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Comparison of the evaluation of the carbon content in solid solution in extra-mild steels by thermoelectric power and by internal friction

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The comparison of the evaluation of the carbon content in solid solution in extra-mild steels by thermoelectric power (TEP) and by internal friction (IF) showed the existence of a population of carbon atoms, which is not detected by IF but is visible by TEP. This population, which contributes to the strain ageing, could be constituted of carbon atoms in interaction with substitutional atoms.

Keywords: Thermoelectric power; Internal friction; Ferritic steels; Strain ageing

1. Introduction

In a recent work [1], a novel method for the quantitative evaluation of the interstitial content in solution in extra-mild steels was proposed. This method, based on thermoelectric power (TEP) measurements [2], uses the segregation of the free interstitial elements to the dislocations which occurs during a static strain ageing: it consists in introducing a high dislocation density in the studied steel by cold-rolling and in treating the cold-rolled steel during 30 min at 120 °C, so that all the interstitials in solution segregate to the dislocations during the ageing. In these conditions, the TEP variation measured between the fully strain aged state and the cold-worked state of the steel, $\Delta S_{a,max}$, is related to the interstitial content in solution before the strain ageing [1]. In the case of a steel which contains only carbon atoms in solution with a content $[C_{ss}]$, $\Delta S_{a,max}$ can be written as follows:

$$\Delta S_{a,max} = |P_C| \cdot [C_{ss}] \quad (1)$$

where P_C is the coefficient reflecting the influence of C in solution on the TEP of pure iron. A comparison of the results of this method with those given by chemical analyses showed that the TEP is likely to detect all the interstitials in solution.

In this context, the aim of the present work is to compare the results of the quantitative evaluation of the carbon content in solution given by this novel method with those deduced from classical internal friction (IF) measurements. This latter type of measurements, commonly used to assess the content of the free interstitial elements in steels, is based on the ability of the interstitials in solution to rearrange in the bcc unit cell of alpha-iron under the combined action of an applied stress and of the thermal activation (Snoek effect) [3]. If the loading of the sample is cyclic, the damping resulting from the rearrangement of each type of interstitial solute presents a maximum for given values of the frequency and of the temperature. According to [4], the height of the peak of each type of interstitial atom is proportional to its content in solution, making the quantification of these atoms possible if the proportionality constants are known.

2. Materials and experimental procedure

Two pure iron samples and four steels (two ultra-low carbon (ULC) steels and two low carbon (LC) steels)

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with different manganese contents were used for the study. Their chemical composition is given in Table 1. Before conducting the comparative study between the results given by TEP and IF, the steels were treated at 750 °C for 5 h to precipitate all their free nitrogen in the form of aluminium nitrides. Indeed, for steels with an excess of aluminium with the stoichiometric [Al]/[N] atomic ratio, this treatment is long enough to precipitate all the nitrogen atoms [5]. The steels were then solutionized at 700 °C for 30 s (ULC steels) and for 5 min (LC steels) before being water quenched. After such a treatment, all the carbon of the ULC steels is assumed to be in solution. Lastly, in order to obtain varying carbon concentrations in solid solution, each steel was isothermally treated at different temperatures over the temperature range from 600 to 270 °C and water quenched. The treatment times at each temperature were chosen to reach the equilibrium carbon concentration in solution. All the treatments were performed in salt baths.

After these treatments, the carbon content of the samples was assessed using: (i) the TEP method presented in [1] which leads to the evaluation of $\Delta S_{a,max}$ and (ii) IF measurements.

The TEP measurements were performed at room temperature on an apparatus giving the relative TEP (S) of the steels with respect to the TEP of pure iron [6]. This relative TEP is the result of various contributions: $S = \Delta S_{ss} + \Delta S_d + \Delta S_{pp}$ where ΔS_{ss} , ΔS_d and ΔS_{pp} are due to the elements in solid solution (ss), to the dislocations (d) and to the precipitates (pp). The contribution due to the elements in solution is given by the Gorter–Nordheim law [7] which can be expressed as: $\Delta S_{ss} = \sum P_i \cdot [i_{ss}]$ if the concentration of the elements is low. $[i_{ss}]$ is the content of the element “ i ” in solution (in wt.%) and P_i is a coefficient reflecting the contribution of this element to the modification of the TEP of pure iron.

