

# Evaluation of dislocation density and interstitial carbon content in quenched and tempered steel by internal friction

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## ABSTRACT

In this work, mechanical spectroscopy (internal friction) is used for a qualitative evaluation of interstitial carbon content in martensite and of the dislocation density in bulk samples of quenched and tempered steel. On one hand, the decrease of the amplitude of a local maximum at 380 K is correlated with the reduction of interstitial carbon content in the martensite matrix, which is due to the carbide precipitation during the first stage of tempering. On the other hand, the amplitude change of an internal friction peak that appears at 500 K is correlated to the variation of the dislocation density. Both amplitude variations follow a similar trend during quenching and tempering, indicating a correlation between the interstitial carbon content and dislocation density in martensite. This correlation is in agreement with the results obtained by X-ray diffraction, thermoelectric power, and hardness. Additionally, it is possible to observe the Snoek effect in samples that contain ferrite and martensite with low tetragonality due to intercritical austenitization or tempering.

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## 1. Introduction

In carbon steels, quenching and tempering allow to obtain a wide range of mechanical properties due to the allotropic transformation of iron, and the hardening caused by interstitial carbon [1]. Mechanical spectroscopy can help in improving the microstructural characterization, and understanding of the hardening mechanism of these steels. This technique measures the mechanical loss (internal friction,  $Q^{-1}$ ) when an oscillating periodic stress is applied to the material, and it is sensitive to microstructural changes such as interstitial atoms diffusion and the dislocation movement [1].

In the last years, some works about internal friction of quenched and tempered steels have been reported for low frequencies (1–3 Hz), correlating several relaxation mechanisms with the microstructure [2–6]. On one hand, a local maximum (a non-thermally activated peak) appears around 380 K in quenched and low temperature tempered steels. This local maximum has been related to the decrease of carbon content in martensitic matrix due to transition carbide precipitation during the first stage of tempering [2–5]. On other hand, a thermally activated peak appears

around 480 K in quenched and tempered steels. The peak amplitude is proportional to the density of dislocation segments,  $\Lambda$ , and the active dislocation segment length,  $L$ , according to  $\Lambda L^2$  [5,6].

In this work, the use of mechanical spectroscopy (internal friction) as a technique for microstructural characterization is promoted. Using several austenitizing conditions, qualitative correlations are established between the amplitudes of internal friction peaks occurring at about 380 K and 500 K, and the interstitial carbon content in martensite, or dislocation density in bulk samples, respectively. From this, a correlation between the interstitial carbon content and dislocation density in martensite is established, which is in agreement with the model of Morito et al. [7]. On the other hand, the Snoek peak appears in samples with lower martensite tetragonality, which could be associated to ductile deformation.

## 2. Experimental

The chemical composition was measured in an optical emission spectrometer, with an error of  $1 \times 10^{-2}$  wt% (Table 1). The samples of 40 mm × 4 mm × 1 mm were encapsulated under argon to avoid decarburization during quenching. In both, quenching and tempering, the cooling was made in water. The Table 2 shows the heat treatments that were carried out.

The microstructure was observed by Scanning Electronic

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**Table 1**  
Chemical composition of carbon steel.

Element	C	Si	Mn	S	P	Cr	Ni	Mo	Cu	Sn	Ti	Sb	Fe
(wt%, 10 <sup>-2</sup> )	70.8	30.2	76.2	1.8	1.6	4.9	2.9	1.4	3.2	0.4	0.2	0.9	–

**Table 2**  
Description of heat treatments.

Sample	Austenitizing temperature (K)	Austenitizing time (min)	Tempering temperature (K)	Tempering time (min)
A1093K5	1093	5	–	–
A1093K10	1093	10	–	–
A1173K5	1173	5	–	–
A1173K10	1173	10	–	–
A1173K5R380K	1173	5	380	10
A1173K5R480K	1173	5	480	10

Microscopy (SEM), etching the polished surfaces with 2% nital solution (2 ml HNO<sub>3</sub> + 98 ml of ethanol). Hardness was measured in a Vickers HV Mitutoyo durometer, with a charge of 1 kg, and five tests on each sample, reporting the mean value. X-Ray Diffraction (XRD) measurements were performed at room temperature using CuK $\alpha$  radiation ( $\lambda = 1.542 \times 10^{-10}$  m), and scanning from 20° to 99°, with a step of 0.01°. The thermoelectric power (TEP) was measured at a temperature of 20 °C  $\pm$  10 °C, with a gradient ( $\Delta T$ ) of 20 °C between the extremes of the sample, which is held by copper blocks. This gradient induces a voltage difference  $\Delta V$  due to Seebeck effect. The value obtained,  $\Delta S$ , is the difference between the absolute value of the sample  $S^*$  and the relative value to the TEP of copper blocks,  $S_0$  (Eq. (1)) [8].

