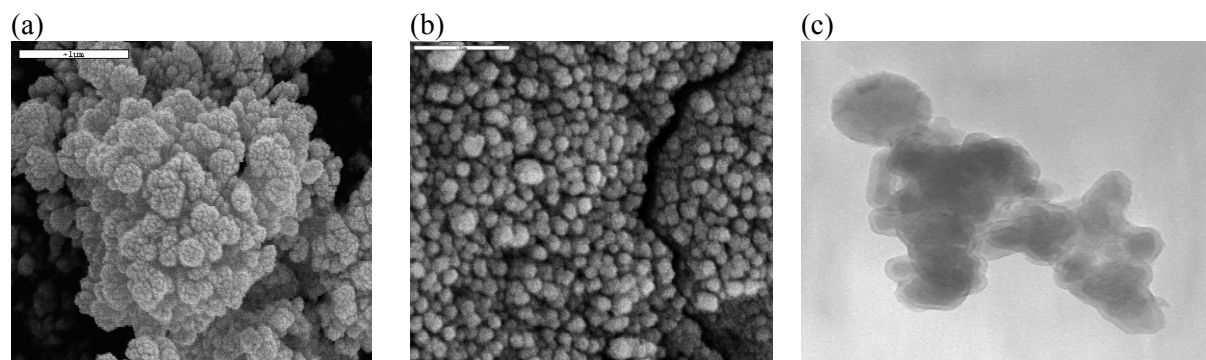
(a) (b) (c)

Figure 1. SEM images of nickel-cobalt-boron samples with Ni:Co ratios of 80:20 prepared using a water:toluene solvent ratio of (a) 80:20 and (b) 50:50; and (c) a TEM image of a sample prepared using 100% toluene.

Compositional analysis of all samples was conducted by EDXA and ICP-MS. The ICP-MS allowed an accurate quantification of boron content in the alloys, which was lacking in the EDXA data, so that together it was possible to determine the empirical composition of the alloys. This also allowed us to measure the transferability of precursor into the final product.

Crystallisation temperatures were determined using DSC, as illustrated in Figure 2 and listed in Table 1. Both series of compounds displayed a similar crystallisation profile. The amorphous powders crystallised over a broad range, as evidenced by the broad peak seen between 70°C and 280 °C in Figure 2. A pre-crystallisation peak was observed in most cases at ca. 340 °C , and the crystallisation temperature for samples made with a 50:50 ratio of Ni:Co was ca. 480 °C. The graph in Figure 2

shows a similarity in the shape of the three different profiles. A general observation was that the greater the cobalt content, the higher was the final crystallisation temperature.
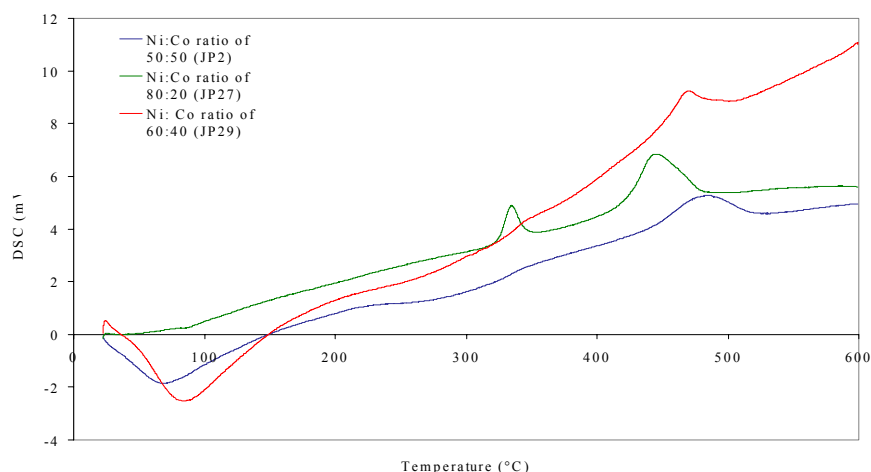

Figure 2. DSC profiles of samples with a variation in Ni:Co ratio.

Table 1. Temperatures of the pre-crystallisation peak, T_1, and the crystallisation peak, T_2, determined by DSC measurement on samples with different Ni:Co ratos.

