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## EFFECTS OF LOW TEMPERATURE DEFORMATION ON THE LATTICE STRUCTURE AND CARBON DISTRIBUTION IN Fe-Ni-C MARTENSITE

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### ABSTRACT

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, 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, which indicates that redistribution of carbon atoms has occurred. Reduction of tetragonality was also observed. Especially in Fe-25Ni-0.7C martensite deformed at 200 K X-ray diffraction measurements revealed no sign of tetragonality.

### 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 the carbon atoms are assumed to lie in c axis octahedral sites (1,2), but in some models also tetrahedral sites are assumed to be possible (3). After aging at very low temperatures only slight effects have been observed in the martensite Mössbauer spectra (4), although tetragonality has changed drastically (5). Virgin martensite is known to be rather ductile, but mechanical properties become worse after aging in the room temperature region (6). Deformation mechanisms have been studied in Ref. (7). Recent experiments have shown that low temperature deformation changes the lattice structure and carbon distribution (8).

### 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 then water quenched. The 3 mm thick pieces were cold rolled 70% and re-austenitized in salt bath for two minutes. Finally they were chemically thinned into 40  $\mu\text{m}$ . These samples were later used in Mössbauer experiments. Carbonless reference specimens were prepared by annealing the foils first in wet hydrogen atmosphere at 973 K for 25 hours, then for six hours in dry hydrogen, and finally for two hours in argon atmosphere in order to remove oxygen and hydrogen from the specimen. Fe-25Ni-0.7C samples were austenitized at 1420 K for three hours and then water quenched. Deformation of the Fe-20Ni-1.15C samples was performed by hammering at liquid nitrogen temperature and at 200 K. Fe-25Ni-0.7C samples were deformed at 213 K by using a rolling machine specially constructed for this purpose.

Transmission Mössbauer measurements were made using the radioactive source  $\text{Co}^{57}$  in chromium matrix (5 mCi). One measurement was performed at room temperature, in order to make sure that the specimen was completely austenitic. After that the specimen was quenched in liquid nitrogen. The sample was hammered at temperatures 77 K and

200 K and then aged at room temperature for 12 hours. Mössbauer measurements were performed at liquid nitrogen temperature after each treatment.

X-ray diffraction experiments of the deformed foils were made at room temperature using  $\text{Cr K}\alpha$  radiation (for Fe-20Ni-1.15C sample) and  $\text{Cu K}\alpha$  radiation (for Fe-25Ni-0.7C specimen). In the latter case the diffractometer was equipped with a curved secondary monochromator. Also low temperature X-ray diffraction experiments were made. In these measurements the pieces of 1mm in thickness were strained two-axially in a special sample holder.

The electrical resistance of deformed and undeformed Fe-25Ni-0.7C samples was measured by using a four point method. Austenitized samples were quenched in liquid helium. Two samples were rolled at 213 K. All the samples were aged at different temperatures and resistances were measured.

### 3 RESULTS

#### 3.1 X-RAY DIFFRACTION MEASUREMENTS

A martensite doublet (110) and an austenite (111) reflection of the sample Fe-20Ni-1.15C are shown in Fig. 1a. This measurement was performed at room temperature after quenching the specimen in liquid nitrogen and aging it for two hours at room temperature. The amount of martensite is 27 % and the tetragonality is 1.075. Retained austenite peak is composed of  $\text{K}\alpha_1$  and  $\text{K}\alpha_2$  components (denoted by  $(111)_\gamma^a$  and  $(111)_\gamma^b$  in the Figure 1a). An identical measurement was made for the sample which was hammered in liquid nitrogen (Fig. 1b.). Peaks are now much broader and the amount of martensite is increased to 97 %, but the peak positions have changed only slightly ( $c/a = 1.067$ ). Hence, deformation at 77 K does not essentially decrease the tetragonality. This result was confirmed also by the measurements made at temperature 77 K with two-axially strained specimens. Tetragonality was then higher because there had been no room temperature aging.

Another Fe-20Ni-1.15C sample (used also in the present Mössbauer experiments) was further deformed at 200 K, and X-ray diffraction measurements were performed at room temperature. The results are presented in Fig. 1c and d. The measurements were preceded by aging for 2 hours (Fig. 1c) and for 12 hours (Fig. 1d) at room temperature. Martensite peaks are even broader than in Fig. 1b and tetragonality is decreased to 1.045. The amount of martensite is now 95 %. The diffraction peaks were fitted using pseudo-Voigt functions. In the fittings of deformed martensite a three-peak model was used, because two-peak fits were not successful. The additional peak in the middle of  $(011)_M$  and  $(110)_M$  reflections are marked by C.

