HYPERFINE FIELD DISTRIBUTION IN DISORDERED Fe-Ni-Mo MARAGING ALLOYS SUBMITTED TO AGEING[1]

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The hyperfine field distribution $P(H)$ of quenched b.c.c. disordered Fe-18.3Ni-
3.4Mo and Fe-15.0Ni-5.7Mo alloys has been described as the result of the con-
volution of the atomic distribution given by the multinomial law over the two
first coordination shells and a gaussian function, the variance of which affects the
upper shells. After 72 hour ageing at 450°C two metastable ultra-fine precipi-
tated phases (Fe-Ni)$_3$Mo and ω(Fe-Ni)$_7$Mo$_2$ are revealed. Their composition is
discussed on the basis of the matrix atomic depletion and the weak paramagnetic
contribution observed by Mössbauer spectroscopy in connection with transmission
electron microscopy experiments.

1. Introduction

In crystalline alloys, the atomic composition can be described by the specifications
of the correlations between pair of atoms. X-Ray diffraction with anomalous scattering
experiments can give the information, however, such approach involves complex proce-
dures. Mössbauer spectroscopy applied to iron-based alloys, more easy to implement
might bring a direct description of the alloy evolution, provided that comparison with
other techniques can be held. The aim of this paper is to reach the atom distribution
in ternary b.c.c. Fe$_{1-x-y}$Ni$_x$Mo$_y$ matrix ($x \simeq 0.15$ - 0.18, $y \simeq 0.03$ - 0.05) in order
to explain the microstructures of aged Fe maraging type alloys. The maraging family
consists of a b.c.c. lattice mainly Fe, Ni and/or Co with additional elements leading,

after thermal treatment, to the precipitation of intermetallic compounds responsible for high mechanical properties. The ultra-fine scale of the precipitates (some nm.) appears as the main limitation of the microstructure analysis. The understanding of the matrix transformation occuring during ageing via the hyperfine field distribution $P(H)$ modifications could bring information about the concomitant metastable precipitate formation.

As the Ni concentration implied in this study is not relevant of the low dilution region, we have, first, defined the Fe nucleus perturbations induced by Ni in binary alloys up to the Ni content involved in the ternary system. In a second step, the $P(H)$ of quenched ternary alloys was fitted. This could be considered as the stage preluding the precipitation process.

Afterwards, the aged $Fe_{1-x-y}Ni_xMo_y$ alloys were investigated in correlation with transmission electron microscopy (TEM) observations under the thermal and time duration conditions corresponding to the highest hardness values: 72 hours at 450°C [1].

2. Experimental

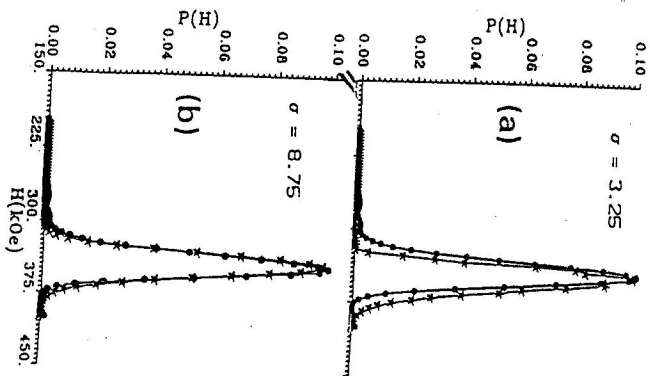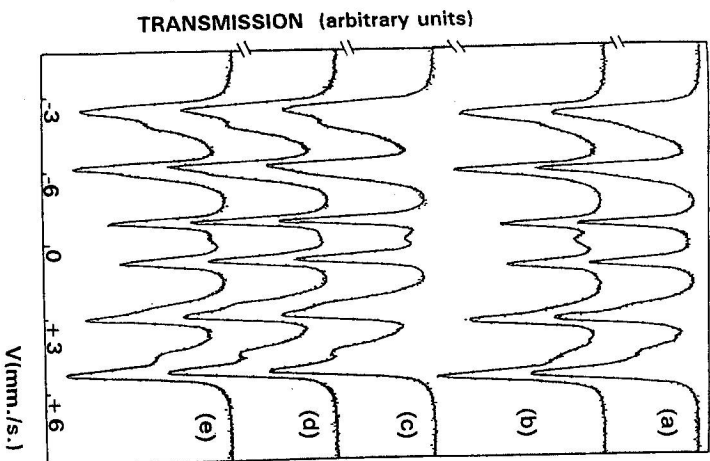The samples were elaborated from high purity powders by sintering process under H_2

