Carbon concentration measurements by atom probe tomography in the ferritic phase of high-silicon steels.

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Abstract

Recent studies using atom probe tomography (APT) show that bainitic ferrite formed at low temperature contains more carbon than what is consistent with the paraequilibrium phase diagram. However, nanocrystalline bainitic ferrite exhibits a non-homogeneous distribution of carbon atoms in arrangements with specific compositions, i.e. Cottrell atmospheres, carbon clusters, and carbides, in most cases with a size of a few nanometers. The ferrite volume within a single platelet that is free of these carbon-enriched regions is extremely small. Proximity histograms can be compromised on the ferrite side, and a great deal of care should be taken to estimate the carbon content in

regions of bainitic ferrite free from carbon agglomeration. For this purpose, APT measurements were first validated for the ferritic phase in a pearlitic sample and further performed for the bainitic ferrite matrix in high-silicon steels isothermally transformed between 200 °C and 350 °C. Additionally, results were compared with the carbon concentration values derived from X-ray diffraction (XRD) analyses considering a tetragonal lattice and previous APT studies. The present results reveal a strong disagreement between the carbon content values in the bainitic ferrite matrix as obtained by APT and those derived from XRD measurements. Those differences have been attributed to the development of carbon-clustered regions with an increased tetragonality in a carbon-depleted matrix.

Keywords. Bainitic steel; nanostructure; tetragonal distortion; atom probe tomography (APT); X-ray diffraction (XRD).

1. INTRODUCTION

It is now accepted that bainitic ferrite formed at low temperatures is super-saturated with carbon when the concentration is evaluated with respect to the ferrite/austenite phase boundary under paraequilibrium (PE) conditions [1]. Experimental results leading to this conclusion were initially drawn from atom probe tomography (APT) data [2-5] and supported later by synchrotron radiation [6], X-ray diffraction (XRD) [7], and *in situ* neutron diffraction [8] experiments. The major discrepancies between the calculated phase boundaries and the experimental carbon concentration values are obtained for

high-carbon high-silicon steels transformed into bainite at temperatures below 300 °C [4], where the carbon content in bainitic ferrite is over forty times above that expected from the PE phase boundary with austenite. Carbon supersaturation in ferrite is not exclusive of low-temperature bainite and it can also be found in the lower and upper bainite forms of high-carbon and medium-carbon high-silicon steels [4, 9].

Besides the carbon in super-saturated solution, nanocrystalline bainitic ferrite exhibits a complex non-homogeneous distribution of carbon atoms in arrangements with a specific composition, a few nanometers in size in most cases. Those carbon-enriched regions have been identified as Cottrell atmospheres (~8 at.% C), carbon clusters (~15 at.% C), the Fe_{32}C_4 carbide (~20 at.% C), and cementite precipitates (~25 at.% C) from the carbon content [3, 4, 10, 11].

APT is a state-of-the-art analytical technique that allows for three-dimensional elemental mapping with near atomic resolution. It is a powerful tool that can provide local compositional information, and therefore, it is currently the most widely used technique to investigate the origin of carbon super-saturation in bainitic ferrite. The method routinely used to evaluate the carbon content in bainitic ferrite is based on 1-D concentration profiles [3, 4, 10, 11], where the carbon content is determined by counting the number of carbon atoms in slices perpendicular to one of the axes of a selected volume. The size of the slices is selected to maximize the number of ions within the slice without sacrificing the spatial resolution; larger slices produce less statistical scatter, but reduce the spatial resolution [12]. However, the volumes of ferrite that do not

contain any of the aforementioned carbon-enriched regions are extremely small and the statistics obtained by concentration profiles are jeopardized.

Besides, proximity histograms are profiles of local atomic concentrations vs. proximity to an isoconcentration surface whose composition is selected to represent an interface[13]. Proximity histograms are primarily designed to investigate the solute distribution and interfacial segregation at interphase interfaces and solute partitioning trends between phases. On very fine scale structures, as in nanostructured bainite [7], they might be used effectively to estimate the solute content and the presence and extent of solute tails. Nonetheless, regarding the complexity of features that one can encounter within a single bainitic ferrite platelet, proximity histograms can be compromised on the ferrite side, and a great deal of care should be taken during sampling to estimate the carbon content in regions of bainitic ferrite free from carbon-enriched regions.

On the other hand, the carbon-enriched regions cannot be unambiguously identified by APT without the use of highly correlative electron microscopy to reveal what kind of feature is actually encountered[14-16]. The identification of the features solely from the carbon content becomes specially challenging for carbon-related Cottrell type features and small stoichiometric cementite in opposition to other carbides. Ab-initio predictions coupled with quasi-harmonic phonon calculations or multi-component diffusion simulations are useful to identify and understand the partitioning behavior of carbon and other alloying elements between bainitic ferrite and different carbides[9, 17, 18]. In this work, we will consider the ferrite matrix as the low-carbon regions in the

material where the solute atoms are randomly distributed so that an accurate identification of all the features present in an APT needle is not needed.

The carbon contents in bainitic ferrite, as determined from APT, are currently used as the grounds for research focused on the origin of the carbon super-saturation. The most sensible hypothesis considered is the increased solubility of a tetragonal (rather than cubic) ferrite lattice, by virtue of experimental results[6, 7, 19] and ab-initio calculations [20, 21]. Carbon-supersaturation in bainitic ferrite is one of the key issues to discuss the transformation mechanism of bainite and thus, it is of primary importance in this research field. Ensuring precise and systematic carbon content values is now crucial for researchers to develop the theoretical approaches which can numerically explain such carbon super-saturation.