The specimen Fe-25Ni-0.7C was quenched in liquid helium in order to decrease the fraction of retained austenite. After that it was heated up to 200 K and cold rolled about 40 %. Measurements were performed at room temperature after 2 hours and 12 hours aging. The results are shown in Fig. 2a and Fig. 2b respectively. The austenite (111) and the martensite (110) peaks are separate in Fig. 3a, and martensite is clearly tetragonal ( $c/a = 1,050$  %). But after cold rolling only one very broad martensite reflection is seen. Retained austenite peak is also broadened.

#### 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.3. These measurements were made at liquid nitrogen temperature. Deformation at 77 K increased the fraction of martensite phase (see also Fig.1) but did not change the shape of the virgin martensite spectrum (not shown here). Deformation at 200 K drastically changed martensite Mössbauer line profiles (Fig. 3b). Room temperature aging for 12 hours had a slight effect on the ferromagnetic spectrum (Fig. 3c). All Mössbauer spectra were computer fitted. The fitting model and spectrum analyses are described below.

##### Fitting model

Mössbauer peaks of the present alloy are broad because of high nickel content. An exact fitting model which takes into account different nickel and carbon environments of  $\text{Fe}^{57}$  atoms is very complicated. In the present study the effects of nickel atoms are treated only mathematically (9). 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

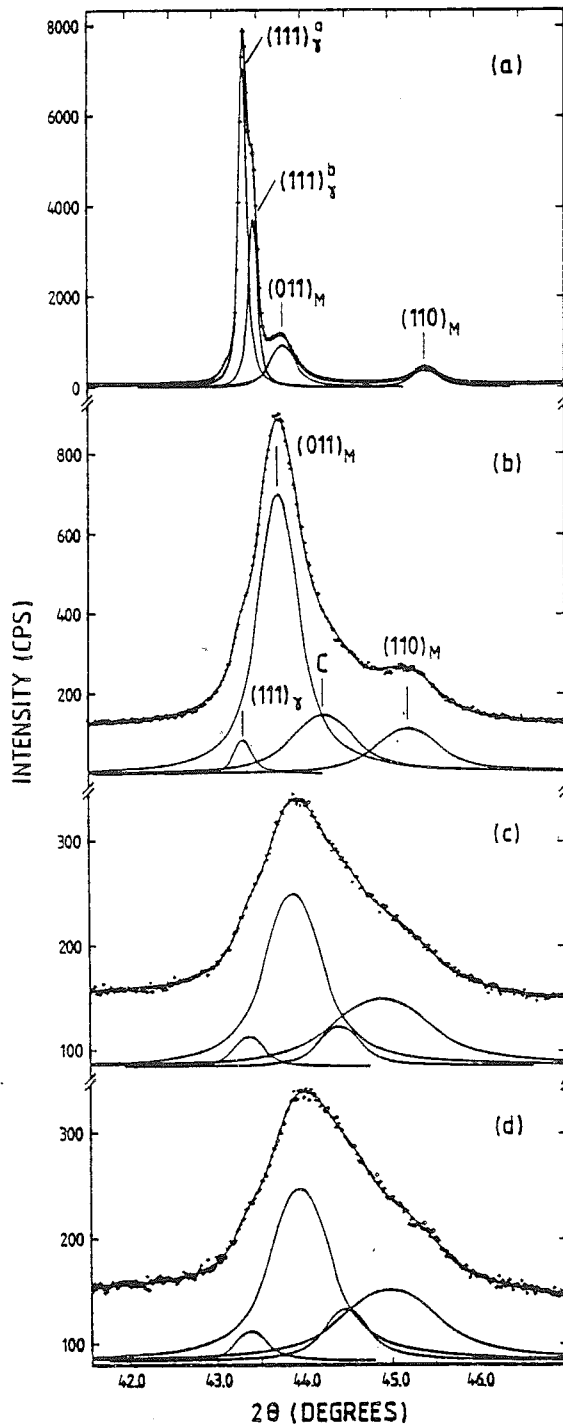


Figure 1. X-ray diffraction patterns of the Fe-20Ni-1.15C samples, quenched in liquid nitrogen  
 (a) sample (1), no deformation  
 (b) sample (2), deformed at 77K  
 (c) sample (3), deformed at 77K and at 200K  
 (d) sample (3), subsequently aged for 12 hour at 300 K