Fig. 1. Theoretical * and experimental ● $P(H)$ curves obtained with: (a) $\Delta H_{Ni,1}=9.4$ kOe and $\Delta H_{Ni,2} = 7$ kOe - (b) $\Delta H_{Ni,1} = 6.1\pm0.5$ kOe and $\Delta H_{Ni,2} = 4.4\pm0.5$ kOe for $Fe_{1-x}-Ni_x$ $x=0.178$

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Fig. 2. Mössbauer spectra at room temperature for
- Fe-18.3Ni-3.4Mo a) quenched at the rate of 300°/h - b) aged 72hours at 450°C
- Fe-15.0Ni-5.7Mo c) quenched at the rate of 300°/h - d) aged at 450°C one hour - e) aged 72hours at 450°C

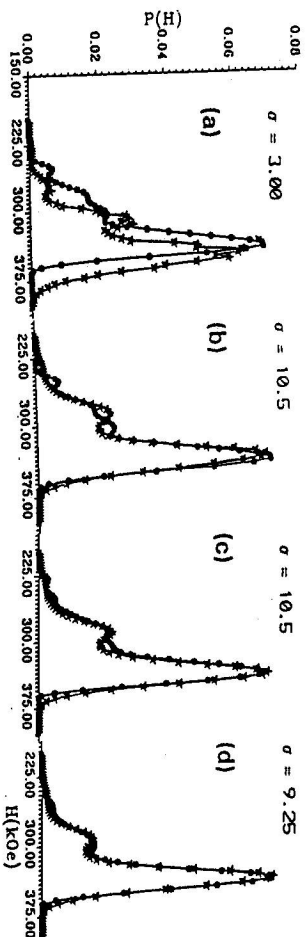
Fig. 3. Theoretical * and experimental ● hyperfine field distribution $P(H)$ for Fe-18.3Ni-3.4Mo : - (a) ΔH_M, given in ref.[6]; (b), (c), (d) $\Delta H_{Ni,1}=5.3\pm0.7$kOe, $\Delta H_{Ni,2} = 3.3\pm0.7$kOe, $\Delta H_{Mo,1} = -49.5$kOe, $\Delta H_{Mo,2} = -24.7$kOe - (b) cooling rate of 80°/s - (c) cooling rate of 300°/h - (d) sample aged 72h at 450°C.

at 1200°C or 1400°C for respectively the binary and ternary alloys. After co-rolling and annealing they were quenched at the rate of 80°/s and 300°/h in order to test the cooling rate influence upon the segregation of the Mo, and, subsequently aged. The atomic

{110}$_M$ || (010)

