EELFS study of the cementite local atomic structure

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The changes in the nearest - neighbour surroundings of carbon atoms in the cementite Fe_3C lattice due to the heat treatment are analysed by the Extended Energy Loss Fine Structure (EELFS) method. To study the local atomic structure of the carbon steel U15 after different heat treatment regimes the electron energy - loss spectra above the C K edge and Fe $L_{2,3}$ edge were measured. The measured experimental EELFS spectra were treated by the standard for the Extended X - ray Absorption Fine Structure method procedure using Fourier transformation to obtain the parameters of the nearest - neighbour atomic surroundings. Qualitatively the assumption was made that the number of the iron atoms in the carbon atom nearest - neighbour surroundings changes due to the heat treatment, the evidence of which was the change in the ratio of the first two feature intensities of the atomic radial distribution function. This assumption is consistent well with the previous Mössbauer data.

Keywords: EELFS, Fe_3C, local atomic structure

1. Introduction

Recent X-ray and electron diffraction and Mössbauer studies (Schastlivtsev et al., 1996, Schastlivtsev et al., 1997) of carbon steels have shown that the structure of the cementite formed in steels due to eutectoid (pearlite) transformation differs essentially for different conditions of heat treatment used to obtain the pearlite. Moreover disagreement between the cementite diffraction patterns and the space group *Pnma* assigned to the cementite structure (Fasiska & Jeffrey, 1965) has been observed. An analysis of NMR spectra of the cementite (Schastlivtsev et al., 1996) has shown that, firstly, nearest-neighbour surrounding of Fe atoms in the cementite lattice during heat treatment changes. Secondly, the probability distribution function of hyperfine fields for the cementite produced by one of the heat treatment regime differs substantially from that of the space group *Pnma*, that points to change of the atomic crystal structure. In other words, some evolution of the cementite structure during long annealing takes place, and at least one form of the cementite have a structure different from *Pnma* cementite structure whose crystallographic parameters are given in the literature (Fasiska & Jeffrey, 1965). The results obtained earlier allow us to suppose that the cementite formed after quite low temperatures of pearlite transformation differs from the cementite formed after additional annealing of carbon steels below the A_1 temperatures. To verify this assumption the nearest-neighbour surrounding of C atoms in the cementite lattice is studied in this paper.

2. Experimental

Extended Energy-Loss Fine Structure (EELFS) in transmission mode was chosen as a research method because of a number of its substantial advantages. Firstly, this is strong locality of the method determined by using electron beam as an excitation source. Secondly, using EELFS in the transmission mode allows to obtain an information on a local domain restricted by the electron beam diameter, on the one hand, and by the thickness of the foil traditionally prepared for the study by Transmission Electron Microscopy (TEM) method, on the other hand. Moreover the combination of the electron microscopy, the electron microdiffraction and the electron spectroscopy possibilities allow to choose the desired local region under study, in particular, great cementite grain, being wholly sure of studying really the cementite grain due to the electron microdiffraction opportunity.

Steel U15 containing 1.53% C prepared from pure components under laboratory conditions was studied. This steel contains substantial part of the cementite (more than 20 wt %). The pearlite structure in these samples was obtained by heating up to 1050°C followed by isothermal tempering at 500°C for 1 min (regime 1). The second group of samples after the same heat treatment was undergone by the additional annealing at 700°C for 20 hours (regime 2).

The structure of carbide obtained by different regimes of heat treatment was studied by EELFS in the transmission mode. The experiment was carried out on transmission electron microscope JEM-2000EX equipped by spectroscopic EELS device. Samples for EELFS studies were prepared using standard technique as foils of ~1000 Å thickness.

Microstructure of the pearlite structure after different regimes of heat treatment is shown in Fig. 1 (regime 1) and Fig. 2 (regime 2). To study the local atomic structure of the steel U15 after different regimes of heat treatment electron energy-loss spectra above C K- and Fe $L_{2,3}$-edges were measured. A typical experimental EELFS spectrum in the transmission mode is given in Fig. 3. The experimental EELFS spectra were treated using