Here, the distribution of isolated atoms for the determination of the matrix composition (hereinafter DIAM) method proposed by de Geuser and Lefebvre [22] was applied to determine the carbon concentration in bainitic ferrite away from dislocations, clusters, and precipitates in an attempt to assess the actual carbon solubility in bainitic ferrite. To this end, the DIAM method was first validated in pearlitic ferrite, where the carbon concentration is known, and further applied to the ferritic phase in bainite.

2. EXPERIMENTAL PROCEDURE

The alloys studied are high-silicon steels whose chemical composition are given in Table 1. Heat treatments were performed in the furnace of an AdamelLhomargy LK02 high-resolution dilatometer on samples of $15 \text{ mm} \times 10 \text{ mm} \times 5 \text{ mm}$. Each sample was heated by radiation in vacuum to the austenitization temperature (T_γ) above A_{c3} for 15 min and subsequently cooled down at $50 \text{ }^\circ\text{C/s}$ to the isothermal transformation temperature (T_{iso}) and held for the necessary isothermal transformation time (t_{iso}) for completion of the bainite transformation. Finally, samples were helium quenched to room temperature. The relevant process parameters, i.e., T_γ , T_{iso} and t_{iso} are presented in Table 2, where samples have been encoded according to the material and heat treatment, expressed as $x\text{C}/y$, where x and y are the carbon content of the steel and the transformation temperature respectively.

Additionally, two reference pearlitic microstructures (expressed as 0.7C/PER and 1.0C/PER) were produced from the 0.7C and 1.0C steels by continuous cooling at $1.5 \text{ }^\circ\text{C/s}$, after fully austenitization at 900 and 950 $^\circ\text{C}$ for 15 min respectively. These steels were selected to ensure a fully pearlitic structure after a slow cooling[23].

XRD was used to determine the lattice parameter and the average carbon content of bainitic ferrite. XRD measurements were carried out with a Bruker AXS D8 diffractometer equipped with a Co X-ray tube, Goebel mirror optics and a LynxEye Linear Position Sensitive detector. XRD data were collected over a 2θ range of 35 to 135° with a step size of 0.015° . The lattice parameter of bainitic ferrite was determined

by applying the Rietveld method to attain a high degree of precision. In this study, version 4.2 of the Rietveld analysis program TOPAS (Bruker AXS) was used for fitting the XRD patterns. In order to characterize the particularities of the diffractometer set-up used, the instrumental profile was empirically parameterized from an XRD pattern of a corundum sample. The refinement protocol used also included the background, zero displacement, the scale factors, peak breath, and texture parameters. The analysis of the diffraction line profiles for deriving quantitative information on crystallite size and microstrain was performed by means of the *double-Voigt* approach, in which both the crystallite size and strain are comprised of Lorentzian and Gaussian component convolution [24].

There are considerable amounts of literature data on the lattice parameters of Fe-C martensite and Fe-C austenite, from which the dependence of the lattice constants for both phases with the carbon content in solid solution was previously determined [25, 26]. In the case of Fe-C martensite, the most widely used expression for calculating the carbon content in solid solution is the well-known empirical relation given by Cohen [25], $c/a = 1 + 0.045x_w$, where x_w is the carbon concentration in wt.%. However, data used for obtaining this linear function present large statistical scatter due to experimental errors associated with the method used for lattice-parameter determination and the presence of residual stresses. Improved relations have been found, such as the one derived by Cheng et al.; $c/a = 1 + (0.0095 \pm 0.001)x_{at}$ where x_{at} is the carbon concentration in at.% [26].

APT needle-shaped samples were cut from bulk material and electropolished with the standard double layer and micropolishing methods, followed by slight focused ion beam (FIB) milling[12, 27]. Atom probe analyses were performed in the CAMECA Atom Probe Tomography Center and Oak Ridge National Laboratory (ORNL) local electrode atom probes (CAMECA Instruments LEAP 5000 R/XR and LEAP 4000X HR). The local electrode atom probes were operated in voltage-pulse mode with a specimen temperature of 50 K, a pulse repetition rate of 200 kHz, and a pulse fraction of 0.2. These conditions were selected so that they reproduce previous atom probe studies where the carbon content bainitic ferrite was determined [2-5].

3. RESULTS AND DISCUSSION

3.1. X-RAY DIFFRACTION MEASUREMENTS

In bainitic steels, additions of 1.5 wt.% silicon prevent the precipitation of cementite between the plates of bainitic ferrite during bainitic transformation, but cannot retard the precipitation of cementite inside the ferrite plates at low transformation temperatures. The carbon that is rejected from the bainitic ferrite enriches the surrounding austenite, so that it can be stabilised down to room temperature. The microstructure in high-silicon bainitic steels roughly consists of bainitic ferrite interwoven by retained austenite regions, though martensite regions might appear when the austenite carbon enrichment is insufficient.