<1$\bar{1}$1>$_M$ || [100] (Fe,Ni)$_3$Mo

{111}$_M$ || (0001)$_\omega$
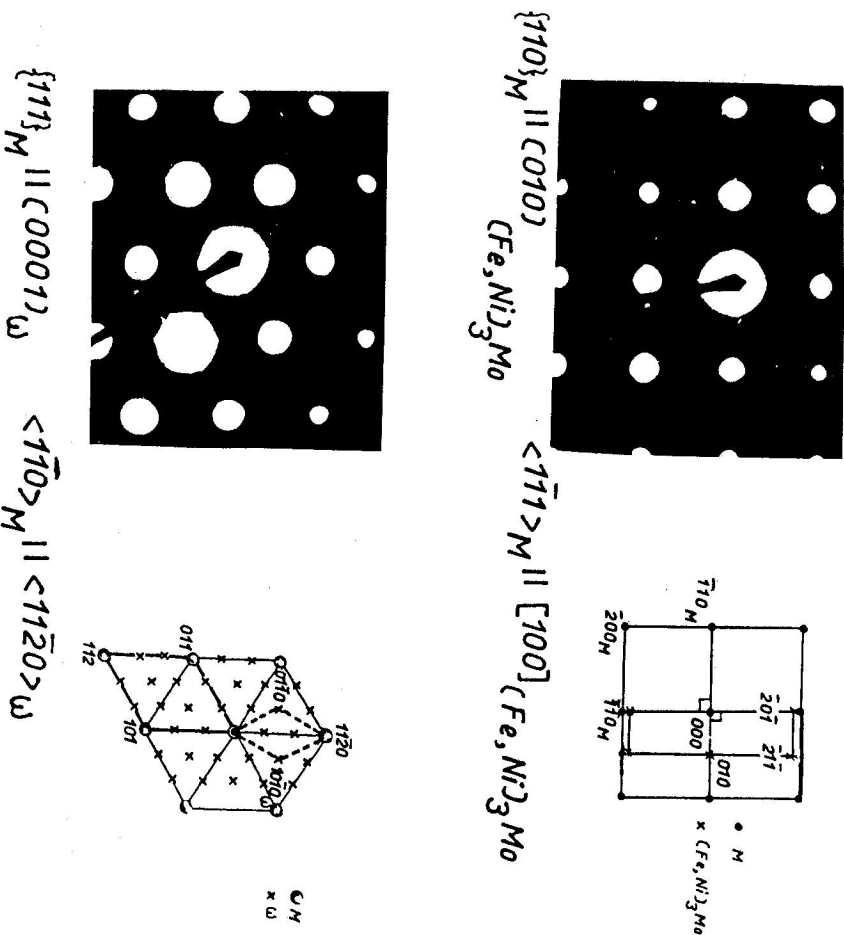
<1$\bar{1}$0>$_M$ || <11$\bar{2}$0>$_\omega$

Fig. 4. Diffraction pattern of the precipitates after 72 hour ageing at 450°C
- (a) (Fe-Ni)$_3$Mo on <001> zone axis of the b.c.c. martensitic matrix lines
- (b) ω phase on <111> zone axis of the b.c.c. martensitic matrix.

composition, controlled by X-Ray microprobe, is given with an accuracy of ±0.2. The Mössbauer spectra were classically collected at room temperature and the data analyzed by two consecutive procedures. They were, first, least square fitted assuming lorentzian lines [2]. The final solution provided the isomer shift (δ) and quadrupole splitting (ϵ) value correlations as a function of the magnetic hyperfine field (H) required for the extraction of the experimental hyperfine field distribution $P(H)_{ex}$ with the method given by Le Caer et al. [3].

The calculated hyperfine field distribution $P(H)_c$, was obtained assuming the in-dependence of the substituting atoms between the two first neighboring shells in the model of a statistical distribution of atoms, the probability P_α for a configuration α

being given by the binomial law extended to ternary alloys [4].

$$P_\alpha = \frac{N_i!}{\prod_{k=0}^{K} m_{k,i}!} \prod_{k=0}^{K} p_k^{m_{k,i}} \qquad (1)$$

$m_{k,i}$ number of atoms of k species on i shell and N_i total number of atoms on i shell

The associated hyperfine field $H(\alpha)$ has been given as a function of the hyperfine field increments $\Delta H_{k,i}$ and the number $m_{k,i}$ of atoms of k species in i shell

$$H(\alpha) = H_0 + \sum_{i=1}^{2} \sum_{k=1}^{K} m_{k,i} \Delta H_{k,i}, \qquad (2)$$

