Mössbauer study of martensitic transformation and collective magnetic excitations in $Fe_{.9}Ni_{.1}$ fine particles*

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Abstract The austenite to martensite transformation in fine $Fe_{.90}Ni_{.10}$ particles prepared by evaporation is studied by Mössbauer technique. Unlike bulk $Fe_{.9}Ni_{.1}$ which is entirely transformed to martensite, these particles show a remarkable austenite stability upon cooling upto liquid nitrogen temperature. This stability is associated with the oxide surface layer formed on the particles and also with their small size. A hyperfine field approach is employed to analyze the martensitic transformation in the particles. It is also shown that, in contrast with large particles, the temperature variation of the Mössbauer average hyperfine field of the fine particles can be satisfactorily explained in terms of the collective magnetic excitations model.

Keywords Mössbauer effect, Martensite, Austenite, $Fe_{.9}Ni_{.1}$, Collective magnetic excitation model, Hyperfine field

1 Introduction

Studies on martensitic transformation in Fe-Ni particles are generally few[1−3]. Although martensitic nucleation is generally believed to be heterogeneous, the nucleation sites have not yet been certainly identified. In the literature, except the work of Kajiwara *et al*[1,2], the particles used so far in such studies are large (10 ∼ 150μm in diameter). Recenty, we have prepared $Fe_{.9}Ni_{.1}$ fine particles whose volume is about 10^{-9} that studied before. Due to the heterogeneity of the nucleation sites, it seems natural to assume that the probability of having such a site in a particle will decrease as its diameter decreases. Consequently, one anticipates the martensitic transformation and some other properties in the fine particles to be different from their counterparts in the corresponding bulk or in larger particles.

In this paper, we present a Mössbauer study of the $Fe_{.9}Ni_{.1}$ fine particles mentioned above. The martensitic transformation in the fine particles is analyzed and the presence of collective magnetic excitations in the particles is briefly discussed.

2 Samples preparation and characterization

A bulk $Fe_{.9}Ni_{.1}$ alloy was prepared by melting appropriate amounts of high purity Fe with electro-deposited Ni in an induction furnace. Then, 2 samples of fine particles were produced by evaporating this bulk alloy under pressure of 1.3 kPa (sample 1) and 10.7 kPa (sample 2). Electron microprobe analysis has shown the composition of the fine particles to be well close to that of the mother bulk.

Transmission electron microscopy (TEM) micrographs have shown most of the particles to be spherical with a tendency to form chains. The average diameter of the particles in sample (1) is found to be 20 nm, while that of those in sample (2) is found to be 80 nm.

The X-ray diffraction (XRD) patterns of the samples have revealed that they are composed of α-b.c.c. and γ-f.c.c. phases (Fig.1). The lattice constant obtained from the XRD measurements is 0.2897 nm for the b.c.c. phase and 0.3571 nm for the f.c.c. one. Furthermore, the b.c.c. phase was shown by the Mössbauer technique to be ferromagnetic martensite while the f.c.c. one is shown to be non-ferromagnetic austenite. The XRD pattern of the fine par-

*The Project Supported by National Climbing Plan (85-06 NMS special subject)
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Manuscript received date: 1996–03–20

ticles consists of weak broadened oxide peaks originating from microcrystalline oxide surface layer. This is confirmed by the electron diffraction pattern of the particles (Fig.2) which consists of bright rings corresponding to the oxide surface layer. The Mössbauer spectra at 80 K indicate that the magnetic portion of the surface oxidation is very weak. Also, no nitride peaks exist in the XRD patterns of the samples. These features are similar to those reported by us - for fine Fe particles prepared by the same technique - elsewhere[4].

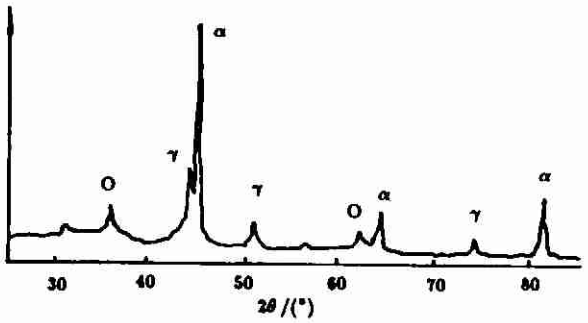

Fig.1 The XRD pattern of the $Fe_{.9}Ni_{.1}$ fine particles
α and γ denote the α-b.c.c. and γ-f.c.c. phases, respectively; O the oxide surface layer

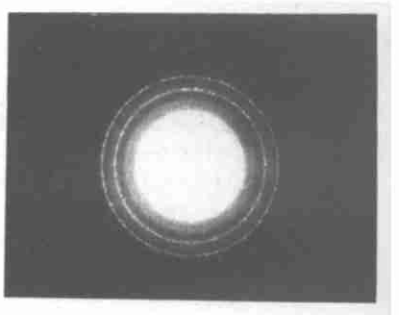

Fig.2 Electron diffraction profile of $Fe_{.9}Ni_{.1}$ fine particles

3 Analysis of phase transformation

In this part we present a hyperfine field analysis of the austenite to martensite transformation in the fine particles. The Mössbauer spectra of the two fine particle samples at 295 K and 80 K are shown in Fig.3.

