This article was published in


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OVERVIEW NO. 99

EFFECTS OF COHERENT INTERFACES IN THE FRESHLY FORMED IRON–NICKEL–CARBON MARTENSITES

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(Received 10 January 1992)

Abstract—Evidence for a coherent bond at the interfaces between retained austenite and as-quenched martensite in Fe–Ni–C alloys and the relation of coherent interfaces to the abnormally high tetragonality of martensite are presented. The iron based alloys with 20 Ni–0.73 C, 28 Ni–0.2 C, 20 Ni–1.2 C, 25 Ni–0.7 C, 30 Ni–0.37 C, 33.5 Ni–0.01 C (in wt%) were studied by means of X-ray and neutron diffraction, Mössbauer spectroscopy, internal friction, electrical resistivity and magnetic susceptibility. It is shown that the break of coherency occurs during heating of the freshly formed twinned martensite in the temperature range of 100–200 K and it is accompanied by a relaxation of stresses in the retained austenite and a decrease of tetragonality. A new internal friction peak centered at 145 K was observed and attributed to movement of coherent interfaces and to the subsequent break of coherency. The relation between abnormally high tetragonality and coherency at the interface was confirmed in experiments with external deformation of virgin martensite at temperatures around 100 K. It is shown that the plate morphology of martensite is a necessary condition for a coherent bond at the interface. A possible role of atomic ordering of austenite in abnormally high tetragonality is discussed. Mössbauer measurements gave evidence for nickel-rich regions in initial austenite. During quenching the regions with the highest nickel content were assumed to remain austenitic inside the martensite plates. The conclusion about the coherency at the interface between the freshly formed martensite and the ordered regions in the retained austenite and at the interface along the martensite plates as a reason for high tetragonality of the Fe–Ni–C martensite with plate morphology is made.

Résumé—Cette publication met en évidence un lien cohérent entre l'austénite restante et la martensite quasi-trempée dans le cas des alliages de formule Fe–Ni–C, ainsi que la relation entre les interfaces cohérentes et la tétragonalité anormalement élevée de la martensite. Les alliages à base de fer: 20 Ni–0.73 C, 28 Ni–0.2 C, 20 Ni–1.2 C, 25 Ni–0.7 C, 30 Ni–0.37 C, 33.5 Ni–0.01 C (en % du poids) y furent étudiés dans le cadre de la diffraction par rayon ou par neutron, de la spectroscopie de Mössbauer, de la friction interne, de la résistivité électrique et de la susceptibilité magnétique. Il y est prouvé qu'une rupture de cohérence apparaît pendant le chauffage de la martensite fraîche à morphologie en plaques à une hauteur de température comprise entre 100 et 200 K et qu'elle s'accompagne d'un relâchement de la tension dans l'austénite restante ainsi que d'une diminution de tétragonalité. On a pu observer à 145 K l'obtention d'un nouveau sommet dans la friction interne, il est attribué au mouvement des interfaces cohérentes et à la rupture subséquente de cohérence. La relation entre la tétragonalité anormalement haute et al cohérence à l'interface fut confirmée par des expériences avec déformation externe de martensite vierge à des températures avoisinant les 100 K. Il y est démontré l'importance de la morphologie de la martensite en plaques, condition nécessaire pour obtenir un lien cohérent à l'interface. On y présente aussi le rôle possible joué par l'ordre des atomes dans l'austénite en cas de tétragonalité anormalement haute. Les mesures de Mössbauer ont aussi permis de mettre en évidence des régions riches en nickel dans l'austénite initiale. On y assume que pendant le trempage, les régions à fort contenu en nickel sont restées austénitiques au sein des plaques de martensites. On en conclut que la cohérence à l'interface entre la martensite fraîchement formée et des régions ordonnées de l'austénite restante ainsi qu'à l'interface entre les plaques de martensite est la raison de la haute tétragonalité de la martensite Fe–Ni–C à morphologie en plaque.
1. INTRODUCTION

The freshly formed Fe–Ni–C martensite is characterized by abnormally high tetragonality. The excessive part of the $c/a$ ratio is compared to that determined by the relation $c/a = 1 + \gamma p (\gamma = 0.046, p$ is the carbon content in wt%) mainly depends on the Ni content [1–4]. The nature of the high $c/a$ ratio in the as-quenched state still remains an object for discussions [5–10]. The hypotheses about the distribution of carbon atoms between the octahedral and tetrahedral interstitial sites [5] or between different sublattices of the octahedral sites [6, 7] and about the coherency at the interface between virgin martensite and retained austenite [8–10] were proposed for the explanation of high tetragonality and for its change during the low temperature ageing. The effects of morphology on tetragonality of Fe–Ni–C martensites were also studied in Ref. [11].

