An EFTEM study of the dissolution of cementite during the graphitisation annealing of a quenched medium carbon steel

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Abstract. Graphitisation annealing at 680°C of a quenched medium carbon (0.38wt%C) steel with high contents of both Al (1.44wt%) and Si (1.82wt%) has resulted in the formation of graphite nodules ~2-5µm in diameter in a very short time (~2 hours). This could potentially improve machinability by an alternative and more commercially viable alloying route to, for example, the addition of lead. The overall graphitisation process involves the dissolution of the Fe₃C iron carbide phase (cementite) as well as formation of the graphite nodules. The evolution of microstructure and composition of cementite during the annealing treatment has been studied by analytical electron microscopy, including energy loss spectroscopy (EELS) and energy-filtered transmission electron microscopy (EFTEM) imaging. The formation of a non-graphitic, carbon-rich amorphous phase was identified during the heat treatment. This amorphous phase could be a previously undetected intermediate stage during the overall graphitisation process, the nodular graphite evolving from it.

1. Introduction
The Fe₃C iron carbide phase (cementite) is the major second phase constituent in a wide variety of commercial carbon and alloy steels. As a consequence, its formation during steel heat treatment and its effect on mechanical properties, have been extensively studied and documented. During the tempering of quenched martensitic steel, however, emphasis has mainly been placed upon relief of carbon supersaturation by the precipitation and eventual coarsening of cementite, to achieve either strength and toughness for service, or softening for future forming, rather than upon its dissolution, and generally not in steels containing high concentrations of graphitising elements. Cementite dissolution is an important event in graphitisation because it is the source of carbon for the formation of graphite nodules. In the case of graphitisation of conventional carbon steel compositions, this is expected to require long times, up to many tens, or even hundreds of hours at temperature [1], but in a steel alloyed with relatively high concentrations of Si and/or Al, graphitisation times can be reduced significantly [2]. Steel machinability, along with cold-workability, should be greatly improved by exchanging a dispersion of cementite for one of graphite nodules and could provide alternative alloying solutions to replace the present practice of adding elements such as Pb, which can give recycling and/or environmental concerns.

Electron energy loss spectroscopy (EELS) is an established technique for the detection and quantification of the light elements (B, C, N etc) with high spatial resolution (down to ~ 1nm or less). By using EFTEM, compositions in the phases involved during graphitisation, in particular, the light elements such as carbon can be revealed. In the present paper, the electron microscopic observations of the evolution of the microstructure and composition from the dissolution of cementite to the formation of graphite nodules during graphitisation annealing, including results obtained using EELS and EFTEM, are reported.
2. Materials and experimental methods
High-purity elements were used to make 50g ingots in an arc-melting furnace under a partial pressure of argon gas. The steel composition is 0.38C-1.82Si-0.07Mn-1.44Al (wt.%). The argon-arc ingot was homogenised at 1150°C for 70 hours and water quenched. Specimens cut from the quenched ingot were annealed at 680°C for various times. Samples for transmission electron microscopy (TEM) were first mechanically ground to a thickness of 80-100µm from thin slices, followed by electropolishing at 20mA, 15V and ~10°C, in a twin-jet unit using an electrolyte of 10% perchloric acid, 30% 2-butoxyethanol and 60% ethyl alcohol.

TEM examination and microanalysis were carried out either in a Philips CM 20, operating at 200kV, with an Oxford ultra-thin window EDX attachment and ISIS software, or a CM200 FEGTEM, fitted with a Schotty emitter source operated with an extraction voltage of 3.99kV. In addition to energy dispersive X-ray analysis (EDX), EELS spectra and EFTEM images were recorded using a Gatan Imaging Filter 200. Processing was performed using Gatan Digital Micrograph and EL/P software. To quantify the carbon content in the precipitates, 0.5eV/pixel EELS spectra that contain both carbon K-edge and iron L₂,₃ edges were collected. Both the Hartree-Slater quantification methods and the hydrogenic quantification with white line correction were used, with the experimental parameters: beam energy 197kV, convergence angle 1mrad, and collection angle 5.9mrad.

