



X-RAY ABSORPTION STUDIES OF NANOCRYSTALLINE Ni

L. Y. Jang¹, Y. D. Yao², Y. Y. Chen², and Y. Hwu²

1 Synchrotron Radiation Research Center, Hsinchu 300, Taiwan, ROC.

2 Institute of Physics, Academia Sinica, Taipei 115, Taiwan, ROC.

Abstract--*The x-ray absorption was investigated for nanocrystalline Ni, bulk Ni, and NiO. The size of nanocrystalline Ni is roughly 22 nm. From the k edge spectrum studies, we find that the bond lengths in both nanocrystalline and bulk Ni are completely the same, however, the ordering factor is manifestly reduced for nanocrystalline Ni. The calculated coordination number of nanocrystalline Ni is 11.7 which is smaller than the number of nearest neighbor 12 in bulk Ni. The ordering factor and the coordination number of nanocrystalline Ni increase to the same value of bulk Ni after annealing in vacuum at 1600 K for 24 hrs. From this study, we can clearly identify the surface oxidation effect in nanocrystalline Ni. This strongly supports the magnetic anisotropy effect which occurs only in nanocrystalline Ni. The magnetization enhancement near 40 K for the nanocrystalline Ni is related to the exchange anisotropy effect. ©1997 Acta Metallurgica Inc.*

INTRODUCTION

X-ray absorption fine structure (XAFS) measurements can provide useful information on the short-range-order structure, thus is well suited for investigating the local environment around the constituent atoms in nanocrystalline materials. Recently, XAFS spectra of nanocrystalline Fe, Cu, and Co etc. have been extensively studied [1-6]. Relatively little research work has been devoted to the XAFS study on the nanocrystalline Ni system. In the present study, the Ni K-edge XAFS spectra is employed to investigate the local environment surrounding of Ni atoms in nanocrystalline Ni, bulk Ni, and NiO particles.

EXPERIMENTAL

Samples used in the study were prepared from commercially available high purity Ni powder (99.999%), NiO (99.99%) powder and Ni fine powders with particle sizes of about 22 nm, which were prepared by the evaporation technique and bought from Vacuum Metallurgical Co., Japan. The X-ray absorption fine structure (XAFS), which includes extended x-ray absorption fine structure (EXAFS) and near-edge absorption fine structure (XANES), measurements were performed at Synchrotron Radiation Research Center (SRRC),

Hsinchu, Taiwan. Data were obtained by measuring the transmission nickel K-edge absorption spectra through layers of powders spread on Scotch tapes. A high-order multiple-scattering approach method [7-9] was used for the calculation of XAFS spectra.

RESULTS AND DISCUSSION

The structure and magnetic properties of nanocrystalline Ni have been reported before [10]. The main peaks of X-ray diffraction pattern of the nanocrystalline Ni are completely consistent with that of the Ni bulk, except that the peaks become more broad. Fig. 1 shows the magnetization as a function of temperature between 4 and 300 K for (a) bulk Ni and (b) nanocrystalline Ni. It is clear that the value of magnetization of nanocrystalline Ni is much smaller than that of bulk Ni, and a change of slope near 40 K for nanocrystalline Ni has been explained by the magnetic exchange anisotropy effect [10].

The Ni K-edge XANES spectra for nanocrystalline Ni with average particle sizes around 22 nm, nanocrystalline Ni annealed at 600 K in air (10^{-2} torr) for 1/2 hr, Ni bulk powder, and NiO powder are shown in Fig. 2. The curve for nanocrystalline Ni after annealing at 1600 K in high vacuum for 24 hrs coincides with that of bulk Ni, therefore, it is not shown in the figures. This suggests that the ordering factor and the coordination number of nanocrystalline Ni increase to the same value of bulk Ni after annealing in vacuum at high temperatures. The intense feature centered around 8350 eV is expected to be composed of bound-state transitions of the 1s electron to levels with substantial p-orbital character. The second derivatives of the same spectra in Fig. 2 are plotted in Fig. 3, which indicates the features shown in Fig. 2 more clearly. In general, Figs. 2 and 3 tell us that the curves of nanocrystalline Ni are located between the curves of bulk Ni and NiO powders. The Fourier transform of the Ni K-edge EXAFS spectra (k^3 -weighted) of the same samples as plotted