The carbon content in solution determined from the TEP method ($[C_{ss(TEP)}]$) was assessed from the following relation:

$$[C_{ss(TEP)}] \text{ (wt.\%)} = \frac{\Delta S_{a,max}}{|P_C|} \quad \text{with} \quad (2)$$

$$|P_C| = \frac{\alpha_c \cdot S_c}{\rho} = \frac{517.5}{\rho}$$

In the expression of P_C , α_c and S_c are the specific resistivity and the specific TEP of carbon in solution in pure iron, whilst ρ is the resistivity of the steel. As ρ depends on the chemical composition of the steel (in particular, of its manganese content), the value of P_C is not identical for all the studied steels. Table 1 gives the values of P_C taken for each studied material. They were calculated knowing that in an extra-mild steel having a resistivity of 11.5 $\mu\Omega\text{cm}$, P_C has been determined experimentally with a precision of 2% and is equal to $-45 \mu\text{V}/(\text{K wt.\%})$ [8]. From these results, it is thus possible to determine the value of the product between α_c and S_c (i.e. 517.5) and to calculate the values of P_C from the knowledge of the resistivity of the different steels. The resistivity of the steels was evaluated from the empirical relation of Meyzaud and Parnière [9] giving the resistivity of a steel at room temperature as a function of the content of its alloying elements in solution expressed in wt.%:

$$\rho \text{ (}\mu\Omega\text{cm)} = 9.9 + 30(C + N) + 6 \cdot \text{Mn} + 13 \cdot \text{Al} \quad (3)$$

With regard to the IF measurements, they were carried out with an inverted torsion pendulum at 1 Hz employing a heating rate of 50 °C h⁻¹ between -40 and 70 °C. At each temperature, the logarithmic decrement (δ) of the samples was measured. For steel samples with only carbon atoms in solution, this decrement reaches a maximum value (δ_{max}) for a temperature of 40 °C and a frequency of 1 Hz.

The carbon content in solution deduced from IF experiments ($[C_{ss(IF)}]$) can be evaluated from the linear relation linking δ_{max} and $[C_{ss(IF)}]$:

$$[C_{ss(IF)}] \text{ (wt.\%)} = \frac{K_C \delta_{max}}{\pi} \quad (4)$$

In this relation, K_C is a factor which depends on several parameters (texture, chemical composition, grain size of the steel...). As a consequence, the value of this coefficient has to be determined for each type of steel, using an approach such that developed by Saitoh and Ushioda [10] for example. As the value of K_C is difficult to determine accurately, it is not easy to deduce the carbon content in solution from the knowledge of δ_{max} . In the present work, it was thus chosen to use δ_{max} as an indicator of the free carbon content assessed by IF when the knowledge of $[C_{ss(IF)}]$ was not absolutely necessary.

Table 1
Chemical composition of the studied materials and values of their resistivity and of their coefficient P_C

	C 10 ⁻³ wt.% (ppm)	N 10 ⁻³ wt.% (ppm)	Mn wt.%	Al wt.%	ρ ($\mu\Omega\text{cm}$)	P_C ($\mu\text{V}/(\text{K wt.\%})$)
Pure iron	0.5 or 1.5 (5 or 15)	0.2 (20)	$\sum \text{Al, Si} \dots \leq 0.050$		9.90	-52.0
Steel ULC ₁	6.0 (60)	4.0 (40)	0.125	0.015	10.89	-47.5
Steel ULC ₂	7.0 (70)	5.0 (50)	0.250	0.016	11.63	-44.5
Steel LC ₁	23.0 (230)	5.3 (53)	0.200	0.050	11.77	-44.0
Steel LC ₂	59.0 (590)	4.8 (48)	0.400	0.048	12.90	-40.0

For the evaluation of the resistivity, the carbon content of the steels in solution was taken equal to $5 \times 10^{-3}\%$.