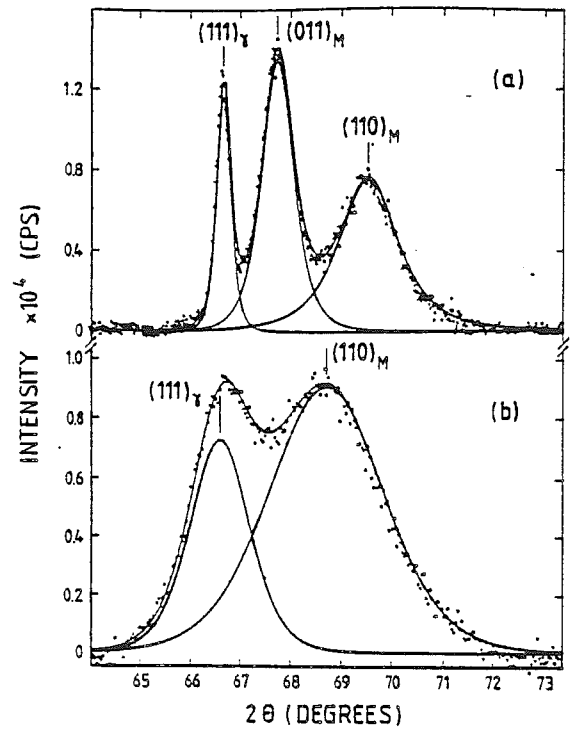


Figure 2. X-ray diffractogram of the Fe-25Ni-0.7C sample quenched in liquid helium, measured at 300 K (a) after quenching and (b) after deformation at 200K.

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 decarburization annealing were omitted. It is evident that this model can be valid only if nickel atoms affect the hyperfine fields of  $Fe^{57}$  nuclei in a similar way both in the Fe-20Ni-1.15C martensite and in the Fe-20Ni reference. 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 slightly the Mössbauer spectra of Fe-Ni-C martensites (4). As for the 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 interstitials. 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 is binomially distributed

$$P_{nml} = \binom{n}{2} \binom{m}{4} \left(\frac{1}{8}\right)^c c^{n+m+l} (1-c)^{14-n-m-l}$$

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 to be 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

The Mössbauer spectrum shown in Fig. 3a could be well fitted using the present model. Hyperfine fields of iron caused by the first, second and third carbon neighbours were 28.8 T, 30.3 T and 34.2 T respectively. The absorptions of the second and fifth peaks were 66 % of the values in the reference Fe-20Ni spectrum. It indicates that magnetic field distribution in the specimen cannot be random but tends to be perpendicular to the sample surface. If the magnetization

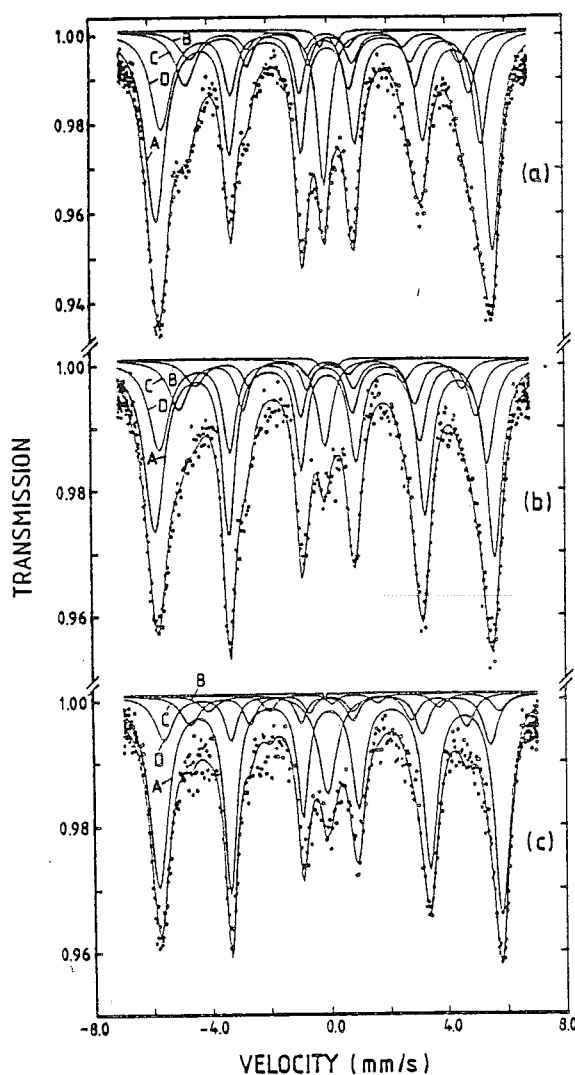


Figure 3. Mössbauer spectra of Fe-20Ni-1.15C martensite (sample 3) measured at 77 K: (a) deformed at 77 K, (b) further deformed at 200 K and (c) aged at RT for 12 hours

vector is assumed to be parallel to the *c* axis, this result means that deformation at 77 K produces an angular dependence in the *c* axis orientation distribution. The amount of martensite was calculated to be 92.3 %.

