Pergamon

NanoStructured Materials, Vol. 6, pp. 933-936, 1995

0965-9773/95 $9.50 + .00

0965-9773(95)00213-8

THERMAL AND MAGNETIC STUDIES OF NANOCRYSTALLINE Ni

Y.D.Yao[1,2], Y.Y.Chen[1], C.M.Hsu[3], H.M.Lin[3], C.Y.Tung[3], M.F.Tai[2], D.H.Wang[2], K.T.Wu[4], and C.T.Suo[4]

1.Institute of Physics, Academia Sinica, Taipei, Taiwan, ROC.
2.Department of Physics, National Chung Cheng University, Chiayi, Taiwan, ROC.
3.Dept. of Material Eng.,Tatung Institute of Technology, Taipei, Taiwan, ROC.
4.Department of Physics, Fu Jen University, Taipei, Taiwan, ROC.

Abstract-- *Ultra-fine Ni particles with average particle sizes from 12 to 100 nm were prepared by the evaporation technique. The calorimetric effects of nanocrystalline Ni as well as the NiO and Ni bulk samples were measured between 300 and 800 K. Both an exothermal effect between 380 and 480 K and an endothermal peak near 560 K were observed for ultra-fine Ni; only endothermal peak was observed for both NiO near 520 K and bulk Ni near 630 K. A shifted magnetic hysteresis loop and a slope change in saturation magnetization were observed below roughly 50 K for ultra-fine Ni particles with average particle sizes roughly below 50 nm. This is explained by the effect of exchange anisotropy interaction between the interfaces of the ferromagnetic region and the layers of antiferromagnetic NiO on the surface of the nanocrystalline Ni particles.*

INTRODUCTION

Research of ultra-fine magnetic particles has been very active because of the potential applications in high density magnetic recording media (1,2). A large fraction of the atoms in ultra-fine particles are surface atoms; this has a significant influence on the thermal and magnetic properties. In this investigation, we report on studies of the calorimetric behavior at high temperatures and the magnetic exchange anisotropy effect at low temperature for nanocrystalline Ni.

EXPERIMENTAL

Samples for this study were prepared from commerically available high purity Ni ingots (99.999%) and NiO (99.995%) powders. Nanocrystalline Ni powders with average particle sizes from 12 to 100 nm were prepared by the evaporation technique.The pressure of the He gas atmosphere during evaporation was varied from 1 to 100 mbar to control the growth of the particle size. The calorimetric effect was measured with a differential scanning calorimeter (DSC). The magnetization below 300 K was studied by using both SQUID and VSM magnetometers. Powder X-ray diffraction and transmission electron microscopy (TEM) were used in structure, morphology and particle size analyses.

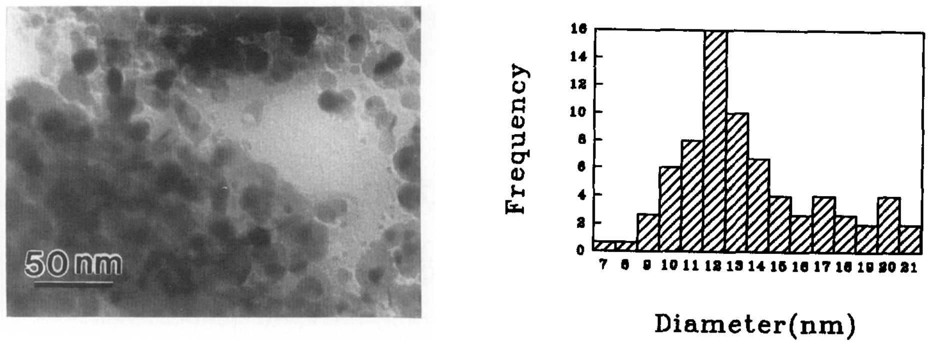

Figure 1. TEM micrograph and particle size distribution for nanocrystalline Ni with average particle size around 12 nm.

RESULT AND DISCUSSION

Figure 1 shows as an example the TEM micrograph and the particle size distribution for Ni particles with average sizes around 12 nm. The particle size distribution was obtained by measuring about 500 Ni particles from TEM micrographs.The calorimetric effect and X-ray diffraction pattern of nanocrystalline Ni as well as NiO powder and Ni bulk samples are plotted in Figure 2. It is clear that the specific heat of nanocrystalline Ni is higher than that of the bulk Ni. A slowly exothermal effect between 380 and 480 K is due to the aggregation of the ultra-fine Ni particles. The endothermal peak near 560 K is related to magnetic phase transition. According to the magnetic study by Schaefer et al (3), it is the magnetic phase transition of the interfacial component. Only an endothermal peak was observed for NiO near 520 K and bulk Ni near 630 K which is ascribed to the magnetic phase transition temperature. The main peaks of X-ray diffraction patterns of all the samples show either pure Ni or NiO phase.

