Comparative study and quantification of cementite decomposition in heavily drawn pearlitic steel wires

A. Lamontagne [a], V. Massardier [a,*], X. Kléber [a], X. Sauvage [c], D. Mari [b]

[a] University of Lyon, INSA Lyon, MATEIS–UMR CNRS 5510, Bât. St Exupéry, 3ème étage, 25 Avenue Jean Capelle, Villeurbanne Cedex 69621, France
[b] Institute of Condensed Matter Physics, Ecole Polytechnique Fédérale de Lausanne, Station 3, Lausanne CH-1015, Switzerland
[c] University of Rouen, GPM, UMR CNRS 6634, BP 12, Avenue de l'Université, 76801 Saint-Etienne du Rouvray, France

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ABSTRACT

Heavily cold-drawing was performed on a pearlitic steel wire and on an ultra-low carbon (ULC) steel wire in order to highlight and quantify the microstructural changes caused by this type of deformation. Both global techniques (thermoelectric power, electrical resistivity, internal fiction background) and local techniques (Atom Probe Tomography) were combined for this study. It was shown that two distinct stages have to be taken into account during the cold-drawing of pearlitic steels. The first stage (below a true strain of 1.5) was attributed mainly to the lamellar alignment, while the second stage (above a true strain of 1.5) was unambiguously interpreted as being due to a gradual enrichment of the carbon content of ferrite arising from the strain induced cementite decomposition. The carbon content in solid solution in ferrite was assessed as a function of the true strain. All the techniques showed that this carbon content exceeds the solubility limit of carbon in the ferrite above a true strain of 2.2. A correlation between the increase in the carbon content of ferrite and the increase in yield strength was also highlighted. Moreover, a scenario was proposed to explain the microstructural changes caused by drawing.

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1. Introduction

Heavily cold drawn pearlitic steel wires are commonly used as structural materials for their high strength (close to 4 GPa for industrial applications and up to 7 GPa at the lab scale) and their acceptable ductility [1,2]. Their microstructure has been extensively investigated over the past decades in order to explain their unusual strain-hardening behavior. In a first step, the cold-drawing process induces a reorientation of cementite lamellae toward the drawing direction [3–5]. This leads to shear band deformation, curling and fragmentation of cementite [4]. This geometrical reorientation of the original pearlitic structure is typically achieved for a true strain of about 1.5 [4,6] and is accompanied by a strong lamellar refinement. It has been shown in earlier works using Mössbauer spectroscopy [7–10], thermomagnetic analyses [11,12], Transmission Electron Microscopy (TEM) [13–15] or Atom Probe Tomography (APT) [14–16] that at higher strains, cementite starts to dissolve. This phenomenon is believed to influence also the mechanical properties [17,18]. Two physical mechanisms responsible for this decomposition have been proposed in the

literature. It could be linked to the binding energy between carbon atoms and dislocations in the ferrite phase that would be higher than that of carbon and iron atoms in the cementite phase [8]. The other proposed mechanism is linked to the strong increase in the ferrite/cementite interfacial energy due to the fragmentation of cementite lamellae during drawing (Gibbs–Thomson effect) [13]. According to some authors, cementite dissolution may even occur through a post-deformation natural ageing mechanism [19–23]. The large range of reported data and of interpretations of the results is probably due to the typical heterogeneous structure of pearlitic steel wires (large interlamellar spacing distribution) and the rather local nature of some analyses like TEM or APT. On the other hand, differences in process parameters (averaged reduction area per step, drawing speed, etc.) or in storage conditions after drawing (time spent at room temperature before analyses) may have a significant influence on microstructure and carbon redistribution in heavily drawn pearlitic wires (natural aging). Besides, the different pearlitic steels that have been probed in the literature have also in part different contents in manganese and silicon as well as chromium. These elements may affect the stability of the cementite. Thus, it is conceivable that the exact chemical composition and hence the carbide stability may also lead to different cementite dissolution rates upon wire drawing.

In this context, the aim of this work was to carry out a comparative study of the microstructure evolution and of cementite

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* Correspondence to: University of Lyon, INSA Lyon, MATEIS UMR5510, Bât. Saint-Exupéry, 25 Avenue J. Capelle, 69621 Villeurbanne, France. Fax: +33 4 72 43 79 30.
E-mail address: veronique.massardier@insa-lyon.fr (V. Massardier).

decomposition as a function of the drawing strain. Both global and local measurements were performed using the thermoelectric power technique (TEP), mechanical spectroscopy, electrical resistivity and APT analyses. In order to achieve quantitative measurements of carbon super saturated solutions in ferrite (resulting from deformation induced cementite dissolution), reference samples were used to calibrate TEP and electrical resistivity measurements. These data were compared to APT measurements and linked to the mechanical behavior.

2. Material

The material used in this study is a pearlitic steel wire of eutectoid composition: Fe–0.91C–0.32Mn–0.22Si–0.22Cr in wt% or Fe–4.10C–0.32Mn–0.43Si–0.22Cr in at%. The wire rod of 5.5 mm in diameter was cold-drawn to 0.26 mm up to the true strain $\varepsilon = 3.81$. As-drawn samples were taken every two dies, immediately immersed in liquid nitrogen and kept at $-80\ °C$ in order to avoid any unintentional ageing at room temperature before measurements.

In order to isolate the effect of the plastic deformation on the measured physical properties (TEP, resistivity), an ultra-low carbon steel wire containing 50 ppm of carbon was also cold-drawn up to the true strain $\varepsilon = 3.81$. It was stored in the same conditions as those used for the pearlitic steel wire.

