

ANALYSIS OF THE PHASE STABILITY OF FINE $\text{Fe}_{1-x}\text{Ni}_x$ ALLOY PARTICLES

H. M. Widatallah¹, R. S. Huang, Y. F. Hsia, X. M. Lee
Department of Physics, Nanjing University, Nanjing 210008, China.

J. H. Wang and H. X. Lu
National Laboratory of Solid State Microstructure, Nanjing University, Nanjing 210008, China.

A set of $\text{Fe}_{1-x}\text{Ni}_x$ ($x = 0.10, 0.25, 0.30, 0.35, 0.50, 0.60, 0.75, 0.85$) fine particles prepared by the gas evaporation technique was studied by Mössbauer, XRD and other techniques. The XRD and Mössbauer patterns of the sample with $x=0.10$ ($\text{Fe}_{90}\text{Ni}_{10}$) were found to be exceptionally different, showing an austenite phase stability when the particles are quenched. This phase stability is quite different from that of the corresponding bulk alloy. Using binomial distribution fits of the Mössbauer spectra of the particles in terms of nearest and next nearest neighbour configurations around the Fe atoms, an analysis of this phase stability is given. The changes in the relative intensities of the resulting magnetic sextets are used to determine the increase in martensite following the austenite-martensite transformation process. The stable austenite can, therefore, be determined. This stability may be related to the oxide surface layer and the small number of atoms of these fine particles.

I. INTRODUCTION

The determination of austenite retention in binary Fe-Ni alloys is an interesting theoretical and technological problem. While in bulk Fe-Ni alloys, the austenite phase is usually unstable and transforms upon quenching into martensite, some authors have reported an austenite phase stability in some quenched Fe-Ni small particles[1]. In studying the austenite phase stability in such alloys, techniques such as Mössbauer and X-ray diffraction (XRD) are used. In particular, Mössbauer spectroscopy has proved to be very effective in retained austenite determination [2,3]. This technique allows one to determine the relative fraction of the paramagnetic austenite phase in the presence of the ferromagnetic martensite phase.

In the present paper we report on and analyse an observed austenite phase stability in $\text{Fe}_{90}\text{Ni}_{10}$ fine particles.

II. PREPARATION AND CHARACTERIZATION OF THE SAMPLES

Bulk $\text{Fe}_{1-x}\text{Ni}_x$ ($x = 0.10, 0.25, 0.30, 0.35, 0.50, 0.60, 0.75, 0.85$) alloy samples were prepared by melting appropriate

amounts of high purity Fe and electrodeposited Ni. Fine $\text{Fe}_{1-x}\text{Ni}_x$ particles were, then, produced by evaporating these bulk alloy samples in a nitrogen atmosphere under pressure of 10 Torr. An additional sample of $\text{Fe}_{90}\text{Ni}_{10}$ fine particles was prepared in a similar way under a pressure of 80 Torr.

Throughout the paper, we shall denote both $\text{Fe}_{90}\text{Ni}_{10}$ samples by (1) and (2) referring to their respective preparation pressures, 10 Torr and 80 Torr.

Electron microprobe has shown the composition of the particles to be in agreement with that of the corresponding bulk samples.

Transmission electron microscope (TEM) micrographs have shown most of the particles to be monocrystalline and spherical with a tendency to form chains. The average size of the $\text{Fe}_{1-x}\text{Ni}_x$ particles, prepared under 10 Torr was found to be 20nm, while that of sample (2) was found to be 75nm.

The electron diffraction patterns of the $\text{Fe}_{90}\text{Ni}_{10}$ particles (both samples) have shown bright rings corresponding to an oxide surface layer. For the rest of the particles ($x > 0.10$), the intensities of the rings in the electron diffraction patterns are found to be very much weaker.

Fig.1 shows the XRD patterns of the $\text{Fe}_{1-x}\text{Ni}_x$ particles. In consistency with the electron diffraction

¹On leave from Khartoum University, P.O.Box 321, Khartoum, Sudan.

results, one can easily observe clear peaks in the XRD pattern of the $Fe_{90}Ni_{10}$ particles that correspond to an oxide surface layer, which do not exist in the patterns of the other particles ($x > 0.10$). This suggests that the oxidation process gets difficult as x increases.

III. MÖSSBAUER MEASUREMENTS

Mössbauer measurements were performed on the fine $Fe_{1-x}Ni_x$ particles, both at 295K and 80K, using a source of $^{57}Co/Pd$ with a nominal activity of 20 mCi. The isomer shifts are given relative to α -Fe. The Mössbauer spectra of the $Fe_{1-x}Ni_x$ particles at 295K and 80K are shown in Fig. 2 and Fig. 3 respectively. A detailed study of these spectra is given elsewhere[4].

