Journal of Magnetics 11(4), 156-159 (2006)

Magnetic Properties of Nano-Sized CuNi Clusters

Y. Jo[1], M. H. Jung[1]*, M. C. Kyum[2], K. H. Park[3], and Y. N. Kim[3]

[1]*Quantum Material Science Team, Korea Basic Science Institute, Daejeon 305-333, Korea*
[2]*Control Development Team, Korea Basic Science Institute, Daejeon 305-333, Korea*
[3]*Mechanical Engineering Department, Korea Maritime University, Pusan 606-791, Korea*

(Received 27 September 2006)

We have studied the magnetic properties of the CuNi nanoparticles for three different sizes prepared by plasma and chemical techniques. The magnetization is enormously enhanced with decreasing the nanoparticle size. This enhanced magnetic moment shows almost inversely linear temperature dependence, which could be interpreted by the Langevin-type superparamagnetism. The field dependence exhibits ferromagnetic-like behavior with weak hysteresis, which could described in terms of uncompensated spin and/or surface anisotropy. In addition, the magnetic data suggest that the CuNi nanoparticles produced by the plasma method result in significantly less oxidized metallic nanoparticles than those prepared by other techniques.

Keywords : CuNi nanoparticle, superparamagnetism, oxygen free, plasma technique

1. Introduction

The recent interest in cluster science stems from the main observation that the physical properties of finely divided powders are very different from the macroscopic well-known properties of the bulk. Particular interest lies in the magnetic properties of transition metal-oxide and pure transition metal clusters, which have been mostly found to exhibit an unusual form of magnetic ordering [1]. When the diameters of the fine particles are comparable to the characteristic length of the magnetic correlation, a special spin polarization can occur. Thus, it could be of interest to know how the magnetic coupling develops with cluster size and how the moments within the cluster are aligned.

Studies on the magnetic properties of monoatomic transition metal clusters have demonstrated that the magnetic moment is increased over the bulk value and is more enhanced as reducing the cluster size. Magnetic behaviors on ferromagnetic Fe, Co, and Ni clusters have been determined earlier measuring molecular beam deflection [1], in which the magnetic moments for clusters of diameter ~ a few nm are atomic like and those for larger clusters approach the bulk limit. The experimental trends have been qualitatively explained using both *ab-initio* [2] and semiempirical tight-binding models [3] in monoatomic transition metal clusters. However, the magnetic properties of mixed transition metal clusters have not yet received similar attention because of the lack of high-quality sample. Fe-Ni alloy, which is one of the most widely used magnetic materials, has been studied as the bulk alloys change into the ultrafine particles ~ a few tens nm in diameter [4]. Although the magnetization for the ultrafine particles has almost the same temperature dependence as that of the bulk alloys, the saturation magnetization of the ultrafine particles was remarkably lower than their bulk value. This is particularly surprising as one expects the particles to have higher magnetic moments due to the increased number of surface atoms with reducing the size. They believed that the lowering of magnetization in the nanophase could be due to coexistence of ferromagnetic and antiferromagnetic solutions. Furthermore, other effects such as disorder and segregation have been suggested to play a role in the decrease of the total magnetization of the system [5].

2. Experimental Details

In the present study, we present experimental results of the magnetic properties of mixed Cu-Ni clusters in comparison with those of the corresponding bulk alloys. Three kinds of CuNi ultrafine particles were prepared by different techniques. The nano-sized composites of CuNi

*Corresponding author: Tel: +82-42-865-3495,
Fax: +82-42-865-3498, e-mail: mhjung@kbsi.re.kr

