LOW TEMPERATURE BAINITIC FERRITE: EVIDENCE OF CARBON SUPER-SATURATION AND TETRAGONALITY

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Abstract

Experimental evidence indicates that bainitic ferrite formed by transformation at low temperatures (200-350°C) contains quantities of carbon in solid solution far beyond those expected from para-equilibrium. A change in the conventional symmetry of the bainitic ferrite lattice from cubic to tetragonal explains the abnormal solid solubility detected. This carbon supersaturation was measured by atom probe tomography, and the tetragonality of the bainitic ferrite, was characterized by means of X-ray diffraction analysis and high resolution transmission electron microscopy.

Keywords: Tetragonal bainitic ferrite, Nanostructured bainite, Atom probe tomography, High resolution transmission electron microscopy, X ray diffraction

1 INTRODUCTION

Atom probe tomography (APT) was recently used to demonstrate that bainitic ferrite grows with a high supersaturation of carbon, when transforming at abnormally low temperatures (200 °C) due to the extremely slow kinetics of a nanocrystalline bainitic steel [1-4]. Results indicated that iron and substitutional atoms, such as Mn, Cr and Si, do not diffuse during the bainite transformation, and that the partitioning of carbon into the residual austenite occurs immediately after growth. The bainite reaction ceases well before the austenite carbon content reaches para-equilibrium. All these results were explained in terms of the diffusionless growth of bainite sub-units [1-4].

In addition, APT revealed the presence of a high level of carbon in bainitic ferrite, which was well above that expected from para-equilibrium with austenite once the reaction proceeds to completion. This reluctance of the carbon to partition was firstly attributed to carbon-trapping at dislocations in the vicinity of the austenite-ferrite interface, Cottrell atmospheres [5], and to the fact that the lower the reaction temperature, the higher the dislocation density of bainitic ferrite [6-8]. However, other recent APT work has shown that as the transformation temperature is decreased, higher amounts of carbon remain in defect-free solid solution in the bainitic ferrite after the transformation. In fact, the recorded composition profiles revealed that the carbon content is rather homogeneously distributed within each phase, indicating that carbon had sufficient time to be distributed to a state close to certain kind of equilibrium that is independent of the initial distribution between bainitic ferrite and parent austenite.

The interesting question is what factors have caused the abnormally high carbon solubility in bainitic ferrite. Bhadeshia and co-workers, using first-principles

calculations, proposed that the apparent reluctance of the excess carbon to partition from bainitic ferrite, is due to a change in the symmetry of the ferrite unit cell originating from the mechanisms of transformation [9]. In other words, when body centered tetragonal ferrite (BCT) is in “*equilibrium*” with austenite, it has a much greater solubility for carbon than is the case for body centered cubic ferrite (BCC) in the same circumstances [10].

In this work, these first principles calculations were validated from APT measurements of the carbon content in bainitic ferrite plates away from any carbon-enriched regions, such as dislocations, boundaries, and carbide particles. A variety of microstructures were studied in two nanostructured bainitic steels after transformation at low temperatures, 200-300 °C. The results are also validated with those obtained as the bainitic transformation progresses at 200°C, and at different tempering stages. In addition, new experimental evidence is provided on the tetragonality of nanostructured bainitic ferrite, based on X-ray diffraction (XRD) measurements, and high resolution transmission electron microscopy (HRTEM).

2 MATERIALS AND EXPERIMENTAL PROCEDURES

The steels studied exhibit a nanocrystalline bainitic structure, as described elsewhere [11-13] with the chemical composition as stated in Table 1.

A Bahr 805D high-resolution dilatometer was used to perform the heat treatments and to track the isothermal decomposition of austenite into bainitic ferrite on samples that were 5 mm in diameter and 10 mm long. In these experiments, by means of an induction system, samples were heated above the A_{c3} and subsequently cooled down to the isothermal temperature. The process parameters, i.e., the austenitisation temperature,

cooling rate to the isothermal temperature and the value of this same temperature, were adapted to the alloy chemical composition and to its hardenability, the latter to avoid the formation of ferrite and pearlite prior to bainite transformation. The nanostructured bainite was produced during the isothermal holding at temperatures ranging between 200 and 350 °C. For most of the experiments, the selected isothermal holding times were those strictly necessary to ensure the end of the bainitic transformation. But, some experiments were kept longer than strictly necessary for reasons later described in further detail, those experiments are identified by the '+' sign followed by the amount of extra time after the end of the bainitic transformation. For example for the case of Alloy 2 treated at 220 °C, the '+6d' means that the sample was held for an additional 6 days after the completion of the isothermal transformation taking place after 24 h of heat treatment. For details in the time needed to finish the bainitic transformation at the different isothermal temperatures see Table 1.