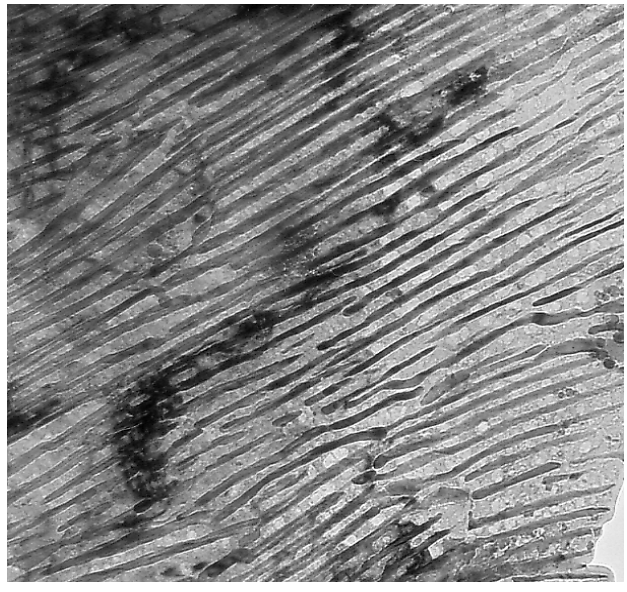

Figure 1
Microstructure of the carbon steel U15 pearlite obtained by quenching from 1050°C followed by annealing at 500°C for 2 min (regime 1)

Figure 2
Microstructure of the carbon steel U15 pearlite obtained by quenching from 1050°C followed by annealing at 500°C for 2 min, cooling to room temperature and additional annealing at 700°C for 20h (regime 2)

the procedure traditional for extended X-ray absorption fine structure (EXAFS) spectra. In Fig. 4 oscillatory parts extracted from the experimental EELFS spectra above C K edge for steel U15 samples after different heat treatments in comparison with the calculated one by FEFF7 (Rehr et al., 1992).

3. Results and discussion

The calculated oscillatory part above the C K edge was obtained by means of FEFF7 using crystallographic bond lengths in the cementite according to the symmetry characteristic for the *Pnma* space group. It is seen from Fig. 4 that the period of the main oscillation is quite the same for all three oscillatory parts. But there are some peculiarities that differ structures of the experimental oscillatory parts for different heat treatment regimes from the calculated one. It is observed also the feature in the range of ~250 eV in the electron energy-loss scale corresponding to the ionization of O K edge and connected with presence of oxygen in surface layers of the samples studied. The oscillatory parts differ also from each other for a number of characteristic features. These differences may give evidence that the nearest-neighbour surrounding of carbon atoms in the cementite formed at the lowest temperature of the pearlite transformation and for the least tempering which are enough however to complete the eutectoid transformation really is not the same as in the cementite formed at the higher temperatures. Therefore there is some evolution of the cementite structure connected probably with changes in the partial lengths of C-Fe pairs.