© 2006 Journal of Magnetics

were produced by an inductively coupled plasma reactor equipped with the liquid nitrogen cooling system. Those of the starting raw materials were 50Cu:50Ni (at.%). The nano-sized CuNi alloy was prepared by thermolysis of single molecular precursor in hexadecylamine. The reaction was carried out at relatively low temperatures without reducing agent under inert atmosphere condition. We denote the nanoparticles prepared by plasma method as *a*- and *b*-types with difference diameters of 10 nm and 20 nm, respectively. And we denote the nanoparticles prepared by chemical method as c-type with a diameter of 80 nm. The results of EDS (Energy Dispersive Spectroscopy) quantitative analysis showed almost 50 at.% Ni and 50 at.% Cu for all the composites. The SEM (Scanning Electron Microscope) and HR-TEM (High-resolution Transmission Electron Microscope) images showed nearly spherical shapes and average sizes of (a) 10 nm, (b) 80 nm, and (c) 20 nm in diameter. This enables us to study the effect of particle size and surface anisotropy on magnetic interaction in the cluster. The XRD (X-ray Diffraction) patterns of all of the alloys could be indexed with a cubic structure. The diffraction peaks show a trend of broadening, which results from the reduced size of the particles. Magnetic measurements were performed using a Quantum Design SQUID magnetometer. The temperature dependence of magnetization was measured in an applied field of 1 kOe between 2 and 350 K and the hysteresis loop was measured at 2 K. We find qualitatively ferromagnetic-like spin polarization when the bulk alloy changes into the nanoparticles, that is the magnetization saturated at high field and there is a hysteresis in the field dependent magnetization. This ferromagnetic spin polarization seems to be dependent of the surface anisotropy, although the nanoparticles exhibit similar reversible magnetic behavior.

3. Results and Discussion

Figure 1 shows the temperature dependence of magnetic susceptibility *M*/*H* measured at 1 kOe for the three kinds of nanoparticles and the bulk alloy of CuNi. For the bulk sample, the *M*/*H* curve satisfies the Curie-Weiss law at high temperatures above 250 K, giving values of the effective magnetic moment $\mu_{eff} \approx 1.5\ \mu_B$ per formula unit and the paramagnetic Curie temperature $\theta_P \approx 240$ K. The large positive value of θ_P is presumed to be due to a ferromagnetic correlation in the CuNi alloy. On the other hand, in the lower temperature regime it increases rapidly below 50 K, which generally agrees with the ferromagnetic transition temperature for the bulk CuNi system [6]. However, the smooth change at the transition may arise

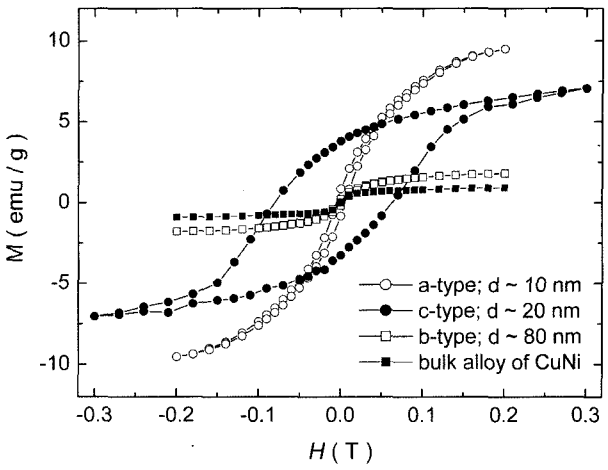

Fig. 1. Temperature dependence of magnetic susceptibility M/H measured at 1 kOe for 10 nm (a-type), 20 nm (c-type) and 80 nm (b-type) CuNi nanoparticles, and the bulk alloy of CuNi.

from additional contributions from unavoidable impurity phases in our bulk sample. When the nanoparticles are approached from the bulk sample, the magnetic moment is enormously enhanced and the *M*/*H* curve is almost inversely linear temperature dependent. There is no substantial difference in the temperature dependence of *M*/*H* except the sudden rise of *M*/*H* for the c-type nanoparticles at low temperatures. If one presumes that the inversely linear temperature dependence is attributed to the conventional Langevin paramagnetism, i.e., the Curie-Weiss term, one can have extraordinary values of $\mu_{eff} \approx 64\ \mu_B$ and $\theta_P \approx$ 507 K for the a-type nanoparticles. Thus, we could exclude this interpretation and have to find another possible origin for the temperature dependence of *M*/*H* in the nanoparticles. We would suggest the Langevin-type superparamagnetism with a high blocking temperature fairly above the room temperature in origin. This interpretation can be supported by the weak hysteresis (Fig. 3) and the ferromagnetic-like behavior observed in the magnetization curve (Fig. 2), and thus it is more reliable than the interpretation of conventional Langevin paramagnetism. Here, the interesting point is that the superparamagnetism appears abruptly to have a very high blocking temperature. The superparamagnetism for nanoparticles is mostly believed to originate from uncompensated spin and/or anisotropic surface effect. The uncompensated spin on the surface of the nanoparticles can be easily aligned along the direction of the applied magnetic field, resulting in the large magnetic moment. The magnetic anisotropic energy can be deduced from the blocking temperature and the size of single nanoparticles [7]. It has been reported for metallic iron nanoparticles that the magnetic anisotropy energy