After the isothermal heat treatment, samples were Ar quenched to room temperature. It is important to note here that, as austenite (γ) is enriched in carbon relative to the average composition of the steel, due to the partial partitioning of carbon from the bainitic ferrite (α_b), during quenching to room temperature, no martensite (α') forms, as the martensite start temperature, M_s , of the C enriched retained austenite is well below room temperature. Finally, the microstructure thus achieved consists of fine platelets of bainitic ferrite in a matrix of carbon-enriched residual austenite. Numerous microstructural studies are available elsewhere and are not reproduced here for the sake of brevity [11-13].

The results obtained in this work could be interpreted as suggesting that martensite and nanostructured bainitic ferrite are the same phase. Indeed, they share many common aspects [14], but they are quite separate phases, since the transformation occurs at very different transformation temperature ranges. Thus, for Alloy 3, dilatometric curves from the austenitisation temperature under different scenarios, Figure 1, illustrates :

- CRYO: The dilatometric curve of a cryogenic test, down to -150°C , where the full martensitic transformation is visible, beginning (M_s) and end (M_f).
- PART: Partial bainitic transformation at 200°C , where not enough carbon enrichment has taken place, and during cooling to room temperature, the martensitic transformation takes place from the untransformed retained austenite.
- ISO: Completed bainitic transformation at 300°C , enough carbon enrichment of austenite has taken place, and therefore, during cooling down to room temperature austenite remains stable.

Therefore, in this work when the term martensite (α') is used, it refers to the tetragonal phase obtained by quenching from the austenitisation temperature down to room temperature, the 'as-quenched' microstructure thus obtained is composed of retained austenite and the aforementioned martensite (α').

X-ray diffraction analysis was used to determine the fraction of retained austenite (V_{γ}) and other structural parameters, such as the lattice parameters, microstrain, crystallite size, etc. For this purpose, specimens of the different bainitic microstructures were prepared by a standard grinding and polishing procedure, which included a final polish with $1\text{ }\mu\text{m}$ diamond paste. In order to remove the deformed layer, where austenite may have transformed to martensite by TRIP effect, several cycles of etching and polishing

were applied. X-ray diffraction 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 for ultra-fast XRD measurements. This type of radiation is specially suited for iron-rich samples to avoid the strong fluorescence arising from copper radiation, and to produce high resolution data. A current of 30 mA and a voltage of 40 kV were employed as tube settings. Operational conditions were selected to obtain XRD profiles of sufficient quality: namely, optimal counting statistics, narrow peaks and detection of the small diffraction peaks of minor phases. The XRD data were collected over a 2θ range of $35-135^\circ$ with a step size of 0.01° .

The volume fraction of the retained austenite was calculated from the integrated intensities of (111), (002), (022) and (113) austenite peaks, and those of (011), (002) and (112) planes of ferrite, with the equation for the ratio of these experimental values to the normalisation factors for peaks intensity (R) given in the ASTM E975-13 [15]. Instead calculating R factors from basic principles, they were obtained from a calibration curve determined from three standard reference materials certified by the National Bureau Standards with a specified amount of austenite. The use of several Bragg peaks in evaluating the amount of retained austenite diminished the detrimental influence of texture, as long as it remains small to moderate. In samples with a strong texture, the diffracted intensity of each peak was corrected by the cubic harmonics model [16].

