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# STRUCTURAL AND MAGNETIC PROPERTIES OF CARBONYL Fe-Ni NANOMETER PARTICLES

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***Abstract*** — *The phases, size, shape, aggregation pattern and chemical composition of carbonyl Fe-Ni ultrafine particles prepared by thermal decomposition of the mixture of* $Fe(CO)_5$ *and* $M(CO)_4$ *were investigated by X-ray diffraction and electron microscopy. It was found that the main phase was* $\gamma$*-(Fe-Ni), including a small amount of* $Fe_3O_4$*. The particle size was about 10 nm and the particles formed a fractal aggregation pattern whose dimension was 1.64. The composition varied from particle to particle, showing an average value of* $Fe_{44}Ni_{56}$*. The magnetic properties of the particles were examined with a vibrating sample magnetometer. © 1997 Acta Metallurgica Inc.*

## INTRODUCTION

Ultrafine magnetic particles (in the nanometer range), showing very interesting properties, have attracted much attention recently; while Fe-Ni alloys have been of special scientific and technical interest because of their high permeability and low coercivity as well as freedom from oxidation. Hence, it is interesting to study the properties of ultrafine Fe-Ni particles.

Different methods can be used to obtain particles in the nanometer range. Among these, chemical reduction and vacuum deposition are the most used ones. As far as Fe-Ni particles are concerned, Kajiwara *et al.* (1) prepared them by the hydrogen plasma-metal reaction method and Ying-Hui Zhou *et al.* (2) prepared them by levitation melting in liquid nitrogen.

Thermal decomposition of metallic carbonyl compound, one of the methods of powder metallurgy, is an efficient way of producing some ultrafine particles, such as Fe (sometimes called carbonyl iron powder), Ni, Co, even Cr, W and Mo (3), and especially efficient to produce iron and nickel particles (4). Furthermore, by the decomposition of the mixture of metal carbonyls, particles of some alloys, such as Fe-Ni, Fe-Co, Fe-Mo and Ni-Mo can be produced, too.

In this paper, ultrafine Fe-Ni particles formed by the thermal decomposition of a mixture of liquid iron pentacarbonyl and nickel quadracarbonyl were studied. The formation of the carbonyl Fe-Ni ultrafine particles could be described by the following reactions:

$$Fe(CO)_5 + Ni(CO)_4 \xrightarrow{\Delta} (Fe - Ni) + 9CO$$

First, liquid iron carbonyl $Fe(CO)_5$ and nickel carbonyl $Ni(CO)_4$ (raw materials) were made. $Fe(CO)_5$ can be prepared by passing carbon monoxide over sponge iron at temperatures in the range of 473K to 493K under a pressure of 70-200 atmospheres; $Ni(CO)_4$ can be prepared in a similar way (4). The boiling points of $Fe(CO)_5$ and $Ni(CO)_4$ were about 376K and 316K, respectively. Then $Fe(CO)_5$ and $Ni(CO)_5$ were mixed together in a certain proportion. Finally, the liquid mixture is decomposed into fine particles in the gas phase at a certain temperature and atmospheric pressure in the reaction vessel. The particle size can be controlled by varying the decomposition temperature and liquid mixture flow rate. Generally, the higher the decomposition temperature, the smaller the particles. In order to further decrease the particle size, some catalysts (for example, a small amount of ammonia) can be used. Though the composition of the particles prepared in this way is inhomogenous, which we will see later, it is very easy to prepare them in mass production level, and this makes the method attractive to industry.

## EXPERIMENTAL

X-ray diffraction (XRD) experiments were performed on a Rigaku x-ray diffractometer (Co Kα radiation) to identify the phases of the particles. The particle size, shape and aggregation patterns were studied with a JEOL-2000FX analytical transmission electron microscope (TEM) and a JEOL-2000EXII high resolution electron microscope (HREM), both operating at 200KV. Selected area diffraction (SAD) patterns from the particles were obtained with the analytical TEM. The chemical composition of the particles was determined by electron energy dispersive spectroscopy (EDS) using a TN5500 X-ray analyzer attached to the analytical TEM. The intensities of Fe-K and Ni-K lines were used for the compositional analysis. The magnetic properties were measured with a vibrating sample magnetometer (VSM) at room temperature.