In the case of 0.7C and 1.0C bainitic steels, the level of carbon in the austenite after the transformation ensures that no martensite will be formed. Here, two phases are mainly present; the austenite and the bainitic ferrite. In the meantime, in the bainitic microstructures produced from 0.3C steel, the carbon enrichment of large regions of austenite is not sufficient for the austenite to be stable at ambient temperature, so that martensite will form during the last quenching stage after bainitic transformation. In these microstructures, martensite and ferrite peaks are not distinguishable in the XRD spectra and definitive conclusions in terms of carbon super-saturation in bainitic ferrite cannot be drawn from the lattice parameters derived from XRD measurements. Detailed microstructural characterization of all the microstructures studied in the present work can be found in [23] for the 0.3C and 1.0C steels and in [28] for the 0.7C steel.

As expected, XRD patterns of the bainitic microstructures showed only diffraction peaks for ferrite and austenite[7]. As reported in previous studies, bainitic ferrite formed in similar steels by isothermal transformation at temperatures ranging between 200 and 300°C present a tetragonal unit cell [7]. Thus, the Rietveld refinement method used here to analyze XRD patterns included the crystal structure model for ferrous martensite and austenite, together with the line-broadening analysis of diffraction peaks with the *double-Voigt* approach [24]. The structural data results of the Rietveld XRD pattern refinements are shown in Table 3. Differences in the $c/a_{\alpha'}$ ratio of bainitic ferrite and the lattice parameter of retained austenite after the isothermal heat treatments are rather small, though tendencies indicate that the $c/a_{\alpha'}$ ratio is increased either when the carbon content of the steel is increased or the bainitic transformation temperature is decreased.

In the case of the pearlitic structures 0.7C/PER and 1.0C/PER, XRD measurements showed a cubic structure of the ferritic phase with a lattice parameter of 2.867 Å in either case. Thus, the composition of pearlitic ferrite in these microstructures is expected to be close to the equilibrium.

3.2. ANALYTICAL PROCEDURE FOR CARBON CONCENTRATION MEASUREMENTS BY ATOM PROBE TOMOGRAPHY

In order to obtain direct measurements of the carbon content in bainitic ferrite, APT analyses were performed. The usual description of a matrix assumes a random distribution of the solute atoms throughout the matrix, which is consistent with the definition of chemical disorder, which states that the probability of an atom to occupy a lattice site is equal to its average concentration on all lattice sites. Therefore, we will consider the ferrite matrix as the low-carbon regions in the material where the solute atoms are randomly distributed. Defining and assessing randomness is not trivial and the interpretation of atom probe datasets where very fine solute clustering is present requires careful consideration. Up-to-date overviews are given in [29, 30] and are not discussed in detail here for the sake of brevity.

In the present work, a recently developed method to be applied in APT datasets containing two phases or more has been used to calculate the carbon content of ferrite, which uses the distribution of isolated atoms for the determination of the matrix composition (DIAM) [22]. The principle of this method relies on the calculation of the

relative amount of isolated atoms (i.e., not surrounded by a similar solute atom) within a sphere of radius d . Thus, the average number of carbon solute atoms n in a sphere of radius d is given by:

$$n = \frac{4}{3}\pi d^3 \frac{N_0}{V} \quad \text{Eq. 1}$$

where N_0 is the total number of carbon atoms and V is the total analyzed volume. The probability of a carbon atom to be isolated, i.e. not to be neighboured by another carbon atom within a sphere of radius d is given by the probability of Poisson $P_0(0, n)$ and can be written as

$$P_{iso}(n) = P_0(0, n) = e^{-n} \quad \text{Eq. 2}$$

Considering a volume containing carbon-rich regions of concentration C_p (i.e. clusters, Cottrell atmospheres, and second phases) embedded in a carbon-depleted matrix of concentration C_m , the probability of a carbon atom to be isolated is different for the fraction of atoms x belonging to the carbon-rich regions and the fraction of atoms $(1 - x)$ belonging to the carbon-depleted matrix. Thus, the probability of an atom to be isolated in the whole volume is

$$P_{iso}(n) = x e^{-\frac{C_p}{C_0}n} + (1 - x) e^{-\frac{C_m}{C_0}n} \quad \text{Eq. 3}$$

where C_0 is the volume overall composition in carbon atoms. Eq. 3 is the sum of two decreasing exponential functions, and given that $C_p > C_m$ the first exponential term

decreases faster and can be neglected for large values of n . The logarithm form of the expression allows the probability to be reduced to a straight line [22]:

$$\ln[P_{iso}(n)] = \ln[1 - P_{1NN}(n)] \approx \ln(1 - x) - \frac{C_m}{C_0}n \quad \text{Eq. 4}$$

The term on the left side of Eq. 4 can be readily computed by the first nearest neighbor distribution, since $P_{1NN}(d)$ is the integral sum (or cumulative sum in the discrete case) of the first nearest neighbors distribution [31]. A change of variable should follow to obtain $P_{1NN}(n)$ and then $P_{iso}(n)$. Finally, C_m can be determined from the slope of $\ln[P_{iso}(n)]$.

