Synthesis and Magnetic Studies of Nanocrystalline Nickel Nitride Material

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Single domain Ni₃N nitride particles are synthesized by simultaneous decomposition and nitridation in ammonia atmosphere of [Ni(NH₃)₆](NO₃)₂ complex crystals at 650 K. The Ni₃N phase crystallizes in the hexagonal structure with unit cell parameters a = 4.624(4) Å and c = 4.316(4) Å, and has a crystallite size of 16 nm. In TEM study, these nanosize particles show spherical shape, and form particle aggregates of 18 nm size. Ni₃N particles exhibit a Curie temperature of $T_{\rm C} = 634$ K. In the field dependence magnetic measurements, the presence of hysteresis loop indicates ferromagnetic behavior with $\sigma_{\rm s} = 1.678$ emu/g, $\sigma_{\rm R} = 0.50$ emu/g and $\mu_0 H_{\rm c} = 0.022$ T. In this phase, the density of states (DOS) of Ni is dominated by 3d states and is mixed with 2p DOS of N. The contribution of d-electrons in the intra-band polarization affects the magnetic moment of Ni and thus the magnetic moment of Ni₃N.

Introduction The transition metal nitrides are very important for technological applications as well as fundamental studies because of their unusual combination of physical properties such as very high melting point, extreme hardness and metallic conductivity [1]. Interestingly, transition metal nitrides in the nanostructured form are most attractive for magnetic storage devices, catalytic studies, sensors, fuel cells, superconducting applications [2, 3]. However the paucity of literature on metal nitrides illustrates that the much greater challenges are both in synthesizing and characterizing them with respect to their composition, structure and physical properties. The metastable Ni₃N phase is reported as nanocomposite films of Ni₃N/AlN along with the presence of elemental nickel [4]. In this paper, we present the synthesis of nanocrystalline nickel nitride (Ni₃N) particles. These particles are obtained in the temperature range 613 to 673 K in NH₃ atmosphere from the nickel hexaamine nitrate complex where M–N linkage is present. Nanocrystalline Ni₃N particles are characterized and studied for their interesting magnetic properties.

Experimental Ni₃N was prepared by simultaneous thermal decomposition and nitridation of $[Ni(NH_3)_6](NO_3)_2$ in ammonia atmosphere in the temperature range of 613– 673 K. The complex was prepared by the addition of 10 ml ammonia solution slowly into 1.0 g of Ni(NO_3)_2 · 6H_2O (Merck, India, 97%) with rapid stirring to get a crystalline complex. The final product obtained was nanocrystalline Ni₃N which was con-

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firmed for its stoichiometry by chemical analyses for nickel and nitrogen amount. The metal to nitrogen content ratio was found to be Ni:N = 3:0.9984.

The powder X-ray diffraction (XRD) patterns of Ni₃N were recorded by using a Rich-Seifert X-ray diffractometer, model Isodebyeflex 2002 with Cu K_{α} radiation in the 2θ range of $20^{\circ}-100^{\circ}$. The crystallite size was determined from line broadening using the Scherrer formula, $D = K\lambda/B \cos \theta$, where D is the particle size, K is a constant (shape factor), B is the half-maximum linewidth, and λ is the wavelength of the X-rays. TEM (Philips model E-301) was used to study the morphology and particle size distribution of powder samples. Magnetization measurements were carried out using a vibrating sample magnetometer, in conjunction with a Varian electromagnet assembly that provides a magnetic field up to 2.1 T.