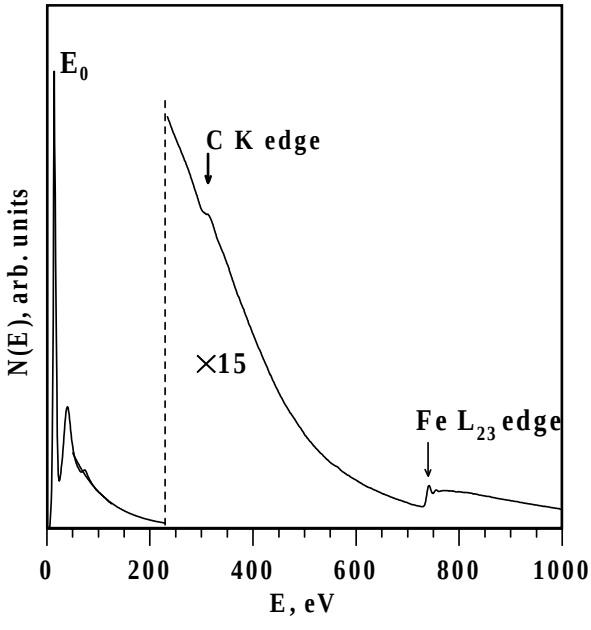

Figure 3
A typical EELFS spectrum measured in the transmission mode

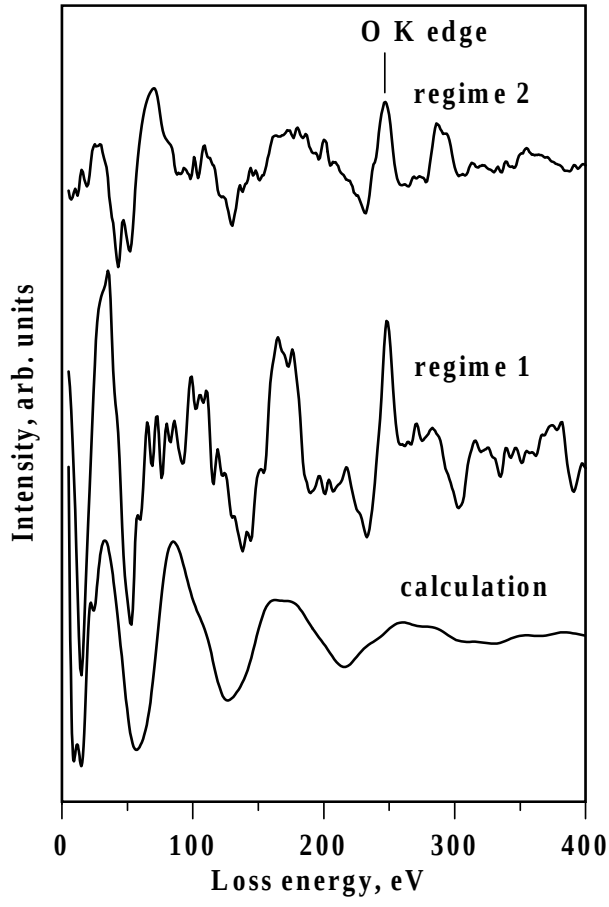

Figure 4
Oscillatory parts extracted from the experimental EELFS spectra above C K edge in comparison with the calculated one (FEFF 7)

Using the standard procedure of EELFS spectra treating we carried out Fourier transformation of oscillatory parts extracted from the experimental spectra. Obtained Fourier transform as compared with Fourier transform of the calculated oscillatory part for C K edge in the cementite lattice according to the *Pnma* space group symmetry are represented in Fig. 5. A comparison has shown that in the range up to ~3Å Fourier transform of

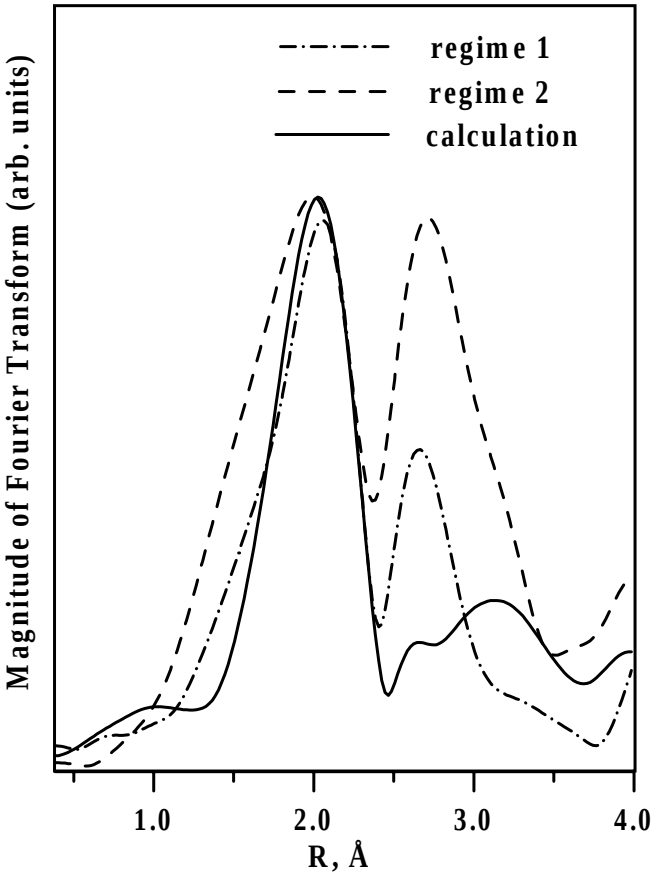

Figure 5
Fourier transform magnitudes of the oscillatory parts extracted from experimental EELFS spectra of the cementite after different heat treatments in comparison with FT of calculated oscillatory part by FEFF7

the oscillatory part of the signal from the cementite obtained at the lowest temperature of the pearlite transformation for the least tempering time is quite similar to the calculated one.

The magnitude of the Fourier transform for oscillatory part of the spectrum above C K edge in the cementite formed during the heat treatment regime 2, i.e. undergone by additional annealing differs essentially both from the magnitude of the Fourier transform for the first experimental oscillatory part and calculated one. Qualitatively it may be suggested that in the cementite formed as a result of the heat treatment regime 2 in the range up to ~ 3Å a change in the number of Fe atoms in the nearest-neighbour surrounding of carbon atoms is observed and a change in the ratio of the intensity of the first two maxima is the evidence of this fact.

To obtain more complete information on the local atomic structure of the cementite using EELFS method it is necessary to study both C K edge and Fe $L_{2,3}$ edge in order to find partial interatomic distances.

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