$$\Delta S = S^* - S_0 = \frac{\Delta V}{\Delta T} \quad (1)$$

Internal friction was measured from the free decay of the oscillations, with resonance frequency of 2 Hz, amplitude of deformation of  $2 \times 10^{-4}$  and heating rate 0.8 K/min, in a temperature range from 100 K to 800 K. The deconvolution of peaks is made with a background exponential, and Debye functions (Eq. (2)),  $\varphi$ , considering a peak broadening factor,  $\alpha$ , where  $\Delta$  is the relaxation amplitude,  $\omega$  is the angular frequency, and  $\tau$  is the relaxation time. The broadening factor is equal to 1 when the peak is symmetrical [5].

$$\varphi = \Delta \frac{(\omega\tau)^\alpha}{1 + (\omega^2\tau^2)^\alpha}, \quad 0 < \alpha \leq 1 \quad (2)$$

### 3. Results and discussion

Fig. 1 shows the microstructure of the sample A1173K5, a martensitic matrix ( $\alpha'$ ), with regions of ferrite ( $\alpha$ ) and undissolved carbides (c). The same phases are present in all quenched samples. The ferrite appears due to incomplete austenitization. Thus, the size and the amount of ferrite areas decrease when the austenitizing temperature is higher. On the other hand, in the samples austenitized at 1173 K, the tempering at 380 K and 480 K does not generate significant changes in the microstructure [1].

Fig. 2 shows the XRD diffractograms of all samples. In quenched samples, the austenite peaks are observed only when the austenitizing temperature is 1173 K, but with a low intensity. The ferrite and martensite peaks appear in all samples, overlapping. Therefore, it is not possible to distinguish between the peaks of these phases. However, the overlapped peaks are broader when the

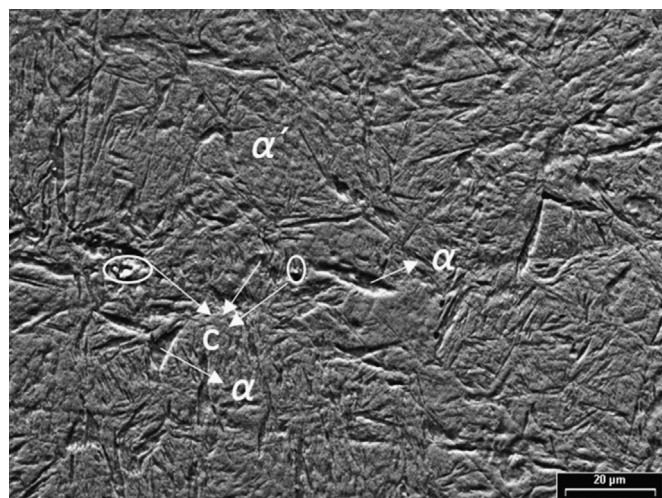


Fig. 1. Microstructure of the sample A1173K5.

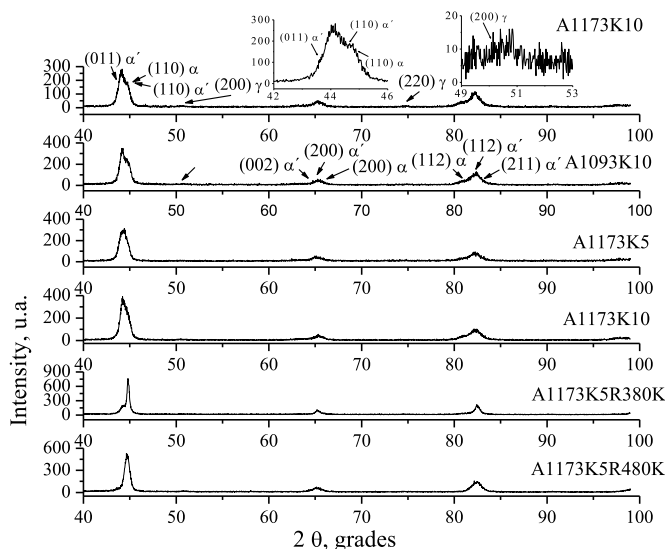


Fig. 2. X-ray diffractograms of quenched and tempered samples.

temperature and time of austenitizing are higher due to the increase of the interstitial carbon content in martensite (martensite tetragonality), which produces a higher separation between the diffraction lines of both phases. During tempering of samples austenitized at 1173 K for 5 min, the width of overlapped peaks decrease in comparison with quenched sample. This is attributed to the decrease of interstitial carbon content of the martensite during tempering, and therefore of martensite tetragonality.

