ISSN 0029-3865

CNPq

CBPF – CENTRO BRASILEIRO DE PESQUISAS FÍSICAS

Notas de Física

CBPF-NF-067/93

Mössbauer Spectroscopy, X-Ray Diffraction and Magnetic Measurements of Iron-Nickel Ultrafine Particles

by

R.B. Scorzelli, E.G. da Silva, C. Kaito, Y. Saito, M. MacElfresh and M. Elmassalami

Rio de Janeiro
1993

ISSN 0029-3865

CBPF-NF-067/93

Mössbauer Spectroscopy, X-Ray Diffraction and Magnetic Measurements of Iron-Nickel Ultrafine Particles

by

R.B. Scorzelli[1], *E.G. da Silva*[2], *C. Kaito*[3], *Y. Saito*[3], *M. McElfresh*[4] *and M. Elmassalami*[1*]

[1]Centro Brasileiro de Pesquisas Físicas — CBPF/CNPq
Rua Dr. Xavier Sigaud, 150
22290-180 – Rio de Janeiro, RJ – Brasil

[2]Universidade Federal de Minas Gerais, Departamento de Física
30270 - Minas Gerais, BH – Brasil

[3]Dep. of Physics, Kyoto Technical University, Kyoto 606-Japan

[4]Purdue University, Physics Dep., West Lafayette IN47906-USA

*On leave from Physics Dep. University of Khartoum,
PO Box 321, Khartoum, Sudam

Iron-nickel ultrafine particles with a composition in the Invar region (38% - 50% Ni) were prepared by the gas-evaporation-coalescence technique. The chemical composition was checked by electronprobe microanalysis while X-ray diffraction Rietveld refinement was used to characterize the structure as well as to estimate the particle size. The temperature and field dependence of the magnetization M (B,T) was measured for $0 \leq B \leq 25$ kOe in the temperature range $4.2\ K \leq T \leq 400\ K$. Transmission Mössbauer spectra were taken at room temperature and at liquid helium temperature. The results obtained show that the predominant phase is a disordered Ni-rich alloy.

Key-words: Fe-N; Fine particles; Mössbauer.

I. INTRODUCTION

Previous studies on samples prepared under non-conventional conditions, such as electron-irradiated and meteoritic samples, have shown that iron-nickel alloys in the Invar region (35% - 50% Ni) can undergo phase transformation involving clustering provided that the conditions favour atomic diffusion /1/.

Experimental investigations of phase equilibria in the Fe-Ni system are strongly hampered, especially at low temperatures (below 500° C), due to the slow diffusion rates of the metallic atoms. Therefore, it is very difficult to observe any segregation effects on samples prepared through conventional, although long, heat treatments. An alternative method of accelerating the approach to equilibrium in some alloys is to prepare them in the form of fine particles, usually by thermal decomposition of mixed salt /2/.

The aim of this work was to prepare Fe-Ni ultrafine particles by a process in which it may be possible to induce a phase transformation in this system. For this purpose, ultrafine particles of Fe-Ni in the Invar composition range were produced by the gas evaporation technique, in which a solid material is heated in an inert gas atmosphere /3/. The vapour of the material is subsequently cooled and condensed in the gas atmosphere, resulting in a smoke which resembles that of a candle.

In this paper we report on the results obtained by electronprobe microanalysis (EPMA), X-ray diffraction (XRD), magnetization and Mössbauer spectroscopy measurements of these ultrafine particles of Fe-Ni.

II. EXPERIMENTAL

The Fe-Ni particles were synthesized from the powders of Fe and Ni in vapour and evaporated in Ar gas pressure at 13 kPa. In order to collect a significant amount of particles for Mössbauer absorbers, a special method of collecting ultrafine particles by gas flow has been used /4/.

The EPMA was done using clumps of powder embedded in epoxy that was polished away to expose the material. Calibration was made on samples of pure Ni and pure Fe. Clumps containing many very fine single grains were analyzed together. Total weight concentration is less than 100% for Ni plus Fe due to epoxy and polishing material that was embedded between grains within the clumps; this lowers the accuracy to about ±0.5 at. %.

The crystal structure was determined by refinement with the Rietveld method applied to X-ray diffraction pattern obtained in a monochromatized Cu-Kα_1 powder diffractometer with Bragg-Brentano focalization geometry operating in a step by step mode.

