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Redistribution of interstitial atoms and ageing of Fe-N α' martensite

J. FOCT and C. CORDIER-ROBERT

Laboratoire de Métallurgie Physique, URA CNRS 234, Université Lille I, Bâtiment C6, 59655 Villeneuve d'Ascq, France

ABSTRACT

Different experimental measurements show that transformations of martensite occur from very low temperature, often below 77K. In order to understand the redistribution of interstitial atoms which is studied by Mössbauer spectroscopy near room temperature the previous low temperature changes are briefly discussed. The Mössbauer data related to cubic γ , γ' , α' and α'' Fe-N alloys are presented. It is shown that the interstitial atom distribution and redistribution of interstitial atoms is partially inherited from austenite and that γ' Fe₄N nuclei corresponds in γ and α' to N-Fe-N chains oriented along $\langle 001 \rangle$ in γ and along $\langle 110 \rangle$ in α' .

I - LOW TEMPERATURE TRANSFORMATIONS OF Fe-N α' MARTENSITE

The internal friction peaks which are observed near 100, 200 and 270K during the first heating of a virgin α' martensite obtained under a M_s temperature low enough to prevent any "auto-ageing" correspond to hysteretic irreversible phenomena [1-3]. In order to understand these changes which occur in $\alpha' + \gamma$ specimen complementary measurements have been done by dilatometry [4], X ray diffractometry [5], Mössbauer spectrometry [6-9], resistivity [10]. Although Mössbauer spectra do not show clear evidences of changes below 270K an unambiguous variation of the tetragonality c/a was measured (table I).

	Fe-33.5Ni	Fe-30Ni-0.37C	Fe-25Ni-0.7C	Fe-2.39N	Fe-3Mn-1.6C
$\Delta c/a$	-0.008	-0.015	-0.01	-0.02	+0.008

Tableau I: Change of tetragonality after heating from 4K to about 250K, from experimental results obtained by K. ULLAKO [10]

The main hypothesis which have been proposed to interpret these variations are:

- A - Redistribution of interstitials between O_x , O_y and O_z sites [11],
- B - Redistribution of interstitials between tetragonal and octahedral sites [12],
- C - Interaction between defects - Interfaces boundaries α / γ - Dislocations - C and N atoms...

Hypothesis B has been rejected and no unambiguous evidence of the A processus was obtained when temperature is below 200K [13] therefore C is the main source of low temperature phenomena. Schematically these very low temperature changes can be considered as relaxation-type processes i.e. by which the free energy of the system decreases by reorganization of the defects which relaxes stresses and strains.

Although low temperature changes of c/a are observed even when virgin martensite does not contain interstitial atoms, they appear to be mainly due to interstitial defect interactions. According to these views it can be proposed that in FeN_x martensite the density of N atoms in O_x , O_y and O_z , and near defects are X_x , X_y and X_z sites and X_D ($X = X_x + X_y + X_z + X_D$).

According to the fact that the interplanar distance measured by X ray diffraction corresponds to an integration of the mean static displacements:

$$a = a_0 \left\{ 1 + \alpha [X_x + X_y] / 2 - \beta [X_z + (X_x + X_y) / 2] + \varepsilon X_D \right\}$$

$$c = c_0 \left\{ 1 + \alpha X_z - \beta [X_x + X_y] + \varepsilon X_D \right\}$$

which lead to $c/a = 1 + (\alpha + \beta) [X_z - (X_x + X_y) / 2]$ and $\Delta V/V = (\alpha - 2\beta) [X - X_D] + 3\varepsilon X_D$. These equations show that the tetragonality c/a as well as $\Delta V/V$ may change if X_D varies.

It is clear that X_D leads to minor changes of the Mössbauer spectra but possibly to important changes of c/a and $\Delta L/L$, both values which should be discussed in parallel. It should be emphasized that all the low temperature relaxation - type transformations of martensite do not suppose any change in the Zener ordering. However in the vicinity of substitutional S atoms, such as Mn or Cr, short range order which is induced by the S-N interaction is likely to delay the Zener ordering, and could explain the important increase of tetragonality in Mn alloyed martensites.

