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## LOW TEMPERATURE AGEING OF Fe-N MARTENSITE

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1. Introduction

A freshly formed martensite in Fe-X-C alloys is characterized by abnormal tetragonality which changes during low temperature ageing. In the Fe-Ni-C martensite tetragonality decreases and in the Fe-Mn-C martensite it increases during heating from liquid helium temperature to room temperature. Among the hypotheses for the nature of abnormal tetragonality the most popular are those explaining the deviations from the relation  $c/a=1+\gamma P_c$  ( $P_c$  = the carbon content in wt%,  $\gamma=0.046\pm 0.001$ ) in three different ways, firstly by the distribution of the carbon atoms between the different sublattices of the octahedral interstitial sites (1) or between the octahedral and tetrahedral sites (2), secondly by short range atomic ordering in the initial austenite inherited to the virgin martensite (3) and thirdly by the coherent bond at the interface between the virgin martensite and the ordered regions in the retained austenite (4-6), i.e. constraint strain by the matrix, as it was assumed in (7). The abnormally high tetragonality in Fe-Ni-C martensite was attributed to the coherency at the austenite-martensite interface and its decrease with temperature was assumed to be caused by the break of coherency according to the neutron diffraction study (8).

The tetragonality of the freshly formed Fe-N martensite and its temperature behaviour has not been studied so far. The isothermal martensitic transformation was found during heating below room temperature using dilatometric analysis (9). By means of Mössbauer spectroscopy the redistribution of nitrogen atoms and the formation of  $\alpha''$ -phase was observed after ageing at temperatures above 300 K and also after long time ageing at room temperature (10,11). On the basis of calorimetric and dilatometric data Mittemeijer *et al.* (9,10) came to the conclusion that clustering of nitrogen atoms does not take place at an early stage of ageing in Fe-N martensite. However, the measurements (9,12) were performed above room temperature with the alloys whose  $M_s$  temperatures were so high that because of autotempering some ageing must have occurred before measurements.

The aim of this report is to present the results of the studies of the virgin Fe-N martensite paying special attention to the change of tetragonality and the redistribution of nitrogen atoms during ageing in the temperature range between 5 K and room temperature.

2. Material and experimental procedure

The samples Fe - 2.39 wt% N and Fe - 2.75 wt% N were prepared by nitriding the foils of 10  $\mu$ m in thickness. The nitriding was performed in the mixture of ammonia and 20 % hydrogen at 800°C for 2.5 hours. The samples were quenched in water immediately after nitriding, and they were fully austenitic at room temperature. The virgin martensite was produced by the cooling to liquid helium temperature. To determine the nitrogen content we used the concentration

dependence of the austenite lattice parameter  $a=3.657+0.0073 P$  ( $P$  is the effective concentration  $100 n/N$ , where  $n =$  a number of nitrogen atoms and  $N =$  a number of iron atoms).

The techniques of X-ray diffraction, Mössbauer spectroscopy, electrical resistivity and magnetic susceptibility were used in the present studies. X-ray diffraction measurements were made using a monochromated  $\text{Co K}_{\alpha 1}$  radiation. The diffracted beam was detected with a  $120^\circ$  curved position sensitive detector (INEL CPS 120). The cooling of the sample was performed by means of a closed cycle cryocooler. X-ray diffraction and Mössbauer spectra were computer fitted using Lorentzian peak shapes. AC susceptibility (1 kHz) and electrical resistivity (25 Hz) were measured simultaneously from the same sample using an equipment the principle of which is described in (13,14).

### 3. Experimental results and discussion

The martensitic transformation start temperature in the alloy Fe - 2.75 wt% N was found to be 120 K according to the electrical resistivity and magnetic susceptibility results. Such a low  $M_s$  temperature implies that we really obtained virgin martensite in our samples. The X-ray diffraction patterns measured after cooling and low temperature ageing are shown in Fig. 1. It is evident that positions of the peaks  $(002)_\alpha$ ,  $(200)_\alpha$  and  $(112)_\alpha$ ,  $(211)_\alpha$  change after ageing in the temperature range of 9-300 K. The  $c/a$  ratio in the freshly formed martensite is equal to  $1.112 \pm 0.004$  which is much higher than the value 1.089 expected from the concentration dependence of  $c/a$  given by (15).

The behaviour of tetragonality due to ageing can be divided into two stages with a decrease of the  $c/a$  ratio at temperatures below 200 K and the increase of that at higher temperatures (Fig.2). It is noteworthy that the value of tetragonality 1.092 after heating to 200 K coincides in the limits of error with the normal value expected from the concentration dependence of  $c/a$  (15).