The Rietveld method has been widely reported as one of the most suitable technique for calculation of structural parameters from XRD patterns of polycrystalline materials [17, 18]. This method involves the calculation of a theoretical diffraction profile from the

actual structures of the phase components (unit cell, space group, atom types, atomic coordinates, occupation number and temperature factors) in the sample. The structural model used in the refinement was a combination of ferrite and austenite. In order to take in account the particularities of the diffractometer set up used in the Rietveld refinement, instrument functions were empirically parameterised from the profile shape analysis of a corundum sample measured under the same conditions. In this study, version 4.2 of Rietveld analysis program TOPAS (Bruker AXS) was used for the XRD data refinement. The refinement protocol included also the background, zero displacement, the scale factors, the peak breadth, the unit cell parameter, and texture parameters. Line broadening effects due to the crystallite size and lattice strain was analyzed with the double-Voigt approach, in which both the crystallite size and strain comprise Lorentzian and Gaussian component convolution [19]. The quality and reliability of the Rietveld analysis was quantified by the corresponding figures of merit: the weighted summation of residual of the least squares fit, R_{wp} , the statistically expected least squares fit, R_{exp} , the profile residual, R_p , and the goodness of fit (sometimes referred as chi-squared), GoF [20]. Since $GoF = R_{wp} / R_{exp}$, a $GoF = 1.0$ means a perfect fitting.

The retained austenite carbon content (X_γ) was calculated making use of the relationship between lattice parameter and chemical composition, as reported in [21], and assuming that during transformation, only carbon diffuses [14], thus, the concentration ratios of all elements but carbon should be equal in the bulk material as in the retained austenite (γ) [22, 23]. The lattice parameter of the austenite phase was determined from the Rietveld method to attain a high degree of precision. As the whole diffraction pattern is fitted, it is possible to correct and adjust the zero offset keeping into account

simultaneously all the (hkl) reflections included in the angular range measured, s , which minimizes errors.

An example of the X-ray spectrums for Alloy 2 are presented in Figure 2 a and b, for the microstructure obtained by bainitic transformation at 220 and 300 °C, and also for comparison purposes to the as-quenched microstructure. It is evident that only diffraction lines corresponding to ferrite and austenite are present.

High resolution TEM (HRTEM) examination was performed on selected samples using a Philips Tecnai F30 300 keV FEG-TEM and a JEOL FS2200 FEG-TEM. Discs of 0.1 mm thickness were punched out from strips using a Gatan Disc Punch Model 659, and mechanically thinned down to 0.06 mm, before being twin-jet electropolished until perforation in a Fischione Instruments Model 120, with an electrolyte of 5% perchloric acid, 25% glycerol and 70% ethanol at 5°C and 45 V.

APT needle-shaped samples were cut from bulk material and electropolished with the standard double layer and micropolishing methods [24, 25]. Atom probe analyses were performed in the Oak Ridge National Laboratory (ORNL) local electrode atom probes (Cameca Instruments LEAP 2017 and LEAP 4000X HR). The introduction of this instrument has made dramatic, orders-of-magnitude improvements in the data acquisition rate and the size of the analysed volume compared to previous types of three dimensional atom probes. The local electrode atom probes were operated in voltage-pulse mode with a specimen temperature of 60 K, a pulse repetition rate of 200 kHz and a pulse fraction of 0.2. APT carbon content values are estimated using concentration profiles in a selected volume within ferrite regions that did not contain any carbon-enriched regions, such as cementite particles, dislocations and boundaries.

For Alloy 2 treated at 300 °C, an example is shown in Figure 3: (a) carbon atom map, (b) 4 at.% C concentration isosurface superimposed with the carbon atom map, and (c) proximity histograms across the bainitic ferrite/austenite interfaces indicated by arrows. The stated carbon concentration has been measured in austenite and ferrite regions far away from any defects and interfaces [1], and is indicated by the boxes in Figure 3 c. It is possible to distinguish multiple austenite plates in these data: austenite piece (8.2 at. %) at the top which is at least 50 nm thick, and two other austenite plates of 10 and 600 nm thick with 7.9 and 12.1 at. %, respectively, in between these austenite plates are the bainitic ferrite regions with carbon concentrations varying from 0.7 to 1.2 at. %. The concentration of carbon is determined by counting the number of carbon atoms in small slices locally perpendicular to the austenite-bainitic ferrite interface. The size of the slices is a compromise between maximizing the number of ion atoms and the spatial resolution. Error bars for APT values represent the statistical scatter due to the number of ions in each slice of the selected volume of analysis.

Necessary thermodynamics calculation were performed using MtData in combination with the SG SOL-SGTE Solution database [26].

