Deformation-induced cementite decomposition in pearlitic steel wires studied by Atom probe tomography

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1 Introduction

Pearlitic steel is a composite material, consisting of ferrite and cementite, which can exhibit tensile strengths higher than 5 GPa upon severe plastic deformation such as cold-drawing [1-3]. Heavily cold-drawn pearlitic wires are therefore known as one of strongest bulk nanostructured materials. Their field of application as engineering materials is broad, ranging from suspension bridge cables to tire reinforcement materials to piano wires. Although the superior mechanical properties of cold-drawn pearlitic wires are undisputed, the origin of their ultra-high strength is still a matter of debate. A convincing correlation between the strength and the microstructural evolution of this composite has not been found yet also due to a lack of information on the elemental distribution below nanometer-scale.

Atom Probe Tomography (APT) is a high-resolution characterization method that enables three-dimensional elemental mapping with sub-nanometer resolution. Therefore, APT is highly useful for the characterization of metallic nanocomposites. In the present work, a state-of-the-art Local Electrode Atom Probe (LEAP) was used to characterize the microstructural evolution of pearlitic steel, cold drawn to strains up to 5.4. We found correlations of the carbon concentration in ferrite with the strain and of the carbon concentration in the cementite lamellae with their thickness. Strong indications for the formation of cell/sub-grain boundaries in ferrite and segregation of carbon atoms at these interfaces were found. Based on the experimental findings, the mechanisms of cementite decomposition are ascribed to solute-dislocation interaction.

2 Experimental

Commercial pearlitic steel wires with eutectoid composition (Fe–0.81C–0.49Mn–0.20Si–0.006P–0.008S wt.% and Fe–3.66C–0.48Mn–0.39Si–0.01P–0.01S at.%), provided by Nippon Steel Corporation, were studied in this work. The wires (having an initial diameter of 1.70 mm) were patented in an austenitization treatment at 1223 K for 80 s, followed by a pearlitic transformation in a lead bath at 853 K for 20 s. The patented wires were cold-drawn (using lubricants) to true strains 0.93, 2, 3.47, 5, and 5.4.

A LEAP (Imago Scientific Instruments, LEAP 3000X HR™) was used to analyze the carbon distribution in three dimensions. The measurements were performed by applying voltage pulses at 70 K under an ultra-high vacuum of 8 × 10⁻⁹ Pa. The applied voltage during the measurement was between 6.2 and 7.2 kV, where the pulse to base voltage ratio was 15%. The pulse repetition rate and detection rate were set to 200 kHz and 0.005 atoms per pulse, respectively.

Samples for APT analyses were prepared with the tips perpendicular to the wire axis using a dual-beam focused-ion-beam (FIB) (FEI, Helios NanoLab 600™) according to the procedure described in Ref. [4]. As the friction between the wire and drawing tools can cause more plastic deformation at the surface than in the center of a wire, the microstructure of the wire may be different from the surface to the center. However, this difference decreases with increasing drawing strain. For instance, at \( \varepsilon = 5 \), the tips taken from regions 5 and 25 \( \mu \)m below the surface show virtually no difference in the maximum carbon concentration in cementite. To achieve consistent analyses, all tips were taken from the surface regions of the wires. During annular ion-milling about 250 nm of the
material was removed from the surface. Thus, the apex of each tip was located about 250 nm below the wire surface.

**3 Results and Discussion**

**3.1 APT investigations of the lamellar structure of cold-drawn pearlitic wires**

Fig. 1 shows the three-dimensional elemental maps of pearlitic wire samples cold-drawn to true strains of \( \varepsilon = 2 \) (left) and \( \varepsilon = 5 \) (right). Carbon and iron atoms are displayed as yellow and red dots, respectively.

Fig.1. Three-dimensional elemental maps of cold-drawn wires for \( \varepsilon = 2 \) (left) and \( \varepsilon = 5 \) (right). For clarity only 1% of the iron (yellow) and 30% of the carbon (red) atoms are displayed. Cementite and ferrite are labeled as \( \theta \) and \( \alpha \), respectively.

A refinement of the lamellar structure with increasing drawing strain can be observed. The average thickness of the ferrite lamellae thickness decreases from about 56 nm in the as-patented state to about 10 nm for \( \varepsilon = 5 \). The average thickness of the cementite lamellae decreases from 17 to 2 nm. This can also be observed in the three-dimensional elemental maps of the wires drawn to \( \varepsilon = 2 \) and \( \varepsilon = 5 \) (Fig. 1). Here, the carbon-enriched (red) and carbon-depleted regions (yellow) can be identified as cementite and ferrite, respectively. The change in the lamellar spacing, also observed with TEM, has been consistently reconstructed in the three-dimensional maps. Quantitatively, the data indicates that the average interlamellar spacing decreases from an initial value of 70 nm (as-patented) to 25 nm for \( \varepsilon = 2 \) and further to about 13 nm for \( \varepsilon = 5 \).