Internal friction method is a powerful tool for studying the relaxation phenomena concerned with redistribution of interstitials and their interaction with the crystal lattice defects or hysteresis processes attributed to the phase transformations and the change of internal stresses. Internal friction studies of the Fe–Ni–C martensites revealed a complicated pattern of peaks below room temperature [12–15]. The aim of this paper is to study the relation between the internal friction peaks and some features of the morphology of martensites with different nickel and carbon contents and to study a possible role of coherent interfaces in abnormally high tetragonality.

2. EXPERIMENTAL

Several iron–nickel–carbon alloys were vacuum melted and the ingots were hot forged. Austenitizing treatments were performed in evacuated quartz capsules. After water quenching the samples were fully austenitic. Analyses, heat treatments and martensitic start temperatures ($M_s$) are given in Table 1. In the alloys of group 1 the $M_s$ temperatures were so low that the transformed martensite was twinned and of plate morphology. Nickel content was varied between 20 and 33.5 wt%. In this range the ordering effects of nickel atoms were expected. The alloys were balanced with carbon to keep $M_s$ temperatures low. The group 2 alloys were transformed to lenticular martensite with a dislocation substructure, because their $M_s$ temperatures were higher.

Internal friction was measured using torsion pendulum equipment described in detail in Ref. [16]. The frequency was around 0.5 Hz and the strain amplitude about $10^{-5}$. A saturating magnetic field was applied in order to avoid the contribution of magnetic domain walls to the internal friction.

X-ray diffraction measurements were carried out using a monochromated Co $K_{\alpha}$ radiation. The equipment was provided with a 120° position sensitive detector system (INEL CPS 120). The specimen was cooled with a closed cycle cryo-refrigerator in the temperature range of 10–330 K. The deformation of the sample at low temperatures was performed by bending of the plate shaped specimen in a specially constructed holder. X-ray diffraction samples were covered with a thin layer of silicon powder for calibration. Neutron diffraction experiments were made in Leningrad Nuclear Physics Institute, Gatchina, Russia, using a high-resolution time-of-flight diffractometer [17]. The diffractometer was provided with a cryostat in which the samples could be quickly quenched in liquid helium and heated to temperatures between 4 and 500 K [16].

Electrical resistivity and AC magnetic susceptibility measurements were made with equipment the principle of which is described in [18]. Four point resistance was measured with an AC bridge (AVS-100 by RV-elektronikka Oy) at a frequency of 20 Hz. The susceptibility device was composed of two coil sets, a test frame and a compensator. The sample was inserted in the test frame. The change of the inductance of the coils was measured. The frequency of the alternating magnetic field was 150 Hz and the amplitude 0.14 mT. In the present measurements a $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ superconductor of a size identical to that of the samples was placed in the compensator.

Because the change of susceptibility at this superconducting transition is close to 1, it was possible to calibrate the susceptibility scale. A special deformation device was constructed for the resistivity and

<table>
<thead>
<tr>
<th>Group</th>
<th>Fe-based alloy</th>
<th>Austenitization temperature and time</th>
<th>$M_s$ temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>20Ni–1.18C</td>
<td>1150°C, 3 h</td>
<td>103 K</td>
</tr>
<tr>
<td>2</td>
<td>28Ni–0.2C</td>
<td>1150°C, 3 h</td>
<td>208 K</td>
</tr>
</tbody>
</table>

Table 1. Heat treatments and $M_s$ temperatures of the alloys (contents in wt%)
susceptibility measurements. In these experiments deformation was performed by twisting, because the change of the cross section and the length of the sample is small. Also a high degree of deformation can be achieved by twisting.

3. RESULTS AND DISCUSSION

3.1. Evidence for coherent interfaces: internal friction, X-ray and neutron diffraction measurements

Temperature dependence of internal friction in the range of 77–350 K is shown in Figs. 1 and 2. Figure 1 presents internal friction evolution during heating of the freshly formed twinned martensites with different nickel contents. Patterns of the two dislocation martensites with the $M_s$ temperature above 200 K are shown in Fig. 2. The internal friction behaviour was found to be quite different for the martensites with plate and lenticular morphologies. Four peaks were observed at temperatures 105, 145, 210 and 250 K in Figs. 1 and 2.