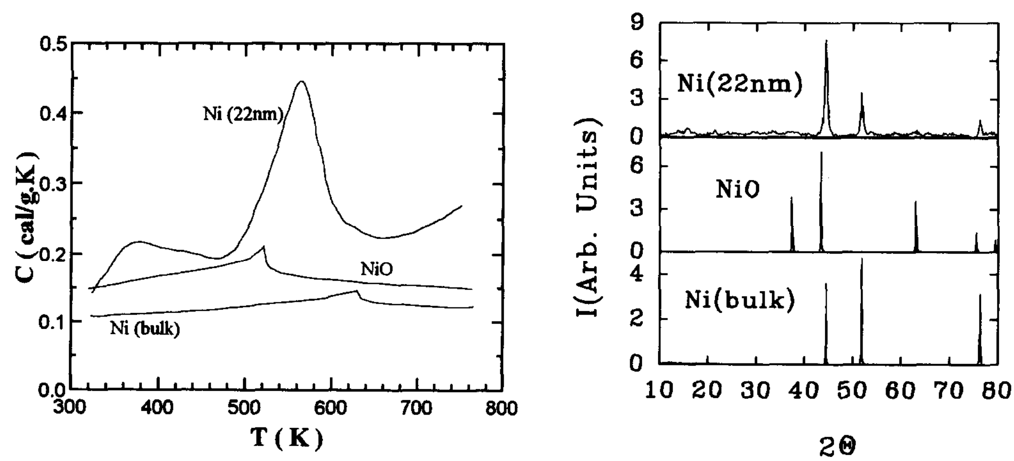

Figure 2. Specific heat of bulk Ni, nanocrystalline Ni (22 nm) and NiO between 300 and 800 K.

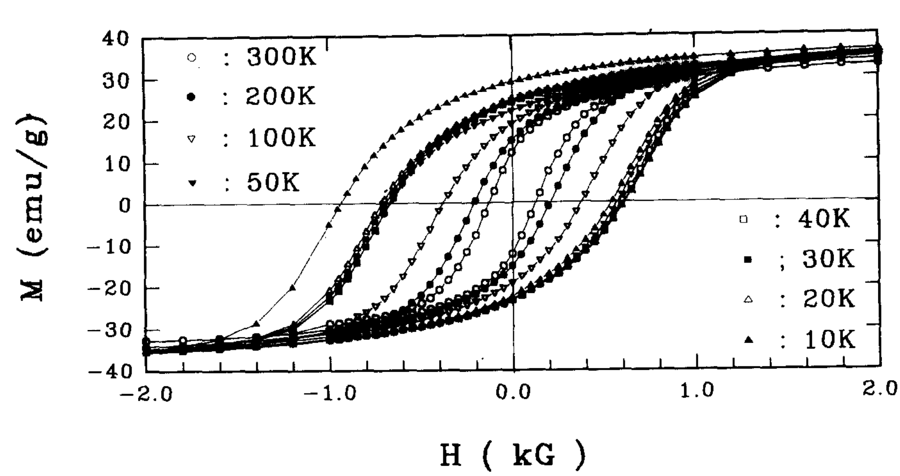

Figure 3. Field (8 kG) cooled M vs H curve for Ni particles with 22 nm at different temperatures.

The exchange anisotropy effect in nanocrystalline Ni particles has been observed below 50 K for all the ultra-fine Ni particles with average particle size roughly below 50 nm. Figure 3 shows as an example the field-cooled (8 kG) magnetic hysteresis loop for Ni particles with average particle sizes around 22 nm. The loops are not symmetrical for temperatures below 50 K. However, they are symmetrical for temperatures above 50 K, and for all the temperature with zero field cooling. Figure 4 shows the magnetization at 8 kG as a function of temperature . A change of slope near 50 K occurs for all samples with particle sizes smaller than 50 nm. Therefore, we conclude that, below 50 K, the shifted loop and the slope change in magnetization are due to the exchange anisotropy ; i.e. coupling between the ferromagnetic Ni core and the antiferromagnetic Nickel oxide shell of the particles. Here, T=50 K is a