An statistical error can be derived from the standard error indirectly evaluated by the DIAM method and the standard error of the calculated slope in Eq. 4, s_m , as follows:

$$s = \sqrt{\frac{C_m(1 - C_m)(1 - Q)}{(1 - f)N_T}} + s_m C_0 = \sqrt{\frac{C_m(1 - C_m)(1 - Q)}{(1 - x)\frac{C_0}{C_m}N_T}} + s_m C_0 \quad \text{Eq. 5}$$

where Q is the detection efficiency, f is the molar fraction of the carbon-rich phases, making $(1 - f)$ the molar fraction of the matrix, and N_T is the total number of atoms in the volume. The multiplier term $(1 - Q)$ in Eq. 5 is added to calculate the standard deviation in a sub-part of the probed volume [32], indicating the standard deviation on the given local concentration as opposed to the standard deviation on an estimate derived from various individual local concentrations.

Figure 1(b) presents the direct application of the DIAM method to the volume presented in Figure 1 (a). The linear fit according to Eq. 4 (black solid line) was performed in the linear regime for large values of n that are attributed to the matrix contribution. The n_{min} and n_{max} parameters between which the linear fit is performed can be determined in an automated way. On the one hand, n_{max} is limited to data of statistical significance, i.e. when $N_C P_{iso}(n) > \beta$, where β is a number of atoms. On the other hand, n_{min} is the value which makes the carbon-enriched features contribution negligible against the matrix contribution, and can be written as [22]:

$$n_{min} = \frac{-C_0}{C_p - C_m} \ln \left[\frac{\varepsilon(1-x)}{x} \right] \quad \text{Eq. 6}$$

where ε is a number sufficiently small to avoid the influence of the carbon-enriched features interfaces. A visual inspection of the fit tells if the value of ε needs to be lowered. In the present work, we have used $\beta = 5$ and $\varepsilon = 10^{-8}$. C_p and x can be obtained from the linear fit in Eq. 4 and a simple mass balance. Though there is a large uncertainty associated to the value of x thus obtained, it can be used for the determination of n_{min} [22].

For the application of the DIAM method, the first nearest neighbor distribution of carbon atoms is needed. Carbon is field-evaporated as molecular ions in the form of monomers (C_1), dimers (C_2), trimers (C_3), and tetramers (C_4). In the case of carbide phases, field-evaporation results in an enhanced formation of molecular ions and their presence is assumed not to be proportional in both the precipitates and the matrix. Thus, the DIAM method was applied separately to the C_1 , C_2 , C_3 and C_4 ions.

On the other hand, for very dilute solid-solutions, the detection limit or the minimum concentration that can be detected in the analyzed material is extrinsically limited by the sources of the background noise. Though the background can never be eliminated, it can be minimized by optimizing the operation conditions. The contribution of the background to the major element is usually slight, but this is not the case for the minor elements. It follows that it is also essential to perform a background correction in the mass spectrum to get precise measurements in the matrix. The first nearest neighbor distribution, as obtained by the IVAS software, contains all the signal and the background atoms for a given mass range. A proper background subtraction after application of the DIAM method becomes necessary to estimate the carbon content in ferritic structures.

To that purpose, a local range-assisted peak decomposition was performed in the mass spectrum of five different volumes within a needle, where a background estimate was calculated for each ranged peak based on the number of counts present on either side of the range. The peak decomposition helps to compute the corrected ionic composition for each of the carbon species C_i^{corr} (C_1^{corr} , C_2^{corr} , C_3^{corr} , C_4^{corr}), as well as the corresponding background of each of the carbon species Bkg_{i0} (Bkg , Bkg_2 , Bkg_3 , Bkg_4). It follows that one can obtain the corrected composition as: $C_i^{corr} = C_i - Bkg_i$, where C_i is the concentration of the carbon ions without background subtraction (uncorrected carbon).

Figure 2 shows the application of the described procedure in five different volumes obtained from a single needle of the 1.0C/PER sample. In all cases, the relationship

between the uncorrected carbon content and the corresponding background follows a straight line with the equation:

$$C_i = a_i Bkg_i + b_i \quad \text{Eq. 7}$$

The carbon content in the matrix, as obtained for each of the species from the DIAM method, can then be corrected as follows:

$$C_{im}^{corr} = C_{im} - Bkg_{im} \quad \text{Eq. 8}$$

$$C_{im}^{corr} = C_{im} \left(\frac{a_i - 1}{a_i} \right) + \frac{b_i}{a_i} \quad \text{Eq. 9}$$

Since the relationship between the uncorrected carbon content and the corresponding background is linear, the application of the process in three volumes within a needle is enough to find the relationship between the uncorrected composition for each of the carbon species and the associated background. The three volumes to be analyzed are the entire needle itself and two other volumes extracted from it. We have typically taken the average carbon composition of the needle as a threshold to obtain both the carbon low-gradient side and the high-gradient side volumes.

However, for the application of Eq. 8, one must consider if the measured carbon content C_{im} is actually detectable, i.e. it can be measured experimentally, or its merely background. This quantity is related to the mass resolution, the background level and the total ion count in the analyzed volume. A criterion of detectability can be expressed

as a function of the standard deviation associated with the background level and that associated with the peak detected[33],

$$N_P - \sqrt{N_P(1 - Q)} > N_B + \sqrt{N_B(1 - Q)} \quad \text{Eq. 10}$$

where Q is the detection efficiency and N_P and N_B are the average counts per interval at the peak maximum and the background respectively. Since for each of the carbon ions all the detected peaks are evaluated simultaneously in order to obtain C_{im} , Eq. 10 can be expressed as a function of the concentration as follows:

$$C_{im} - \sqrt{C_{im}(1 - Q)} > Bkg_{im} + \sqrt{Bkg_{im}(1 - Q)} \quad \text{Eq. 11}$$