All the spectra exhibit an overlap of an unsplit central singlet due to austenite and a broadened sextet corresponding to the martensite phase. Although the counting statistics is not of a very high quality, it is adequate for measuring the amounts of both b.c.c. and f.c.c. phases as well as the hyperfine magnetic fields due to the isolated environments of the Ni around the ^{57}Fe nucleus. The austenite component has been fitted with only a singlet. All the spectra consist of a weak central doublet, apparent from the deviation of the "large" relative intensity of the inner-most peaks from the usual 3:2:1 ratio. The position of this doublet is consistent with that expected from a non-magnetically split oxide surface layer. The martensite spectra of both samples show hyperfine structure within other lines, suggesting that each spectrum is composed of several sextets. The intensities of these sextets and other hyperfine parameters can be related to local arrangements within the fine particles. We assume for these Fe-rich particles a b.c.c. lattice structure, with the Fe atom having n first and m second Ni nearest neighbours that are randomly distributed. The different atomic arrangements will then result in different magnetic hyperfine fields that superimpose to produce the observed broadened spectra. The relative intensities $I(x)$ of these fields, which reflect the corresponding configuration shells, are computed from the binomial relation:

$$I(x) = \Sigma_{n=0}^{8}\Sigma_{m=0}^{6}\binom{8}{n}\binom{6}{m}x^{n+m}(1-x)^{14-n-m}$$

where $\binom{8}{n}$ and $\binom{6}{m}$ are binomial coefficients, x the mol fraction of Ni in the alloy. We shall limit ourselves only to configuration shells each populated by not lower than 0.10 of the total number of atoms. It follows from the above relation that when $x = 0.10$, only the first four configurations satisfy this requirement. Consequently, the Mössbauer spectra of the $Fe_{.9}Ni_{.1}$ both at 295 K and 80 K have been fitted with four magnetic sextets (A, B, C and D) corresponding to martensite, an austenite singlet E and a weak oxide doublet F. The relative intensities (areas) of these subspectra and their hyperfine parameters are given in Tables 1 and 2, respectively.

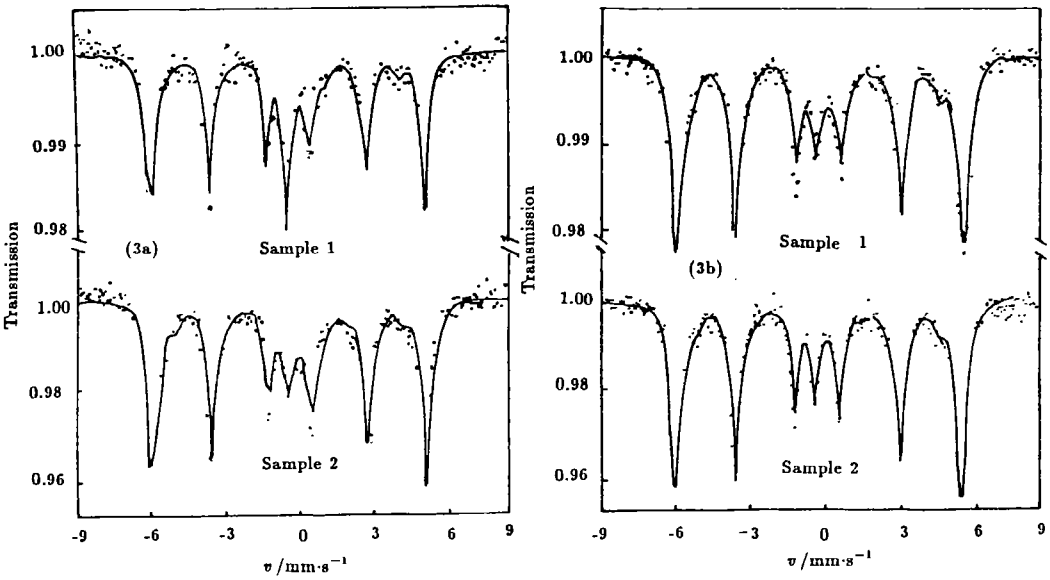

Fig.3 Mössbauer spectra of $Fe_{.9}Ni_{.1}$ fine particles at 295 K (a) and at 80 K (b)

