

## **LATTICE STRUCTURE OF LOW TEMPERATURE DEFORMED Fe-NI-C MARTENSITE**

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Low temperature deformed Fe-20Ni-1.15C and Fe-25Ni-0.7C martensites were studied using Mössbauer spectroscopy and X-ray diffractometry. After quenching the austenitic Fe-20Ni-1.15C sample in liquid nitrogen only a small amount of martensite was observed. During deformation at 77 K the fraction of martensite phase increased up to 95 %, but this deformation did not essentially affect the Mössbauer spectrum and lattice parameters of virgin martensite. Instead, deformation at 200 K drastically changed the martensite Mössbauer peaks and also a reduction in tetragonality was found. The latter effect was more clearly seen in Fe-25Ni-0.7C martensite. In the present work, carbon redistribution during deformation is discussed.

### **1 INTRODUCTION**

Carbon redistribution in ferrous martensites during aging in the room temperature region has been extensively studied using Mössbauer spectroscopy. In most of the models carbon atoms are assumed to be in c axis octahedral sites (1,2), but in some models also tetrahedral sites are assumed to be possible (3). At very low temperatures only slight effects have been observed in the martensite Mössbauer spectra (4), although tetragonality is found to be drastically changed (5).

Virgin martensite is known to be rather ductile, but the mechanical properties become worse due to aging effects (6). Deformation mechanisms were studied in Ref. (7).

### **2 EXPERIMENTAL PROCEDURE**

An alloy Fe-20Ni-1.15C was vacuum melted and hot forged into bars. Pieces of 1 mm and 3mm in thickness were austenitized at temperature 1420 K for three hours and water quenched. The 3 mm thick pieces were cold rolled 70 % and reaustenitized in salt bath for two minutes. Finally the reaustenitized samples were chemically thinned into 40  $\mu\text{m}$ . These samples were used in Mössbauer experiments. Carbonless reference specimens were prepared by annealing the foils in wet hydrogen atmosphere at 973 K for 25 hours and for six hours in dry hydrogen and still for two hours in argon atmosphere in order to remove oxygen and hydrogen from the specimen. Samples Fe-25Ni-0.7C were austenitized at 1420 K for three hours and water quenched. Deformation of the samples was performed in liquid nitrogen temperature by hammering and at 200 K also using a specially constructed rolling machine.

Transmission Mössbauer measurements were made using a sinusoidal velocity wave form. The radioactive source was  $\text{Co}^{57}$  in chromium matrix and its activity was about 5 mCi. One measurement was made at room temperature in order to make sure that the specimen was fully austenitic. Thereafter, the specimen was quenched in liquid nitrogen. A sample was hammered at temperatures 77 K and 200 K and then aged at room temperature for 12 hours. Mössbauer measurements were performed after each treatment at liquid nitrogen temperature.

X-ray diffractio experiments of the deformed foils were made at room temperature using Cr  $K_{\alpha}$  radiation (for Fe-20Ni-1.15C) and Cu  $K_{\alpha}$  radiation (for Fe-25Ni-0.7C). In the latter case the diffractometer was equipped with a curved secondary monochromator. In addition, low

temperature X-ray diffraction experiments were made. In these measurements the samples of 1mm in thickness were strained two axially in a special sample holder.

### 3 RESULTS

#### 3.1 X-RAY DIFFRACTION MEASUREMENTS

A martensite doublet (110) and an austenite (111) reflection of the sample Fe-20Ni-1.15C is shown in Fig. 1a. This measurement was run at room temperature after quenching in liquid nitrogen and aging for two hours at room temperature. The amount of martensite is seen to be rather small. Retained austenite peak is composed of  $K\alpha_1$  and  $K\alpha_2$  components. Identical measurement was made for the sample which was hammered in liquid nitrogen (Fig. 1b.). A drastic increase in the peak widths and in the amount of martensite is observed, but the peak positions are unchanged. Hence, deformation at 77 K does not decrease the tetragonality. This result was confirmed also by the measurements which were made at temperature 77 K from the two-axially strained specimens. Tetragonality was then higher because of no room temperature aging.