If the detectability criterion is fulfilled a correction according to Eq. 9 is applied, otherwise no atoms of the given carbon ions are considered to belong to the matrix. The corrected average carbon composition in the matrix (at.%) is finally obtained by decomposing the complex carbon species into carbon atoms:

$$C_m^{corr} = \frac{C_{1m}^{corr} + 2C_{2m}^{corr} + 3C_{3m}^{corr} + 4C_{4m}^{corr}}{1 + C_{2m}^{corr} + 2C_{3m}^{corr} + 3C_{4m}^{corr}}$$

The errors associated to each of the carbon ions are propagated to account for Eq. 12:

$$s_m = \sqrt{\sum_{i=1}^4 \left(\frac{\partial C_m^{corr}}{\partial C_{im}^{corr}} \right)^2 s_i^2}$$

3.3. MASS-TO-CHARGE SPECTRA

Figure 3 (a) shows a representative mass-to-charge spectrum of a bainitic structure obtained from the 1.0C/250 sample. Carbon has several peaks corresponding to various species in the mass spectrum. According to its mass-to-charge (Da) ratio, peaks at 6, 6.5, 12 and 13 Da are assigned to C_1 monomer ions and peaks at 18, 18.5 and 36 Da to C_3 trimer ions. In most of the analyses, peaks within the 24–26 Da range were detected. The peak at 24.5 is assigned to the carbon tetramer C_4 and the peak at 25 Da to the carbon dimer C_2 , while the peak at 24 Da can be due either to C_2^+ or C_4^{2+} , or a mixture of both. A peak decomposition algorithm supplied by the IVAS software was applied to decompose this peak.

Regarding substitutional elements, and depending on the alloy compositions given in Table 1, peaks for Fe, Si, Mn, Cr, Ni, Mo and Cu can be identified in addition to minor impurity elements, Co, Al and P. Fe is identified at 18.7, 27, 28, 28.5, 29 and 56 Da. Si is unambiguously assigned to peaks at 14, 14.5 and 15 Da; Mn is assigned to the peak at 27.5 Da; Cr to peaks at 25, 26, 26.5 and 27 Da; Ni to peaks at 29, 30 and 31 Da; Mo to peaks at 30.6, 31.3, 31.6, 32, 32.3, 32.6, 33.3, 46, 47–49 and 50 Da; Cu to peaks at 31.5, 32.5, 63 and 65 Da; V to peak at 25.5 Da; Co to the peak at 29.5 Da; Al to peaks at 9 and 13.5 Da; P to peaks at 15.5 and 31 Da; and Ga to peaks at 34.5 and 69 Da. Overlaps are found for the peak at 25 Da for $^{50}\text{Cr}^{2+}$ and $(^{13}\text{C}^{12}\text{C})^+$; the peak at 27 Da for $^{54}\text{Cr}^{2+}$ and $^{54}\text{Fe}^{2+}$; the peak at 29 Da for $^{58}\text{Fe}^{2+}$ and $^{58}\text{Ni}^{2+}$; and the peak at 31 Da for $^{62}\text{Ni}^{2+}$ and $^{31}\text{P}^+$. These overlapped peaks have been decomposed according to the natural abundance of the isotopes, as calculated by the peak decomposition algorithm provided by IVAS [34].

Figure 3 (b) and (c) show part of two APT mass-to-charge spectra of the 0.7C/PER sample containing only pearlitic ferrite and a cementite/pearlitic ferrite interphase respectively. Only the carbon monomer ions are identified in pearlitic ferrite (Figure 3 (b)), whereas the presence of all the carbon molecules is revealed when cementite is also present in the dataset (Figure 3 (c)). Other APT studies conducted in pearlitic steels after severe plastic deformation show that the carbon tetramer C_4 is generally absent in ferrite if the compositions of both ferrite and cementite are separately determined, but the C_2 dimer ions exist in ferrite at the peak at 24 Da [35-37]. Plastic deformation of pearlite promotes the decomposition of cementite with the subsequent migration of carbon atoms towards the ferrite close to the interphase boundary or along dislocation cell boundaries [35, 36, 38-41]. In the present case, the absence of all carbon multiples in the pearlitic ferrite phase can be interpreted as an evidence of the repulsive component of C-C interaction in cubic ferrite [42, 43], i.e. carbon atoms are sufficiently far from each other not to produce a molecular bonding during field evaporation.

3.4. VALIDATION OF THE ANALYTICAL PROCEDURE

Figure 4 shows two APT carbon atom maps of the 1.0C/PER sample containing only pearlitic ferrite (Figure 4a) and a cementite/pearlitic ferrite interphase (Figure 4b). These two volumes were chosen to test the differences in the carbon composition measurements when evaluating a pure matrix volume and the same matrix in the presence of a precipitate. It is reminded here that local magnification effects often occur in the vicinity of precipitates given the differences in the evaporation field between

these and the matrix. Local magnification effects are reflected as focusing or defocusing artifacts and overlaps of the ion trajectories in the vicinity of the precipitate/matrix interface. The lower evaporation field of carbides leads to a widened apparent carbon concentration gradient at the interfaces between the ferrite matrix and the precipitate. In the case of pearlite, the reconstruction parameters of the APT atom maps can be optimized; first by probing perpendicularly to the pearlitic lamellae [44], and second by using correlative High-Resolution Scanning Transmission Electron Microscopy (HRSTEM) images as templates in order to minimize distortions of the reconstructed volume [38, 39, 45, 46]. In principle, local magnification artifacts affect only the precipitates regions and a good estimate of the matrix composition can be obtained if n_{min} is suitably chosen so that every other phase or interface contribution can be neglected [22].