Once the relaxation of the martensite is accomplished one can estimate $X_D \approx 0.1 X$ and $X_z \approx X - X_D = 0.9 X$.

After relaxation of the α' lattice because $X_D \neq 0$, it seems very probable that the values of the local deformation based on the variation of a and c versus X are underestimated. When the relaxation stage is achieving, ageing of martensite resulting from a redistribution of interstitials on O_z sites, which preserves Zener order, may occur (figure 1).

II - MÖSSBAUER RESULTS AND DISCUSSION

Since early studies of ageing of Fe-C and Fe-N martensites, it was clear that Mössbauer spectra led to characterize iron environments in the different phases and that the main source of identification of the hyperfine parameters and therefore of the Mössbauer peaks is the number of interstitial nearest neighbours. Let us identify environments by the number of first nitrogen nearest neighbours O, I, II [14] in the different FeN_x phases γ , γ' , α' , α'' : O^γ , $\text{O}^{\gamma'}$, $\text{O}^{\alpha'}$, $\text{O}^{\alpha''}$ - I^γ , $\text{I}^{\gamma'}$, $\text{I}^{\alpha'}$, $\text{I}^{\alpha''}$ - II^γ , $\text{II}^{\gamma'}$, $\text{II}^{\alpha'}$, $\text{II}^{\alpha''}$.

Figure 2 shows the peaks corresponding to these environments during ageing of α' . II^γ has been clearly identified in FeN_x austenite since twenty years [15]. This II^γ environment essentially corresponds to N-Fe-N $\langle 100 \rangle$ chains which are isomorphous to those observed in γ' and which correspond to $\text{II}^{\gamma'}$. These environments act as nuclei for γ' precipitation during ageing of austenite [14].

The spectrum of γ' is also unambiguous, the splitting of $\text{II}^{\gamma'}$ into two $\text{II}_{\parallel}^{\gamma'}$ and $\text{II}_{\perp}^{\gamma'}$ environments corresponds to the two possible angles formed by the direction of easy magnetization with the electric field gradient axis [16]. It must be mentioned that when nitrogen content X of $\gamma' \text{FeN}_x$ is slightly lower than 0.25 an environment $\text{I}^{\gamma'}$ has been identified and corresponds to iron atoms of type $\text{II}^{\gamma'}$ for which one nitrogen nearest neighbour is replaced by a vacancy.

An unambiguous interpretation of α'' has been proposed [16] which shows that the splitting of $\text{I}^{\alpha''}$ into $\text{I}_{\parallel}^{\alpha''}$ and $\text{I}_{\perp}^{\alpha''}$ corresponds to sites at the corner of the irregular octahedron and is consistent with the expected abundances ratio: 2. The very high value of the hyperfine magnetic field corresponding to $\text{O}^{\alpha''}$ higher than 40T is the reason for the high saturation magnetization of $\text{Fe}_{16}\text{N}_2 \alpha''$ and corresponds to the expansion of the Fe-Fe distances when N atoms are further from iron atoms than $a_0 \sqrt{2}/2$.

In virgin α' martensite $\text{O}^{\alpha'}$, $\text{I}_{\parallel}^{\alpha'}$ and $\text{I}_{\perp}^{\alpha'}$ isomorphous to O^{α} , $\text{I}_{\parallel}^{\alpha''}$ and $\text{I}_{\perp}^{\alpha''}$ are clearly identified. An important site $\text{O}^{\alpha'}$ is also visible on the spectra. Up to now and curiously, no clear interpretation of $\text{O}^{\alpha'}$

was proposed. In austenite N-N interactions are highly repulsive and therefore the N distribution forms N-N <110> doublet building the frame of the γ'' -like structure likely to lead to α'' by a Bain transformation (figure 3). If the nitrogen distribution on the possible sites of γ'' , i.e. α'' , is nearly random, the density of sites O having i N third nearest neighbours ($0 \leq i \leq 4$) is:

$PO_i\alpha' = (1 - 6x') C_4^i (8x')^i (1 - 8x')^{4-i}$, where x' is the isolated nitrogen interstitial concentration i.e. x diminished by interstitials forming N-Fe-N chains. Measurements of peaks area show that $O'\alpha'$ corresponds to environments $O_i\alpha'$ with $i \geq 3$.