3 RESULTS AND DISCUSSION

3.1 APT RESULTS ON LOW TEMPERATURE BAINITIC FERRITE

The carbon contents in bainitic ferrite, as determined from APT, after transformation at different temperatures in nanostructured bainitic steels, Alloy 1 and 2 are shown in Figure 4 a. Highlight the fact that the APT values reported are estimated from concentration profiles in selected volumes of ferrite that did not contain any C enriched

regions, such as cementite particles, dislocations, and boundaries. In order to gain some perspective, the results are also plotted with the same type of measurements on two bainitic steels with a medium carbon content, 0.3 wt. %, and two different Si contents, 1.5 wt.% Si (MC-HSi) and 0.25 wt.% (MC-LSi), transforming at intermediate temperatures and allowing for the evaluation that cementite precipitation has on the carbon supersaturation of bainitic ferrite. Although bainitic range of transformation is mainly consequence of the C content ,300-525 °C for MC-HSi and MC-LSi steels, and 123-350 °C for Alloy 1 and 2 steels, the inhibition of cementite precipitation during the transformation is controlled by the addition of ~1.5 wt.% Si, known for retarding the precipitation of cementite from austenite due to its low solubility in the cementite crystal structure [27, 28]. The APT results show the presence of a significant amount of carbon in bainitic ferrite, up to 1 at. %, which lies within the region delimited by the para equilibrium (PE) phase boundaries when ferrite is considered as a cubic (BCC) and a tetragonal (BCT) structure, the latter estimated according to first-principles calculations by Jang *et. al.* [10]. It is interesting to note that, for the lowest transformation temperatures, the results lie closer to the PE (BCT) line, and when the temperature increases there is a progressive approach towards the PE (BCC) line. This behaviour could be interpreted as a possible loss of tetragonality when the transformation temperature increases.

What is more, tracking the carbon content of ferrite in Alloy 1 at different stages of the 200 °C transformation, Figure 4 b, provides clear evidence of carbon supersaturation in bainitic ferrite from the beginning of the transformation exhibiting, again, a carbon level well above the PE (BCC) line and closer to that for the PE (BCT) assumption.

Not only that, when comparing the APT results of the Alloy 1 and 2, with and without extra time, Figure 4 a and b, it is possible to assure that the C in solid solution in the bainitic ferrite is reluctant to partition into the residual austenite despite the high quantities and the opportunity given by the extended heat treatment. For example, in the case of Alloy 2 the detected variation of carbon in bainitic ferrite is from 0.8 to 1 at.%, which, within the margins of error, it can be considered almost negligible despite the 6 extra days at 220 °C.

Furthermore, the same reluctance of the carbon to move from bainitic ferrite is shown even when the microstructure is subjected to tempering. APT results obtained as a result of tempering Alloy 1 treated at 200 °C for different temperatures and times is shown in Figure 4 c. The bainitic ferrite still shows great inertia to release the *apparent excess* of carbon. The amount of carbon in solid solution in the ferrite was similar to that measured in the initial microstructure even after tempering at 500 °C for 30 min. The loss of carbon in ferrite due to carbon partitioning into austenite starts to be evident after tempering at 550 °C. Apart from carbon partitioning, the other competing reactions must be activated if carbon atoms in supersaturated ferrite do not partition to retained austenite during tempering at 400 °C as reported elsewhere [29]. The presence of carbon accumulation randomly dispersed throughout the ferrite matrix during tempering at 400 °C for 30 min. was also revealed in Alloy 1 by APT [30]. It is likely that these carbon-enriched regions may signify the onset of the transition carbides observed during tempering at 450 °C for 30 min. [30].

The APT results indicate that bainitic ferrite is able to accommodate significant quantities of carbon in solid solution in a stable and not transitory state. The amount of C is far greater than that expected from theory when bainitic ferrite is considered to be

BCC instead of BCT. The APT technique cannot provide the crystallographic information that might be necessary to rationalize this abnormal behaviour, as already proposed [10]. The intention of the following sections is to provide such supporting evidence.