Composition	T_1 (°C)	T_2 (°C)
$Ni_{31}Co_{40}B_{29}$	351 ± 10	485 ± 5
$Ni_{54}Co_{13}B_{33}$	334 ± 10	445 ± 5
$Ni_{40}Co_{24}B_{34}$	348 ± 10	469 ± 5

XPS analysis of certain samples showed the connectivity of elements to one another, and whether the element was in its elemental or oxidised form. A typical XPS survey of this type of alloy is shown below in Figure 3. The binding energies that are observed for the B1s level, maybe assigned to oxidised boron. The main nickel peak at 852.6 eV corresponds to the Ni 2p 3/2 level. This is representative of elemental nickel. Another peak for this level was observed at 870.0 eV and is due to Ni 2p 1/2 level. The peak at 782.9 eV is due to oxidised cobalt, and is the Co 2p level.
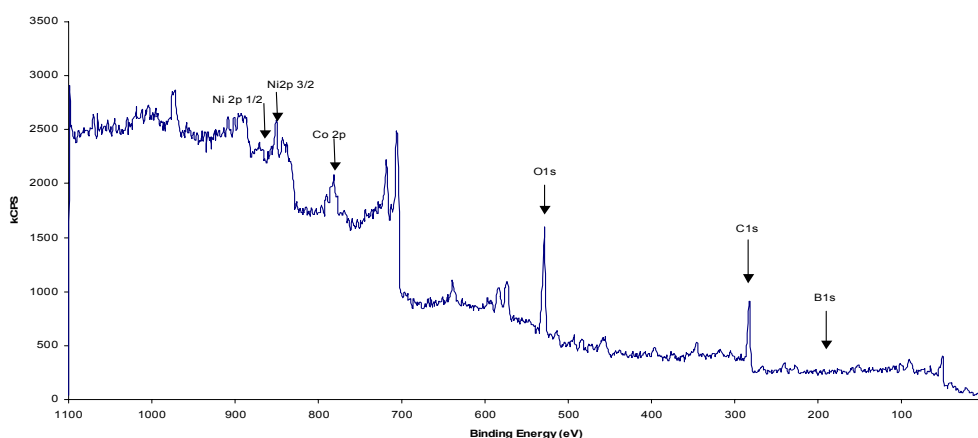

Figure 3. XPS survey of a sample of composition $Ni_{32}Co_{38}B_{30}$.

Magnetic properties were determined using VSM. A composition that yielded a saturation magnetisation (M_s) of ca. 80 emu/g and a coercivity (H_c) of ca. 200 Oe was sought. An alloy of particular composition, with these magnetic properties would be ideal for application in high-density storage. Samples were also annealed at 500 °C for one hour (above the crystallisation temperature determined for the alloy) with the intention of crystallising the alloy cores. Magnetic data was collated for the as-prepared and annealed samples. Two alloys stood out in terms of magnetic data after the annealing process with saturation magnetisation and coercivity values in the correct region range: $Ni_{20}Co_{44}B_{36}$ with M_s = 84 emu/g and H_c = 170 Oe; and $Ni_{54}Co_{13}B_{33}$ with M_s = 37 emu/g and H_c = 486 Oe.

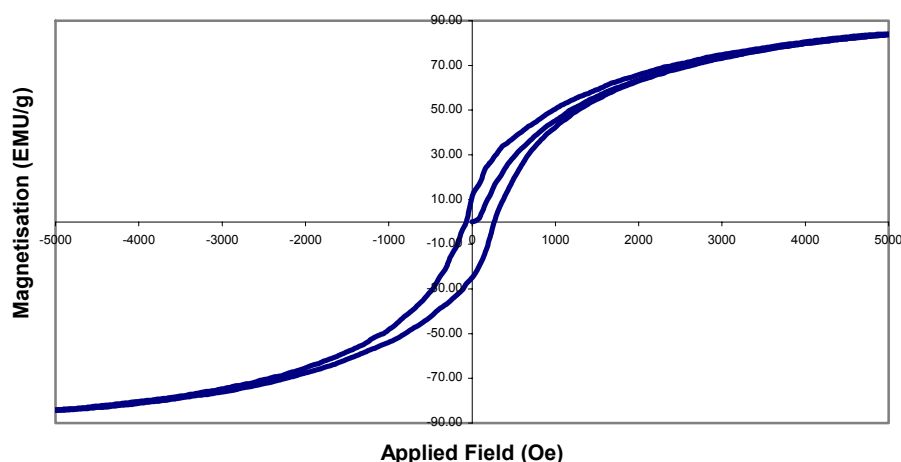**Figure 4.** Hysteresis loop of $Ni_{20}Co_{44}B_{36}$: M_s = 84 EMU/g, H_c = 170 Oe and M_r = 12.62 EMU/g. Recorded at room temperature with a vibrating sample magnetometer.

4. Conclusions

Amorphous nickel-cobalt-boron alloys were synthesised using CRS. The products were nanoparticulate and had core-shell morphology. The alloys had crystallisation temperatures of between 445°C and 485°C, dependent on the percentage of nickel in the alloy. Magnetic data showed that some products had desirable saturation magnetisations and coercivities of the order of 80 emu/g and 170 Oe respectively, making them suitable for a potential use as an exchange-pinned magnetic material [6]. However, most products had substantially smaller magnetisations and coercivities. We conclude that further optimisation is needed before technological applications can be fully explored.

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