Fig. 2 shows elemental maps (top and middle) and the corresponding one-dimensional carbon concentrations profiles (bottom) of selected regions taken of Fig. 1. It can clearly be recognized that in addition to the refinement of lamellar spacing the cementite filaments also become thinner, while the phase boundaries become more diffuse.

Fig.2. (a) Elemental map of a selected region of \( 4 \times 20 \times 50 \text{ nm}^3 \) from the whole detected volume shown in Fig. 1 for the cold drawn pearlitic steel wire at \( \varepsilon = 2 \). (b) for the wire drawn to \( \varepsilon = 5 \). (c) One-dimensional carbon concentration profiles for \( \varepsilon = 2 \) and 5 along the direction perpendicular to the lamellar interfaces between ferrite and cementite.

**3.2 Carbon concentration in ferrite and cementite**

Fig. 3 shows the carbon concentrations measured in ferrite as a function of wire strain, where each data
point is obtained from averaging over three to ten measurements. The values measured in all wires are below 0.6 at.% C. The solubility of carbon atoms in ferrite does not monotonically increase with drawing strain, but saturates at a certain strain ($\varepsilon = 3.47$ in the present work). This observation suggests that cementite decomposition may also saturate at the same strain.

3.3 Segregation of carbon atoms in ferrite

Fig. 3. (a) Carbon concentration in ferrite as a function of true drawing strain. (b) Dependence of carbon concentration in the cementite on the lamellar thickness for as-drawn wires at various drawing strains.

Fig. 3. (b) shows the carbon concentration in cementite as a function of the lamellar thickness. The carbon concentration was measured from the APT dataset by cutting out the middle of each cementite lamella to avoid errors due to variations in the local magnification (the so-called local magnification effect, see [5] for more details). All samples of different strain share a common feature: the carbon concentration decreases with decreasing thickness of the cementite lamellae. For the same cementite thickness the carbon concentration decreases upon further straining from ($\varepsilon = 2$ to $\varepsilon = 3.47$). It should be noted that the influence of strain is inverse to the lamellar thickness. The curves show a tendency that in the cementite lamellae with sufficient thickness the strain effect becomes negligible and the carbon concentration matches the stoichiometric value of 25 at.% for Fe$_3$C. For $\varepsilon \geq 3.47$ the influence of the drawing strain disappears so that the cementite filaments with the same thickness exhibit the same carbon concentration. This observation is consistent with the results shown in Fig. 3 (a), where the carbon concentration in ferrite saturates at the same strain level.

3.4 Possible mechanisms for cementite decomposition

There are two common models for cementite decomposition in cold-drawn pearlitic wires in the
literature. One is based on the decomposition of cementite lamellae due to the Gibbs-Thompson effect [6], while the other one is based carbon dislocation interaction [7].

Based on our APT results, we consider the interaction between carbon atoms and dislocations to be the dominating mechanism for cementite decomposition. This assumption is supported by the observation that both the carbon concentrations in ferrite and cementite saturate for $\varepsilon \geq 3.47$. At the same strain level, saturation of the dislocation density was detected by means of X-ray line profile analyses. Furthermore, it is known from literature that dislocations in ferrite and carbon atoms exhibit a higher binding energy [8] than carbon and iron atoms in cementite [9,10]. Altogether, there are strong indications that upon cold-drawing carbon atoms are dragged by dislocations from cementite into ferrite. This process may occur via dislocations cutting the entire cementite lamella or via dislocations formed at the ferrite/cementite interface due to a mismatch in elastic moduli between the two phases and stress concentration. Hence, dislocation activity and cementite decomposition are associated phenomena and occur simultaneously during cold-drawing. Upon severe plastic deformation dislocation walls can be formed inside the ferrite lamellae which can eventually develop into cell or low-angle grain boundaries. At these boundaries the carbon atoms are found to be segregated (as observed with APT).

In addition to the elementary interaction between carbon atoms and lattice dislocations in the ferrite, a transphase dislocation-shuffle mechanism may also act as a mechanism for the decomposition of cementite [11]. According to the mechanism discussed in Ref. [11], the shearing of atomic planes along mutually inclined directions can create slip steps and embed small cementite particles in ferrite, provided that dislocations penetrate from ferrite into cementite on more than one active slip system. Such tiny cementite particles can be further cut by dislocations gliding through them, which increases the free interfacial energy of the particles. Finally, these particles dissolve via the Gibbs–Thomson effect.

4 Conclusions

The three-dimensional elemental distribution in cold-drawn pearlitic steel wires was studied as a function of true drawing strain by means of APT. Cementite decomposition was found to be promoted by plastic deformation. However, it saturates for $\varepsilon \geq 3.47$. Strong indications for the formation of cell–grain boundaries in ferrite, at which most of carbon atoms in ferrite are segregated, were found. Based on the experimental findings, we suggest that the strong carbon-dislocation interaction in ferrite is probably the underlying mechanism for cementite decomposition.

References