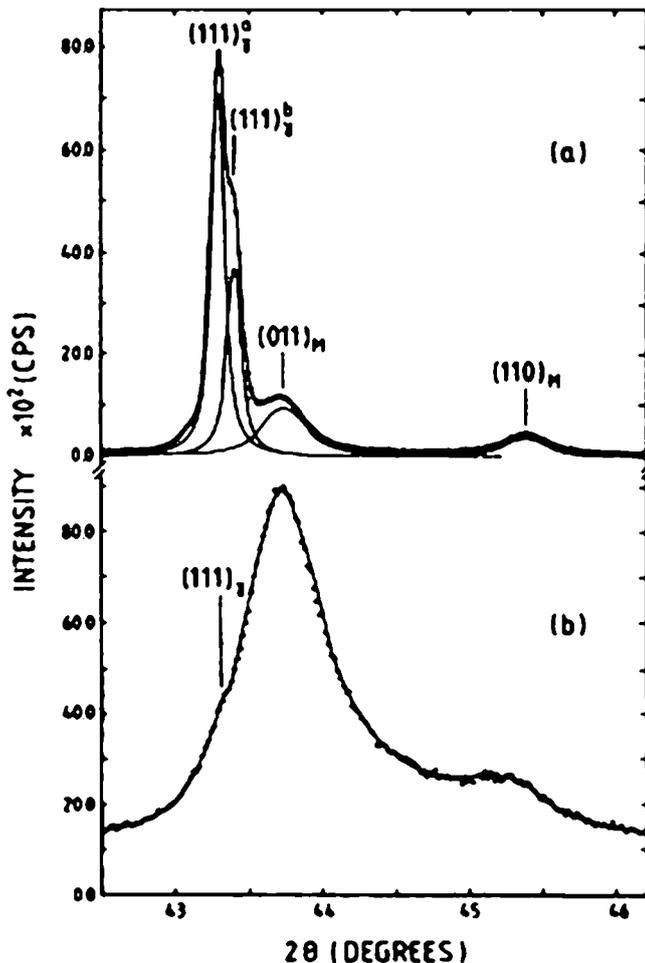


Figure 1. X-ray diffraction patterns of the Fe-20Ni-1.15C sample after quenching (a) and after deformation at 77K (b).

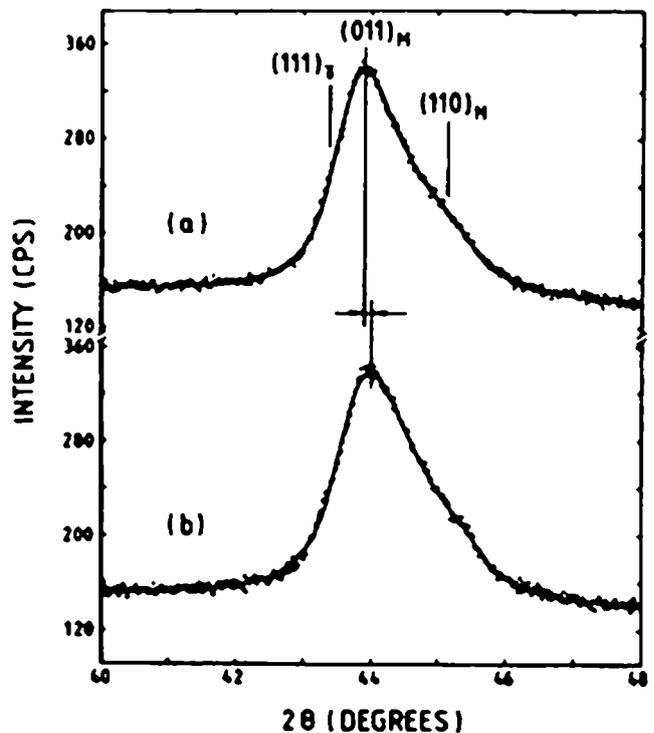
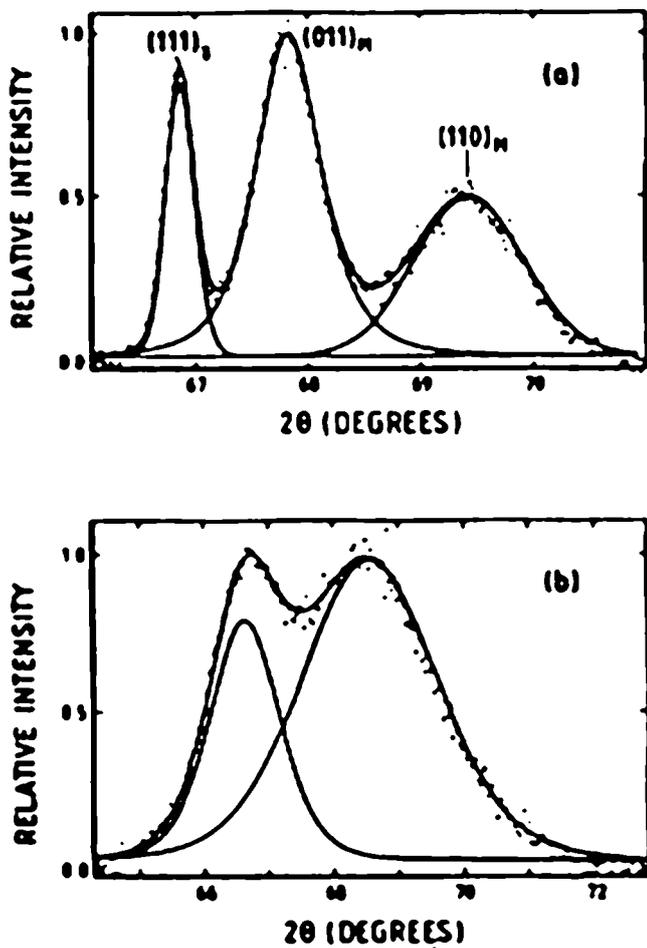