Mössbauer spectroscopy was used to study the redistribution of nitrogen atoms in martensite. The redistribution can be accompanied with a change of the nearest surroundings of iron atoms. The Mössbauer spectrum of the virgin martensite has a multicomponent structure (Fig.3) substantially different from that observed in (10,11). The central lines 0 and 1 belong to iron atoms in the retained austenite. The interpretation of the sextets 2-6 will be discussed below.

The ageing of the virgin martensite at different temperatures below 300 K does not lead to any change in Mössbauer spectra (Fig.3b,c), which indicates that there is no change in the nearest

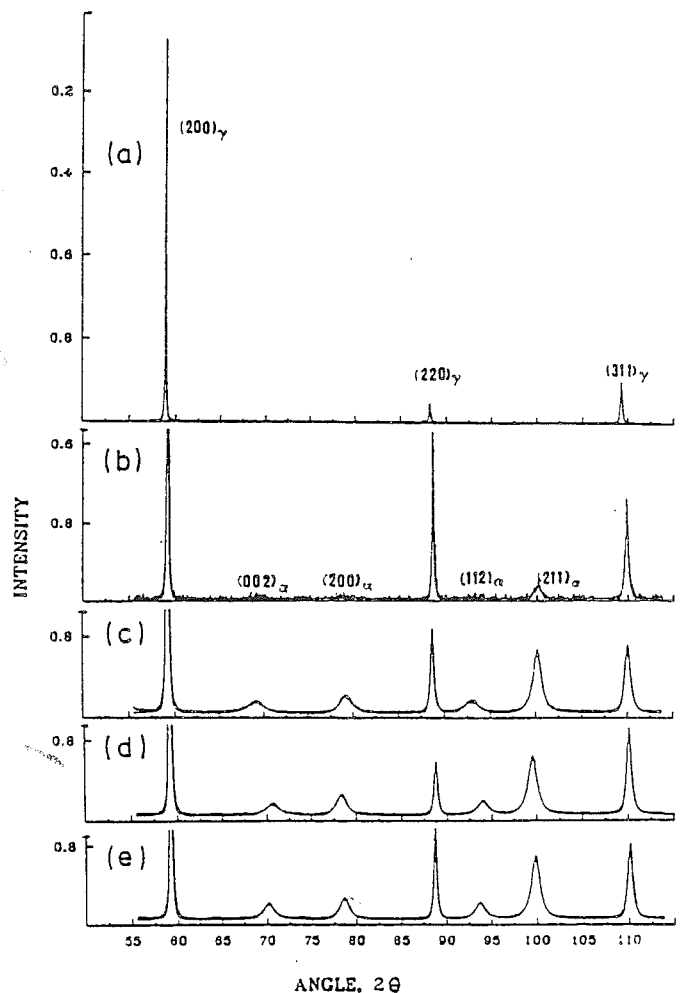


FIG.1. X-ray diffraction pattern of the alloy Fe-2.39wt%N: initial austenite measured at 300 K (a), martensitic transformation during cooling at 102 K - 87 K (b), martensite measured at 9 K as freshly formed (c) and after ageing for 1 hour at 200 K (d) and at 300 K (e)

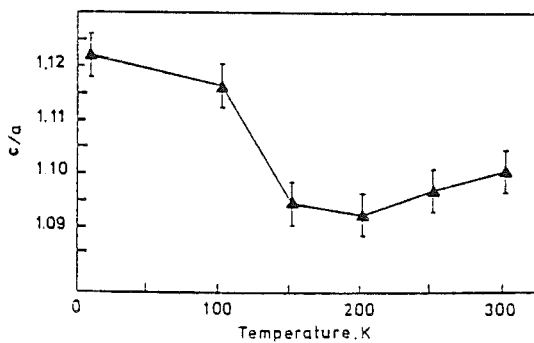


FIG.2. Dependence of the  $c/a$  ratio of the Fe - 2.39 wt% N martensite on the ageing temperature. Measurements were made at 9 K.

neighbourhood of iron atoms. The increase of the measurement temperature above 100 K causes a significant change in the spectra. The intensities of the central lines increase nearly 100%, sextets 5 and 6 disappear and the sextet 2 decreases in intensity (Fig.3d). This effect is reversible and the Mössbauer spectrum shown in Fig.3a-d can be reproduced after cooling back below 100 K.