Magnetization measurements were performed using a Quantum Design Squid-based magnetometer. A 5.0 cm scan length was used and temperatures were stabilized to better than ±0.05 K prior to measurement. The temperature and field dependence of the magnetization M (B,T) was measured for $0 \leq B \leq 25$ kOe between $4.2\ K \leq T \leq 400\ K$.

Absorbers for Mössbauer spectroscopy measurements were prepared by pressing the ultrafine particles in a plexiglass sample holder. The spectra were recorded at RT and 4.2 K with a ^{57}Co/Rh source in a conventional spectrometer.

III. RESULTS AND DISCUSSION

The results of EPMA showed a composition that ranged from (38%Ni - 62%Fe) to (50%Ni - 50%Fe) in atomic concentration. The mean composition is (44%Ni - 56%Fe).

The predominant crystalline phase indicated by the XRD pattern (fig. 1) is an fcc Fe-Ni alloy (Ni-rich taenite), space group Fm3m, and lattice parameter ao=3.5819±0.001Å. The particle size, which was estimated from the linewidth of the (111) reflexion (2θ = 43.74° for $CuK\alpha_1$ radiation) using the Scherrer equation, was found to be 165 ± 15Å.

As can be clearly seen in fig. 2, for low field, the magnetization rises very steeply and saturation is obtained at relatively low fields as expected for a ferromagnet with low coercivity. Moreover, since the Curie-temperature is high, the magnetization is found to change very little with temperature for T < 350° C (insert). This is in agreement with the Mössbauer results where the hyperfine field is found to vary ~ 10% between RT and 4.2 K.

The Mössbauer spectrum at RT showed a distribution of hyperfine fields with a maximum distribution peak H_i=310 kOe (fig. 3a), with asymmetric intensities and very broad lines, typical of Fe-Ni disordered alloys in the composition range 35% - 50% Ni /5/. A small amount of a paramagnetic phase has also been observed. From the 4.2K spectrum (fig. 3b) we can see that this minor phase splitted magnetically with a hyperfine field that may correspond to the presence of iron oxide, probably formed during the collection process and it is not detected by XRD.

Moreover, the Mössbauer results of these ultrafine particles showed that segregation and ordering has not been achieved, since the ordered phase $Fe_{50}Ni_{50}$ (superstructure $L1_0$) has not been detected, in spite of the nearly similar growth conditions as shown in previous papers /6/, wherein very small amounts of sample have been collected for electron microscopy measurements which showed the presence of the ordered superstructure (tetrataenite). However, for this particular phase equilibrium problem, this technique does not allow the detection of segregation of phases with different compositions, due to the crystallographic similarity of the resultant phases. Mössbauer spectroscopy, on the other hand, is the most sensitive technique for distinguishing such phases with different magnetic states, showing clearly the coexistence of Fe-Ni γ-phases with different compositions (a magnetic phase with quadrupole splitting, corresponding to the ordered Fe_{50}-Ni_{50} and a paramagnetic phase due to the Ni-poor taenite with less than 30% Ni).

It is important to mention that the $Fe_{50}Ni_{50}$ ordered phase, tetrataenite, is a magnetic mineral with uniaxial magnetocrystalline anisotropy exhibiting high coercivity independent of the grain size /7/. When tetrataenite is heated to 550° C, it changes into taenite (disordered Ni-rich alloy) of low coercivity /8/. Our magnetization measurements showed a complete different picture. The low coercivity, as shown in fig. 2, is a clear evidence that the dominant phase is the disordered one confirming the absence of tetrataenite phase in our sample. The magnetic behaviour, as shown by the Mössbauer spectroscopy as well as magnetization studies can be explained if we assume these samples to be composed by an aggregate of ferromagnetically-ordered microparticles. Inside each particle, although individual spins are well ordered, a random orientation of magnetic domains reduces the total magnetization to zero. The temperature-dependent as well as the field-dependent magnetization behaviour for this system is well known: the dependence of the local magnetization as a function of temperature is governed by the spin-wave type excitation while the field-dependent magnetization is dictated by the dynamics of the domain walls. This picture is in agreement with disordered (Ni-rich) Fe-Ni alloys in the Invar composition.