The variation of the interstitial carbon content in martensite is also evaluated by TEP (Fig. 3). This technique shows that interstitial carbon content increases when the temperature and time of austenitizing get larger. Tempering clearly produces a major drop in interstitial carbon content as shown by the increase of TEP. It is known, that TEP at room temperature is inversely proportional to the carbon concentration in ferrite and martensite [5]. The contributions due to other defects such as dislocations and carbides

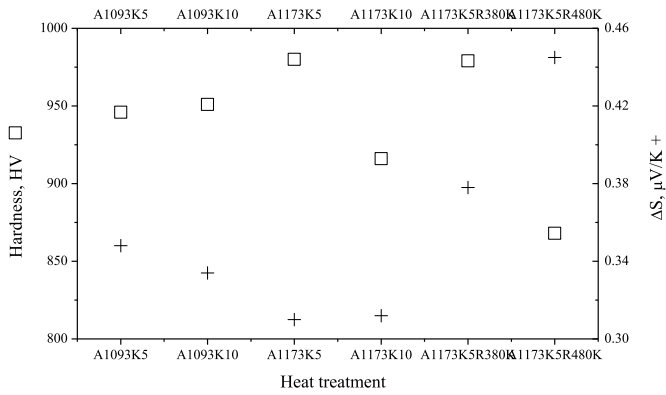


Fig. 3. Variation of hardness and TEP of quenched and tempered samples.

can be considered as negligible [8,9].

On the other hand, Fig. 3 also shows the hardness of the bulk samples. In quenched samples, hardness increases when increasing the austenitizing temperature to reach a maximum value in the sample A1173K5, and then it decreases due to the increase of retained austenite. During tempering of the sample A1173K5, hardness tends to decrease when the tempering temperature is higher due to the martensite decomposition. The increase of hardness suggests a higher dislocation density due to the influence of interstitial carbon content in martensite. However, hardness is also influenced by the presence of the other phases, and the distribution and size of carbide precipitates [1].

The internal friction spectrum of sample austenitized at 1173 K for 5 min and quenched into water was decomposed in an exponential thermal background and three peaks at 220 K, 415 K and 500 K (Fig. 4). The peak that appears at 220 K is attributed to the edge dislocation–point defects interaction, and is broader in comparison to Debye mechanisms. The broadening of this peak is due to the non-uniformity of the active dislocation segment, and the overlapping of multiple relaxation mechanisms. These mechanisms are associated with the interaction between dislocation lines and particles such as carbides and segregated carbon, involving several activation energies [3]. On the other hand, the peak that appears at 500 K is attributed to the Snoek–Köster relaxation, which is related to the dragging of carbon atoms by kink pairs formed on screw dislocations. As it was indicated before, its amplitude is proportional to  $\Lambda$  and  $L$  [4,5].

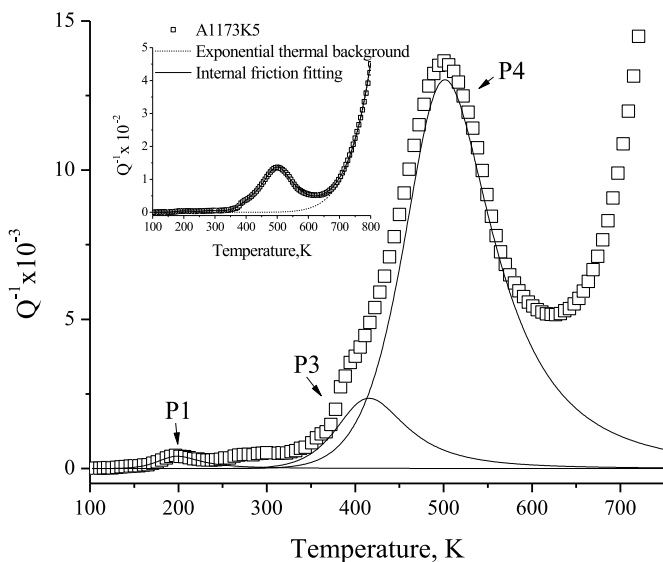


Fig. 4. Internal friction spectrum of sample A1173K5 measured at 2 Hz.