The distribution of the carbon atoms in pearlitic ferrite for both 0.7C/PER and 1.0C/PER samples is random (shown in supplementary Figure S 1). Thus, the application of the DIAM method is not necessary in this case and the carbon composition was obtained by the peak decomposition algorithm provided by IVAS, giving a value of 0.01 at.% in 0.7C/PER and 0.03 ± 0.01 at.% in 1.0C/PER. When applying the DIAM method to the 1.0C/PER volume shown in Figure 4(b) the carbon content obtained is 0.04 ± 0.01 at.%. The apparent carbon obtained in the analogous volume of 0.7C/PER is 0.02 ± 0.01 at.%. The carbon content in pearlitic ferrite under thermodynamic equilibrium is expected to be lower than 0.02 at.%, so that it is slightly overestimated in either case.

There are several examples in the literature where atom probe tomography analyses indicate an anomalous carbon-supersaturation in pearlitic ferrite at thermodynamic equilibrium; e.g. 0.06 at.% [47], 0.11 at.% [48], 0.18 at.% [49] and 0.48 at.% [50]. Such a high carbon content is often ignored, if ever, it has been attributed to a non-equilibrium state in the microstructure [47, 51] but not to the validity of the measurements nor the actual solubility of carbon in ferrite in complex alloy systems. Indeed, silicon has been recently shown to increase the carbon solubility limit in ferrite up to 0.03 at.% at 700 °C [52]. In any case, the values obtained in both the pure ferrite and the pearlite volumes are consistent and within the order of magnitude of what it is expected. Accordingly, the described procedure can be fearlessly applied for the determination of the carbon content in a bainitic ferrite matrix.

It should be mentioned that neighbor correlations cannot be readily established for carbon when the detector event histogram shows specific low-index poles. These low-index poles could cause deviations in the carbon spacing within the pole regions, which would affect the carbon concentration calculated using the DIAM method. The [110] pole was observed in the detector event histogram retrieved from pure ferrite. However, neither the bainitic nor the pearlitic samples showed strong evidence of a pole structure due to the complexity of the microstructures, and therefore, poles could not be extracted for the NNDs (see supplementary Figure S 2). The DIAM method was tested using a pearlitic steel to verify that the C content of ferrite can be accurately calculated such that concentration deviations due to detector event histogram poles are minimal.

3.5. CARBON CONCENTRATION MEASUREMENTS IN THE BAINITIC FERRITE MATRIX

Table 3 collects the carbon content in bainitic ferrite as obtained by different techniques and methodologies. Carbon content in ferrite values are given according to the procedure described in this work (C_{α}^{APT}) as compared to the APT values found in the literature (Fig. 4a in [7]) for the same steel and transformation conditions (C_{α}^{Ref}), the carbon content values as derived from the $c/a_{\alpha'}$ ratio obtained by XRD experiments according to [26] (C_{α}^{XRD}) and the calculated values for bainitic transformation under PE conditions (C_{α}^{PE}).

There is a notable difference between the carbon content values obtained in this work and the APT values previously given in the literature. In the case of the bainitic structures obtained from the 0.7C and 1.0C steels, the new values corroborate that bainitic ferrite out of carbon-enriched features is super-saturated with respect to the ferrite/austenite phase boundary under PE conditions. Tendencies indicate that for a given steel the level of carbon supersaturation decreases as the transformation temperature is increased, with depletion of carbon in the ferrite matrix after prolonged heat treatment.

On the contrary, the bainitic ferrite matrix in the 0.3C steel meets the carbon solubility value that is predicted by the PE with the austenite. This result is not surprising, since it is usually assumed that carbon diffusivity is enhanced as the transformation temperature is increased, providing an opportunity for the decarburization of the super-saturated ferrite soon after the growth event [7].

It should be lastly mentioned that the present APT measurements errors are based solely on counting statistics ignoring all other sources of uncertainties, e.g., complex ion dissociation, multi-hit/pile-up effects, reconstruction artifacts, etc. Stating here that a difference of 0.1 at.% between what is measured and what is expected is a clear evidence carbon-supersaturation means pushing the capacity of the APT to its limits. The discussion will hereinafter be focused in the significant differences found between the APT and the XRD technique.