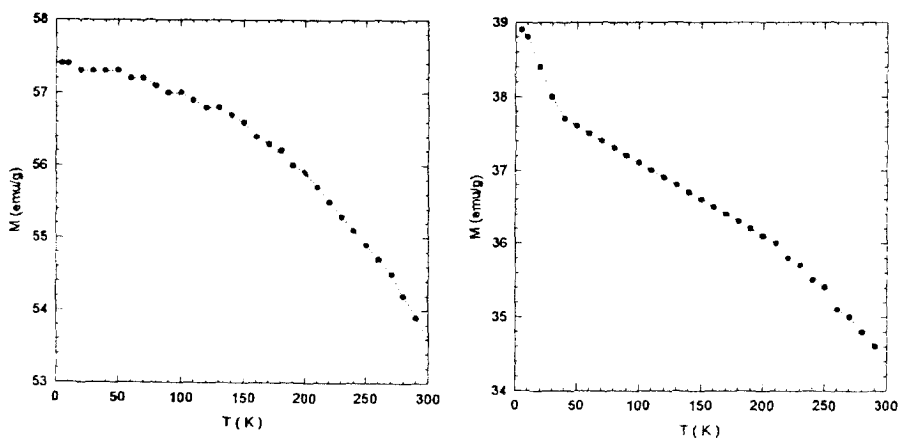


Fig.1 Magnetization of bulk Ni (a) and nanocrystalline Ni (b) as a function of temperature between 4 and 300 K.

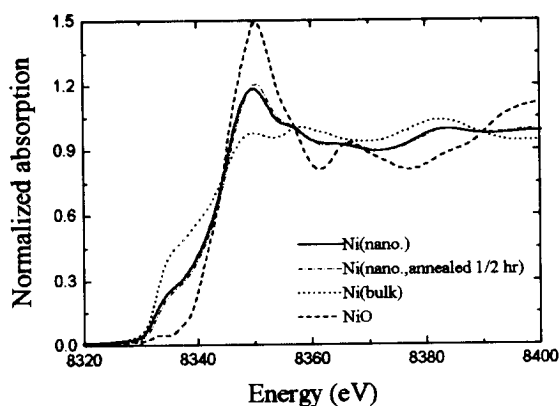


Fig. 2 Normalized absorption spectra of nanocrystalline Ni, nanocrystalline Ni annealed at 600 K in 10^{-2} torr air condition for 1/2 hr, bulk Ni, and NiO powder.

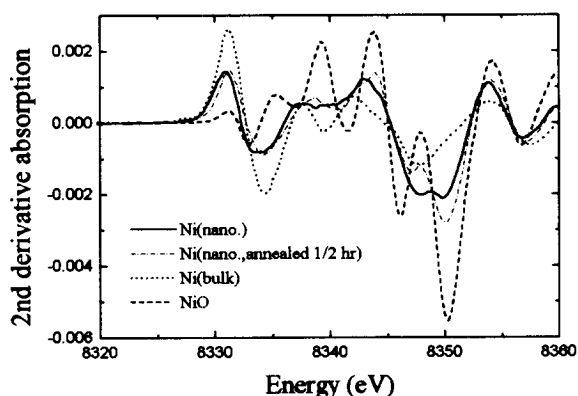


Fig. 3 The second derivatives of the absorption spectra shown in Fig. 2.

in Fig. 2 are shown in Fig. 4. The calculated coordination number of nanocrystalline Ni is 11.7 which is smaller than the number of nearest neighbor 12 in bulk Ni. It is clear that the bond lengths in both nanocrystalline and bulk Ni are completely the same, however, the mean-square disorder factor of nanocrystalline Ni is larger than that of bulk Ni, this means that the ordering factor is significantly reduced in nanocrystalline Ni. The quite large peaks observed near 2.6 Å (Ni-O bond) for nanocrystalline Ni tell us that the surface oxidation is manifest. This can confirm the magnetic exchange anisotropy effect between the Ni core and the surface NiO layers of the nanocrystalline Ni.

In summary, we have studied the XAFS measurements for nanocrystalline Ni. The bond lengths in both nanocrystalline and bulk Ni are completely the same, however, the ordering factor is manifestly different. The calculated coordination number of nanocrystalline

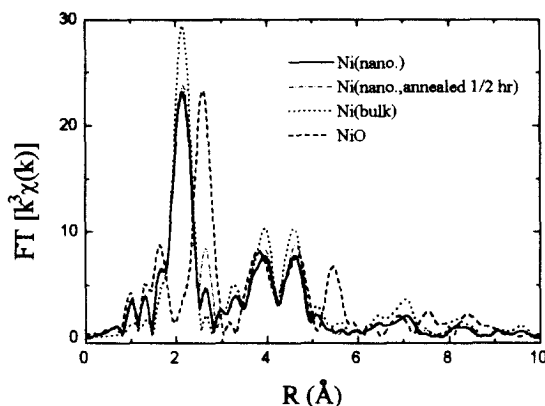


Fig. 4 The Fourier transform of the Ni K-edge EXAFS spectra of same samples in Fig. 2.

Ni is smaller than that of bulk Ni. The surface oxidation behavior is clearly observed in nanocrystalline Ni system, this can be an explanation for the magnetic exchange anisotropy effect which occurs only in the nanocrystalline Ni system.

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