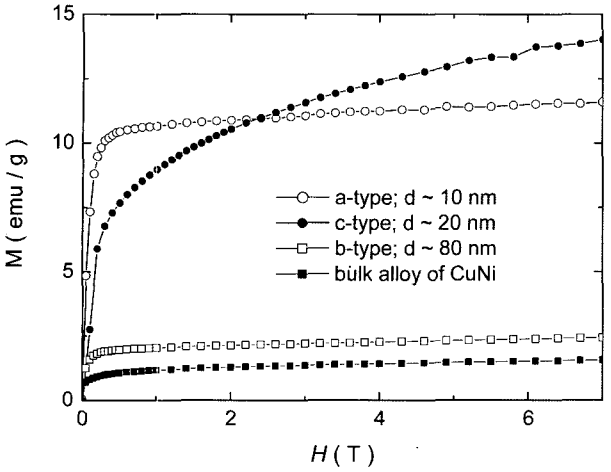

Fig. 2. Magnetic field dependence of magnetization M(H) measured at 2 K for three kinds of CuNi nanoparticles and the bulk alloy.

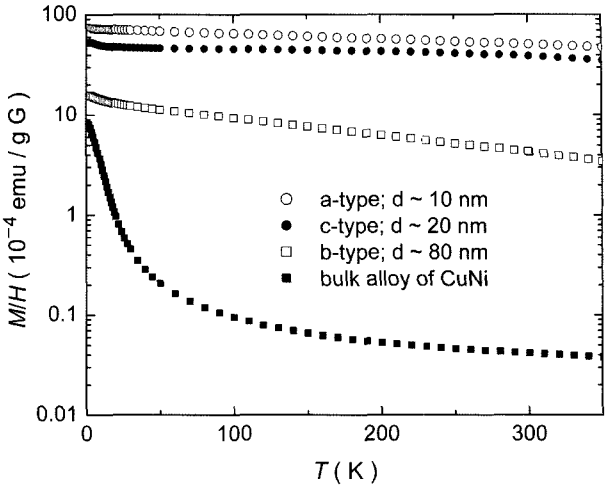

Fig. 3. Hysteresis loops measured at 2 K for three kinds of CuNi nanoparticles and the bulk alloy.

increases with decreasing particle size, presumably because of the influence of surface anisotropy [8].

In order to take a careful look at the magnetism of the CuNi nanoparticles, we have measured the magnetization $M(H)$. It is worth noting from Fig. 2 that $M(H)$ increases significantly with decreasing the particle size of CuNi. At 2 K, the magnetization at 5 T is about 11.5 emu/g and 2.4 emu/g for the a- and b-type particles, respectively, far from the saturation value for the bulk alloy of CuNi. This increased magnetic moment is most likely to be the outcome of anisotropic surface effects, as found in monoatomic transition metal nanoparticles like Fe, Co, and Ni [1]. For the c-type particles, monotonic increase of $M(H)$ is observed at 2 K, where the temperature dependence of M/H shows a sudden increase. Such behavior is presumed to be associated with the oxidization of the CuNi nanoparticles. In general, the metallic nanoparticles are easily oxidized in air, which leads to the formation of an oxide layer on the surface of the metallic particles. Due to the presence of exchange interaction at the interface between the metal and metallic oxide, the system would exhibit an exchange bias [9]. The exchange bias can be reflected by the shift of the hysteresis loop. As seen in Fig. 3, the hysteresis loop of the c-type nanoparticles is asymmetric, giving a quantitative value of $\Delta H_C = (H_C^+ + H_C^-)/2 \sim 72$ G, where H_C^+ and H_C^- are defined as the coercive fields with increasing and decreasing fields, respectively. On the other hand, the hysteresis loop of the a- and b-type nanoparticles is symmetric with respect to zero field. This indicates that the CuNi nanoparticles produced by the plasma technique are free of any oxide layer. Furthermore, the coercivity at 300 K (that is not shown here) is nearly negligible, corresponding to superparamagnetism, which is most likely to be associated with uncompensated spin and/or anisotropic surface effects.