Figure 2. Fe-20Ni-1.15C martensite (110) doublet after deformation at 200 K (a) and after room temperature aging (b).

The Fe-20Ni-1.15C sample was further deformed at 200 K and X-ray diffraction measurements were run at room temperature. The results are presented in Fig. 2. The measurements were preceded by aging for 2 hours (Fig. 2a) and for 12 hours (Fig. 2b) at RT. Martensite peaks are seen to be broader and tetragonality smaller than after deformation at 77 K. During room temperature aging a small reduction in tetragonality is observed.

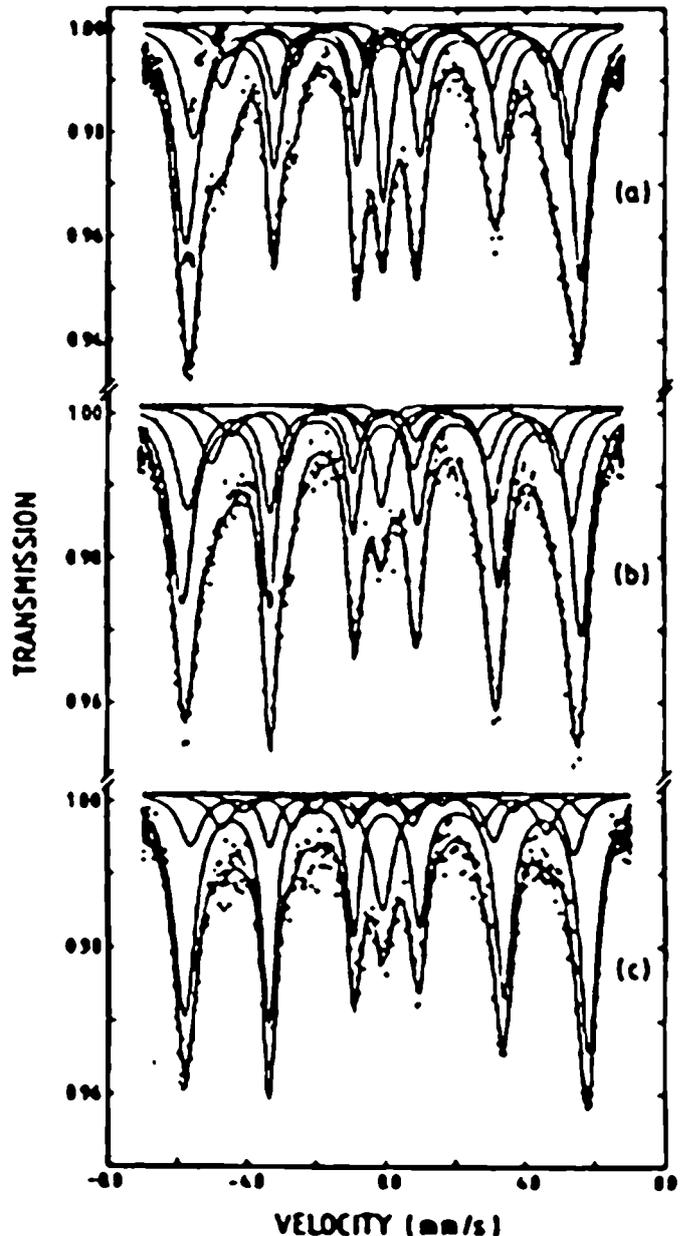
The specimen Fe-25Ni-0.7C was quenched in liquid helium in order to decrease the fraction of retained austenite. Thereafter it was heated up to 200 K and cold rolled about 40 %. Measurements were then performed at room temperature after two hours and 12 hours aging. The results are shown in Fig. 3a and Fig. 3b, respectively. The austenite (111) and the martensite (110) peaks are separated in Fig. 3a and martensite is clearly tetragonal. Instead, after cold rolling only one very broad martensite reflection is found.