The effects of higher coordination shells was thought as random variables of zero mean and finite variance, $G(0,\sigma)$, so that the correct distribution $P(H)_c$ could be described by the convolution of the distribution given by the generalized binomial law acting on the two first coordination shells and the gaussian distribution of the superimposed field, H_D, brought by the more distant shells.

$$P(H)_c = P(H(\alpha)) \times P(H_D) \qquad (3)$$

where $P(H_D)$ equal to $G(0,\sigma)$

The adjustable parameters interfering in the $P(H)_c$ calculation remain the alloy composition defining $P(H(\alpha))$ the ($\Delta H_{k,i}$) values and the variance σ of the gaussian function.

The correct agreement between $P(H)_c$ and $P(H)_{ex}$ was evaluated from the following R factor

$$R = \sqrt{\frac{\sum_i (P_i(H)_c - P_i(H)_{ex})^2}{N}}$$

N represents the number of experimental data.

In the case of the quenched alloys the composition was fixed and the field increment adjusted. For the aged samples, the field increment were fixed and the composition varied.

The TEM studies were systematically performed on the samples studied previously by Mössbauer spectroscopy.

3. Results and discussion

In the case of the binary Fe$_{1-x}$Ni$_x$ alloys ($x=0.03$ to 0.18), the experimental mean hyperfine field Hi and isomer shift δ were, for all x content, in agreement with the experimental values reported previously [5]. However, with the known $\Delta H_{k,i}$ increments (+9.4kOe, +7.0kOe) [6], $P(H)_c$ was systematically shifted relatively to $P(H)_{ex}$ (Fig1). The statistical distribution of Ni atoms could not be suspected because of the good homogeneity of our samples, demonstrated by X-Ray microprobe analysis. A significant

better fit was found for other $\Delta H_{Ni,i}$ values. The new available $\Delta H_{Ni,i}$ values can be regarded as constant with z and equal respectively to 6.1 ± 0.5kOe and 4.4 ± 0.5kOe. The subsequent σ value increases logically with z from 6kOe up to 8.7. It reflects the effect of all solutes neighbors without limitation of the shell distances. However a specific ΔH value assigned to individual shell upper than 2 remains out of physical meaning. From those results, we can conclude that the additivity model is fully obeyed in the case of the binary alloys $Fe_{1-x}Ni_x$ up to $x=0.18$.

Noticeable disparities appear in the behavior of the quenched Fe-18.3Ni-3.4Mo and Fe-15.0Ni-5.7Mo alloys (Fig2).

Whatever the quenching rate no paramagnetic line was revealed on the Mössbauer spectrum of the lowest Mo content alloy. On the contrary, a paramagnetic line appeared with amplitude increasing up to 1.3 % for the 300°/h cooling rate in the case of Fe-15.0Ni-5.7Mo sample. After an ageing of one hour at 450°C, this peak vanished. This extra line is then relevant of segregation of atoms within the martensite more extensively as the cooling rate is slower and it may result from Cottrell clouds. We focussed consequently our attention on the samples free from any paramagnetic line and considered the ageing duration of one hour as the initial stage of the precipitation process.

Nevertheless, for both compositions, the $P(H)_c$ calculated with the known $\Delta H_{k,i}$ increments [6] were shifted too towards higher fields suggesting that the Ni increments were too large and the Mo ones too small. The best agreement between $P(H)_c$ and $P(H)_{ex}$ was obtained with the modified $\Delta H_{Ni,i}$ increments found for the binary alloys within the experimental accuracy (5.3±0.7kOe, 3.3±0.7kOe), while $\Delta H_{Mo,1}$, $\Delta H_{Mo,2}$ were found equal respectively to −49.5±1.0 and −24.7±1.0kOe.