The fitting of Mössbauer spectra revealed that the parameters of the components 2,5,6 correspond to the structure  $Fe_4N$ . The sextets 3,4 belong to iron atoms in the martensite phase.

The reversibility of the changes in the spectra when cycling the temperature between 100 K and RT and the existence of the  $Fe_4N$  hyperfine structure below 100 K indicate that magnetic ordering occurs in the retained austenite. Clusters with the imperfectly ordered structure  $Fe_4N$  may exist, because the distribution of nitrogen atoms in austenite corresponds to a diluted solid solution on the basis of the chemical compound  $Fe_4N$  (16,17). These clusters are nonmagnetic at room temperature and they may undergo magnetic ordering when the temperature decreases.

We observed no changes in Mössbauer spectra which could be attributed to the redistribution of nitrogen atoms between octahedral interstitial sites of different sublattices or between octahedral and tetrahedral sites. It means that from the two possible explanations for the abnormally high tetragonality of the virgin Fe-N martensite (the redistribution of nitrogen atoms or the constraint strain by a matrix) we can exclude the first one. The present data show that the coherent bond at the interface between the freshly formed martensite and the retained austenite is the reason for high tetragonality. We have got the evidence that the ordered clusters exist in the retained austenite and at low temperatures the atomic order causes the magnetic structure with

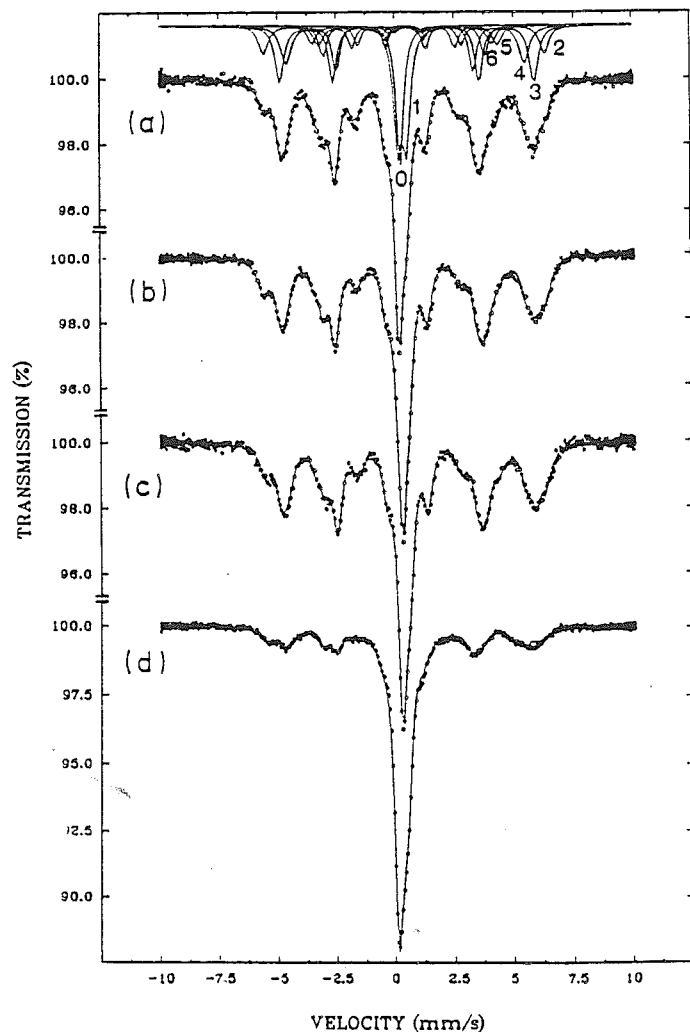


FIG.3. Mössbauer spectra of the Fe-2.75wt%N martensite as freshly formed (a) and after ageing for 1 hour at 200 K (b) and at 300 K (c,d). Measurements a,b,c were made at 5 K and the measurement d at 300 K. (Source Co<sup>57</sup>: Cr)

hyperfine parameters typical of the  $Fe_4N$  structure. The existence of such ordered regions may assist the abnormally high tetragonality if the coherent bond exists between the virgin martensite and the retained austenite. The temperature behaviour of the  $c/a$  ratio (Fig.2) is consistent with this explanation because the rise of temperature increases the mobility of dislocations and in such a way can assist the break of coherency.