Table 1 The relative intensities of Mössbauer subspectra of $Fe_{.9}Ni_{.1}$ fine particles at 295 K and 80 K

Sample and temperature	Relative intensity /%					
	A	*B*	*C*	*D*	*E*	*F*
Sample (1) at 295 K	26(2)	21(2)	17(2)	14(3)	8(4)	14(2)
Sample (1) at 80 K	30(2)	22(3)	20(2)	14(3)	5(3)	9(3)
Sample (2) at 295 K	29(5)	21(3)	18(2)	14(2)	7(3)	11(2)
Sample (2) at 80 K	28(2)	24(2)	23(2)	11(2)	8(4)	6(3)

Table 2 The Mössbauer parameters of $Fe_{.90}Ni_{.10}$ fine particles at 295 K and 80 K

Sample and temperature	Hyperfine parameters	Spectral components					
		A	*B*	*C*	*D*	*F*	*E*
		($m = n = 0$)	($m = 1, n = 0$)	($m = 1, n = 0$)	($n = m = 1$)		
Sample (1) 295 K	*H*/T	35.2(5)	34.3(7)	33.5(4)	29.5(6)		
	IS/mm·s^{-1}	0.02(3)	0.02(4)	0.01(3)	−0.07(7)	−0.09(2)	0.91(10)
	QS/mm·s^{-1}	0.06(4)	0.02(6)	0.02(4)	−0.19(4)		0.06(17)
Sample (1) 80 K	*H*/T	35.8(3)	34.7(2)	33.4(2)	29.7(4)		
	IS/mm·s^{-1}	0.10(2)	0.09(2)	0.06(2)	0.00(2)	−0.01(3)	1.19(25)
	QS/mm·s^{-1}	0.00(2)	0.03(2)	0.04(3)	0.04(4)		0.73(40)
Sample (2) 295 K	*H*/T	35.8(5)	34.5(2)	33.3(2)	29.0(4)		
	IS/mm·s^{-1}	0.05(2)	0.02(4)	0.03(7)	−0.06(3)	−0.03(2)	1.11(12)
	QS/mm·s^{-1}	0.06(4)	0.04(6)	0.03(5)	0.01(9)		0.79(16)
Sample (2) 80 K	*H*/T	35.7(3)	34.7(2)	33.4(3)	29.7(4)		
	IS/mm·s^{-1}	0.09(2)	0.08(2)	0.06(2)	0.03(2)	−0.02(6)	0.49(22)
	QS/mm·s^{-1}	−0.04(3)	0.01(3)	0.03(4)	0.02(6)		0.93(37)

Notes: *H*=Hyperfine field, IS=Isomer shift relative to α-Fe, QS=Quadrupole splitting

Now, comparing the relative intensities of the martensite sextets, the following assignments can be made: *A* is due to Fe atoms with free Ni environment ($n = m = 0$); similarly, *B* is due to $n = 1$, $m = 0$; *C* due to $n = 0$, $m = 1$; *D* due to $n = 1$, $m = 1$.

Concerning the doublet *F*, we note that Abe and Schwartz[5] had found a similar doublet in the study of $Fe_{.73}Ni_{.27}$ powders, assigned to FeO. In the present case, additional

investigation is required for an accurate assignment of the doublet (note the computed error for this weak doublet).

The fact that the relative intensities of the martensitic sextets at 80 K are higher than those at 295 K indicates that some austenite has been transformed, upon cooling, to martensite. However, the presence of the central singlet E in both spectra at 80 K, shows that a considerable fraction of austenite remains stable at this temperature (see Table 1).

There seem 2 reasons to account for the austenite phase stability in these fine $Fe_{.90}Ni_{.10}$ particles as opposed to their corresponding bulk. First, the fact that the increase in the relative intensities of the magnetic sextets due to cooling is rather weak, indicates some hindrance for atoms to adjust at different lattice sites. This may be associated with the small number of atoms in the particles ($\approx 10^6 \sim 10^7$) which may hamper the adjustment process. Indeed, as seen from Table 1, for the particles with the smaller size (sample 1) the austenite phase is stabler. The other reason in this context may be the oxide surface layer. One notes that the area of the oxide surface layer is much larger for the fine particles than for their corresponding bulk. Therefore, it seems reasonable that the higher phase stability in the particles may relate to their larger oxide surface layer. The role played by this layer in stabilizing austenite in the fine particles may be thought of the same as that played by additive elements used to prevent $\alpha - \gamma$ phase transition in Fe-Ni alloys.