It is clear from our results that it is very difficult to keep the temperature distribution conditions during the production of the ordered ultrafine particles. The collection of an amount of ~ 100 mg for Mössbauer absorbers had to be done repeating the gas evaporation experiments several times. For the previous electron microscopy and magnetic measurements /9/ the amount of the collected samples were 0.01mg - 0.4 mg. In the present case a 1000 - 500 times bigger amount were collected, making difficult to maintain the ideal growth conditions. A collection method for this purpose keeping the growth conditions to obtain segregation and ordering is now being planned and the results will be published elsewhere.

Acknowledgments

We are grateful to R.A. Pereira and C.A.C. Perez for XRD analysis.

FIGURE CAPTIONS

Figure 1 - XRD diffraction pattern of Fe-Ni ultrafine particles.

Figure 2 - Field and temperature (insert) dependence of the magnetization .

Figure 3 - Mössbauer spectra of Fe-Ni ultrafine particle at RT and 4.2 K.

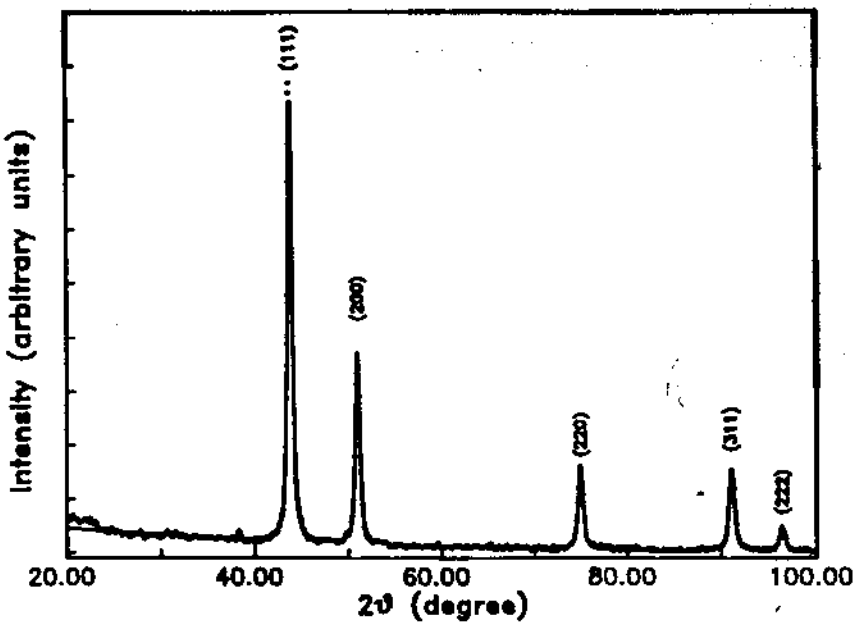
Intensity (arbitrary units)
(111)
(200)
(220)
(311)
(222)
20.00
40.00
60.00
80.00
100.00
2ϑ (degree)

FIG. 1

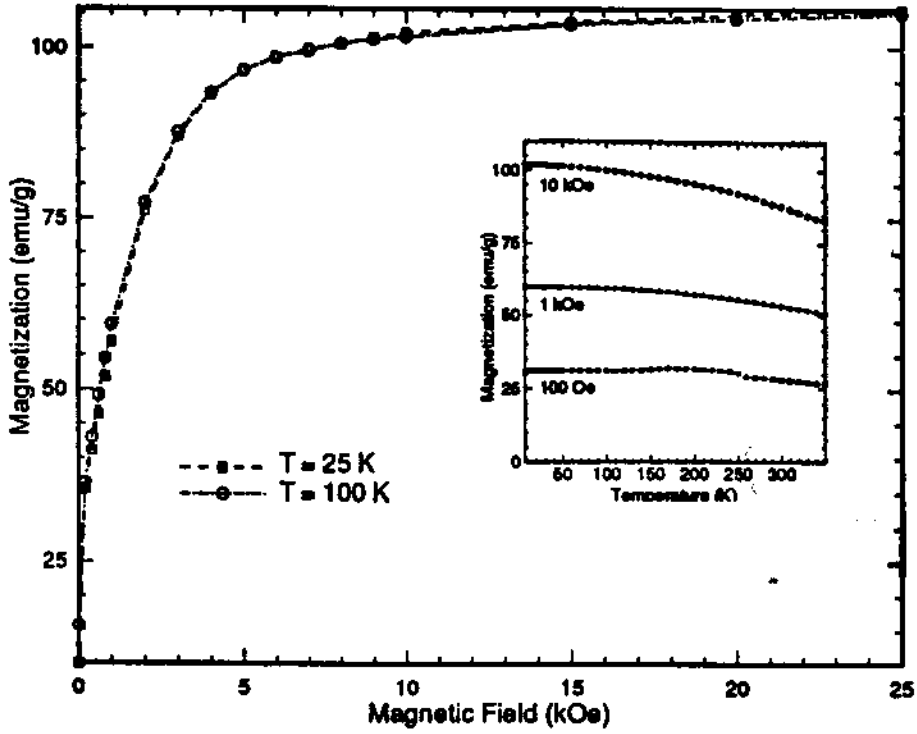
Magnetization (emu/g)
Magnetic Field (kOe)
T = 25 K
T = 100 K
10 kOe
1 kOe
100 Oe
Temperature (K)