3.6. CARBON SUPER-SATURATION IN FERRITE AND TETRAGONALITY

As stated, the most reasonable explanation up to now for carbon supersaturation in bainitic ferrite is that the unit cell is non-cubic. The diffusionless transformation of the austenite containing carbon necessarily leads to a body-centered tetragonal (bct) lattice in the very beginning of the transformation [53-55]. Carbon interstitial atoms occupy octahedral sites in both ferrite and austenite, but only one set of such sites, Z, is common to both lattices. Upon a diffusionless transformation, the octahedral symmetry of the interstitial carbon atoms in the original face-centered cubic (fcc) lattice is maintained in the body-centered cubic (bcc) lattice, increasing the number of carbon atoms at Z sites. However, the carbon atom expands the octahedral void in the bct lattice by pushing apart two iron atoms in a direction that becomes the *c* axis of the bct cell, which align in parallel. The preferred location (ordering) of carbon atoms on one set of octahedral interstices leading to a bct lattice is usually referred to as the Zener order [56]. However, tetragonality is not merely an effect of the diffusionless transformation, and the elastic (strain induced) interactions in the Fe-C bct lattice may cause ordering. The atoms will tend to randomize if the temperature is above the

required temperature for Zener ordering and the bct lattice will turn into bcc [56]. Based on Zener's considerations, Kurdjumov and Khachaturyan[57] later developed a model for the order-disorder transition using their microscopic elasticity theory. In their recent work Djaziri and Liet *al.*[58] have developed a full thermodynamic approach of Zener coupling which also considers any type of internal or external lattice strains, such as from applied loads or microstructural strains of second or third order. These effects have been shown to change the critical transition temperature for Zener ordering in a direction to similar to the works of Kurdjumov and Khachaturyan, extending the stability region of bct[58].

Carbon concentration values derived from XRD analyses are five to nine times as much as the ones obtained by APT (see Table 4). The question then arises as to what extent the observed tetragonality is related to the ferrite matrix. The difficulties in making comparisons between XRD and APT data in nanocrystalline bainite have been recently reviewed [59], pointing towards the huge differences in sampling volumes, combined with the fact that the scale of the heterogeneous distribution is much greater than that of the sample size in atom probe. However, the characteristic length of nanocrystalline bainitic ferrite (~40 nm as determined by XRD) allows sampling various platelets in a single APT needle, that could be representative enough of the whole matrix. It is true that the carbon content of each bainitic subunit may vary depending on its thickness, the presence of carbides, and the density of dislocations [10], but these variations hold in a very limited composition interval around the average value.

A shift in the solute distribution away from the randomized distribution is indicative of correlations of occurrence of ions (ordering) or other microstructural phenomena [60]. The carbon contents determined in this work have been forced to be randomly distributed, i.e. disordered. Each set of atoms occupies one set of positions in the fully ordered state, while the atoms are randomly distributed among the sites they occupy in disordered solutions. Short-range order is a description of the atomic configuration in the immediate vicinity of an atom; if the average number of unlike neighbors of an atom is higher than expected from a random distribution, the alloy possesses short-range order. The extent to which this ideal arrangement is achieved is a measure of the long-range order of the structure. It is usual for there to be an appreciable short-range order, but not long-range order[61]. The bct phase inherits the spatial distribution of atoms, which was present in austenite. The austenite before transformation could be considered as an ordered structure with iron occupying one position, and a mixture of carbon and vacancies occupying the other (short-range ordering). The reality is a random distribution of carbon on interstitial sites because the stress-induced energies of the C atoms' interaction in austenite are small [62, 63]. Accordingly, APT measurements over a random, and thus, disordered distribution of carbon in the long-range, are in principle compatible with a bct phase which inherits the random distribution of carbon atoms in the austenite, holding specific positions of the carbon atoms in the bct lattice.

However, the discrepancies between XRD and APT results suggest that the increased tetragonality detected by XRD would rather come from tetragonal carbon-enriched features within ferrite, i.e. carbon clusters. The development of local enrichments of carbon (clusters), in association with a locally increased tetragonality, may produce the

overall c/a ratio that is detected by XRD. Such a distribution of carbon into clusters with an increased tetragonality surrounded by a depleted matrix has been thoroughly studied in the early stages of decomposition of Fe-C, Fe-N, Fe-C-N, and Fe-C-X martensites [64-67]. Here, the random distribution of interstitial atoms developed by the martensite transformation rapidly transforms into a clustered arrangement of carbon and/or nitrogen atoms on one set of sublattice octahedral sites in the depleted ferrite matrix. The C content detected by APT in the present work does not agree with the C content derived from XRD measurements due to the fact that XRD measurements average the structure of the carbon cluster regions and non-carbon cluster regions within the ferrite. The origin and nature of carbon clusters in bainitic ferrite is the focus of future research.

4. CONCLUSIONS

An APT data analysis method has been successfully tested in a pearlitic ferrite sample with a known carbon composition for its application to the ferrite matrix of different bainitic structures. However, there is a strong disagreement between the carbon content values in the bainitic ferrite matrix as obtained by APT and those derived from XRD measurements. XRD analyses average the carbon content in bainitic ferrite. As this phase includes carbon-clustered regions with an increased tetragonality in a carbon-depleted matrix, a significantly lower carbon content is determined in bainitic ferrite away from carbon-enriched features by APT.

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Figure captions

Figure 1. (a) APT carbon atom map of the 0.7C/220+6d sample and (b) Probability of carbon to be isolated as a function of n in the volume shown in (a). The black solid line represents the linear fit for the matrix contribution regime according to Eq. 4.

Figure 2. Relationship between the uncorrected carbon and the corresponding background in the mass spectrums extracted from the volume shown in Figure 1(a). The solid line at the bottom delimits the region where the carbon concentration is greater than the background. Note that the carbon axis is represented in logarithmic scale.

