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C-vacancy concentration in cementite, Fe_3C_{1-z}, in equilibrium with α-Fe[C] and γ-Fe[C]

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Abstract—New data are presented on the ambient-temperature values of the orthorhombic lattice parameters of cementite (θ, Fe_3C_{1-z}). The cementite was obtained by electrolytically etching away the ferrite or martensite from quenched dual-phase Fe–C alloys equilibrated at $823\ K \leqslant T \leqslant 1323\ K$, i.e. in the α (ferrite) + θ or γ (austenite) + θ two-phase fields, followed by quenching. In qualitative agreement with earlier data (Petch, 1944), the decrease in the lattice parameters *a* and *c* and the simultaneous increase in *b* with increasing equilibration temperature *T* can be attributed to an increase in the fraction of C vacancies, *z*, in Fe_3C_{1-z} in equilibrium with the corresponding Fe[C] terminal solid-solution phase (α or γ). The experimental data are compared with results on C-vacancy-induced lattice-parameter changes obtained by first-principles calculations performed within the framework of density-functional theory (DFT). The anisotropy of the changes in the lattice parameters *a*, *b* and *c* predicted by DFT agrees qualitatively with the experimentally observed changes occurring with increasing equilibration temperature. Eventually, the equilibration-temperature dependence of the unit-cell volume of the cementite, $V = abc$, was used to calculate *T*-dependent values of the vacancy fraction *z*, thereby yielding data for the α + θ/θ and γ + θ/θ phase boundaries in the metastable phase diagram of Fe–Fe_3C. In particular, the α + θ/θ phase boundary determined could be interpreted in terms of Gibbs energy of C-vacancy formation in cementite, whereby its enthalpy contribution agrees well with the results of the first-principles calculations.

Keywords: Cementite; Diffraction; Iron alloys; First-principles calculations; Thermodynamic modeling

1. Introduction

Cementite (θ, Fe_3C) is the most prominent intermediate phase in the Fe–C system [1]. It occurs as a constituent in many (low-alloying element) steels and other Fe–C-based alloys. The importance of cementite as a metastable phase is reflected by the relevance of the metastable Fe–Fe_3C phase diagram for many heat-treatment processes of carbon steel and other Fe–C alloys, in which formation of the thermodynamically stable graphite is largely suppressed. The rate of graphitization relies heavily on the temperature and on the presence of alloying elements [2]; the presence of, for example, some Cr in the alloy can make the cementite phase thermodynamically stable against graphitization.

The orthorhombic[1] crystal structure of cementite contains two inequivalent crystallographic sites for the Fe atoms and one for the C atoms [3], where the formula Fe_3C results in the case of full occupation of all these sites. In most published phase diagrams and thermodynamic descriptions of the Fe–C system, the 25 at.%/6.69 wt.% C corresponding to this formula are adopted as a fixed composition for cementite, i.e. it is regarded as a line compound [1,4,5].

Nevertheless, there is considerable experimental evidence for a homogeneity range of the cementite phase, implying that the C content can amount to <25 at.% in equilibrium with ferrite (α) or austenite (γ). As early as 1944, Petch [6] reported minor but significant changes in the lattice parameters of cementite (always measured at ambient temperature) extracted from Fe–C alloys. These were equilibrated at and subsequently quenched from $T \leqslant 1173$ K, at which the alloys were in the α + θ or γ + θ dual-phase region. With increasing equilibration temperature *T*, a decrease in the lattice parameters *a* and *c* and an increase in the lattice parameter *b* (see fn. 1) as well as a decrease in the unit-cell volume *V* (= *abc*) were encountered. These changes were attributed to a *T*-dependence of the cementite's composition in equilibrium with the (mainly) γ phase: Whereas cementite in equilibrium with the α phase is basically stoichiometric, cementite in equilibrium with the γ phase contains C vacancies on the sites,

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[1] Here the setting indicated by the space group *Pnma* will be employed, implying *c* (~4.5 Å) < *a* (~5.1 Å) < *b* (~6.7 Å). Note that also the *Pbnm* setting implying *a* < *b* < *c* is used in many current works. Note that the indices for planes (*hkl*) and directions [*uvw*] have to be permuted upon switching from one setting to the other.

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which are fully occupied in stoichiometric Fe_3C (the interstitial C sublattice). Thereby, the vacancy content in the cementite in equilibrium with the γ phase increases (i.e. the carbon content decreases) with increasing equilibration temperature. Such variations in the lattice parameters were later reproduced [7–9], particularly on alloys containing elements such as Cr and Mn. Moreover, C-deficient cementite with characteristic lattice metrics was obtained by modest decarburizing of Fe_3C powder by H_2 at low temperatures [10,11] or by rapidly quenching Fe–C alloys from the liquid state [12].