FIG. 2

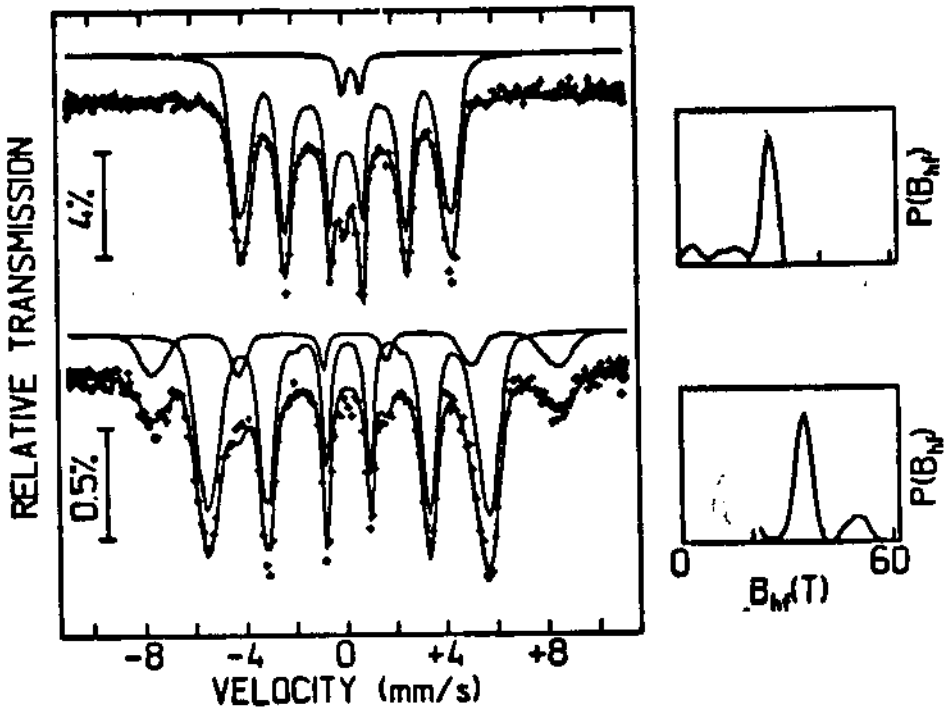
RELATIVE TRANSMISSION
4%
0.5%
-8
-4
0
+4
+8
VELOCITY (mm/s)
P(B_hf)
P(B_hf)
0
60
B_hf(T)

FIG. 3

REFERENCES

/1/ L.Néel, J. Paulevé, R. Pauthenet, J. Laugier and D.J. Dautreppe, J. Appl. Phys. 35 (1964) 873.
/2/ H. Franco and H.R. Rechemberg, J. Phys. F: Met. Phys. 15 (1985) 719.
/3/ K. Kimoto, Y. Kamiya, M. Nunoyama and R. Uyeda, Jpn. J. Appl. Phys. 2 (1963) 702.
/4/ C. Kaito, Y. Yoshimura and Y. Saito, Jpn. J. Appl. Phys. 30 (1991) 559.
/5/ H.R. Rechemberg, PhD Thesis Université Grenoble (1973).
/6/ C. Kaito, Y. Saito and K. Fujita, Jpn. J. Appl. Phys. 28 (1989) L694.
/7/ T. Nagata, C. Kaito, Y. Saito and M. Funaki, Proc. NIPR Symp. on Ant. Meteorites 4 (1991) 404.
/8/ P. Wasilewski, Lunar and Planetary Science XIII, Houston, Lunar Plant. Inst. (1982) 843.
/9/ Minoru Funaki, Proc. NIPR Symp. on Ant. Meteorites 6, (1993) 391.