Three of the peaks, $A_1$, $A_3$, and $A_4$, were described earlier by Prioul et al. [12–14]. The isothermal martensitic transformation occurs during heating after the quenching in liquid nitrogen and causes peak $A_1$. The increase of temperature assists the mobility of the dislocations contributing to the damping (the left side of peak $A_3$), while carbon atoms become mobile at temperatures above 200 K leading to the pinning of dislocations, which results in a decrease of internal friction (the right side of peak $A_3$). Neither of these peaks is of relaxation nature, which is consistent with the nearly vanishing values of the activation enthalpy obtained. Peak $A_4$ was attributed to the formation of the Snoek atmospheres, i.e. jumps of carbon atoms into more favourable interstitial sites in the stress field of the moving dislocations [14]. The activation enthalpy of this process is smaller than that of the Snoek relaxation (see, for example, [19]).

Peak $A_2$ was earlier reported by the present authors in [15] with some preliminary conclusions. This peak exists only in alloys with a low $M_s$ temperature (Fig. 1), which is a sign relating this peak to the plate morphology of martensite. It is not observed in the patterns of Fe–20 Ni–0.7 C and Fe–28 Ni–0.2 C martensites (Fig. 2), because the $M_s$ temperatures of these alloys are higher and martensites transformed...
are lenticular. The relative intensity of peak A₂ is reduced by decreasing the nickel and increasing the carbon content, as is clearly evidenced in Fig. 1. For the alloy Fe–33.5 Ni this peak is pronounced but in the curve of the lowest nickel alloyed sample Fe–20 Ni–1.2 C it is only slightly distinguishable, although its Mₙ temperature is the lowest. Hence, nickel and carbon contents play an essential role in the appearance of peak A₂. We shall use the concept of coherency at the interface between virgin martensite and retained austenite for the interpretation of peak A₂. The coherent bond remains between austenite and virgin martensite transformed at low temperatures, because dislocations are "frozen" and cannot provide a relaxation of the stresses which are caused by the coherency at the interface. Coherency is broken at temperatures where dislocations in austenite become sufficiently mobile. With the following experiments we shall test this interpretation.

Figure 3 displays internal friction of the freshly formed Fe–33.5 Ni martensite during step-wise heating to different temperatures (the intermediate cooling curves to 77 K are not shown).

The measurement reveals the reversibility of the left side of peak A₂. We attribute the left side to the movement of coherent interfaces the mobility of which is increased with temperature. The right side of peak A₂ is irreversible [see Fig. 3(a), curves 2–5], which can be interpreted as evidence for the coherency break. The frequency of the aged martensite is quite independent of temperature [Fig. 3(b), curve 5], which is typical for invar alloys. In the case of the freshly formed martensite frequency increases with temperature during each step of heating, which is attributed to the decrease of the modulus defect due to pinning of dislocations by carbon atoms. Hence, the data obtained for the origin of the A₂ are consistent with the interpretation proposed above.

As mentioned above, the concept of coherency was proposed as an explanation of the abnormally high tetragonality in the freshly formed Fe–Ni–C martensites [8, 9]. It was used to explain the tetragonality of the carbon-free Fe–Ni martensite, too [10]. The behaviour of the c/a ratio during heating the virgin Fe–33.5 Ni martensite is shown in Fig. 4. The c/a value of the as-quenched martensite is so high and the carbon content (0.01 wt%) so low that the origin of tetragonality cannot lie in the ordering of carbon atoms in one of the three sublattices of the octahedral interstitial sites. We assume that the reason is the coherency between martensite and retained austenite,
especially at the interfaces of the small ordered austenite regions inside of the martensite plates. During heating in the temperature range of 100–200 K the martensite lattice becomes nearly cubic. The temperature ranges of the decreasing tetragonality and the internal friction peak \( A_2 \) coincide. A small tetragonality can remain even after ageing at room temperature. This can be explained by the short range atomic order in the Fe–Ni austenite according to Winchell et al. [20]: atoms of one kind (Fe) surrounded by atoms of the other kind (Ni) tend to retain the former atomic configuration in martensite which resists the Bain strain and causes the tetragonal distortion of the martensite crystal lattice.

Tetragonality behaviour of the Fe–30 Ni–0.37 C and Fe–25 Ni–0.7 C martensites is also shown in Fig. 4. In both of the alloys the \( c/a \) ratio is remarkably higher as compared to the relation \( c/a = 1 + 0.046 \rho \) and they display a similar decrease of \( c/a \) between 100 and 200 K. Tetragonality reduction in these martensites also coincides with the temperature range of the internal friction peak \( A_2 \) and is attributed, by the present authors, to the break of coherency at the interface between martensite and austenite. The further decrease of tetragonality above 250 K is associated with the clustering of carbon atoms and it will be discussed elsewhere. For the dislocation martensites Fe–20 Ni–0.7 C (see Fig. 4) and Fe–28 Ni–0.2 C no decrease of tetragonality was observed during heating in the temperature range of 100–200 K, which is in accordance with the absence of the internal friction peak \( A_2 \) for these alloys as shown in Fig. 2.