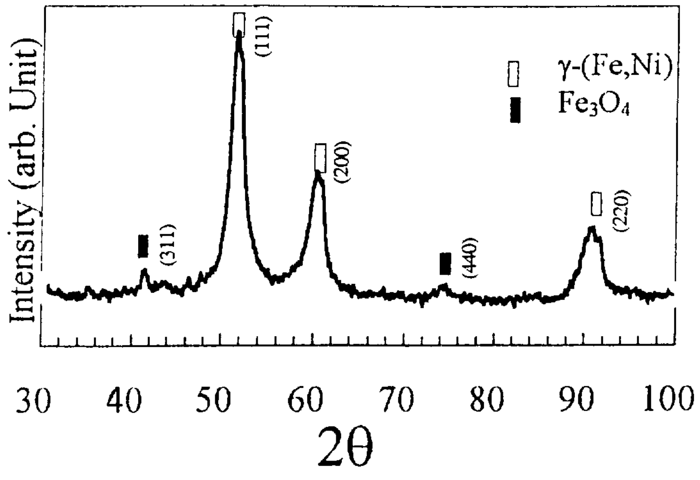

Figure 1. XRD pattern of the carbonyl Fe-Ni particles.

## RESULTS AND DISCUSSION

Figure 1 shows an XRD profile of the Fe-Ni alloy particles. Obviously, the sample mainly contains the γ-(Fe-Ni) phase, but small diffraction peaks of $Fe_3O_4$ phase are also discernible. The intensity of the peaks of $Fe_3O_4$ are very small, indicating there is only a small amount of $Fe_3O_4$. It can also be seen that the diffraction peaks are very broad, which is characteristic of ultrafine particles, suggesting that the size of the particles is very small.

A set of TEM bright-field images for the particles obtained with the analytical TEM are given in Figure 2. As shown in Figure 2A, the particles formed chain-like aggregates, which were a typical fractal pattern, with a fractal dimension of 1.64 measured with box-counting methods. This value is smaller than that of the nonmagnetic particles which is typically 1.75~1.85, suggesting the existence of dipole-dipole interaction among the carbonyl Fe-Ni particles or even exchange interaction between neighboring particles (5). At first glance, one may think the particle size is 40-50 nm from Figure 2A, but this is not the case. Figure 2B are higher magnification micrographs of the particle-formed-chains; the image in the frame is a local magnified image of the area marked by the arrow, and Moiré fringes can be seen in this image, which indicate overlapping of the particles. As shown in these figures, the average size of the ultrafine Fe-Ni alloy particles was about 10 nm. These particles first formed compact (nonfractal) chains with a diameter of about 40-50 nm, and then these compact chains formed the fractal pattern. Figure 2C shows a selected area diffraction (SAD) pattern of the particles. In this SAD pattern only rings of fcc γ-(Fe,Ni) alloy can be seen; maybe the rings of $Fe_3O_4$ are too weak to be seen.

However, under HREM, we clearly found several $Fe_3O_4$ particles, as shown in Figure 3. As can be seen, there is an obvious twin boundary in this $Fe_3O_4$ particle. Figure 4 shows the particles of γ-(Fe,Ni). It is seen that the γ-(Fe,Ni) particles are not spherical. No crystal defect such as twin boundary or dislocations was found in these γ-(Fe,Ni) particles.