What is of interest in this paper is that only for the $Fe_{90}Ni_{10}$ fine particles, is the spectrum, both at 295K and 80K, composed of a clear central paramagnetic singlet flanked by a broadened magnetic sextet. Combining this with the XRD pattern of Fig. 1, one concludes that these

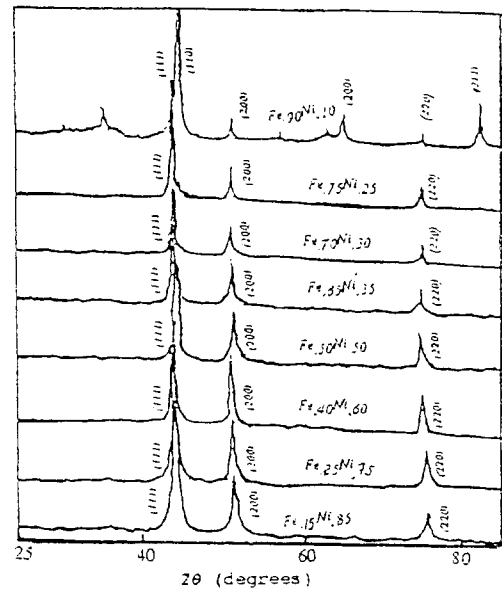


Fig. 1. The XRD Patterns of the $Fe_{1-x}Ni_x$ Fine Particles

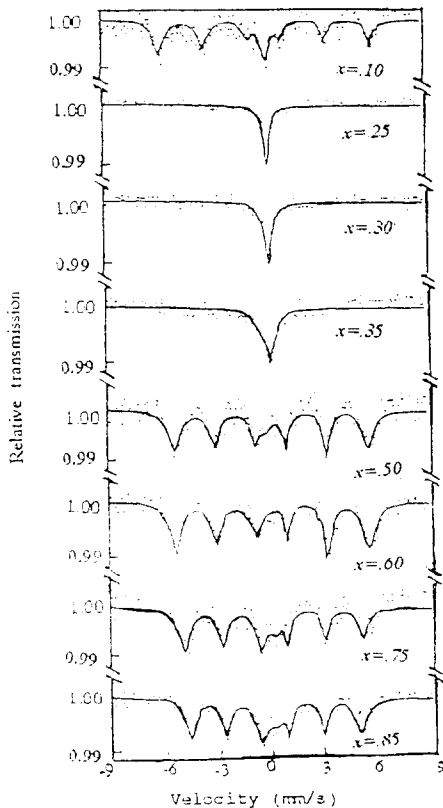


Fig. 2. The Mössbauer Spectra of $Fe_{1-x}Ni_x$ Fine Particles at 295K.

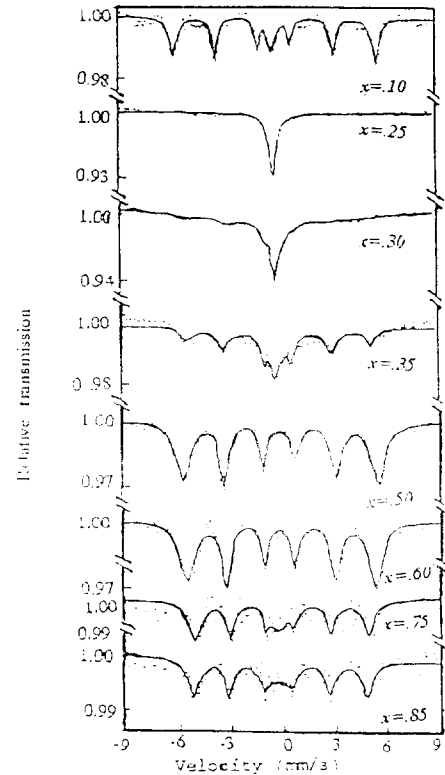


Fig. 3. The Mössbauer spectra of the $Fe_{1-x}Ni_x$ Particles at 80K

particles are two-phased. The Mössbauer central singlet corresponds to an f.c.c. phase (austenite), while the sextet corresponds to a b.c.c. phase (martensite).

The persistence of both phases at 80K, shows an austenite stability in these particles at this low temperature. The spectra of the other particles do not reflect similar phase stability. In the remaining part of this study, a hyperfine field analysis of the phase stability in the Fe₉₀Ni₁₀ fine particles, based on their Mössbauer spectra at 295K and 80K, will be given.

IV. ANALYSIS OF THE PHASE STABILITY OF THE Fe₉₀Ni₁₀ FINE PARTICLES

A. Theoretical Considerations

Figures 4 and 5 show the Mössbauer spectra of sample (1) and sample (2) at 295K and 80K respectively. The austenite component in all the spectra is fitted with a central singlet. A weak doublet exists in all spectra, whose position is consistent with that expected from the presence of an oxide surface layer. Abe and Schwartz [2] found a similar doublet in studying Fe₇₂Ni₂₈ powders and assigned it FeO. In our case, however, it seems that more investigation is required for an accurate assignment of this doublet.