After ageing at temperatures between 200 K and 300 K the  $c/a$  ratio increases again. At the same time the nearest surroundings of iron atoms remain unchanged according to the Mössbauer data (Fig.3c). Nevertheless, electrical resistivity and magnetic susceptibility decreases after ageing at temperatures above 200 K (Fig.4). It means that the redistribution of nitrogen atoms really occurs in this temperature range. Compared to the resistivity and susceptibility results obtained for Fe-Ni-C martensite (18) it is evident that clustering does not take place here. The present results confirm the idea of Mittemeijer *et al.* (12) who proposed that unlike the iron-carbon martensite the ageing of iron-nitrogen martensite is not accompanied with clustering. By clustering we mean such a redistribution of interstitial atoms which leads to an increase of the number of interstitials in the nearest surroundings of metal atoms. Mössbauer studies of the early stage of ageing of the freshly formed Fe-C martensite gave the evidence for clustering of carbon atoms at temperatures above 200 K (19). The electrical resistivity, magnetic susceptibility and Mössbauer data obtained in this study reveal that ordering of nitrogen atoms occurs during low temperature ageing without clustering. According to (20,21) (see also [22]) the definition of short-range order parameter can be written in the following form

$$\alpha_i = 1 - \frac{N_i^{AX}}{N C_A (1 - C_A) Z_i},$$

where  $N_i^{AX}$  is the number of the atom pairs A and X for the  $i^{\text{th}}$  coordination shell around an interstitial, N is the total number of the sites,  $C_A$  is the relative concentration of atoms A,  $Z_i$  is the coordination number for the  $i^{\text{th}}$  coordination sphere,  $N C_A (1 - C_A) Z_i$  is the number of the pairs of the atoms A and X for a random distribution. Taking into account what is mentioned above one can consider the short-range atomic order in terms of the increase of the number of the interatomic bonds between atoms of the different kind A-X (short-range ordering) or of the same kind A-A, X-X (short-range decomposition) (20). If this definition is used, we can conclude that the redistribution of nitrogen atoms below room temperature cannot be considered as any kind of short-range atomic order, because the number of the Fe-Fe or Fe-N interatomic bonds does not change according to the present Mössbauer data. It is possible to define such a redistribution of nitrogen atoms as a long-range atomic ordering in local regions preceding the formation of the  $\alpha'$ -structure  $Fe_{16}N_2$ . It means the decomposition of solid solution with formation of the ordered phase. The increase of the  $c/a$  ratio in the temperature range between 200 K and 300 K is consistent with such kind of ordering.

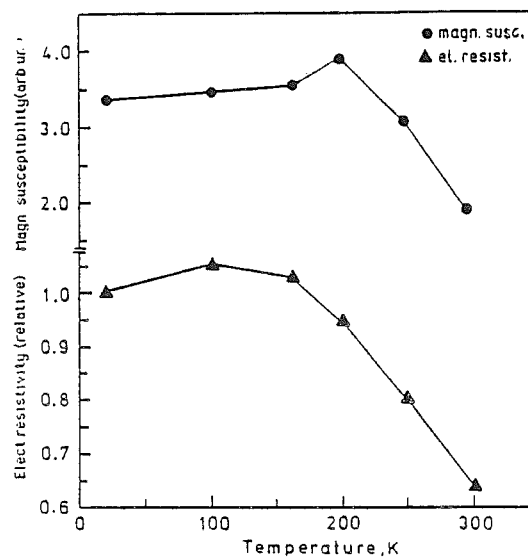


FIG.4. Magnetic susceptibility and electrical resistivity of the alloy Fe-2.39wt%N as a function of ageing temperature, measured at 20 K.

#### 4. Conclusions

1. The freshly formed Fe-N martensite has the abnormally high tetragonality which decreases during heating to 200 K and increases between 200 K and 300 K.
2. The ordered regions with the imperfect structure of Fe<sub>4</sub>N exist in the retained austenite and they undergo the magnetic ordering at temperatures between 100 K and room temperature.
3. The high tetragonality of the freshly formed martensite can be explained as a result of the coherent bond at the interface between virgin martensite and retained austenite. The decrease of the *c/a* ratio during heating to 200 K is assumed to be caused by the coherency break possibly because of the increased mobility of dislocations.
4. The ageing of the freshly formed Fe-N martensite at temperatures above 200 K is accompanied with a redistribution of nitrogen atoms. This redistribution does not lead to any change in the nearest surroundings of metal atoms and it can be considered as a long range atomic ordering before the precipitation of  $\alpha'$  phase. Unlike carbon the nitrogen atoms do not form clusters at the early stage of ageing.

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