**Figure 3.** X-ray diffractogram of the liquid helium quenched Fe-25Ni-0.7C sample measured at RT

(a) after quenching

(b) after deformation at 200 K



**Figure 4.** Mössbauer spectra of Fe-20Ni-1.15C martensite run at 77 K. (a) deformed at 77 K, (b) further deformed at 200 K and (c) aged at RT for 12 hours

### 3.2 MÖSSBAUER MEASUREMENTS

Mössbauer spectra of Fe-20Ni-1.15C martensite after deformations at 77 K and at 200 K and after subsequent aging for 12 hours at room temperature are presented in Fig.4. This measurement was made at liquid nitrogen temperature. Deformation at 77 K was observed to increase the fraction of martensite phase (see also Fig.1), but it does not affect the structure of the virgin martensite spectrum (virgin spectrum not shown here). Deformation at 200 K drastically changes martensite Mössbauer line profiles (Fig. 4b). Room temperature aging for 12 hours is seen to have a slight effect on the ferromagnetic spectrum (Fig. 4c). All Mössbauer spectra were computer fitted and the fitting model and spectrum analyses are described below.

#### Fitting model

Mössbauer peaks of the present alloy are broad due to high nickel content. An exact fitting model which takes into account different nickel and carbon environments of Fe<sup>57</sup> atoms is very complicated. In the present study the effects of nickel atoms are treated only mathematically (8). The martensite fitting procedure is based on the utilization of the Mössbauer spectrum of a carbonless reference Fe-20Ni sample. The reference spectrum which was measured identically with the Fe-20Ni-1.15C martensite spectrum was fitted using six independent Lorentzian lines. The fitting function of the martensite spectrum consists of a number of these reference patterns. Each pattern was modified by the changes in the hyperfine parameters due to different carbon environments of Fe-atoms. In the present study three neighbour shells were taken into account. The effects of nickel and carbon atoms on hyperfine parameters are treated here as additive. Nickel clusters and other possible effects taking place during decarburizing annealing were omitted. It is evident that this model can be valid only if nickel atoms affect the hyperfine fields of Fe<sup>57</sup> nuclei similarly in the Fe-20Ni-1.15C martensite and in Fe-20Ni reference systems. The reference alloy is lath martensite with a bcc lattice while the lattice of Fe-20Ni-1.15C martensite is bct. The difference in lattice symmetries may cause a slight change in electrical quadrupole splitting. These effects are assumed to be negligible, because tetragonality changes in general are known to affect very little on the Mössbauer spectra of Fe-Ni-C martensites (4). As for magnetic structures of the present martensite and the reference alloy, both are ferromagnetic and the orientation distribution is random in undeformed samples.

Martensite spectra were fitted using four Fe-20Ni sextets A, B, C and D. The sextet A is an unchanged Fe-20Ni pattern and it is attributed to those iron atoms which are not disturbed by carbon atoms. The three other patterns B, C and D correspond to the iron sites where carbon atoms are in the first, second and third neighbour shells, respectively. Assuming that carbon atoms are distributed randomly in c-axis octahedral sites the probability of different carbon environments are binomially distributed

$$P_{nml} = \binom{n}{1} \binom{m}{4} \binom{l}{8} c^{n+m+l} (1-c)^{14-n-m-l}$$

where n, m and l are the numbers of carbon atoms in the first, second and third neighbour shells and c is the atomic fraction of carbon. As the present carbon content is small, only P(n,m,l) with n,m,l = 0 and 1 are taken into account. Hence, the relative integral absorptions of the patterns A, B, C and D are (scaled to A) 1, 0.154, 0.291 and 0.528, respectively.