3.2 XRD RESULTS ON LOW TEMPERATURE BAINITIC FERRITE

As expected, the X-ray diffraction patterns of nanostructured bainite after isothermal holding at temperatures ranging between 200 and 350 °C showed only the diffraction lines of ferrite and austenite, as already illustrate in Figure 2. Thus, the Rietveld refinement used to analyze XRD patterns included the crystal structure model for both phases, together with the line-broadening analysis of diffraction peaks with the “double-Voigt” approach. For Alloy 2 and Alloy 3 treated at 250 °C, the XRD patterns after the Rietveld refinement are shown in Figure 5, where the observed data are the blue open circles and calculated data are the red solid line. The difference between experimental data and the fitted simulated pattern is plotted as a continuous grey line at the bottom, and the contribution of the component phases in different colours (orange for ferrite and green for austenite). As shown, the calculated peaks (red solid line) are too narrow when compared with the measured peak shapes (blue open circles). Beside, some misfit in the ferrite peaks position between measured and calculated diffraction pattern can be observed. Since peak broadening could not be associated only to crystallite size and microstrain effects, and carbon concentration profiles in bainitic ferrite measured by APT showed some fluctuations in the carbon content, the broadening could be also associated to two ferrite structures with different lattice

parameters with different carbon content. To check this point, ferrite was inserted in the Rietveld refinement a second time with slightly different starting lattice parameters, Figure 5 b. The figures of merit used to estimate the quality of the least squares refinement in both cases, Table 2, and the difference curve (grey line) of Figure 5 a and b indicate that the fit does not improve significantly, and therefore the inhomogeneity hypothesis cannot explain the characteristic misfit in the difference curve. A closer inspection to the difference curve (grey line) showed that broadening differences between measured and calculated diffraction peaks only affect some ferrite peaks, especially the (200) reflection. As the reason could be a symmetry reduction of the crystal structure of bainitic ferrite, a lower symmetry version of the cubic structure was used in the Rietveld refinement, i.e., a tetragonal structure with a $I4/mmm$ space group, similar to the crystal structure of ferrous martensite [31]. A visual examination of Rietveld refinement with this crystal structure is shown in Figure 5 c, and the values for the figures of merit in Table 2. Both sets of results indicate a good fit. The results are essentially the same after applying this same procedure to all the remaining transformation temperatures. Thus, it was concluded that bainitic ferrite formed by isothermal holding at temperatures ranging between 200 and 350°C did not present a cubic structure as reported in previous studies [14], but a tetragonal unit cell, BCT. The structural data results of the Rietveld X-ray diffraction pattern refinements and the volume fraction of retained austenite are shown in Table 3, as a function of the bainite transformation temperature (T). In this table, the values for an as-quenched microstructure have been also included. It is necessary to highlight the fact that the average volume-weighted crystallite size of the bainitic ferrite plates, determined by the double-Voigt approach, increases as the transformation temperature increases, while the

measured microstrain decreases, a behaviour which is consistent with the bainitic transformation itself, the microstructure becoming thinner and more dislocated when transformation temperature is lowered [14, 32]. Furthermore, the crystallite size values, ranging from 40 to 50 nm, are very close to the plate mean thickness determined by electronic microscopy [13, 32-34].

Results on the evolution of the BCT lattice parameters a and c determined in the Rietveld refinement, and the c/a ratio as a function of the bainite transformation temperature are shown in Figure 6. In this figure, the dotted lines represent the corresponding values for the as-quenched microstructures, composed by austenite (γ) and martensite (α').

It is interesting to note the big differences between the martensite (α') a and c parameters, which reflects in the form of broad and asymmetrical ferrite diffraction peaks, see Figure 2 a and b, clearly composed by the overlapping of two peaks. While in the case of the bainitic ferrite, the calculated a and c parameters are close together and the diffraction peaks are therefore narrower and more symmetrical.

Carbon occupies octahedral interstitial positions in the iron lattices of both austenite and martensite. In austenite, the iron atoms forming the corners of the octahedron are equidistant from the interstitial site; hence when the site is occupied by a carbon atom the lattice is expanded symmetrically. In martensite, the octahedral sites have two iron atoms closer to the other four iron atoms, thus forming a distorted octahedron. When such a site is occupied, the lattice distortion is asymmetrical. There are three sets of octahedral sites in BCC iron. If only one set of sites is occupied, the asymmetric

distortions will lead to expansion in one of the three $\{001\}$ directions and contractions in the other two [35].

