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X-RAY ABSORPTION STUDY IN NANOCRYSTALLINE Fe, Co, Ni AND Cu METALLIC POWDERS

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Abstract *- The X-ray absorption was investigated for nanocrystalline, bulk, and oxides of Fe, Co, Ni, and Cu. From the k edge spectrum measurements, we have found that the band lengths in both nanocrystalline and bulk metallic powders we studied are roughly the same. However, the coordination number in nanocrystalline samples for Fe and Co is 8.6 and 7.4 respectively, which is a little bit larger than that of bulk samples; and it is 11.7 and 11.2 for Ni and Cu, which is a little bit smaller than that of bulk samples. Difference between their crystal structure is used to explain our experimental results. The mean-square disorder factor of nanocrystalline samples is always larger than that of the bulk samples. This indicates that both ordered and disordered crystalline phases may exist in nanocrystalline metallic powders.* ***©1999 Acta Metallurgica Inc.***

INTRODUCTION

Nanocrystalline (NC) materials are single- or poly- crystalline materials with grain sizes roughly below 100 nm. This means NC materials contain a higher volume percentage of the grain or interphase boundaries. It is expected that the structure of grain boundaries plays an important role in determining and controlling the physical properties of NC materials. 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 NC materials. In recent years, the study of XAFS spectra of nanocrystalline metallic materials have been gradually increased [1-7]. In the present study, the k-edge spectra is employed to investigated the local environment surrounding of the NC metallic atoms in Fe, Co, Ni and Cu.

EXPERIMENTAL

The nanocrystalline Fe, Co, Ni, and Cu samples were prepared from commercially available high purity fine particles with particle sizes of about 20 nm for Fe, Co, and Ni, and about 50 nm for Cu, 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 k-edge absorption spectra through layers of powders spread on Scotch tapes. A high-order multiple-scattering approach method [8-10] was used for the calculation of XAFS spectra.

RESULTS AND DISCUSSION

The k-edge XANES spectra for NC Fe, Cu, Ni and Co with their oxides and bulk materials are shown in Figs. 1(a) to 1(d), respectively. All the materials were prepared in powder forms. There are three oxides for Fe (i.e. FeO, Fe_3O_4 and Fe_2O_3), two oxides for Cu (i.e. Cu_2O and CuO), one oxide for Ni (NiO), and two oxides for Co (i.e. CoO and Co_3O_4). The energy range studied is from 7100 to 7180 eV for Fe system, from 8970 to 9010 eV for Cu system, from 8320 to 8360 eV for Ni system, and from 7700 to 7760 eV for Co system.

In general, the curves for nanocrystalline powders are located between the curves of bulk material and oxides. The Fourier transform of the k-edge EXAFS spectra (k^3 - weighted) for all the samples were used for calculation of the XAFS spectra. The calculated coordination number of nanocrystalline Fe and Co is 8.6 and 7.4, respectively, which is a little bit larger than that of bulk samples; and it is 11.7 and 11.2 for Ni and Cu, which is a little bit smaller than that of bulk samples. This is explained due to their different crystal structure. We know that both Ni and Cu are F.C.C. structure with a theoretical packing fraction of 0.740, and Fe is B.C.C. structure, and Co is H.C.P. structure both with a smaller theoretical packing fraction than that of F.C.C. structure. The order factor is variable which is dependent on the historical conditions and the annealing condition etc. of the samples. As an example, for annealed NC Ni samples, a quite large peak near 2.6 Å (Ni-O bond) for nanocrystalline Ni was observed [11], this tells us that the surface oxidation is manifest. This was confirmed by the magnetic exchange anisotropy effect studies between the Ni core and the surface NiO layers of the nanocrystalline Ni. For electronic configuration, also for example, considering the nanocrystalline Ni samples after annealing between 300 and 900 °C, their ordering factors and coordination numbers slowly approach the bulk value: however, according to their absorption curves, the electronic configuration remains the same.

The mean-square disorder factor of nanocrystalline samples is always larger than that of the bulk samples. This means that the ordering factor is significantly reduced in nanocrystalline materials. For example, the mean square disorder factor for nanocrystalline Fe, Cu, and Co samples is 0.0064±0.0008, 0.0083±0.0005, and 0.0117±0.0025, respectively; they are slightly larger than the values of 0.0044±0.0003, 0.0078±0.0004, and 0.0068±0.0005 for bulk Fe, Cu, and Co, respectively.

EXAFS spectra contain important information on their near neighbor configurations. Changes in the radial distribution functions around the atoms studied are reflected in the Fourier transform. As an example, the Fourier transform of the k-edge EXAFS spectra (k^3 - weighted) of nanocrystalline and bulk Co and Cu samples is plotted in Figs. 2(a) and 2(b), respectively. It shows that the bond lengths in both nanocrystalline and bulk samples are roughly the same. The mean-square disorder factor about the average distance can be calculated from these curves, and it shows that the mean-square disorder factor of nanocrystalline samples is always larger than that of the bulk samples.