![Figure 6](image)

**Fig. 6.** The effect of deformation *in situ* on the diffraction peaks (112)\(_x\) and (211)\(_x\) of the virgin Fe–33.5 Ni martensite: (a) undeformed; (b) deformed at 40 K; (c) further deformed at 110 K. Both measurements were made at 40 K.

The decrease of tetragonality in Fe–Ni–C martensites at low temperatures was observed by Hayakawa et al. with X-ray diffraction [3, 21] and by the present authors with neutron diffraction [22]. A detailed analysis of the tetragonality behaviour of different Fe–Ni–C martensites was performed by Kajiwara et al. [4, 11]. Unlike in X-ray diffraction, information is obtained from a real bulk sample in the case of the neutron diffraction measurements and therefore it is a useful method for studying the effects of internal stresses. Figure 5 shows the change of the width of the Fe–20 Ni–1.2 C austenite peak (311), during cooling and during the subsequent heating to room temperature. The behaviour of the other austenite peaks was similar. During martensitic transformation the austenite lines become broader indicating the increase of stresses in the retained austenite.

Stresses in retained austenite were studied by Hayakawa and Oka [23], Golovchiner [24], Jershov and Oslon [25] and Gridnev and Trephilov [26] by means of X-ray diffraction. Conclusion about hydrostatic compression of the retained austenite during martensitic transformation was made in Refs [24–26] while according to [23] stresses in austenite, not of
hydrostatic nature, are created in austenite before martensitic transformation due to rapid cooling from the homogenization temperature and they are relaxed during transformation. This discrepancy between different X-ray results and between the X-ray and neutron diffraction data, too, could be explained by the fact that X-ray diffraction is obtained from a surface layer. This can lead to incorrect conclusions about compression or dilatation of the retained austenite or absence of stresses, because depending on treatments (homogenization temperature, cooling rate), stresses in surface layers can have different values and directions. Neutron diffraction data provide the opportunity to evaluate the average stresses in the whole of the sample. According to the present measurements the positions of the retained austenite peaks in a neutron diffraction pattern at different temperatures do not differ from those of the initial austenite. Thus there is no hydrostatic compression nor dilatation in austenite due to martensitic transformation in accordance with [23], while broadening of the peaks, in contrast to [23], gives evidence for increase of the stresses during transformation.

During heating the austenite line width is significantly decreased (Fig. 5). We attribute this reduction to the stress relaxations in austenite as a result of the break of coherency at the martensite–austenite interface. The austenite peak positions remain unchanged. The changes in line widths were remarkably smaller in the alloy Fe–18 Ni–0.7 C, whose Ms temperature is higher and morphology is lenticular [22].

If the break of coherency is assisted by some dislocation process, as we assume, tetragonality should also be reduced by applying an external stress. In order to test this idea the virgin Fe–33.5 Ni and Fe–25 Ni–0.7 C martensites were deformed in situ at two temperatures 40 and 110 K during the X-ray diffraction measurement. 110 K was selected for the deformation temperature, because it is there that we have the onset of the break of coherency effects, according to tetragonality measurements (see Fig. 4). The fitted diffraction patterns are shown in Fig. 6. The clearly resolved diffraction peaks (112)_α' and (211)_γ of the undeformed Fe–33.5 Ni martensite in Fig. 6(a) are evidence for a high axial ratio c/a. Tetragonality was decreased after a slight deformation at 40 K [Fig. 6(b)], while the deformation at 110 K led to a total disappearance of tetragonality [Fig. 6(c)], which is a sign of a broken coherency at the interface between martensite and retained austenite. It is noteworthy that the peak in the Fig. 6(c) is narrow, which indicates that stresses have relaxed during deformation. This is in accordance with the neutron diffraction data about the correlation between stresses at coherent interfaces and abnormally high tetragonality [22]. The break of coherency really releases stresses in the retained austenite.