The Bain distortion part of martensite formation is the collapse of the FCC austenite lattice into the BCT martensite lattice. Due to the nature of this distortion, if there are some carbon atoms in solution, they will occupy one of the three sets of octahedral sites. The accumulative effect of the asymmetric distortions of the occupied sites leads to the martensite being BCT. Winchell *et al.* [36] have offered a systematic treatment of those situations in which tetragonality may be produced in martensite as a result of asymmetric point defects.

The results shown in Figure 6 clearly indicate that as transformation temperature increases there is a significant contraction of the c_α bainitic ferrite lattice parameter, while the a_α parameter expands, i.e., a decrease in the c_α/a_α ratio. This tendency resembles that observed in the c and a martensite lattice parameters as the carbon concentration decreases [37], and is summarized by the following expression $c/a = 1 + 0.045 X_w$, where X_w is the carbon concentration in wt% [37, 38]. The carbon content in the bainitic ferrite after isothermal transformation at different temperatures, using this dependence of the axial c/a ratio on the carbon content, is shown in Figure 7. For both alloys, the carbon concentration in α_b compares well with the results reported by APT, see Figure 4. For example in Alloy 2, the calculated carbon concentration between 220 and 300 °C ranges from 0.19 wt.% (0.88 at. %) to 0.16 wt.% (0.71 at. %), and for Alloy 3 at 250 and 300 °C varies from 0.18 wt.% (0.81 at. %) and 0.16 wt.% (0.71 at. %), when compared with those measured by APT, ranging from 0.99 at. % to 0.60 at. %, for Alloy 1 and 2, Figure 4, depicting an excellent level of agreement.

The same calculations were performed on the as-quenched microstructures of Alloy 2 and 3, Figure 7, clearly showing that martensite formed from the bulk austenite has a carbon concentration close to that of the alloy, see Table 1. On the other hand, the austenite carbon concentration was calculated to be lower than the bulk from the lattice parameter measured by X-ray. This is due to the fact that the retained austenite in the as-quenched microstructure is compressed due to martensite transformation of its surrounding region [39]

As with the APT results, where almost no variation was observed in the amount of carbon in solid solution in bainitic ferrite despite the extended heat treatments, the X-ray results also indicate that this variation was negligible, see results in Figure 7 corresponding to Alloy 2 treated at 220 °C with extra time (+6d) and without extra time, ~0.19 wt.% in both cases. Furthermore, this result also agrees with that reported by APT, i.e., 0.19 wt.%.

From the fraction of the present phases (V_i), Table 3, and their corresponding carbon contents (X_i), as in Figure 7, it is possible to estimate the carbon deficit defined as $\bar{X} + V_\gamma(X_\alpha - X_\gamma) - X_\alpha$, where α stands for either α_b or α' . It is interesting to note that according to the results in Figure 7 for the bainitic microstructures, the carbon deficit tends to decrease as the transformation temperature increases, from 0.39 wt.% (1.7 at. %) to 0.08 wt.% (0.4 at. %) for the 220 and 350 °C cases, respectively. If this same exercise is done with the APT results of the nanostructured bainite transformed at 200° C in Figure 4, where $V_\gamma = 29\%$ and its corresponding carbon in solution, also measured by APT, amounts for $X_\gamma = 8.3$ at. % [23], the carbon deficit is ~1.4 at. %, which again shows an excellent agreement with the X-ray results.

Although purely qualitative, there are two facts to point out, firstly, the carbon deficit decreases as the bainitic transformation temperature increases, and secondly, it seems to be higher than that detected for the as-quenched $\gamma+\alpha'$ microstructure. As discussed earlier the carbon content in the as-quenched is underestimated and so it is expected that carbon deficit is even lower than that calculated.

There are a number of possibilities for the location of this carbon. Although carbon atom maps of annealed samples of Figure 3, where only carbon atoms (red dots) are displayed, showed a homogeneous distribution of C throughout the ferrite and austenite, a progressively decreasing carbon profile in the austenite close to the interface is observed. However, there is no evidence of segregation of either carbon or substitutional elements to the austenite-ferrite interface, although it is difficult to define the exact location of the interface with respect to the carbon composition, because the interface may not be planar over the intercepted surface. Herbig et al. has found that segregation of C at the ferrite-ferrite interfaces in a nanocrystalline Fe-4.40C-0.30Mn-0.39Si-0.21Cr (at. %) alloy can reach also high levels, up to 14 at. % [40].