The Mössbauer spectrum of the aged Fe-18.3Ni-3.4Mo alloy shows a broad central paramagnetic line with a δ value equal to −0.077±0.005mm/s and a relative abundance equal to 3.4±0.2 % (Fig.2). With the hyperfine field increments found above, the relative Ni and Mo population were adjusted to fit $P(H)_c$ and $P(H)_{ex}$. Such analysis led to the relative atomic Ni and Mo contributions to the matrix hyperfine field distribution. However, the number of Fe atoms involved in the precipitates and the matrix can only be defined from the knowledge of the relative Lamb-Mössbauer f factors. The possible assumptions about their values can only be justified by experiments with other methods. That is the reason of the TEM experiments.

The assumption of equal-f factors led to a precipitate composition $Fe_{50\pm5}$-$Ni_{30\pm5}$-$Mo_{20\pm5}$. A careful analysis for the TEM diffraction patterns revealed the presence of two kinds of precipitates identified as a (Fe-Ni)$_3$Mo type phase (orthorhombic Pmmn) and as the ordered (Fe-Ni)$_3$Mo ω phase (hexagonal P6$_3$/mmc (Fig4). The hypothesis of one ferromagnetic family can be ruled out as the unique possibility should be a b.c.c. Fe enriched Fe-Ni-Mo phase excluded from TEM experiments. It results that the observed paramagnetic line on the Mössbauer spectra is assigned to both precipitated phases. In the case of such observed phases, it is possible to assimilate their volume fraction to their atomic fraction having in mind their unit cell parameters with the corresponding number of atoms as the volume per atom is equal to 0.0118nm³ for the Ni$_3$Mo and ω phase, and 0.0107nm³ for the martensitic matrix. Moreover, the

volume fraction of the precipitates evaluated from the TEM observations lies around 5-10% in agreement with the weak fraction of the various components Fe, Ni, Mo involved in the precipitates and deduced from the Mössbauer spectrum supporting our hypothesis of similar f factors, the TEM micrographs leading to an evaluation of the two phase ratio.

The same remarks can be formulated about the Fe-15.0Ni-5.7Mo alloy. The overall composition of the precipitates can be defined as $Fe_{25\pm5}$-$Ni_{40\pm5}$-$Mo_{35\pm5}$ showing an increase in Ni and Mo content. TEM micrographs give evidence for the (FeNi)$_3$Mo phase and the superstructure of A_7B_2 type (ω) as previously [7]. However the Ni and Mo content are higher than for the Fe-18.3Ni-3.4Mo alloy. This ensures that the ω phase evolves to its limit form of Ni$_2$Mo type [8].

We must finally outline that in the case of these precipitates, we are concerned with very fine entities in the nanoscale level. From the accurate overall composition of the precipitates given by the Mössbauer spectra we have been able to identify the composition modification between the precipitate families revealed by TEM micrographs; the richest alloy favors the precipitation of depleted Fe phases.

4. Conclusion

We have explained the magnetic field perturbations experienced by the Fe nucleus in binary $Fe_{1-x}Ni_x$ alloys up to $x=0.18$ with the model of additivity of the solute influences in the assumption of a statistical atomic distribution. No departure from this model is observed in the case of the ternary $Fe_{1-x-y}Ni_x Mo_y$ with $x\simeq0.15-0.18$ $y\simeq0.03-0.05$.

In the case of the present alloys after an ageing of 72 hours at 450°C two precipitates $(Fe_{(1-x)}Ni_x)_3$ Mo and ω $(Fe_{(1-y)}Ni_y)_7$ Mo$_2$ have been detected by TEM experiments with an overall Fe/Ni+Mo atomic ratio, given by Mössbauer spectroscopy, twice smaller for the sample with the highest Mo content. The necessary assumptions about relative Lamb-Mössbauer f factors of the matrix and precipitates were correctly corroborated by the volumic fraction evaluations performed with the TEM measurements.

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