The decrease of tetragonality during deformation was also found in the alloy Fe–25 Ni–0.7 C. Figure 7(a) shows the diffraction patterns after deformations at 60 and 110 K. Tetragonality was decreased from the value of the virgin martensite. Further deformation at 120 K led to a drastic change in tetragonality: the c/a ratio decreased to the value of 1.018 which is much less than even in the case of aged martensite (see Fig. 4). In Ref. [27] it was shown that during a heavy deformation at 200 K the tetragonal doublets were reduced to symmetrical single peaks indicating that the lattice became cubic. It means that besides the break of coherency, a redistribution of carbon atoms has taken place, which was evidenced by Mössbauer measurements. It was obvious that low temperature deformation changes also the ageing behaviour of martensite possibly by preventing clustering of carbon atoms. The effects of low temperature deformation on the martensite lattice structure was earlier studied by Kurdjumov et al. [28]. In [27, 28] the decrease of tetragonality was explained by a movement of carbon atoms from the c-axis octahedral sites to sites a and b. Although virgin martensite is rather ductile at low temperatures a possible microcracking has to be taken into account with the capture of carbon atoms from the solid solution.

All X-ray samples in the present study were covered with a silicon powder for calibration. This method is of special importance in the deformation experiments where a slight displacement of the specimen is possible. Figures 6 and 7 show that the martensite doublets are shifted during deformation, which may indicate changes in martensite unit cell volumes. A possible role of macrostresses of the sample in the holder can not be completely excluded either. However, the shifts were not observed in the

![Fig. 7. Diffraction patterns of Fe–25 Ni–0.7 C martensite: (a) deformed at 60 K and further at 110 K, (b) subsequently deformed at 120 K. Measurements were made at 60 K.](image-url)
retained austenite peak positions in Fig. 7, which can be regarded as evidence for real changes in the martensite unit volume.

The internal friction peak \( A_2 \) (Fig. 1) above was attributed to the mobility of coherent interfaces between martensite and retained austenite. As shown by X-ray measurements the coherency can be broken by deformation. If the present interpretation for peak \( A_2 \) is correct, it should disappear during low temperature deformation. In order to test this argument the virgin Fe–33.5 Ni martensite sample was deformed 10% by twisting at 77 K in the internal friction sample holder. The subsequent measurement in the temperature range of 77–200 K revealed no sign of the 145 K peak within the limits of error. This curve is shown in Fig. 1 (denoted by filled circles). Also the isothermal martensite peak \( A_1 \) was absent, because the martensitic transformation was completed during deformation.

### 3.2. Break of coherency: electrical resistivity and magnetic susceptibility data

It was possible to perform electrical resistivity and magnetic susceptibility measurements simultaneously with the same sample, which is of special importance when precise comparisons are made and high resolution is required. Figure 8(a) shows a change of electrical resistivity during cooling of the Fe–33.5 Ni alloy to 20 K and during the subsequent first and second heatings. The martensitic transformation occurred at 125 K. The electrical resistivity and magnetic susceptibility patterns of the second heating were subtracted from those of the first heating and the difference curves are shown in Fig. 8(b) and (c) respectively. Using this method, irreversible effects can be separated from the reversible thermal ones.

Isothermal martensitic transformation occurs during the first heating below 120 K (as evidenced by internal friction measurements) and it is accompanied by a decrease of magnetic susceptibility shown in Fig. 8(c). This is due to the fact that the magnetic domain walls can move more easily in the ferromagnetic austenite than in martensite. The formation of the isothermal martensite is accompanied by a decrease of electrical resistivity. The noteworthy feature in the electrical resistivity change during heating is the continuation of its reduction above 120 K [Fig. 8(b)] at which temperature the formation of isothermal martensite has been completed according to the internal friction (Fig. 1) and susceptibility [Fig. 8(c)] measurements. The resistivity curve 8(b) levels off at 170–200 K. As shown by the X-ray results (Fig. 4) tetragonality disappears in this temperature range. Hence, the decrease of resistivity above 120 K can be explained by the stress relaxation during the break of coherency, which is consistent with the present model. This explanation is close to the interpretation given by Hoffman and Cohen [29] for a change of resistivity during low temperature ageing of martensite. However, the \( M_S \) temperatures of the alloys studied in [29] were not low enough for the present coherency effects to occur. Probably, the low temperature resistivity reduction reported in [29] was due to the formation of reheat martensite. Magnetic susceptibility increases in the temperature range of 120–200 K [Fig. 8(c)] where the break of coherency occurs. This is natural, because the relaxation of internal stresses increases the mobility of the magnetic domain walls. The susceptibility curve levels off at temperatures above 170 K where the break of coherency is completed. The small reduction between 210–240 K and the final increase of susceptibility above 250 K are attributed to the redistribution of carbon atoms (see Table 1).