All this implies that the (metastable) cementite phase shows, at least in equilibrium with the γ phase, a homogeneity range where the $\gamma + \theta/\theta$ boundary is located at a C content <25 at.%, whereby this C content decreases with increasing temperature. Thereby, the lowest C content of cementite is probably found at the temperature of the eutectic reaction at ~1421 K [5]. However, there have been only a few quantitative assessments of the course of this phase boundary $\gamma + \theta/\theta$ (or $\alpha + \theta/\theta$ below the eutectoid temperature of 1000 K [5]). This is because, although lattice-parameter changes can be observed, it is not trivial to quantitatively interpret the lattice-parameter changes in terms of composition changes. Independent data on the extent of the homogeneity range of cementite came from chemical analysis of cementite extracted from cast and quenched specimens, containing some Cr to stabilize the cementite [7]. Thereby, 6.4 wt.% C was determined, compared with 6.69 wt.% C for Cr-free stoichiometric cementite. This C content was used to assess the composition of the phase boundary $\gamma + \theta/\theta$ at the eutectic temperature (1421 K; see above) as 24.1 at.% C or as given by the formula $Fe_3C_{0.95}$ (5% of the C sites are vacant). The 24.1 at.% C was indicated in several published phase diagrams [13–16]. Authors from the same group stated that the C content of cementite in equilibrium with the γ phase approaches the stoichiometric content for decreasing equilibration temperatures, as demonstrated, for example, by phase-content determination using planimetry on the basis of micrographs of dual-phase alloys [14]. The composition $Fe_3C_{0.98}$ of cementite in liquid-quenched Fe–C alloys was estimated [12] assuming (i) a proportionality of the unit-cell volume with the C content and considering the estimated unit cell volume of a hypothetical C-free cementite derived in Ref. [3], and (ii) from the decrease in the Curie temperature as a result of C vacancies. Much smaller C contents in cementite, even at $T \leqslant 900$ K (i.e. below the eutectoid temperature) were reported [17]: Rietveld refinements performed on neutron powder-diffraction patterns collected from dual-phase $\alpha + \theta$ Fe–C alloys gave C contents in cementite decreasing with increasing temperature. C contents corresponding to a formula of $Fe_3C_{0.75}$ were encountered close to the eutectoid temperature. Such high vacancy contents seem to contradict all the above-mentioned estimates.

In the present paper, new data on the orthorhombic lattice parameters of cementite obtained by electrolytically etching away the ferrite or martensite from quenched dual-phase Fe–C alloys equilibrated at $823\ \text{K} \leqslant T \leqslant 1323$ K are reported. For quantitative interpretation of the lattice parameters in terms of the C-vacancy fraction z (with the help of which the chemical formula reads Fe_3C_{1-z}), it will be assumed that the lattice parameters change linearly with the (small) values of z. If one expresses the lattice parameters as strains relative to the lattice parameters of stoichiometric cementite, a_0, b_0 and c_0, one obtains

$$\varepsilon_{11}(z) = \frac{a(z) - a_0}{a_0} = K_{11} z \qquad (1)$$

as well as corresponding expressions for ε_{22} and ε_{33} calculated from $b(z)$ in connection with b_0 (factor K_{22} on the right-hand side) and from $c(z)$ in connection with c_0 (factor K_{33} on the right-hand side). The K_{ij} are components of a 2nd-rank tensor (a "composition-induced strain tensor"), which connects the (relative) lattice-parameter change with the fraction of C vacancies z and thus with the composition of the cementite, whereby $K_{12} = K_{13} = K_{23} = 0$ holds, owing to the orthorhombic symmetry. The values of these K_{ij} will be obtained from first-principles calculations performed within the framework of the density-functional theory (DFT). The lattice parameters as they contribute to the unit-cell volume were employed to determine absolute values of the C-vacancy fraction and thus of the C content of the cementite considered, leading to assessment of the $\alpha + \theta/\theta$ and of the $\gamma + \theta/\theta$ phase boundaries in the metastable Fe–Fe_3C phase diagram.

2. Methods

2.1. Experimental: alloy production, heat treatment and cementite extraction

Fe–C alloys were prepared by induction melting of iron granules (Alfa Aesar, 99.98%) and graphite, weighted in accordance with target compositions of 0.8 wt.% C, 2.0 wt.% C (graphite fibres, Alfa Aesar, 2N5) and 4.0 wt.% (spectral carbon, Ringsdorff; the graphite fibres were no longer available for preparation of the third alloy). The melts were cast into water-cooled copper moulds to obtain rods. The C content of the alloys was determined by combustion analysis as 0.63, 1.6 and 4.2 wt.% C (reproducibility in the region of 5% for different alloy pieces).

The Fe–0.63 wt.% C alloy was cold rolled and machined to obtain plates of thickness 1 mm. These were sealed under vacuum in quartz tubes to be annealed (equilibrated) at 823 K, 873 K, 923 K, 973 K or 988 K for 7–14 d, followed by water quenching, including crushing of the quartz tube. Pieces of the rods of the Fe–1.6 wt.% C and Fe–4.2 wt.% C were sealed under vacuum in quartz tubes to be annealed for 16 h at 1273 K. In a second step, the Fe–1.6 wt.% C alloy pieces were annealed (equilibrated) for 17 h at 1073 K, 1123 K, 1173 K or 1223 K, whereas the Fe–4.2 wt.% C alloy pieces were annealed (equilibrated) for 17 h at 1223 K, 1273 K or 1323 K. The second annealing step was always terminated by water quenching, including crushing of the quartz tube.

The specimens were cross-sectionally embedded, polished, etched with 1 vol.% nital, and some of them were stained with Groesbeck solution (4 g $KMnO_4$, 1 g NaOH and 1 g KOH per 100 ml H_2O). The cementite was extracted from the alloys by electrically contacting the embedded cross sections from the back and anodically oxidizing the alloy in 0.1 wt.% HCl solution with a voltage of 2.4–3.2 V. This leads to preferential dissolution of the ferrite or martensite phase coexisting with the cementite in the alloys. After some treatment time, the remaining cementite was removed by gently scratching. The powder was then washed with water, then with ethanol, and dried.