3. Comparison of the evaluation of the carbon content in solution by TEP and by IF

To compare the results given by the two methods of evaluation of the carbon content in solution, the value of δ_{\max} of each studied sample was reported, in Fig. 1, as a function of the corresponding amount of carbon in solution evaluated by TEP ($[C_{ss(\text{TEP})}]$). Fig. 1 shows that the evolution of δ_{\max} with $[C_{ss(\text{TEP})}]$ is linear for all the studied materials and is characterised by a slope which is not rigorously the same for all the materials due to their difference of texture. However, whilst the evolution of δ_{\max} with $[C_{ss(\text{TEP})}]$ is directly proportional for pure iron, this is not the case for the steels. Indeed, after having treated these materials for 3 h (LC steel) or for 24 h

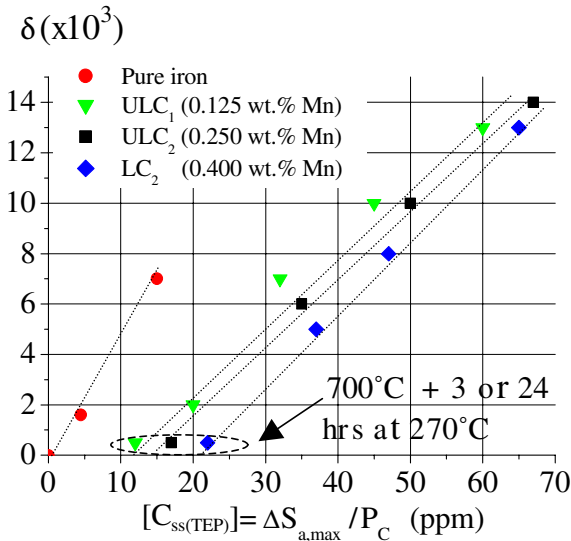


Fig. 1. δ_{\max} as a function of $[C_{ss(\text{TEP})}]$.

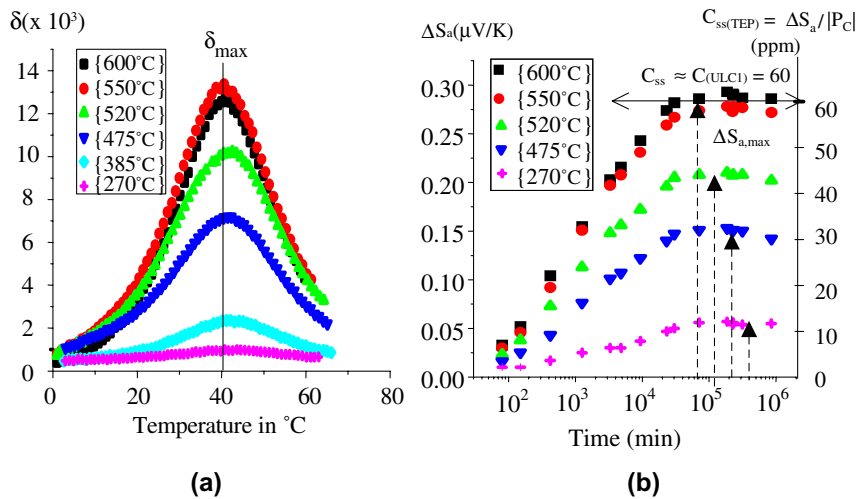


Fig. 2. (a) IF spectra at 1 Hz measured on the steel ULC₁ treated at different temperatures; (b) TEP variations measured during the strain ageing at 20 °C of the steel ULC₁ treated at different temperatures and cold rolled with a reduction ratio of 50%: the final TEP variation corresponds to $\Delta S_{a,\max}$.

(ULC steels) at 270 °C, the TEP technique detects the presence of a given amount of carbon atoms in solution while $\delta_{\max} = 0$. Moreover, as can be seen in Fig. 1, this amount of carbon atoms, detected by TEP but not by IF, depends on the manganese content of the steels: it increases from 12 to 22 ppm when the manganese content of the steels varies from 0.125 to 0.400 wt.%.

Fig. 2 refers to the steel ULC₁. It shows the IF spectra of this steel treated at different temperatures to obtain varying carbon contents in solution, together with the corresponding strain ageing kinetics of the steel followed by TEP during an ageing at room temperature. As was shown by [11], these kinetics reflect the segregation of the carbon atoms to the dislocations. When the steel has been treated at 550 or at 600 °C before the strain ageing, the TEP kinetics are identical. This can be explained by the fact that all the carbon of the steel (60 ppm) is in solution after treatment at these two temperatures. This explanation is confirmed by the quantitative evaluation by TEP of the carbon content which segregate to the dislocations during the ageing. Lastly, the comparison between Fig. 2a and b clearly proves that after having treated the steel for 24 h at 270 °C prior to the strain ageing, the TEP detects the segregation of about 12 ppm of carbon on the dislocations, whilst the IF spectrum is flat.