Electrical resistivity and magnetic susceptibility of the Fe–33.5 Ni alloy were measured during deformation at liquid nitrogen temperature. Resistivity vs degree of deformation is presented in Fig. 9. It is noteworthy that resistivity decreases during deformation. It can be explained by the formation of stress assisted and strain induced martensites and by the break of coherency between martensite and austenite phases. The overall reduction of about 13 \( \mu \Omega \text{cm} \) is larger than the difference between the first and second heatings shown in Fig. 8(b). This is because during
deformation more martensite is transformed than during heating. The measurement which was performed during heating after the deformation at 77 K revealed only negligible effects, which means that the formation of martensite and the break of coherency had mostly occurred during the deformation, which is in accordance with the present internal friction and X-ray measurements. Thus the electrical resistivity and magnetic susceptibility data are consistent with the proposed model of coherent interfaces.

3.3. Effect of $M_s$ temperature and morphology: two-stage cooling

Coherency at the interface between martensite and retained austenite can be expected only for the plate morphology, i.e., for the twinned martensite and not for the dislocation martensite. All measurements made with Fe–Ni–C alloys support this assumption. As seen in Fig. 2, the coherency peak $A_2$ does not exist in the internal friction curve of the Fe–20 Ni–0.7 C martensite. Neither the X-ray nor the neutron diffraction measurements made with the alloys Fe–20 Ni–0.7 C and Fe–18 Ni–0.7 C revealed any sign of the coherency effects (see also [22]), which is obvious taking into account the high $M_s$ temperature and correspondingly the lenticular morphology of those martensites.

We shall further test the relation between the internal friction peak $A_2$ and the coherency. We shall also study, whether the coherency is dependent on the morphology of martensite or whether the low $M_s$ temperature itself could be a sufficient condition for the coherency to exist. The possibility for such a test is provided by the procedure of the two-stage cooling [16, 30]. Using this method it is possible to produce dislocation martensite at low temperatures.

Temperature dependence of magnetic susceptibility of the Fe–20 Ni–0.7 C alloy during coolings and heatings is shown in Fig. 10a. The martensitic transformation started at 208 K ($M_{S1}$) during the first cooling. The decrease of susceptibility just below the burst is typical for lenticular martensites. It is of magnetic origin and indicates no reduction in the amount of martensite, which was evidenced by resistivity and dilatometric measurements. The cooling was interrupted at 150 K and after that the sample was heated back to room temperature and then cooled to 77 K. Martensitic transformation in the retained austenite occurred starting from 110 K ($M_{S2}$). The stabilization of the retained austenite is caused by ageing of the previously formed martensite during its heating to room temperature in accordance with studies performed in [31]. It would be natural to expect that thin plate martensite with twinned structure would be formed in such a low temperature range according to [32]. However, the martensite obtained during the second stage of cooling is dislocation martensite. This was also proved by transmission electron microscopy studies [30].

The difference of electrical resistivity between the second and third heatings is shown in Fig. 10(b). Finally the third heating [not shown in Fig. 10(a)] was performed to ensure that all irreversible effects had occurred. The significant difference, as compared to the resistivity behaviour of the alloy Fe–33.5 Ni [compare Fig. 8(b)], is that resistivity is decreased mostly at temperatures below 120 K where isothermal martensitic transformation takes place. It levels off at 140 K at which temperature there is a minimum in the internal friction curve of this alloy indicating the completion of the formation of reheat martensite. No change in resistivity is observed in the temperature range where the break of coherency occurs in the twinned martensites (compare Fig. 8b).

The internal friction behaviour during heating after the first and second cooling is shown in Fig. 11.
Fig. 11. Internal friction of the Fe–20 Ni–0.7 C alloy during the first (a) and second (b) heatings in the two-stage cooling experiment [compare Fig. 10(a)].

Peaks \( A_3 \) and \( A_4 \) appeared during the first heating from 150 K to room temperature [Fig. 11(a), see also Fig. 2] due to the interaction between dislocations and carbon atoms: pinning of dislocations and the formation of the Snoek atmospheres respectively. The heating after the second stage of cooling [Fig. 11(b)] reveals the isothermal martensitic transformation at about 100 K (peak \( A_4 \)) and a small peak \( A_3 \) at about 200 K. Peak \( A_3 \) is the "dislocation" peak of the secondly obtained martensite. Peak \( A_3 \) belongs to the martensite transformed below 110 K during the second stage of cooling and also during the following heating. The martensite transformed during the first cooling gives no contribution to internal friction now because of the irreversibility of the peaks \( A_3 \) and \( A_4 \) shown in Fig. 11(a). Internal friction serves as a unique method to study selectively the effects in martensites which have transformed at different temperatures.

It is noteworthy that the 145 K peak \( A_3 \) concerned with the break of coherency is not observed in Fig. 11(b). This result confirms the relation of the peak \( A_3 \) to the twinned martensite, i.e., plate morphology.