We now discuss the origin of enhanced magnetic moments of the nano-sized CuNi clusters. The bulk CuNi system shows long-range ferromagnetic order above 45 at.% Ni composition [6], which is about twenty times larger than the critical concentration (2.3 at.% Ni) for the bulk PdNi system [10]. The magnetic and transport properties of bulk CuNi alloy are described in terms of quasi-localized moments [11]. Such isolated but fluctuating Ni moments seems to play an important role in the enhanced magnetic moments of our nano-sized CuNi system. As reported for a variety of other nanoparticles, the magnetic properties are a result of contributions from both interaction and size effects.

4. Conclusion

In conclusion, the preparation of the CuNi nanoparticles has been achieved through plasma and chemical techniques with different sizes. The magnetization is remarkably higher than the bulk value and is further enhanced with decreasing the particle size. This enhanced magnetic moment in the nanoparticles is most likely to be associated with the Langevin-type superparamagnetism, which is supported by the weak hysteresis and the ferromagnetic-like behavior. The results could be understood within a framework of uncompensated spin and/or surface anisotropy. The magnetic data suggests that the CuNi nanoparticles produced by the plasma method results in significantly less oxidized metallic nanoparticles, whereas the CuNi nanoparticles prepared by the chemical method makes an sudden increase of magnetization at low

temperatures due to the oxide layer on the surface of the nanoparticles.

This work is supported by NPC CO. Ltd. and "dual use technology project" of MOST, MONT, and MOCIAE and in part by Korea Research Council of Fundamental Science & Technology (KRCF).

References

[1] I. M. L. Billas, A. Chatelain, and W. A. de Heer, Science **265**, 1682 (1994).
[2] M. Castro, C. Jamorski, and D. R. Salahub, Chem. Phys. Lett. **271**, 133 (1997).
[3] A. N. Andriotis, N. Lathiotakis, and M. Menon, Chem. Phys. Lett. **260**, 15 (1996).
[4] X. G. Li, A. Chiba, and S. Takahashi, J. Mag. Mag. Mater. **170**, 339 (1997).
[5] B. K. Rao, Susana Ramos de Debiaggi, and P. Jena, Phys. Rev. B **64**, 024418 (2001).
[6] Q. Chen and Z. J Zang, Appl. Phys. Lett. **73**, 3156 (1998).
[7] F. Bodker, S. Morup, and S. Linderoth, Phys. Rev. Lett. **72**, 282 (1994).
[8] B. D. Cullity, *Introduction to Magnetic Materials*, Addision-Wesley, Reading, MA, 1972.
[9] J. C. Ododo and B. R. Coles, J. Phys. F: Met. Phys. **7**, 2393 (1977); P. A. Stampe and G. Williams, J. Phys.: Condens. Matter **9**, 9251 (1997).
[10] H. P. Kunkel, Z. Wang, G. Williams, J. Phys.: Condens. Matter **1**, 3381 (1989); A. P. Murani, A. Tari, and B. R. Coles, J. Phys. F: Met. Phys. **4**, 1769 (1974); A. Tari and B. R. Coles, J. Phys. F: Met. Phys. **1**, L69 (1971).
[11] R. W. Houghton, M. P. Sarachik, and J. S. Kouvel, Phys. Rev. Lett. **25**, 238 (1970); J. S. Kouvel and J. B. Comly, Phys. Rev. Lett. **24**, 598 (1970); C. G. Robbins, H. D P. A. Beck, Phys. Rev. Lett. **22**, 1307 (1969); T. J. Hicks, B. D. Rainford, J. S. Kouvel, G. G. Low, and J. B. Comly, Phys. Rev. Lett. **22**, 531 (1969).