As a consequence, the preceding results indicate that the TEP method used for the quantitative evaluation of the free carbon in steel samples is sensitive to the presence of a population of carbon atoms in solution which contributes to the strain ageing of the steels but which is not seen by IF. This fact can be explained by the two following assumptions: (1) the IF technique does not detect all the carbon atoms in solution and/or (2) the protocol used for the evaluation of $\Delta S_{a,\max}$ modifies the amount of carbon in solution.

The first assumption implies the existence of two populations of carbon atoms (P_1 and P_2), one of which (P_2) is invisible by IF but is detected by TEP. As the carbon atoms of the population (P_2) are assumed to be invisible by IF, they have to be located in particular sites of the iron matrix of the steel samples. The most probable hypothesis is that these atoms are located near one or several substitutional atoms. As the potential energy of these carbon atoms is different from that of single carbon atoms, their contribution to the IF spectrum is thus assumed to be different.

This explication is supported by the works of different authors [10,12,13] who showed that the presence of substitutional atoms has a strong influence on the height of the Snoek peak of carbon. In particular, Saitoh and Ushioda [10] observed that for a given amount of carbon in solution present in low carbon steels with varying manganese contents, the height of the Snoek peak gradually decreases as the amount of manganese increases. According to Abe et al. [14], this phenomenon can be attributed to the presence of C–Mn complexes, which do not contribute to the height of the Snoek peak [15].

In these conditions, it can be concluded that the carbon atoms of (P_1) are single carbon atoms, while the carbon atoms of (P_2) are in interaction with substitutional atoms. As manganese is the only substitutional element present at an appreciable content in the solution of the studied steels, it can lead to the formation of C–Mn dipoles which are not taken into account in the height of the Snoek peak. However, these dipoles contribute to the strain ageing involved in the quantitative evaluation of carbon by TEP. In fact, if the preceding explanations are valid, they imply that the amount of carbon atoms of (P_2), which is invisible by IF, increases with an increase in the manganese content of the steel. This is in perfect agreement with the preceding experimental results which showed that the disagreement between the evaluation of the carbon content by TEP and IF increases with increasing the manganese content and is not observed when this content is equal to zero (case of the pure iron samples).

The second assumption to explain the disagreement between the TEP and IF techniques is based on the idea that $\Delta S_{a,max}$ overestimates the free carbon content. This overestimation could be due to the fact that the cold-rolling involved in the TEP method can lead to an increase in the carbon content in solution. This increase cannot be due to a partial dissolution of the carbides present in the studied steels before cold rolling, as the thermal treatments performed on the steels were chosen to lead to the formation of coarse incoherent Fe_3C particles. However, it could be due to a desegregation of carbon atoms initially segregated to the grain boundaries or to the quenched-in dislocations.

In fact, the desegregation of carbon atoms located at the grain boundaries during the cold rolling is not pos-

sible from a thermodynamic point of view, as the grain boundaries are very stable sites for the carbon atoms and the desegregation of carbon atoms can occur only after very long times (≈ 100 h) at high temperatures ($T \geq 500$ °C) [15]. In contrast, the desegregation of carbon atoms initially located on the quenched-in dislocations is possible during the cold rolling. In order to check this assumption, the steel LC₂ was submitted to different thermal treatments aimed at obtaining varying dislocation densities in the steel. In all cases, the steel samples were solutionized at 700 °C. They were then either water-quenched to obtain a high density of quenched-in dislocations or slowly cooled until 550 °C in the salt bath used for the treatments and then air-cooled in order to reduce, as much as possible, the amount of quenched-in dislocations. After these two types of treatment, the steel samples were treated for 3 h at 270 °C in order to obtain the equilibrium carbon concentration at this temperature. Lastly, the TEP protocol used for the quantitative evaluation of the carbon content in solid solution was applied to the different samples of the steel LC₂. The carbon content in solution evaluated by TEP was found to be of: (i) 19 ppm for the slowly cooled sample and (ii) 20 ppm for the water-quenched sample. This result indicates that the disagreement between the results given by TEP and by IF cannot be explained by the desegregation of carbon atoms initially located on the quenched-in dislocations during the cold rolling, as the carbon content in solution evaluated by TEP is not markedly affected by the amount of quenched-in dislocations in the steel.

As a conclusion, the carbon atoms which are not detected by IF can be considered as being in interaction with substitutional atoms.