In the preceding analysis, the Mössbauer central singlet was assumed to solely be due to austenite. It is possible, however, that in addition to austenite, some small superparamagnetic particles in the samples contribute partially to this singlet. In this case, the change in the relative area of the central singlet subsequent to cooling will largely be due to the relaxation of these superparamagnetic particles. Accordingly, the presence of the central singlet at 80 K will largely be due to the stable austenite. Also, it may be argued that in the case of fine particles it is not completely valid to assume that the Mössbauer sextets result from hyperfine fields due to different atomic arrangements, since other factors may play role and influence the Mössbauer line shape (e.g. surface effects). It is to be noted, however, that since the relative areas of the ferromagnetic and nonferromagnetic parts reflect the relative amounts of both martensite and austenite, one can obtain a reliable information about the martensitic transformation in the particles using the above fitting procedure for the Mössbauer spectra.

4 Collective magnetic excitations

Table 2 shows that the average hyperfine field for these $Fe_{.9}Ni_{.1}$ fine particles is larger at 80 K than at 295 K. This indicates that, unlike Fe-Ni particles of earlier studies, these fine particles show collective magnetic excitations. The comparisons between these particles and bulk Fe-Ni as well as samples of intermediate crystallite size seem to be needed, and will be published elsewhere[6]. In what follows, we briefly discuss this phenomenon starting from the magnetic hyperfine field at the ^{57}Fe nucleus site given by:

$$H_{\rm hf} = H_{\rm S} + H_{\rm L} - H_{\rm dip} + H_{\rm int}$$

where $H_{\rm S}$ is the Fermi field, $H_{\rm L}$ the orbital field, $H_{\rm dip}$ the dipolar field due to the interaction between the nuclear spin and the electron spin and $H_{\rm int}$ is given by:

$$H_{\rm int} = H_{\rm ext} + H_{\rm dem} + \frac{4}{3}\pi M$$

where $H_{\rm ext}$ is the external field, $H_{\rm dem}$ the demagnetization field and $\frac{4}{3}\pi M$ the Lorentz field. So, $H_{\rm hf}$ can be written:

$$H_{\rm hf} = H_0 + H_{\rm ext} + H_{\rm dem} - H_{\rm dip}$$

where

$$H_0 = H_{\rm S} + H_{\rm L} + \frac{4}{3}\pi M$$

Now, using the collective excitations model[7], we get the average hyperfine field at the site of the ^{57}Fe nucleus:

$$\overline{H}_{\rm hf}(T) = < \cos\theta >_{\rm T} [H'_{\rm hf}(T) + H_{\rm dem}(T) - H_{\rm dip}(T)]$$

where θ is the angle between the magnetization vector and the direction of easy magnetization, T stands for temperature and $< \cos\theta >_T$ denotes a thermal average. If the exchange interaction between the particles is ignored, one gets

$$< \cos\theta >_T = \frac{\int_0^\pi \cos\theta \exp[-E(\theta)/k_B T] \sin\theta \mathrm{d}\theta}{\int_0^\pi \exp[-E(\theta)/k_B T] \sin\theta \mathrm{d}\theta}$$

where k_B is Boltzmann's constant, M the magnetization and $E(\theta)$ the energy of displacing the spin direction through the angle θ given by:

$$E(\theta) = -VM(T)H_{dip}(T)\cos\theta - 2J\Sigma_{i,j}\vec{S}_i \cdot \vec{S}_j$$

where V is the volume of the particles, J an exchange integer, $\vec{S}_i$ and $\vec{S}_j$ the spin values for the interacting pair of atoms i and j.

Using the approximation:

$$< \cos\theta >_T \cong 1 - \frac{k_B T}{VM(T) + 4INJS^2}$$

and assuming that H_{hf}, H_{dem} and $M(T)$ for the fine particles are the same as those of the bulk alloy, the average hyperfine field is got

$$\overline{H}_{hf}(T) = < \cos\theta >_T [H_{hf}(0) + H_{dem} - H_{dip}] \left[1 - AT^{3/2} - BT^{5/2}\right]$$

where A and B are constants.

The values for the average hyperfine field at the site of the ^{57}Fe nucleus obtained from Table 2 are in agreement with the above relation. This, in turn, shows the presence of collective magnetic excitations in the fine particles that fluctuate the magnetization vector in directions close to that of the easy magnetization direction.

5 Conclusion

Fine alloy particles prepared by evaporation possess better austenite stability when compared with their corresponding bulk. By assuming the Mössbauer spectra of these particles originated from various configuration shells around the Fe atom, the martensitic transformation in the particles is analyzed and the amount of stable austenite at 80 K is determined. The austenite stability in the particles is found to be size-dependent. The oxide surface layer and the small size of the particles are regarded as possible reasons for the phase stability. The different values of the average hyperfine field at 80 and 295 K indicate the presence of collective magnetic excitations in the particles — a feature that is missed for the larger particles studied previously.

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