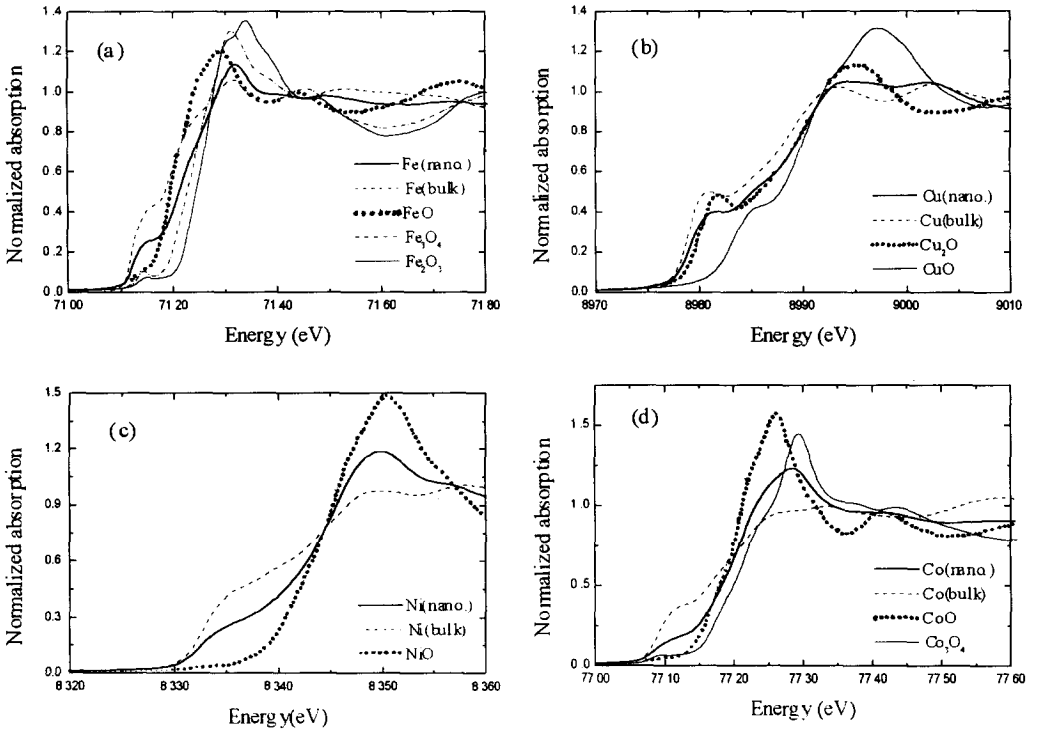

Figure 1 Normalized absorption spectra of NC Fe (Fig. 1a), Cu (Fig. 1b), Ni (Fig. 1c), and Co (Fig. 1d) compared with their oxides and bulk materials.

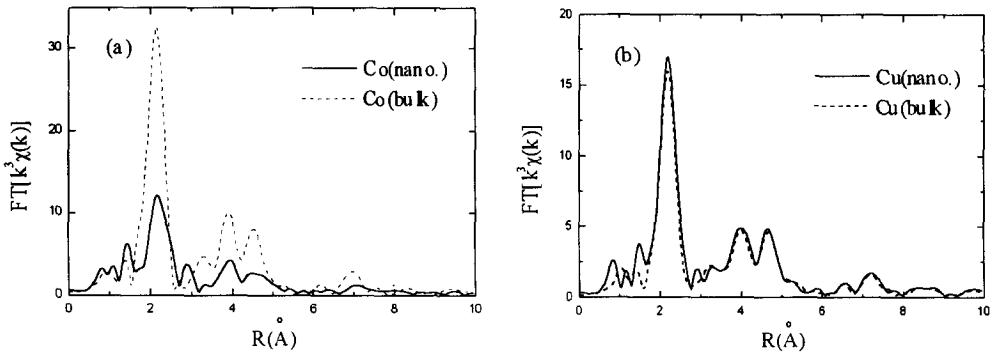

Figure 2 The Fourier transform of the k-edge EXAFS spectra of nanocrystalline and bulk (a) Co and (b) Cu samples.

CONCLUSION

In conclusion, our measurements of the k-edge spectrum of nanocrystalline, bulk, and oxides for Fe, Cu, Ni, and Co show that the bond lengths in both nanocrystalline and bulk metallic powders we studied are roughly the same. However, the coordination number in nanocrystalline samples for Fe and Co is 8.6 and 7.4, respectively, which is a little bit larger than that of bulk samples; and it is 11.7 and 11.2 for Ni and Cu, which is a little bit smaller than that of bulk samples. Difference between their crystal structure is used to explain our experimental results. The mean-square disorder factor of nanocrystalline samples is always larger than that of the bulk samples. This indicates that both ordered and disordered crystalline phases may exist in nanocrystalline metallic powders.

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