Figure 3. (a) Example of an APT mass spectrum of bainite obtained from the 1.0C/250 sample. Significant peaks for the alloying elements C, Fe, Si, Mn, Cr, Mo, Ni and Cu are marked. (b) and (c) mass spectra for pearlitic ferrite and pearlite respectively in the 0.7C/PER sample.

Figure 4. APT carbon atom maps of the 1.0C/PER sample in (a) pearlitic ferrite region and (b) cementite/ferrite interphase.

Supplementary Figures

Figure S 1. First nearest neighbor distributions for the pearlitic ferrite APT reconstructions of (a) 0.7C/PER and (b) 1.0C/PER.

Figure S 2. Detector event histograms for (a) pearlitic ferrite APT reconstruction obtained from sample 1.0C/PER and (b) bainite APT reconstruction obtained from sample 0.3C/350. Note the presence of a low-index pole in pearlitic ferrite (enclosed by the white circle).

Table captions

Table 1. Chemical composition of the high-silicon steels studied.

Table 2. Relevant transformation parameters of the bainitic samples. T_γ is the austenitization temperature, T_{iso} is the bainite transformation temperature and t_{iso} is the bainite transformation time.

Table 3. Results of the Rietveld XRD pattern refinement analyses on the studied structures, where V_γ is the volume fraction of austenite, a_γ is the lattice parameter of austenite, $c/a_{\alpha'}$ is the lattice parameter ratio in bainitic ferrite and ε is the microstrain.

Table 4. Analyzed volumes and carbon content in ferrite for the studied structures as obtained by APT measurements.

Figure_1

Figure_2

Figure_3

Figure_4

Table 1. Chemical composition of the high-silicon steels studied.

Steel		C	Si	Mn	Cr	Ni	Mo
0.3C	wt.%	0.29	1.48	2.06	0.43	–	0.27
	at.%	1.32	2.87	2.04	0.45	–	0.15
0.7C	wt.%	0.66	1.45	1.35	1.02	0.10	0.24
	at.%	2.96	2.78	1.32	1.06	0.09	0.13
1.0C	wt.%	0.98	2.90	0.77	0.45	0.16	–
	at.%	4.28	5.42	0.74	0.45	0.14	–

Table 2. Relevant transformation parameters of the bainitic samples. T_{γ} is the austenitization temperature, T_{iso} is the bainite transformation temperature and t_{iso} is the bainite transformation time.

Sample	T_{γ} , °C	T_{iso} , °C	t_{iso} , h
0.3C/325	925	325	0.5
0.3C/350	925	350	0.5
0.7C/220	900	220	24
0.7C/220+6d	900	220	168
0.7C/250	900	250	8
0.7C/300	900	300	5
1.0C/200	950	200	40
1.0C/250	950	250	15

Table 3. Results of the Rietveld XRD pattern refinement analyses on the studied structures, where V_γ , is the volume fraction of austenite, a_γ is the lattice parameter of austenite, c/a_α , is the lattice parameter ratio in bainitic ferrite and ε is the microstrain.

Sample	V_γ , %	a_γ , nm	c/a_α	Ferrite crystallite size, nm	$\varepsilon \times 10^{-3}$ in ferrite
0.3C/325*	17±2	3.612±0.002	—	—	—
0.3C/350*	18±2	3.612±0.002	—	—	—
0.7C/220	17±2	3.605±0.002	1.0083±0.0004	35±3	5.1±0.2
0.7C/220+6d	12±2	3.610±0.002	1.0082±0.0004	40±2	5.2±0.2
0.7C/250	19±2	3.615±0.002	1.0077±0.0004	37±3	4.9±0.2
0.7C/300	25±2	3.623±0.002	1.0071±0.0004	51±3	4.0±0.2
1.0C/200	28±2	3.619±0.002	1.0090±0.0004	29±3	5.6±0.2
1.0C/250	32±2	3.628±0.002	1.0084±0.0004	34±3	4.9±0.2

*Given that both martensite and bainitic ferrite are present in the microstructures, and these phases cannot be distinguished by XRD analyses, Rietveld refinement results are omitted in the bcc/bct phase.

Table 4. Analyzed volumes and carbon content in ferrite for the studied structures as obtained by APT measurements.

	C_α , at. %	C_α^{Ref} , at. %	C_α^{XRD} , at. %	C_α^{PE} , at. %
0.3C/325	0.05±0.01	0.29±0.09	—	0.05
0.3C/350	0.05±0.01	0.28±0.09	—	0.06
0.7C/220	0.22±0.01	0.76±0.36	0.87±0.04	0.02
0.7C/220+6d	0.13±0.01	1.00±0.14	0.86±0.04	0.02
0.7C/250	0.14±0.01	0.95±0.24	0.81±0.04	0.03
0.7C/300	0.14±0.01	N/A	0.73±0.04	0.05
1.0C/200	0.13±0.01	N/A	0.95±0.04	0.01
1.0C/250	0.10±0.01	N/A	0.90±0.04	0.03

C_α is the carbon content in ferrite according to the procedure described in this work, C_α^{Ref} is the carbon content in ferrite according to the APT values found in the literature [7] for the same steel and transformation conditions, C_α^{XRD} is the carbon content in bainitic ferrite as determined in [20] from XRD data and C_α^{PE} is the calculated carbon content in ferrite for bainitic transformation under paraequilibrium conditions. N/A stands for Not Available.