Beside, extensive segregation of C occurs around dislocations in the ferrite to form carbon Cottrell atmospheres. Wilde et al., on the basis of 3D reconstruction of Cottrell atmospheres around dislocations in iron, have calculated that peak carbon concentration within these atmospheres is ~8 at. %, and this high carbon region can extend ~7 nm from the dislocation core [41]. Despite all these results, as recently proved by Bhadeshia [42], we are still far from an accurate answer.

Therefore, it seems that regardless of the high transformation temperatures applied, up to 350 °C, and/or extended heat treatments, tetragonality persists, being a clear

indication of the reluctance of carbon to partition from supersaturated bainitic ferrite into the adjacent austenite.

3.3 HRTEM ON LOW TEMPERATURE BAINITIC FERRITE

The tetragonality of ferrite can be investigated by the lattice image from high resolution TEM (HRTEM). HRTEM images of the general microstructure and across the bainite/austenite interface in Alloy 1 that was isothermally held at 200 °C are shown in Figure 8 a and b. The corresponding diffractogram (Figure 8 c) obtained by fast-Fourier transformation (FFT) indicate that the bainitic ferrite and the retained austenite keep approximately the Nishiyama-Wassermann (NW) orientation relationship (OR) $\{0 \bar{1} 1\}_{\alpha_b} || \{1 \bar{1} 1\}_{\gamma}$ and $\langle 1 0 0 \rangle_{\alpha_b} || \langle 0 1 1 \rangle_{\gamma}$ [43, 44]. The lattice spacings of austenite, directly determined from the lattice image, are 0.360 nm along $[1 0 0]$ direction and 0.255 nm along $[0 1 -1]$ direction, holding a ratio extremely close to $\sqrt{2}$. The half widths at half maximum (HWHM) of the intensity profiles are 0.07 nm and 0.05 nm, respectively, along the $[1 0 0]$ and $[0 1 -1]$ directions. However, in the bainitic ferrite, the peak intervals along the $[0 0 1]$ direction are larger than those along the $[0 1 0]$ direction, as shown in Figure 8 c. The slight extension along the $[0 0 1]$ direction of ferrite can be apparent after several periods of contrast peaks. The lattice spacing is 0.286 nm along $[0 1 0]$ direction, whereas the lattice spacing is 0.289 nm along $[0 0 1]$ direction. The HWHMs are 0.05 nm and 0.06 nm along $[0 1 0]$ and $[0 0 1]$ directions, respectively. It is suggested that the bainitic ferrite could have a BCT structure instead of a BCC structure. These results shows excellent agreement with those measured by X-ray analysis, see Figure 6. The concentration of carbon in bainitic ferrite can be

estimated to be ~0.23 wt. %, based on the measured c/a value [38], which is consistent with the value of 0.18 wt.% measured by APT, Figure 4.

From the theoretical point of view, tetragonality is explained on the basis of a displacive bainite nature, triggering the change of the lattice from cubic-F to cubic-I achieved by means of the Bain deformation [14, 45]. The carbon atoms in both the parent and product phases occupy octahedral interstices, but there are three times as many of these interstices per atom of Fe in the ferrite than in austenite. This means that the Bain strain places all the carbon atoms on to one sublattice of octahedral interstices in the ferrite when the latter forms without diffusion, resulting in a tetragonal unit cell. The location of carbon atoms on just one set of octahedral interstices is sometimes referred to as Zener order [46, 47], and in this context is a natural consequence of the Bain strain. This leads to a dramatic increase in the solubility of carbon in ferrite that is in equilibrium with austenite [10]. But one cannot ignore that for tetragonal Fe-C martensite Zener [48] proposed a theory to account for the ordering of carbons to one set of sites predicting that, for a given carbon concentration, there is a critical temperature below the structure can minimize its free energy, and accommodate the anisotropic strain due to the interstitial atoms, by allowing them to occupy one set of octahedral sites in preference to the other two. Thus, below this critical temperature, there is a driving force for an ordering reaction that converts the BCC structure to BCT. The prediction for the critical temperature for ordering, namely T_c , is approximately 1000 times the weight percent carbon in the alloy. Owen et al [49] suggested that such as order-disorder reaction may be at play in the formation of BCC martensite in alloys with low carbon content. In such alloys, $T_c < M_s$ leading to carbon disordering immediately on martensite formation. They cite, as supporting evidence, some observations of actual ordering and disordering