In order to fit the martensite spectra, one notices that the lines of all the sextets show hyperfine structure within them. One, therefore, assumes that the martensitic part of each spectrum is composed of several hyperfine sextets. A binomial distribution of the Ni atoms in the Fe-b.c.c. structure is assumed, with the Fe atom having *n* and *m* Ni nearest and next nearest neighbours respectively. The different magnetic hyperfine fields resulting from the different atomic configurations superimpose to give the observed broadened sextets. The relative intensities of the different sextets can be calculated from the following double summation[5]:

$$\sum_{n=0}^8 \sum_{m=0}^6 \binom{8}{n} \binom{6}{m} x^{n+m} (1-x)^{14-n-m} \times \frac{1}{1-(E-\alpha n-\beta m)^2}$$

where $\binom{n}{m}$ is the binomial coefficient, *x* is the Ni content, *E* is an independent variable measured in terms of the resonance linewidth, α and β are the shifts in the absorption due to the presence of *n* and *m* Ni nearest and next nearest neighbours respectively. By comparing the calculated relative intensities and the measured ones, the hyperfine fields can be assigned to various configurations.

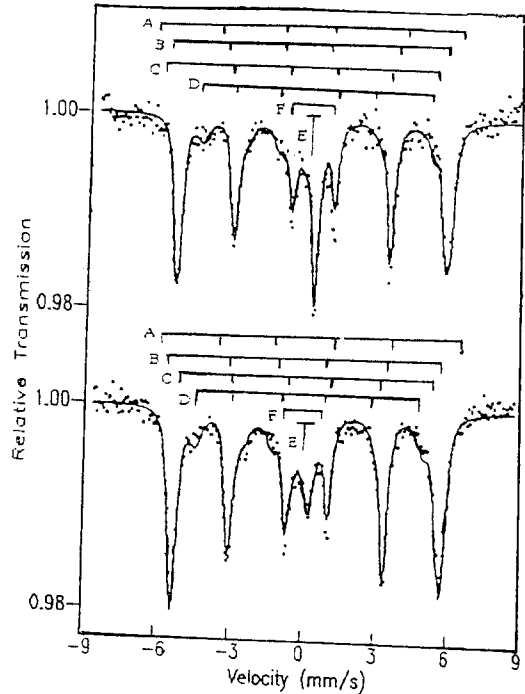


Fig. 4. The Mössbauer Spectra of the Fe₉₀Ni₁₀ Particles at 295K.

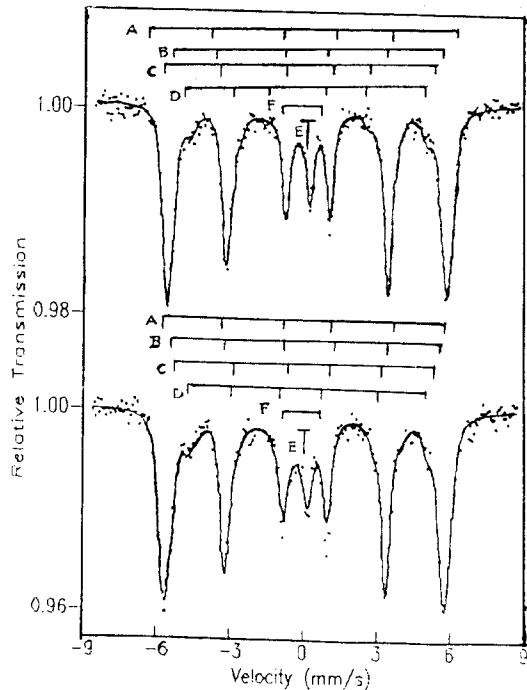


Fig. 5. The Mössbauer Spectra of the Fe₉₀Ni₁₀ Fine Particles at 80K.

B. RESULTS AND DISCUSSION

Tables I and II show the Mössbauer parameters of both samples of the Fe₉₀Ni₁₀ fine particles at 295K and 80K respectively. In line with the above fitting scheme, all the spectra were fitted with four magnetic sextets A, B, C and D assigned to martensite, a central singlet E corresponding to austenite and a weak doublet F for the oxide surface layer.

Table I
The Mössbauer Parameters of the Fe₉₀Ni₁₀ Particles at 295K.