Results and Discussions Nanocrystalline Ni₃N particles in the size range 15.0 to 20.0 nm were prepared by simultaneous thermal decomposition and nitridation of [Ni(NH₃)₆](NO₃)₂ in the ammonia atmosphere for 4 to 12 h duration in the temperature range of 613-673 K. The reactivity and particle size are significantly influenced by the calcination temperature and thus the formation of pure Ni₃N materials. Figure 1a shows the XRD pattern of Ni₃N. The decomposition of Ni₃N starts above 683 K and leads to a mixture of Ni₃N and Ni metal with the escape of interstitial nitrogen. The metastability of Ni₃N is attributed to the low maximum solubility of nitrogen in Ni lattice. The stepwise decomposition is unique to nickel nitride and takes place because of the formation of an intermediate Ni₄N phase in the conversion of nitride to metallic nickel [5]. At high temperature, the removal of nitrogen is enhanced with simultaneous reduction of Ni₃N by the hydrogen molecules from the ammonia decomposition. The main gas evolved is nitrogen and the final product at 873 K is pure Ni metal (Fig. 1b). The XRD pattern of Ni₃N was indexed to a crystal structure with the symmetry found in the disordered Ni₃C [6]. Ni₃N belongs to the hexagonal system with lattice parameters a = 4.624(4) Å and c = 4.316(4) Å. These parameters also match with the reported values of a = 4.621 Å, c = 4.304 Å [7]. The lattice param-



eters of Ni metal having cubic (fcc) system are 3.523 Å [8]. It means that fcc Ni metal changes to hexagonal Ni₃N by considering the cubic diagonal as the hexagonal *c*-axis. There is a regular placement of nitrogen atoms in one third of the distorted octahedral interstices. Nitrogen–nitrogen distance is large compared to the nickel–nitrogen which leads to strong hybridization. The Ni₃N peak positions are uniformly shifted to

Fig. 1. XRD Patterns of a) Ni_3N and b) Ni metal



Fig. 2. TEM micrograph of Ni₃N particles

lower angles of 2θ value by 0.4° , compared to pure Ni and suggests an increase of lattice parameters. The crystallite size of 16 nm was calculated by using Scherrer's formula from the line broadening. Figure 2 shows the TEM micrograph of Ni₃N particles obtained at 633 K. The average particle size observed was about 18 nm which is close to the XRD crystallite size. These particles are spherical in size and showed uniform distribu-

tion. The formation of particle aggregates or magnetic clusters is observed because of strong interaction among the magnetic dipoles of particles. However, we did not find evidence for the crystalline nickel metal in Ni_3N matrix either by XRD or electron diffraction.

Figure 3 shows the temperature dependence of magnetization of Ni₃N particles of 16 nm size, when the applied field was 0.005 T and the inset figure shows the magnetization as a function of field. The Ni₃N sample exhibits ferromagnetic behavior with a coercivity of 0.022 T. The loop is saturated when the maximum field applied is raised up to 1.1 T. The σ -value rises rapidly with a sizable hysteresis (up to the field of 1.1 T), expected for the domain rotation in a ferromagnetic/ferrimagnetic substances [9]. The specific saturation magnetization (σ_s) is found to be 1.6 emu/g and the retentivity (σ_R) 0.5 emu/g at room temperature. The reported value is 1.2 emu/g where the sample is a nanocomposite film of Ni₃N on alumina substrate having an excess amount (3.0%) of elemental nickel [4]. The magnetic moments reported for Ni and Ni₃N are $0.615\mu_{\rm B}$ at 273 K and $0.057\mu_B$ at 292.5 K respectively [9]. Oyama [10] has also reported that Ni₃N shows ferromagnetic behavior. In our study, the σ_s values observed for Ni₃N at a saturation field of 1.1 T are 1.678 emu/g and 1.793 emu/g in the +ve and -ve directions, respectively. This difference is due to the forced magnetization as the single domain rotation in the field direction is predominant at higher fields [9]. The coercivity measured from the hysteresis is 0.022 T at room temperature and is expected from the



Fig. 3. Specific magnetization as a function of temperature. Inset shows the field dependence of magnetization

non-interacting Stoner-Wohlfarth type particles. However, the bulk σ_s of Ni metal is 54.39 emu/g at room temperature [9]. This value is different from the values of Ni₃N nitride material. The Curie temperature (T_c) for Ni₃N is 634 K (Fig. 3) which is higher than for the nickel (fcc) metal at 627.4 K [10].