An other environment is detected in α' : $\Pi\alpha'$ of which the hyperfine field is near that of $\Pi\gamma'$. This led other authors to conclude to the presence of γ' in α' [17]. In fact this corresponds to γ' embryos inherited from the $\Pi\gamma'$ environment. These γ' embryos are formed by N-Fe-N <110> α' chains according to the evolution of site abundances during ageing (figure 4) [18].

III - CONCLUSION

The following sequence for the appearance of sites may be proposed:

- (1) Martensite transformation:

$\gamma\{O\gamma, \Pi\gamma, \Pi\gamma'\} \rightarrow \gamma_R + \alpha'_V\{O\alpha', O'\alpha', I_{\parallel}\alpha', I_{\perp}\alpha', \Pi\alpha'\}$, with a tetragonality of martensite $(c/a)_O$.

- (2) Relaxation stage:

$\alpha'_V\{O\alpha', O'\alpha', I_{\parallel}\alpha', I_{\perp}\alpha', \Pi\alpha'\} \rightarrow \alpha'_R\{O\alpha', O'\alpha', I_{\parallel}\alpha', I_{\perp}\alpha', I_D\alpha', \Pi\alpha', \Pi_D\alpha'\}$, with $(c/a)_R \neq (c/a)_O$.

- (3) Ageing of FeN_x martensite:

Spinodal like decomposition of α'_R : $\alpha'_R \rightarrow \alpha'' + \alpha_A$

$\alpha'_R\{O\alpha', O'\alpha', I_{\parallel}\alpha', I_{\perp}\alpha', I_D\alpha', \Pi\alpha', \Pi_D\alpha'\} \rightarrow \alpha_A\{O\alpha', \Pi\alpha'\} + \alpha''\{O\alpha'', I_{\parallel}\alpha'', I_{\perp}\alpha''\}$

with $\langle c/a \rangle_A \approx f_{\alpha''}(c/a)_{\alpha''} + (1-f_{\alpha''})$, where $f_{\alpha''}$ is the volume fraction of α'' .

- (4) Tempering:

$\alpha_A\{O\alpha', \Pi\alpha'\} + \alpha''\{O\alpha'', I_{\parallel}\alpha'', I_{\perp}\alpha''\} \rightarrow \alpha_T + \gamma'\{O\gamma', \Pi\gamma', \Pi_{\parallel}\gamma', \Pi_{\perp}\gamma'\}$ with $(c/a)_T = 1$.

The N-Fe-N chains inherited from γ act as nuclei for γ' precipitation.

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Figure 1: Evolution of the mean tetragonality $\langle c/a \rangle$ of BCC and BCT phases vs. temperature.

Figure 3: γ' like structure.

Figure 2: Mössbauer spectra at 293K of a) virgin α' $\text{FeN}_{0.1}$; after b) 3 seconds, c) 5 minutes and d) 13 hours ageing at 473K.

Figure 4: Variation of environment abundances A_{ϕ_i} vs. Lnt during ageing of α' $\text{FeN}_{0.1}$ martensite at 473K. First stage of ageing up to τ_1 corresponds to α'' ordering. Second stage corresponds to the formation of γ' nuclei arising from "C" clusters in α'_p which ends as α ferrite. Third stage corresponds to the growth of γ' in $\alpha'' + \alpha$ as well as in γ [18].