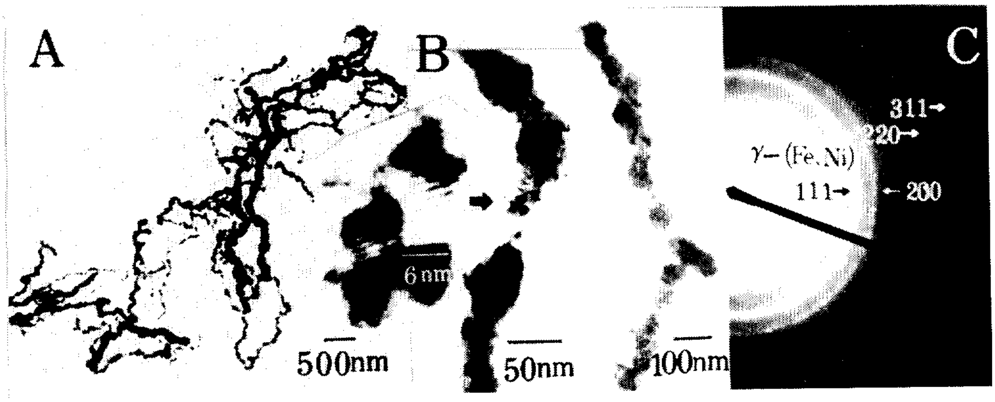

Figure 2. Images (A), (B) and diffraction pattern (C) of carbonyl Fe-Ni ultrafine particles.

Figure 3. High resolution electron microscopy image of an $Fe_3O_4$ particle.

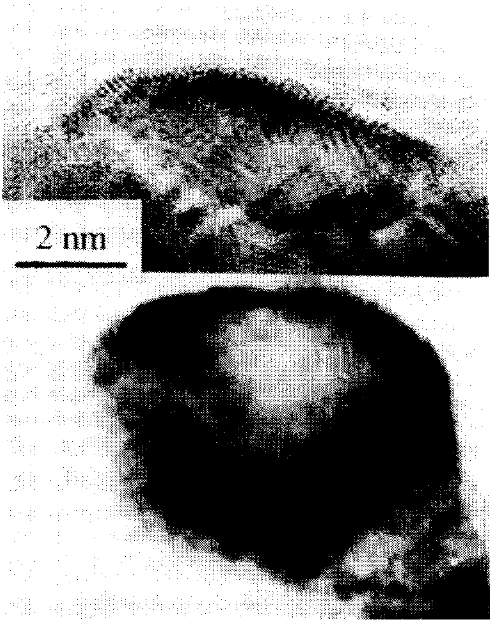

Figure 4. High resolution electron microscopy images of two carbonyl Fe-Ni particles.

EDS indicated that the Fe/Ni ratio varied from particle to particle, as shown in Figure 5, in some cases Fe rich, in some cases Ni rich and in some cases roughly equal amounts. The highest Ni content of the particles detected was about 86 at.%, while several particles showed only Fe x-ray peak, indicating there was no Ni in these particles. The average content of Fe was about 44 at.% and Ni 56 at.%. Note in Figure 5 that the X-ray peak from the Mo specimen grid is also observed. It was reported that the composition of the ultrafine Fe-Ni particles prepared by vacuum deposition is homogeneous, so it may be the method we used here that led to the inhomogeneity in composition of the carbonyl Fe-M particles; and other methods that involve chemical decomposition, for example solgel, may also have this problem, which needs further experimental support.

We measured the composition of more than 200 particles. Figure 6 shows the chemical composition distribution of the particles. It is seen that most particles (about 91%) are in the range of 40-70 at.% Ni, and about 46% of the particles are in the 55-65 at.% Ni range. Two particles are in the range of 90-100 at.% Fe, which may be $Fe_3O_4$ particles as those detected with HREM because the EDS detector we used here was unable to detect the x-ray signal of light elements including oxygen. A small amount of Ni was detected in these particles, which may be because the size of the electron beam was a little bigger than the size of the particles whose composition was examined.