Sample	Subspectra:	A	B	C	D	E	F
(1)	H(T)	35.2(5)	34.3(7)	33.5(4)	29.5(6)		
	IS(mm/s)	0.02(3)	0.02(4)	0.01(3)	-0.07(7)	-0.09(2)	0.91(10)
	Q.S.(mm/s)	0.06(4)	0.02(6)	0.02(4)	-0.19(14)		1.06(17)
	Area %	25.7	20.5	17.5	14.2	14.1	8.0
(2)	H(T)	35.8(5)	34.5(2)	33.3(2)	29.0(4)		
	IS(mm/s)	0.02(5)	0.02(4)	0.03(7)	-0.06(3)	-0.03(2)	1.11(12)
	Q.S.(mm/s)	-0.06(4)	-0.04(6)	0.03(5)	0.01(9)		0.79(16)
	Area %	26.1	22.6	17.9	14.3	11.4	7.7

H=hyperfine field; IS=isomer shift relative to α -Fe; Q.S.=quadrupole splitting

Table II
The Mössbauer Parameters of the Fe₉₀Ni₁₀ Particles at 80K.

Sample	Subspectra:	A	B	C	D	E	F
(1)	H(T)	35.8(3)	34.7(2)	33.4(2)	29.7(4)		
	IS(mm/s)	0.10(2)	0.09(2)	0.06(2)	0.02(5)	-0.01(3)	1.19(25)
	Q.S.(mm/s)	0.02(2)	0.02(2)	0.04(3)	0.04(9)		0.73(20)
	Area %	30.3	22.2	20.4	14.2	8.7	4.2
(2)	H(T)	35.7(3)	34.7(2)	33.4(3)	29.7(4)		
	IS(mm/s)	0.09(2)	0.08(2)	0.07(2)	0.03(2)	-0.02(6)	0.48(22)
	Q.S.(mm/s)	-0.04(3)	0.01(3)	0.03(4)	0.02(6)		0.93(37)
	Area %	28.6	23.6	20.2	14.3	6.3	8.0

H=hyperfine field; IS=isomer shift relative to α -Fe; Q.S.=quadrupole splitting

The values of the measured relative intensities of the four sextets and those calculated from the most probable atomic configurations are given in Table III. Using these values, the sextets A, B, C and D are assigned as follows:

- A results from Fe atoms with Ni-free environments (n=0, m=0);
- B results from Fe atoms with only one Ni nearest neighbour (n=1, m=0);
- C is due to Fe atoms with only one next nearest neighbour

(n=0, m=1);
D is due to Fe atoms with one Ni atom at both nearest and next nearest neighbour configurations.

Table III
Comparison of Measured and Calculated Relative Intensities of the Fe₉₀Ni₁₀ Particles for the Various Configurations (The intensity of the highest field is arbitrarily taken equal 1.0).

Sample + Temperature	Relative Intensities				Remarks
	(n=0, m=0)	(n=1, m=0)	(n=0, m=1)	(n=1, m=1)	
Sample (1) 295K	1.0	0.80	0.68	0.55	measured
	1.0	0.89	0.67	0.59	calculated
Sample (2) 295K	1.0	0.86	0.69	0.55	measured
	1.0	0.89	0.67	0.59	calculated
Sample (1) 80K	1.0	0.73	0.67	0.46	measured
	1.0	0.89	0.67	0.59	calculated
Sample (2) 80K	1.0	0.83	0.71	0.50	measured
	1.0	0.89	0.67	0.59	calculated

As shown in Table I and Table II, the measured relative intensities (relative areas) of the various sextets have slightly increased at 80K with respect to their values at 295K. This indicates that some austenite has transformed to martensite due to the quenching process. However, the relative areas of the austenite singlet for both samples show that a considerable fraction of the austenite remains stable. Following reference [2], we find that due to the cooling process, the austenite portion of sample (1) has decreased by 38% and that of sample (2) by 45%. This is to be contrasted with the total austenite-martensite transformation in bulk Fe₉₀Ni₁₀.

Two reasons seem to account for this phase stability in Fe₉₀Ni₁₀ fine particles. Firstly, we consider the presence of the clear oxide surface layer, discussed before. In a bulk Fe₉₀Ni₁₀ sample, one notes that the area of the oxide surface layer is much smaller than that of the fine particles. The role played by the oxide surface layer in stabilizing austenite in these fine particles may be thought of in a similar way to that of additive elements (such as carbon) used to prevent γ - α transition in Fe-Ni alloys. Secondly, the small size of the particles may, also, be regarded as a possible reason in this context. The austenite-martensite transformation is a phase transition that involves no atomic diffusion, but mere atomic sites adjustment. The small number of atoms, due to this small size may hinder such an adjustment.

IV. CONCLUSION

1. The Mössbauer magnetic subspectra for The Fe₉₀Ni₁₀ fine particles correspond to various lattice configurations.
2. Fe₉₀Ni₁₀ particles prepared by gas evaporation are

found to have better phase stability in comparison to their corresponding bulk alloy, or to other Fe_{1-x}Ni_x fine particles prepared by the same method.

3. The observed phase stability is linked with the oxide surface layer of the particles and to the small number of atoms within the particles as well.

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