4. Influence of the carbon atoms invisible by IF on the bake-hardening properties of the steels

In order to show the role played by the carbon atoms invisible by IF on the mechanical properties measured after deformation and ageing of the steels, the bake-hardening (BH) index of the steel LC₁ was determined after a prestrain of 2% and a thermal treatment of 20 min at 170 °C. This index gives the increase in the yield strength of the steel between its prestrained state and its final state and results from the segregation of the carbon atoms to the dislocations during the ageing at 170 °C. In Fig. 3, the BH₂ index of the steel was reported as a function of its carbon content in solution evaluated by TEP and by IF before bake hardening. For the determination of $[C_{ss(IF)}]$, it was chosen to take a value of K_C equal to 1.28, as this value is the most common admitted value for steels comparable to the one considered in this study [16].

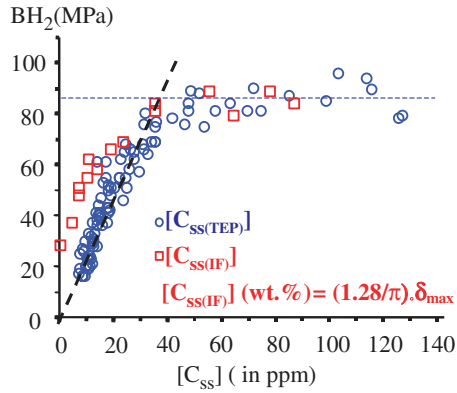


Fig. 3. Evolution of the BH_2 of the steel LC_1 as a function of $[C_{ss(TEP)}]$ and $[C_{ss(IF)}]$.

As can be seen in Fig. 3, two different curves are obtained. The curve giving the BH_2 index as a function of $[C_{ss(IF)}]$ is characterised by very high BH_2 values for $[C_{ss(IF)}]$ values lower than 10 ppm and by a BH_2 value of the order of 30 MPa for $[C_{ss(IF)}] = 0$. This unexpected result is in agreement with previous results found in the literature [17,18]. In contrast, the evolution of the BH_2 index as a function of $[C_{ss(TEP)}]$ is more gradual and is characterised by a linear increase as long as the carbon content does not exceed 30 ppm, followed then by a stabilisation for $[C_{ss(TEP)}]$ values higher than 40 ppm. Furthermore, when the BH_2 index is lower than the BH_2 value at saturation, the carbon content in solution estimated by IF is about 15 ppm lower than that evaluated by TEP for the same BH_2 value.

As a result, all these observations confirm the existence of a given amount of carbon atoms in solution, which is not detected by IF but which contributes to the mechanism of bake hardening of the steels and leads to an increase in their yield strength.

5. Conclusion

The present work showed that the evaluation of the carbon content in solution in extra-mild steels by TEP and by IF leads to different results. This was interpreted by the existence of a population of carbon atoms which is evaluated by TEP but which does not contribute to the height of the Snoek peak. This population could be constituted of carbon atoms in interaction with substitutional atoms. Although these atoms are not seen by IF, they are very important to take into account, as they contribute to their mechanism of bake hardening.

Lastly, it has to be noted that the combination of the quantitative evaluation of the carbon content in solution

by TEP and IF should be very promising for the study of the steels containing both carbon and manganese atoms in solution. Indeed, the preceding results obtained on these steels showed that the TEP is sensitive to the presence of all the carbon atoms in solution (whatever their environment) and gives an evaluation of the total carbon content in solution, while the IF can only estimate the content of single carbon atoms. The consequence is that the combination of the quantitative evaluation of the carbon content in solution by TEP and IF is likely to allow us to determine the content of the single carbon atoms ($[C_f]$) and that of the carbon atoms located near manganese atoms ($[C_i]$). Thus, assuming that the repartition of the carbon atoms in the iron matrix is controlled by a Maxwell–Boltzmann distribution which can be expressed, for dilute solutions, as follows:

$$\frac{[C_i]}{[C_f]} = \frac{2[Mn]}{1 - 2[Mn]} \exp\left(-\frac{B}{kT}\right) \quad (5)$$

where $[Mn]$ is the manganese concentration in solution, it should be possible to assess the binding energy (B) of the C–Mn dipoles. This will be done in a further investigation. Furthermore, the combined use of the TEP and IF techniques could be interesting to study the influence of the C–Mn dipoles on the mechanisms of bake hardening of extra-mild steels.

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