According to the phase diagram of the iron-nickel system (6), above 30 at.% Ni fcc structure is expected. From Figure 6 we know that the Ni-content of almost all the particles is larger than

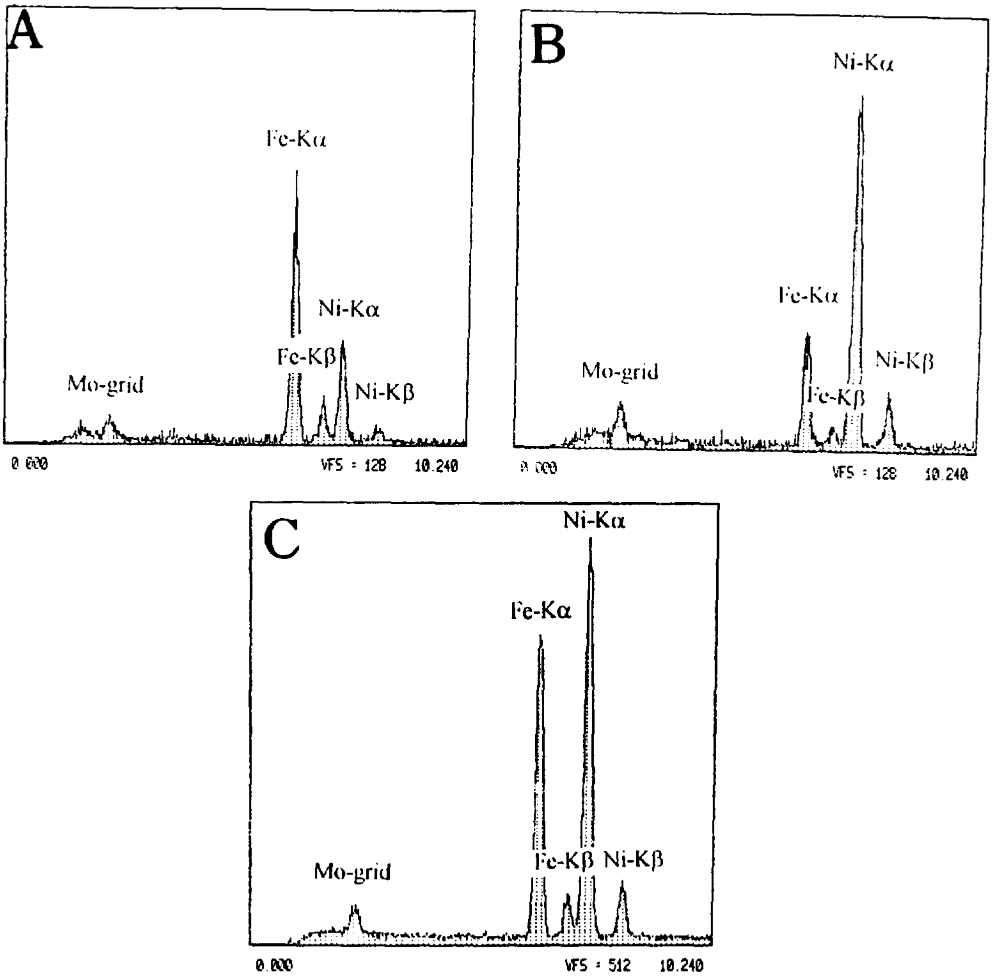

Figure 5. Typical EDS spectra of the carbonyl Fe-M particles, (A): Fe-rich particle, (B): Ni-rich particle and (C): average value showing an Fe:Ni ratio of 44:56 at.%.

30% at.% Ni; hence the main phase should be of fcc structure, and this was proven by XRD data as shown in Figure 1. It is seen that the EDS data are consistent with the results of XRD and SAD.

Magnetic measurements at room temperature showed that the saturation magnetization (Ms) of the particles was 72.2 emu/g, the coercivity (Hc) was 245.2 Oe which was more than $10^3$ larger than that of the bulk material due to their small particle size. It is well known that the most attractive properties of Fe-Ni alloy is its high initial permeability and high antioxidation. Because the initial permeability is difficult to measure, here we compare the initial magnetization curve of $\gamma$-(Fe,Ni) with that of another sort of ultrafine particle, carbonyl iron particles, which was made in the same way and whose Ms and Hc were 96.6 emu/g and 402.7 Oe, respectively. Figure 7 shows the initial magnetization curves of the two sorts of carbonyl particles while Figure 8 shows the hysteresis loops. From Figure 7 it can be seen that the initial permeability of carbonyl $\gamma$-(Fe,Ni) is higher than

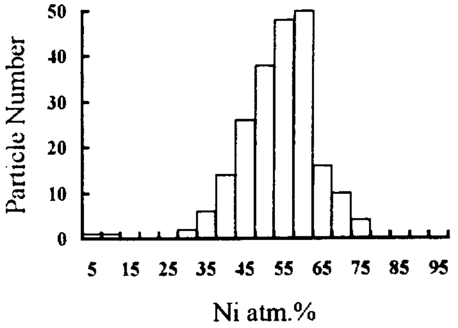

Figure 6. Composition distribution of the carbonyl Fe-Ni particles.