During further deformation at 200 K (Fig. 3b) the amount of martensite increased up to 95 % which is well in accordance with the X-ray diffraction result (see Fig. 1c). The orientation distribution of magnetization is now almost 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. 3a, isomer shifts caused by the first and second neighbour carbon atoms became nearly equal. Also quadrupole splitting changed clearly. The spectrum 3b was also fitted using a model where carbon atoms are assumed to lie in *a* and *b* octahedral sites. In some attempts a fourth neighbour shell was included. Those results did not essentially differ from the present ones.

The spectrum of the room temperature aged martensite (Fig. 3c) 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.

### 3.3 ELECTRICAL RESISTANCE MEASUREMENTS

Electrical resistances for rolled and non-rolled samples are shown in Figure 4. The temperature range for aging was 213-404 K. Intervals of 5, 10 and 15 K were used. Aging time at every temperature was 20 minutes. After each aging stage resistance in liquid nitrogen was measured. The curves for non-rolled and slightly rolled samples show that relative resistance clearly starts to increase at 250 K. The maximum value of resistance is reached at about 320 K. For the rolled sample maximum value is somewhat smaller. When the degree of deformation is raised to 60 %, resistance hardly increases at all. It is also seen (Fig. 4) that maximum value is reached already at 290 K. Electrical resistivities were also calculated, but on resistivity deformation had only a slight effect. Optical microscopic study revealed that the degree of deformation had no significant effect on the amount of martensite. Heavily deformed structure with bended martensite lenses is shown in Figure 5.

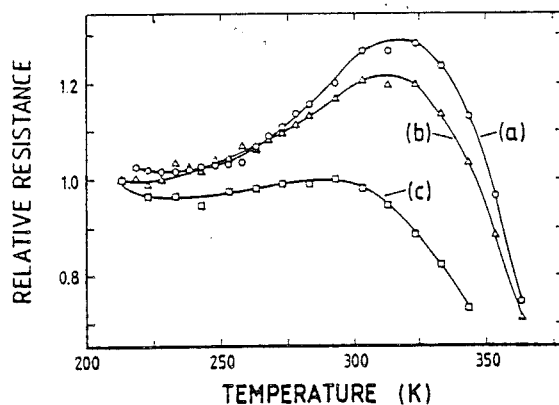


Figure 4. Effects of deformation degree on electrical resistance: (a) no deformation (b) 5% deformation, (c) 60 % deformation



Figure 5. Heavily rolled Fe-25Ni-0.7C martensite.

## 4 DISCUSSION

X-ray diffraction measurements revealed that tetragonality of martensite does not change essentially during deformation at liquid nitrogen temperature. Diffraction peaks are, however, very broad, which 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 observed not to be random. If magnetization is assumed to be parallel to *c*-axis, as shown by Entin et al. using neutron diffractometry (10), the result indicates an angular dependence in *c* axis distribution. Further deformation at 200 K broadened X-ray diffraction peaks and reduced the tetragonality. For the alloy Fe-25Ni-0.7C only one martensite peak was present. Martensite lattice might have transformed to cubic. On the other hand, single diffraction peak could be composed of a distribution of tetragonal doublets with several axial ratios

whose average is smaller than that of the undeformed martensite. The existence of the intermediate peak C in Figures 1b-d might be understood also as a rough approximation of the tetragonality distribution. Mössbauer 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, but they did not confirm that carbon atoms would be 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 the unit cell any more (it is not probable that the structural texture would disappear during further deformation at 200 K). According to the present experimental data, the authors assume that carbon atoms could be driven to a and b interstices by deformation stress fields at a suitable temperature and the cubic lattice structure would result. At very low temperatures this process would be impossible. Collective order in tetragonal Fe-Ni-C martensites is known to be very stable at low temperatures. Tetragonal structure normally transforms to cubic only above room temperature when clustering and precipitation of carbon occur.

Deformation at 200 K changed the behaviour of electrical resistance. The typical increasing tendency (11, 12, 13) in the beginning of the curve (Fig. 4) was absent. The increase is generally attributed to the first stages of carbon clustering (14). The authors assume that tetragonality reduction accompanied by the redistribution of carbon atoms during deformation has changed the aging behaviour and clustering process. Large deformation seems to prevent, or at least retard, cluster formation.

It has formerly been shown that the brittleness of martensite is caused by redistribution of carbon atoms during aging in the room temperature region (6). As the carbon redistribution and aging behaviour can be changed by the deformation at low temperatures, it should be possible to affect also the mechanical properties. Research in this field continues.

## 5 CONCLUSIONS

Effects of low temperature deformation on the lattice structure and the first stages of aging in two Fe-Ni-C martensites were studied. Deformation at 77 K did not cause major changes in the lattice. Instead, during deformation at 200 K, both tetragonality and probably also the carbon distribution changed. Most of the present results could be explained if at least part of the carbon atoms were driven from c axis interstices to a and b interstices. Electrical resistance measurements revealed that the first stages of aging were changed.

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