In the present model hyperfine fields and isomer shifts of the patterns B, C and D and quadrupole splitting in the pattern B were fitted. The integral absorptions of the second and fifth peaks of the Fe-Ni-C spectrum were also left free parameters, because of the changes in the orientation distribution of the magnetic field. In addition, all martensite line widths were

multiplied by one free parameter. Compared to many other models the number of fitting parameters is very small in this model, which is due to the utilization of the reference Fe-Ni spectrum. The paramagnetic peaks of retained austenite were fitted in a normal way (8).

## Results

Mössbauer spectrum shown in Fig. 4a could be well fitted using the present model. Hyperfine fields of iron caused by the first, second and third carbon neighbours were obtained 28.8 T, 30.3 T and 34.2 T, respectively. The absorptions of the second and fifth peaks were 68 % of the values in the reference Fe-20Ni spectrum. It indicates that magnetic field distribution in the specimen cannot be random but it strongly favours to be perpendicular to the sample surface. If the magnetization vector is assumed to be parallel to the c axis, this result would mean that deformation at 77 K produces an angular dependence in the c axis orientation distribution. The phase fraction of martensite was calculated 92.3 %.

During further deformation at 200 K the amount of martensite was increased up to 95 % (Fig. 4b). The orientation distribution of magnetization is now nearly random. Hyperfine field values are 28.1 T, 31.3 T and 34.7 T for first, second and third neighbours. Different to the fits shown in Fig. 4a, isomer shifts caused by the first and second neighbour carbon atoms became nearly equal. Quadrupole splitting was also clearly changed. The spectrum 4b was also fitted using a model where carbon atoms are assumed to be in a and b octahedral sites. In some attempts fourth neighbour shell was included. The results did not essentially differ from the present ones.

The spectrum of the room temperature aged martensite (Fig. 4c) was fitted with free absorptions for the patterns B, C and D. The fraction of the retained austenite and the orientation distribution of magnetization remained unchanged.

## 4 DISCUSSION

X-ray diffraction measurements revealed that tetragonality of martensite is not essentially changed during deformation at liquid nitrogen temperature. Diffraction peaks are, however, very broad, which is may be due to stress fields of lattice defects caused by plastic deformation. The structure of Mössbauer peaks of this strain induced and deformed martensite is similar to that of virgin martensite. Hence, carbon atom distribution is assumed to remain unchanged during deformation at 77 K. Orientation distribution of magnetization was found not to be random. If magnetization is assumed to be parallel to c-axis, as shown by Shilstein *et al* using neutron diffractometry, the result indicates an angular dependence in c axis distribution (9). Further deformation at 200 K was found to broaden X ray diffraction peaks and reduce the tetragonality. For alloy Fe-25Ni-0.7C only one martensite peak was present, which could be explained in two ways. First martensite lattice might have transformed to cubic, because carbon atoms have moved to a and b octahedral sites or secondly single diffraction peak is composed of a distribution of tetragonal doublets with several axial ratios. Mössbauer spectral peak analyses clearly indicated that carbon atoms were redistributed during deformation at 200 K. Special fitting models where different carbon environments of iron atoms were tested (not presented here) did not confirm that carbon atoms were equally distributed in a, b and c sites. However, the fact that orientation distribution of magnetization becomes random indicates that there is no preferred direction in unit cell any more (it is not probable that the structural texture would disappear during further deformation). According to the present experimental data the authors assume that carbon atoms could be driven to a and b interstices by deformation stressfields at a favourable temperature. At very low temperatures this process is not possible. Collective order in tetragonal Fe-Ni-C martensites is known to be very stable at

low temperatures. Tetragonality transforms to cubic only above room temperature due to clustering and precipitation of carbon. The possibility of normal clustering process caused by deformation as an explanation for the present results is not probable firstly because samples remain rather ductile (normally aged and clustered samples are brittle) and secondly Mössbauer spectra were different.

It has been shown that the brittleness of martensite is due to the aging effects (redistribution of carbon atoms) at the room temperature region (6). As the carbon redistribution can be affected by deformation at low temperatures, it would be possible to change the aging behaviour also. In this field studies are continued.

## 5 CONCLUSION

Effects of low temperature deformation on the lattice structure and carbon atom redistribution in two Fe-Ni-C martensites were studied using X-ray diffractometry and Mössbauer spectroscopy. Deformation at 77 K did not cause drastic changes in the lattice, but during deformation at 200 K tetragonality and probably also the carbon distribution were changed. Most of the present observations could be explained, if at least a part of carbon atoms were driven from c axis interstices to a and b sites.

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