3.4. Evidence for the short range ordering of the nickel atoms in austenite

As it was shown above the nickel content plays an important role in the existence of the internal friction peak \( A_4 \) which is caused by the movement of coherent interface and break of coherency. We attribute the abnormally high tetragonality to the coherency bet-

Fig. 12. Mössbauer spectra of Fe–33.5 Ni austenite after cold rolling (a) and subsequent annealing at 1200°C for 1 h (b) and further at 900°C for 18 h (c).

between martensite and retained austenite and assume that nickel-rich regions which can have remained untransformed inside martensite plates have an important role. The existence of nickel-rich regions in the Fe–Ni–C martensite was evidenced by the Mössbauer measurements [33]. The atomic ordering in Fe–Ni alloys is accompanied by the magnetic ordering [34, 35]. Thus it is possible to evaluate the degree of atomic ordering by means of the Zeeman splitting in the Mössbauer spectra.

Figure 12 shows Mössbauer spectra of Fe–33.5 Ni austenite after different treatments. There the increase of the high field components (outer peaks) in

Fig. 13. Mössbauer spectrum of the Fe–33.5 Ni alloy after quenching the austenitic sample [aust. at 1200°C, 1 h and further at 900°C, 18 h; Fig. 12(c)] in liquid nitrogen; measured at room temperature.
the austenite spectra when the austenitizing temperature is decreased is clearly seen. In accordance with the correlation between atomic and magnetic ordering in Fe–Ni alloys it is evidence for the short range atomic ordering in the present alloy, i.e. formation of the nickel-rich regions in austenite. The Mössbauer spectrum of martensite measured after quenching of this specimen in liquid nitrogen is shown in Fig. 13. The remarkable feature of the martensite spectrum is that the retained austenite component (the shaded area) is characterised by a larger relative intensity of the outer lines than in the initial austenite. It can be interpreted as a result of preferential martensitic transformation in the austenite regions depleted of nickel. Therefore, on the basis of the data obtained and in accordance with the idea developed by Kokorin [36] we can assume the existence of the nickel rich austenitic regions in the freshly formed Fe–33.5 Ni martensite and attribute the abnormally high tetragonality to the coherency at their interfaces besides the coherency at the interfaces of the martensite plates.

A test for the existence of such small austenitic regions can be provided by a comparison between the fractions of the retained austenite evaluated from the Mössbauer data and the microscopic analysis. (It was not possible to use X-ray diffraction here because of incorrect intensities due to a large grain size.) The idea of such a comparison is that austenitic regions of any size can be revealed by means of Mössbauer spectroscopy while inclusions beyond the limit of resolution of microscopy are not detected. A preliminary evaluation was performed using optical microscopy and the values of the fractions of the retained austenite were 32 ± 0.5% and 26 ± 1.5% for the Mössbauer and optical microscopy data respectively. The difference exceeds the limits of error and it reveals that about 20% of the retained austenite is distributed in martensite plates in regions smaller than 500 nm. The high-resolution electron microscopy studies will be performed later. In addition, we refer to the unpublished data by Kardonisky [37] who observed the retained austenite regions inside the martensite plates in the binary iron–nickel alloys by means of dark field transmission electron microscopy. The size of those regions was smaller than 10 nm. In accordance with calculations [36], coherency is sustained at the particle sizes 3–5 nm. Thus, we can conclude that nontransformed small regions of the ordered nickel-rich austenite exist inside the martensite plates in the Fe–Ni and Fe–Ni–C martensites. Taking into account the coherency at the interface of such regions it is possible to explain the data obtained by Kourjumov and Mikhailova [38] who observed an increase of tetragonality in the freshly formed Fe–Ni–C martensite when the temperature of the austenitizing treatment was decreased. Of course in such an experiment it is necessary to take into account the phenomenon of graphitization which can screen the effect of ordering on tetragonality.

Also magnetic susceptibility measurements revealed the short range ordering of nickel atoms. Figure 14(a) and (b) show magnetic susceptibility of the alloys Fe–25 Ni–0.7 C and Fe–28 Ni–0.2 C after different austenitizing treatments. All samples were first annealed at 1230°C for 3 h in order to get the same grain size and after that at temperatures of 1050° or 950°C (for 17 h) as shown in Fig. 14. M₅ temperatures were decreased after annealing at 1050°C [Fig. 14(a)] and at 950°C [Fig. 14(b)] as compared to the higher soaking temperatures despite the graphitization took place at temperatures below 1200°C. Higher stability of austenites after lower temperature treatments has to be attributed to the short range ordering of nickel atoms, because the effect of the grain size was excluded and the decrease of the carbon content in solid solution due to graphitization could only cause the opposite effect on the M₅ temperature. Both of the alloys were paramagnetic at room temperature and the ferromagnetic transition took place at about 200 and 260 K in the alloys Fe–25 Ni–0.7 C and Fe–28 Ni–0.2 C respectively. The ordering also affects the magnetic properties of austenite, which displays as a change of the onsets,