3. Experimental techniques

3.1. Thermoelectric power (TEP)

The TEP technique [24–26] is based on the Seebeck effect: when two junctions formed between the studied sample and two blocks of a pure metal are submitted to a temperature gradient (ΔT), a voltage difference (ΔV) can be measured between the two junctions. The apparatus used in this work gives the relative TEP of the sample with respect to the TEP of pure copper at room temperature in nV/°C. The temperature of the copper block is T and $T + \Delta T$ with $T = 15\ °C$ and $\Delta T = 10\ °C$. Knowing the TEP of pure iron (noted S_{Fe}^*) with respect to the TEP of pure copper (noted S_{Cu}^*), the relative TEP values given in this work (noted S) are given with respect to the TEP of pure iron. This relative TEP is defined by: $S = (S^* - S_{Fe}^*) = \Delta V / \Delta T$ where S^* is the absolute TEP of the sample. The value of this relative TEP is affected by the defects present in the iron matrix and can be defined as the sum of several contributions: $S^* = S_{Fe}^* + \Delta S_{ss} + \Delta S_d + \Delta S_p$ where ΔS_{ss}, ΔS_d, and ΔS_p are the TEP variations due to elements in solid solution, lattice defects (dislocations…) and precipitates, respectively.

Fig. 1 illustrates the different effects which have to be taken into account for the analysis of the TEP variations induced by a thermo-mechanical treatment.

The atoms in solid solution in iron (especially, when they are in interstitial position) have a great influence on the TEP of iron which depends both on their nature and their concentration in solution. In the case of interstitial carbon atoms, their influence on TEP is negative and is much higher (in absolute value) than that other elements in solution (such as Mn, Al, Cu, Cr and Mo) [25,27,28]. As a consequence, the contribution of the carbon atoms to the TEP of iron (noted ΔS_{ss}) is expected: (i) to become more and more negative with increasing the amount of carbon atoms in solid solution and (ii) to increase when carbon atoms leave the solid solution either to form precipitates or to segregate on defects (such as dislocations, grain boundaries or interfaces).

In the case of the carbon atoms segregated to the above mentioned defects, it has been clearly shown by [26] that these carbon atoms are not detected by TEP, as shown in Fig. 1 (case b). Hence,
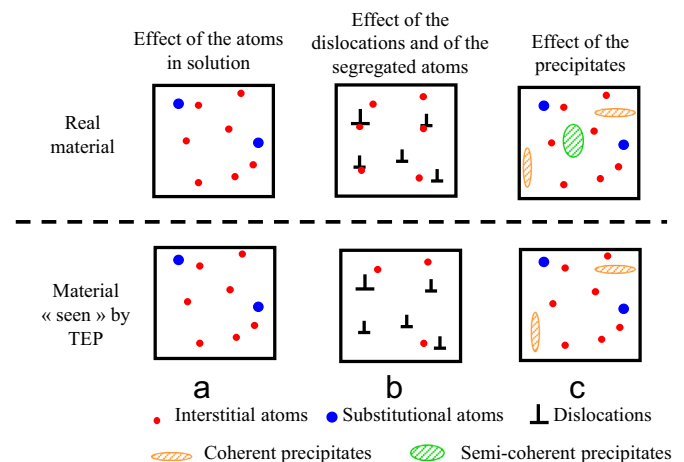

Fig. 1. Schematic representation of the effect of the atoms in solid solution or segregated to dislocations, of the dislocations and of the precipitates on the TEP. Comparison of the real material with that "seen" by TEP.

when carbon atoms leave the solid solution to segregate to these defects, TEP detects only the departure of these atoms from solid solution.

As far as the dislocations are concerned, they tend to decrease the TEP of iron and lead to a TEP variation which is related to the dislocation density [28].

Lastly, the precipitates have an effect on the TEP in the particular case where they are small and coherent (Fig. 1, case c) [29,30]. However, in the case where the precipitates are coarse and incoherent (Fig. 1, case c), it has always been observed that they have no effect on the TEP [30]. As a consequence, during the formation of such precipitates, the measured TEP variations are essentially linked to the decrease in the solute content in solid solution.

From the preceding considerations, one can conclude that the transfer of carbon atoms from cementite to dislocations or interfaces is not expected to lead to a TEP variation. By contrast, TEP may be sensitive to the transfer of carbon atoms from cementite to ferrite.

In present experiments, the length of the samples was approximately 4.5 cm. All the measurements were performed at $20\ °C$.

3.2. Electrical resistivity

Electrical resistivity was determined by measuring the potential drop across both a standard resistance ($1\ \Omega$) and the specimen connected in series and supplied by a source of continuous current (0.5 A). The four-point method, two for the application of the current and two for reading the voltage, was used to avoid contact resistance. The resistance of the sample was calculated by: $R = \Delta V / I$ where ΔV is the potential drop in the sample and I is the instantaneous current. This current was calculated from the potential drop in the standard resistance. Knowing the specimen dimensions, the electrical resistivity could be assessed. Specimens were 350 mm in length with variable diameters, depending on the considered strain. In order to compare TEP and electrical resistivity evolution, measurements were performed at $20\ °C$, in a temperature-controlled oil bath to avoid thermal fluctuations. It is worth noting that despite a precision of 0.1% in the electrical resistance measurements, electrical resistivity was measured with an accuracy of 5% because of the uncertainty in the specimen dimensions. This experimental technique is also sensitive to lattice defects and interstitial elements: electrical resistivity increases with increasing dislocation density and interstitial carbon content [31].