3. Results and discussion
In the as-quenched samples, only inclusion particles of aluminium nitride and aluminium oxide were observed in a martensitic matrix. After annealing at 680°C for 0.5 hours, a dispersion of cementite particles, ranging from approximately 0.1 to 1µm diameter with an average diameter of ~0.3µm, was observed, mainly located at the remaining interfaces of ferrite plates (Fig. 1a). In addition, a much lower density of graphite particles, formed on the aluminium nitrides or oxides, was also found. These graphite particles developed with an irregular morphology as annealing time increased (Fig.1b). As the annealing time was increased to 1 hour, most of the cementite particles disappeared and many more graphite nodules were formed. This increase involved the appearance of smaller more regularly spheroidal graphite nodules that did not appear to contain a nucleating core inclusion particle (Fig.1c). After 1.5 hours, no cementite particles remained and only graphite nodules were present, but now in a more polygonal ferrite matrix (Fig. 2).

![Figure 1](image-url)

**Figure 1.** Bright Field (BF) TEM images (a) showing coarsening cementite particles located mainly at the interfaces of ferrite laths, after 0.5 hours; (b) a graphite nodule associated with an Al nitride inclusion, after 1 hour; (c) a small regular spheroidal graphite nodule without a nucleating inclusion particle, after 3.5 hours.

Examination by microanalytical TEM methods revealed unexpectedly that some of the particles observed after the annealing treatment, and some apparent regions of cementite precipitates, did not have the structure and composition of cementite or graphite, and nor were they oxides or nitrides in nature. Many of the particles either surviving, or formed, after annealing for more than 0.75 hours had a
partly non-crystalline or amorphous structure. Moreover, many of the surviving cementite particles had an average Mn concentration around 2at%, much higher than that of cementite particles annealed for 0.5 hours, which was closer to the steel composition. In a number of cases observed, these particles were complex, consisting of apparent regions with different structure and also different chemical composition, as shown by the EFTEM jump ratio images from elements such as C, Fe and Mn. An example of non-quantitative Fe\textsubscript{L\textsubscript{23}}, Mn\textsubscript{L\textsubscript{23}}, O K- and C K-edge jump ratio images (with contrast levels set in the range from 0.6 to 5.0) of a complex particle is shown in Fig. 3 (these images are obtained by using a ‘two-window’ method: an EFTEM image formed by dividing a post-edge image by a pre-edge image to minimise specimen thickness and diffraction effects). These EFTEM jump ratio images showed clearly that one part of the complex particle was carbon-rich whilst the remaining (generally smaller) part was rich in both iron and manganese. EDX analysis and electron diffraction confirmed that the smaller part was still crystalline cementite containing a higher concentration of Mn (1.83at% for the example shown in Fig. 3). Mn is known to stabilise cementite \cite{3} and so it is not unexpected that the surviving cementite part should contain the higher

\textbf{Figure 2.} BF TEM image showing only graphite nodules present after 1.5 hours.

\textbf{Figure 3.} An example of EFTEM jump ratio images showing a complex particle consisting of an amorphous C-rich part and a smaller cementite region with a high Mn content (1.83at%). Fe\textsubscript{L\textsubscript{23}}, C k, Mn\textsubscript{L\textsubscript{23}}, O K jump ratio images and TEM image.
Mn concentration. EELS analysis showed that the carbon-rich part was nearly amorphous. Quantitative EELS analysis of the C/Fe ratio from the different parts in a complex particle showed that the carbon content increased substantially from around 30at% for a cementite region to around 70at% for the amorphous part. Figure 4 presents the PEELS spectra chronicling the transition from cementite to graphite, characterised by the carbon K-edge.

The above results show that the dissolution of cementite, a key process during graphitisation, can be complete in this experimental steel within a time scale of as little as ~2 hours, and also suggest that cementite may act as a graphite nucleation site during its dissolution, as evidenced by the complex particles, consisting of an amorphous carbon-rich region and a separate crystalline Mn-rich cementite part that were discovered. The amorphous C-rich part could thus be an intermediate stage in the overall graphitisation process, forming the core of the small regularly spheroidal graphite nodules, whilst the Mn-rich part continued to dissolve as annealing continued. A study of the effect of different starting microstructures on graphitisation in steel [4], showed that bainite was more effective than martensite, which could be interpreted as being due to the different state of the carbide dispersions between the two structures, thus lending indirect support to the present hypothesis.

**Summary**

The formation and dissolution of cementite during graphitisation annealing of a medium carbon steel with high contents of Al and Si have been investigated by electron microscopy, including EELS and EFTEM. The results showed that graphitisation could be virtually finished within a time scale of ~2 hours. Importantly, the cementite appeared to be directly involved in nucleation of the graphite phase. Complex particles consisting of a cementite region but with an amorphous part rich in carbon were discovered to develop during cementite coarsening and dissolution that could be interpreted to act as an intermediate stage during the transition from cementite to graphite.

**References**

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