Finally, the peak at 415 K is not thermally activated [5]. This local maximum or shoulder is related to the interstitial carbon content in martensite, and the resulting carbide precipitation during the first stage of tempering [2,3,5]. The mechanism producing internal friction is not clear, but usually it is related to the precipitation of transition carbides [2,5,9–11]. It is important to take in account that the kinetics of the precipitation process depends on the chemical composition, and this could modify the mechanism that produces internal friction [1,12]. For carbon steels, a reasonable explanation is the presence of an internal friction athermal background, which is proportional to the concentration of interstitial carbon. According to the model of Gremaud and Kustov, this non-thermally activated background can be generated by the interaction of dislocations with point defects situated away from the dislocations glide plane [5]. As this background is proportional to carbon content in solid solution, it decreases during tempering due to the carbon segregation and/or the precipitation of transition carbides, producing a curve with a peak shape.

In total, the deconvolution of the internal friction spectra of the quenched and tempered samples allows to observe an exponential thermal background and four peaks (Fig. 5). P1, P3 and P4 appear in all samples. The peak P2 at 345 K is observed only in the quenched sample that was austenitized at 1093 K, and in the tempered samples at 380 K and 480 K. In the other samples, P2 does not appear but an increase of internal friction around this temperature is observed. This peak can be identified as the Snoek relaxation because all samples contain ferrite, and it appears in the samples with lower martensite tetragonality [10]. This relaxation mechanism consists in the preferential redistribution of interstitial atoms under applied cyclic stress, and it takes place in ferrite or martensite tempered at high temperatures. In a fully martensitic sample, this mechanism does not appear since the martensite tetragonality generates energetic differences between the octahedral sites, avoiding stress induced diffusion [10]. In that sense, the formation of P2 could be associated to ductile deformation. It is known, that in this steel, a brittle mechanical behavior is dominant in quenched samples [1].

Fig. 6 shows the frequency spectrum of all samples. The frequency tends to decrease with the temperature is higher. The variation of the frequency around the temperatures of internal friction peaks P1, P2, P4 and P5 can be related to modulus decreases, which is in according with the attribution of these peaks

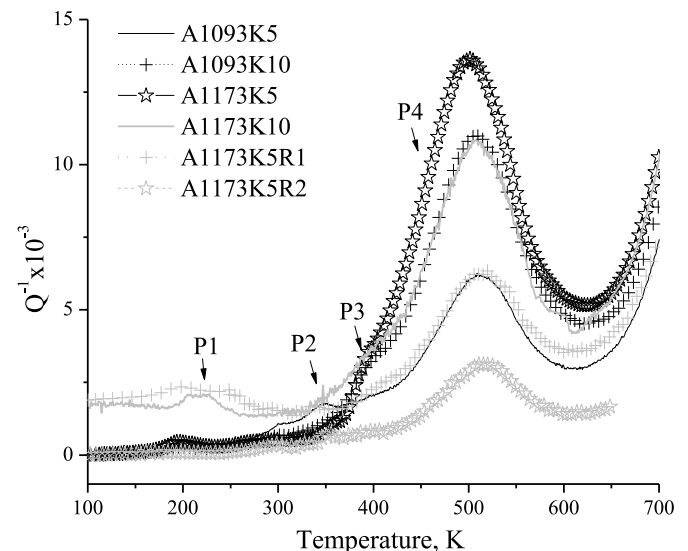


Fig. 5. Internal friction spectra of quenched and tempered samples measured at 2 Hz.

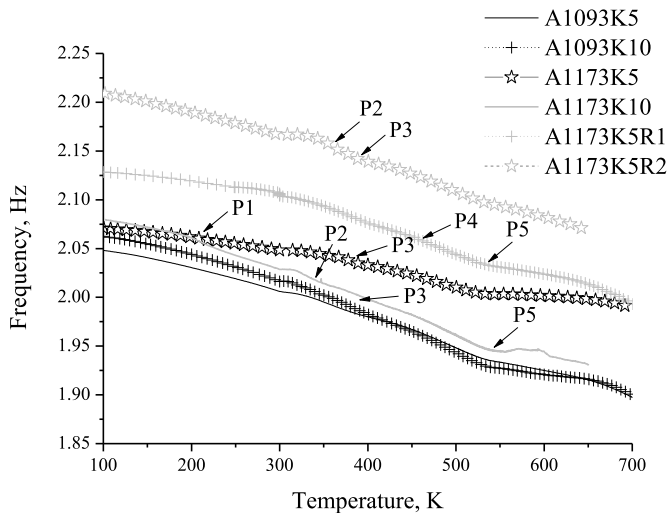


Fig. 6. Frequency spectrum of quenched and tempered samples, showing the modulus change.

to relaxation mechanisms. On the other hand, the plateau formed above 500 K indicates a stronger increase in the modulus, which can be related to the cementite precipitation. In relation to P3, the curvature of the frequency spectrum changes around its temperature, indicating an increase in the modulus, which can be attributed to the transition carbide precipitation and is an indication that P3 is not a relaxation peak. This is in accordance with the work of Tkalec et al. [5].