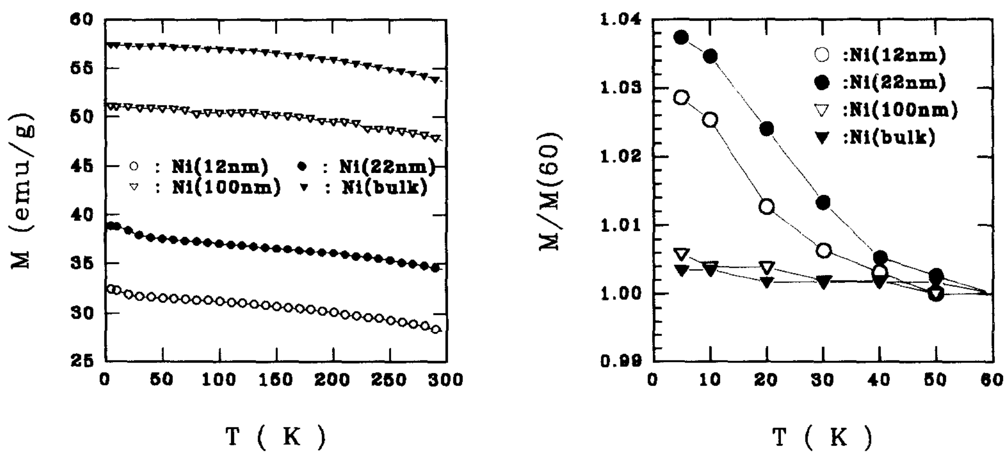

Figure 4. M and M(T)/M(60) vs T curves.

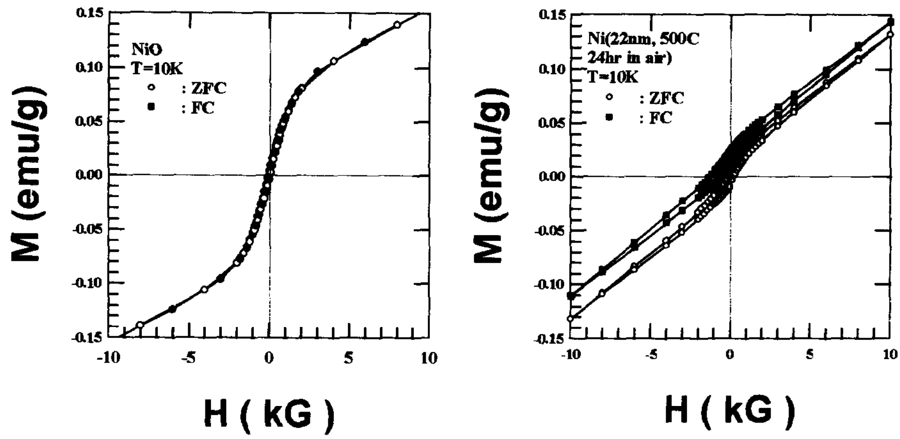

Figure 5. FC & ZFC curves of M vs H at T=10 K for NiO and Ni (22nm) annealed at 500 C in air for 24 hrs.

characterictic temperature for Ni ultra-fine particles; this is quite similar to T=150 K as a characteristic temperature for Co ultra-fine particles (4). Figure 5 presents the field cooled and zero field cooled M vs. H curves at 10 K for NiO powders and Ni ultra-fine powders with annealing at 500 C in air for 24 hrs. This shows that the exchange anisotropy also exists in the system with small amount of pure Ni in the core of a ultra-fine NiO particle.

In conclusion, both an exothermal effect between 380 and 480 K and an endothermal peak near 560 K were observed for nanocrystalline Ni from thermal study ; only an endothermal peak was observed for both NiO near 520 K and bulk Ni near 630 K. From magnetics study, a shifted magnetic hysteresis loop and a slope change in saturation magnetization below roughly 50 K were observed for ultra-fine Ni particles with average particle sizes below rougly 50 nm. This is explained by the effect of exchange anisotropy interaction of the interfaces of the ferromagnetic region and the layers of antiferromagnetic NiO on the surface of the nanocrystalline Ni particles.

ACKNOWLEDGMENTS

This work was supported in part by the National Science Council of ROC (NSC84-2112-M-001-042).

REFERENCE

1. E. Matijevie, MRS Bull. **14**, 19 (1989).
2. H. Gleiter, Prog. Mater. Sci. **33**, 223 (1989).
3. H. -E. Schaefer, H. Kisker, H. Kronmuller, and R.Wurschum, NanoStruc. Mater.**1**, 523 (1992).
4. S. Gangopadhyay, G. C. Hadjipanayis, C. M. Sorensen, and K. J. Klabunde,NanoStru., **1**, 449 (1992).