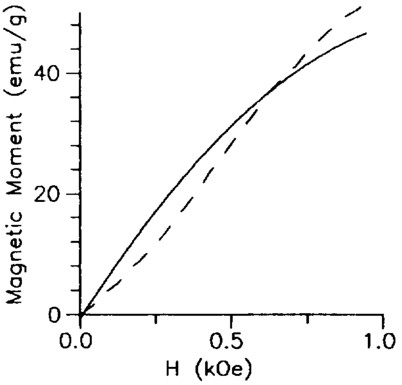

Figure 7. Initial magnetization curves of carbonyl Fe- Ni and Fe particles, solid line: FeNi; dashed line: Fe.

that of the carbonyl iron particles. Figure 8 shows that the hysteresis loop of carbonyl iron particles is flatter than that of γ-(Fe,Ni), suggesting the soft magnetic property of γ-(Fe,Ni) is better than that of the carbonyl particles.

In order to study the antioxidation property of the particles, XRD experiments were performed for the freshly made particles and those that had been stored in air for about two years. It was found that the XRD pattern of the γ-(Fe,Ni) particles that had been stored in air for more than two years was almost the same as that of the freshly made sample, except the latter showed a very

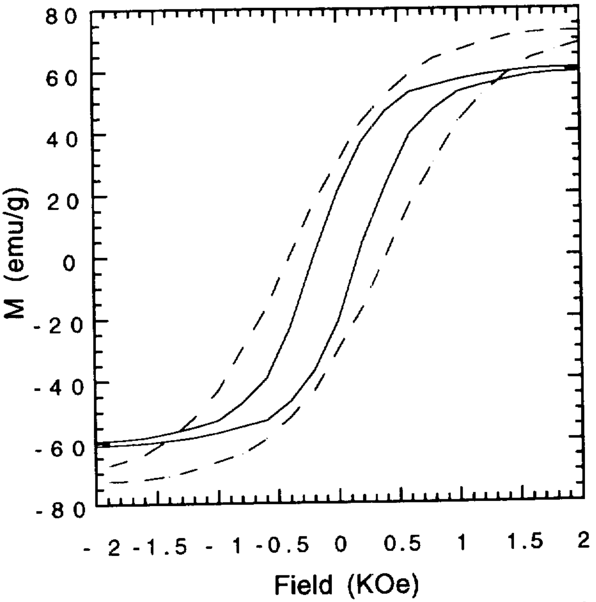

Figure 8. Hysteresis loops of carbonyl Fe- Ni and Fe particles, solid lines: Fe-Ni; dashed lines: Fe.

small amount of α-Fe. We believe that the α-Fe particles in the freshly made particles changed into $Fe_3O_4$ particles due to oxidation, but γ(Fe,Ni) particles showed no change, indicating their antioxidation property is quite good.

## SUMMARY

The main phase of the carbonyl Fe-Ni ultrafine particles was γ(Fe,Ni). The particle size was about 10 nm and the shape was not spherical. The particles formed fractal aggregates whose dimension was 1.64, smaller than that of the nonmagnetic particles due to the dipole-dipole interaction. The particle composition varied from particle to particle, showing an average value of $Fe_{44}Ni_{56}$. From the composition distribution data it was found that about 91% of the particles were in the range of 40~70 at.% Ni.

Magnetic properties of the particles were measured with VSM and it was found that the saturation magnetization and coercivity of the particles were 86.6 emu/g and 198.9 Oe respectively, and with a higher initial permeability than that of carbonyl iron particles.

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