Fig. 7 shows the amplitude of internal friction peaks P3 and P4 for all samples. The peak amplitude of P3 (shoulder) increases when the temperature and time of austenitizing are larger and decreases when the tempering temperature is higher. This behavior can be explained by the variation of the interstitial carbon content during quenching and tempering, and is in agreement with the results obtained by XRD and TEP. On one hand, the interstitial carbon in the martensite matrix increases during austenitizing. On the other hand, precipitation of secondary carbides leads to carbon depletion.

The amplitudes of P3 and P4 follow a similar trend during heat treatments. This indicates a correlation between the dislocation density in bulk and interstitial carbon content in martensite. It is important to take in account that the sample A1173K10 has the highest content of interstitial carbon in martensite, but it has also the highest content of retained austenite. Consequently, in quenched samples, the amplitude of P3 reaches the maximum value in this sample, which is in agreement with XRD and TEP results. Whereas, the amplitude of P4 reaches the maximum value in the sample A1173K5, following the same trend as hardness. Both have the same trend because the highest active dislocation density increase the amplitude of P4 and the hardness [1,5,6]. On the other hand, both amplitudes decrease when the tempering temperature is increased due to the decomposition of the martensitic matrix.

Furthermore, this correlation between dislocation density in bulk and interstitial carbon content indicated by internal friction is in agreement with the model of Morito et al. [7]. This model establishes that an increase of interstitial carbon content in martensite as found by XRD results in an increase of dislocation density [7]. As was indicated before, the amplitude of P4 depends on both the dislocation density and the active dislocation segment length, according to  $\Delta L^2$  [5,6]. Thus, the amplitude of P4 decrease when both are decreased. During tempering of carbon steels, the dislocation density is decreased while the active dislocation segment length is increased. However, the recovery during tempering has a more significant effect on the dislocation density than on the

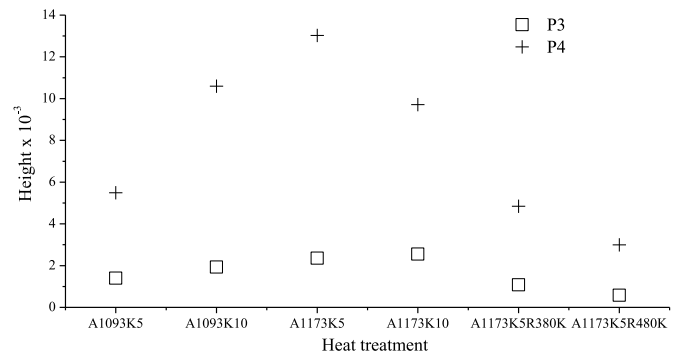


Fig. 7. Peak amplitudes of P3 and P4 of quenched and tempered samples.

active dislocation segment length [11]. This is way, the amplitude of P4 can be used for a qualitative evaluation of the dislocation density.

#### 4. Conclusion

Mechanical spectroscopy can be used for microstructural characterization, in quenched and tempered steels. The amplitude of internal friction peaks at 415 K and 500 K allows a qualitative evaluation of the variation of interstitial carbon content in the martensitic matrix, and of the dislocation density of steel. The Peak found at 415 K is not a relaxation peak. This local maximum or shoulder is related to the presence of interstitial carbon in martensite. When carbides form, the matrix is depleted from carbon. The variation of such maximum can therefore be related with the presence of interstitial carbon. The Peak found at 500 K is attributed to the Snoek–Köster relaxation, which is related to the dragging of carbon atoms by kink pairs formed on screw dislocations. Its amplitude is increased when the dislocation density is higher. The amplitude of such peak follows the same trend as hardness and interstitial carbon in the martensite. This behavior is attributed to a proportional increase of dislocation density in martensite with the content of interstitial carbon. However, the evaluation of dislocation density can be only qualitative. The Peak that appears at 220 K is attributed to the interaction of edge dislocations with point defects. This relaxation peak is broader than a Debye mechanism due to the overlapping of multiple relaxation mechanisms. The peak P2, found at 345 K, is observed only in the quenched sample with the lowest austenitizing intensity and in the tempered samples at 380 K and 480 K. This peak can be identified with the Snoek relaxation and it can be associated with the presence of ferrite and martensite with low carbon content. The occurrence of this peak can be associated with an increase of ductility of the material.

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