Abstract

Much effort has been devoted in recent years in preparing nanosized, spherical particles of ferromagnetic transition metals and alloys. One of the challenging tasks is to produce spherical particles with negligible shape anisotropy and narrow particle size distribution. There are essentially two ways to prepare such materials, namely the top-down and bottom-up approaches. Among the bottom up approaches, the gas condensation and chemical methods are widely used for the production of particles with the above said qualities. Although chemical methods have been used for the past two decades to prepare fine particles, new and interesting results as far as structure is concerned are pouring in. The borohydride reduction technique is one method, the samples prepared by which still remain a fertile ground for the exploration of intriguing structure and magnetic properties. These nanoparticles present an attractive choice in wide areas of application. However, the efficiency of their applications will depend to a large extent on their thermal stability or their stability against oxidation and obviously on their magnetic attributes. Yet few investigations have aimed at identifying their structure or exploring their magnetic properties so that they can be tailored for the manufacture of commercially viable products.

The present research study elucidates the synthesis of Ni nanoparticles by the borohydride reduction of $NiCl_2$ (nickel chloride) solution and is concerned with the understanding of the structure and magnetic properties of these particles. Samples have been prepared using four different concentrations of $NiCl_2$ solution. The following studies have been carried out in detail.

- X-ray diffraction (XRD) has been used to check the amorphous or crystalline nature of the samples and also to identify their structure. Transmission Electron Microscopy (TEM) studies have been used for estimating the particle size. Differential Thermal Analysis and Thermo Gravimetric Analysis (DTA / TGA) techniques have been used for studying the thermal stability or phase stability of the samples and identifying the precise temperature at which the structural phase transformation takes place.
- The field variation of magnetization (M – H plots) at room temperature (300 K) and the thermal variation of magnetization (M – T plots) have been used

to identify the room temperature magnetic state of the samples. The change of magnetic state with change in molar concentration of the starting $NiCl_2$ solution has been pointed out. The M – T curves have also been used for checking the existence of low temperature magnetic transitions.

- Temperature and frequency dependence of low field AC susceptibility has been used to identify the nature of these low temperature transitions in the investigated samples.
- Ageing experiments and critical dynamics study has been used to confirm the critical character of the transitions.
- Isothermal annealing studies at several temperatures under different atmospheres have been carried out and the M – H, M – T and AC susceptibility data of the resulting samples recorded in order to investigate the evolution of structure on heat treatment and identify the close link between structure and magnetic properties.
- Structural and magnetic studies on silver coated Ni nanoparticles have been performed in order to see the modifications (if any) related to these aspects, induced by the silver coating.

The above systematic investigations of the structure and magnetic properties permitted us to draw a number of conclusions. These are:

- Ni nanoparticles prepared by the borohydride reduction method in aqueous medium and ambient atmosphere have a tetragonal crystal structure stabilized by the incorporation of oxygen atoms at the Ni lattice. This is a new crystal structure which we have proposed for the as-prepared samples.
- The room temperature magnetic state of the as-prepared samples is dependent on the molarity of the $NiCl_2$ solution from which the samples have been prepared. The lower molarity samples (0.1 M and 0.5 M) are paramagnetic (PM) while higher molarity samples (1 M and 2 M) show hysteresis at room temperature.
- The dissolved oxygen atoms play the central role in modifying the usual magnetic attributes of FCC Ni and give rise to some unusual magnetic properties such as a paramagnetic state of tetragonal Ni at 300 K. Each particle remains internally disordered with a PM collection of atomic spins

within it. On the contrary, hysteresis and large magnetization enhancement is observed for the same sample at 5 K.

- Magnetic phase transitions are observed at 20 K and 12 K for all samples having tetragonal Ni as majority component. The low temperature transitions are thus intrinsic to the tetragonal phase of Ni.
- The transition at 20 K is a PM (paramagnetic) → FM (ferromagnetic) transition of the oxygen-stabilized tetragonal Ni phase and simply reflects the internal magnetic ordering of each particle, without the particles themselves being ferromagnetically aligned with respect to one another. The 12 K transition is a "superspin glass" transition of the macromoments or 'superspins' formed at 20 K.