![Magnetic Susceptibility](image)

Fig. 14. Magnetic susceptibility (real part χ') of the alloys Fe–25 Ni–0.7 C (a) and Fe–28 Ni–0.2 C (b) during cooling. The two curves in each figure correspond to different austenitizing treatments after annealing at 1230°C. A high-Tₜ superconductor (YBa₂Cu₃O₇₋ₓ) was used to calibrate the susceptibility scale (the change of susceptibility is positive in the figure, because the superconductor was placed in the compensator coil).
widths and intensities of the magnetic transitions. Unfortunately, simultaneous graphitization makes the quantitative analysis difficult. Electron irradiation at room temperature is a better method than annealing for studying the effects of ordering on the tetragonality of Fe–Ni–C martensites, because graphitization can be avoided in the former case. These results will be reported later.

It has been shown above, using different experimental methods, that the necessary condition for the effects of the coherent interfaces between martensite and retained austenite is the plate morphology of martensite with twinned microstructure. In the following we shall test the sufficiency of this condition, which can be done using twinned Fe–Mn–C martensite with abnormally low tetragonality (see, for example, [39]). The Fe–3 Mn–1.6 C martensite with $M_s$ temperature 117 K was selected for this study. Tetragonality in the as-quenched state was abnormally low without any change during subsequent heating between 100 and 170 K. The change of the internal friction during heating of the freshly formed Fe–3 Mn–1.6 C martensite is presented in Fig. 15. Only the reheat martensite peak at 115 K and the dislocation peaks around 250 K (at higher temperatures than for Fe–Ni–C alloys) were observed. No evidence for occurrence of the coherency effects was obtained.

Neither magnetic susceptibility nor electrical resistivity measurements made with the Fe–3 Mn–1.6 C martensite revealed any sign of the present coherency effects. Hence, low $M_s$ temperature and twinned microstructure are not sufficient condition for these effects. Different orientation relationships of the nickel and manganese alloyed martensites may be a reason for different conditions at interfaces. It has to be stressed that Fe–Mn and Fe–Mn–C austenites display no tendency to short range atomic ordering and the opposite effect of decomposition of solid solution accompanied by the formation of manganese clusters takes place according to Mössbauer data and theoretical calculations presented in [40, 41].

We conclude from experimental results shown above that the coherent interfaces and atomic ordering in the retained austenite cause the abnormally high tetragonality of Fe–Ni–C martensites. The coherent bond at the interface between the retained austenite and plates of the as-quenched martensite prevents to complete the Bain strain and sustain the high $c/a$-ratio. In addition, the coherency at the interface of the small regions of the ordered austenite inside the martensite plates largely contributes to tetragonality.

4. SUMMARY

Effects of coherency at the interface between the freshly formed martensite and the retained austenite were studied by means of X-ray and neutron diffraction, internal friction, magnetic susceptibility and electrical resistivity. An interpretation is proposed for a new internal friction peak centered at about 145 K. It is attributed to the movement of coherent interfaces between virgin martensite and retained austenite with a subsequent break of coherency during heating of the virgin martensite. It was shown that the plate morphology of martensite with low $M_s$ temperature and atomic ordering in austenite are necessary and sufficient conditions for the coherency. By means of a two-stage cooling experiment it was shown that the low $M_s$ temperature itself is not a sufficient condition. The measurements made on the iron–manganese–carbon martensite with the low $M_s$ temperature revealed that the twinned substructure alone is not sufficient either. The atomic ordering in the Fe–Ni–C austenite increases the tetragonality of the virgin martensite due to coherency at the interface of the nontransformed small regions of the ordered austenite inside the martensite plates. Some experimental evidence for existence of such small inclusions was given.

Acknowledgements—This research was mainly financed by the Academy of Finland. One of us (K.U.) is indebted to the Oskar Oflund and the Wihrui Foundations and the Foundation of Technology for support. The authors express their appreciation to Dr A. Ustov and Dr D. Mirzajev for discussions and Mr A. Tarasenko for assistance in internal friction measurements.

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![Fig. 15. Evolution of internal friction during heating of the freshly formed Fe-3 Mn-1.6 C martensite.](image-url)
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