The contribution to the magnetic moment in Ni₃N system could be due to an unbalanced charge distribution between spin-up and spin-down states. From the magnetic valence model discussed for Fe₃N [10, 11], both N and Ni contribute to the magnetic moment in Ni₃N. The density of states of Ni (DOS) is dominated by 3d states and mixed with 2p (DOS) of N. This results in the electron exchange processes having some sort of covalent bonding between Ni and N atoms. However, in Ni₃N, N acts as the electron donor, and ionic bonding or charge transfer is also expected. These aspects are confirmed from the electrical resistivity measurements and our Ni₃N showed a higher electrical resistivity of $151.7 \times 10^{-6} \Omega$ cm. compared to $7.0 \times 10^{-6} \Omega$ cm. of Ni metal at 300 K [13], where metal-metal bonding (Ni–Ni) only is present. It means that there is a covalent bonding between Ni and N in Ni₃N in addition to Ni–Ni bonding resulting into high resistivity. Therefore, the number of unpaired d-electrons available for intraband polarization in Ni is reduced resulting in lower magnetization value for Ni₃N phase compared to Ni metal.

Yue et al. [6] have reported Ni₃C phase exhibiting ferromagnetic nature with a roomtemperature coercivity of 70 Oe and a magnetization of 0.8 emu/g. But the observed ferromagnetic behavior does not agree with the theoretical predictions. Such kind of effects cannot be ruled out in case of Ni₃N nitride material because of metastable nature and the observation of ferromagnetic nature of Ni₃N can be explained by the disorder in the structure. The magnetic and structural measurements are consistent with the microscopic observations of nanostructured materials with locally produced Ni-rich Ni₃N regions of aggregates/clusters which may permeate the Ni₃N particles. These aspects are under investigation even though we have not found the presence of Ni in Ni₃N by XRD or electron diffraction.

Conclusions In the present study, we have discussed the synthesis and characterization of nanocrystalline Ni_3N particles that are stable up to 683 K in ammonia atmosphere. TEM data showed spherical morphology, uniform distribution and strong dipolar interactions among particles. Ni_3N exhibited ferromagnetic behavior having a coercivity of 0.022 T and Curie temperature 634 K. The contribution to the magnetic moment in Ni_3N system is due to an unbalanced charge distribution between spin-up and spindown states of Ni-3d and N-2p orbitals.

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References

- [1] L. E. TOTH, Transition Metal Carbides and Nitrides, Academic Press, New York 1971.
- [2] H. GLEITER, Prog. Mater. Sci. 33, 223 (1989).
- [3] P. KROLL, B. ECK, and R. DRONSKOWSKI, Adv. Mater. 12, 307 (2000).
- [4] L. MAYA, T. THUNDAT, J. R. THOMPSON, and R. J. STEVENSON, Appl. Phys. Lett. 67, 3034 (1995).
- [5] L. MAYA, J. Vac. Sci. Technol. A 11, 604 (1993).

- [6] L. YUE, R. SABIRYANOV, E. M. KIRKPATRICK, and D. L. LESLIE-PELECKY, Phys. Rev. 62, 8969 (2000).
- [7] V. R. JUZA and W. SACHSZE, Z. Anorg. Allg. Chem. 251, 201 (1943).
- [8] H. E. SWANSON and E. TATGE, Natl. Bur. Standards (U.S.) Circ. 539, 95 (1953).
- [9] B. D. CULLITY, in: Introduction to Magnetic Materials, Addison-Wesley, Reading (Mass.) 1972.
- [10] S. T. OYAMA, in: The Chemistry of Transition Metal Carbides and Nitrides, Blackie Academic & Professional, New York 1996.
- [11] R. N. PANDA and N. S. GAJBHIYE, J. Appl. Phys. 81, 335 (1997).
- [12] R. N. PANDA and N. S. GAJBHIYE, J. Appl. Phys. 86, 3295 (1999).
- [13] C. KITTEL, Introduction to Solid State Physics, 7th ed., Wiley, New York 1996.