of interstitials, thus confirming the existence of a critical temperature. However, this may be due to the intervention of ageing effects removing the carbon atoms from solution before disordering could be observed. As the mechanism of bainite transformation is displacive, it is necessary a condition that the carbon atoms will be ordered, irrespective of whether the transformation is above or below the ordering temperature. This is because the one site per iron atom in austenite, changes into three sites per iron atom in ferrite, consistent with the symmetry of the two lattices, and with the nature of the Bain strain. What happens to the carbon after that is a kinetics issue, but the presence of the carbon in a tetragonal arrangement stabilizes it when compared with its presence in a cubic lattice. Therefore, partitioning will be lower.

In other words, if the mechanism is displacive, then immediately after transformation the ordering of carbon atoms is forced automatically by the Bain strain. Fresh formed bainitic ferrite plates should be fully supersaturated in carbon and non-cubic in the displacive assumption. Subsequently, the atoms may then disorder or partition.

4 CONCLUSIONS

The results presented have demonstrated that the carbon that persists in solid solution within the bainitic ferrite even after extended heat treatments or tempering, is sufficiently Zener ordered to cause the bainitic ferrite unit cell to be non-cubic. The high level of carbon supersaturation is accompanied by a change in symmetry of the unit cell from cubic to tetragonal.

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Table 1. Chemical composition of the alloys studied in wt.% and at. %. T and t_{finish} indicate the bainitic isothermal temperature, in °C, and the time needed to finish the transformation at such temperature.

		C	Si	Mn	Cr	Mo	Co	Al	Ni	V	T	t_{finish}
Alloy 1	wt. %	1.0	1.5	1.9	1.3	0.26				0.1	200	6d
	at. %	4.4	2.8	1.8	1.3	0.1				0.1	300	12h
Alloy 2	wt. %	0.7	1.4	1.3	1.0	0.24			0.1		220	24h
											250	14h
											300	5h
	at. %	3.1	2.7	1.3	1.0	0.1			0.1		350	4.5
Alloy 3	wt. %	0.8	1.6	2.0	1.0	0.24	4.0	1.7			250	12h
	at. %	3.5	2.9	1.91	1.0	0.1	3.6	3.3			300	6h

Table 2. For Alloy 2 and Alloy 3 transformed at 250 °C, R factors obtained from the Rietveld analysis of the XRD patterns using different crystal structure models for the diffraction peaks fitting of bainitic ferrite.

		Cubic Ferrite	2 Cubic Ferrites	Tetragonal Ferrite
Alloy 2	Rp	2.16	2.07	1.77
	Rwp	3.02	2.92	2.31
	Rexp	1.63	1.63	1.63
	GoF	1.85	1.79	1.42
Alloy 3	Rp	1.88	1.52	1.38
	Rwp	2.57	2.14	1.79
	Rexp	1.29	1.29	1.29
	GoF	1.98	1.65	1.38

Table 3.Result of Rietveld X-ray diffraction pattern refinement and volume fraction of retained austenite as a function of the bainite transformation temperature (T), where ϵ stands for the microstrain.

	T (°C)	V_γ (%) ± 3	a (nm) ± 0.0001	c (nm) ± 0.0001	c/a	Crystallite size(nm) ± 2	$\epsilon \times 10^{-3}$ ± 0.2
Alloy 2	220	16	0.2856	0.2880	1.0084	40	5.1
	220(+6d)	13	0.2855	0.2879	1.0084	41	5.1
	250	19	0.2856	0.2878	1.0077	41	4.9
	300	25	0.2857	0.2877	1.0070	49	4.0
	350	44	0.2859	0.2876	1.0059	46	2.6
	As quenched	16	0.2856	0.2932	1.0266	>100	7.3
Alloy 3	250	34	0.2860	0.2884	1.0084	37	5.1
	300	33	0.2862	0.2883	1.0073	50	4.5
	As quenched	18	0.2859	0.2954	1.0332	>100	6.5

Figure 1. Alloy 3 dilatometric curves from the austenitisation temperature down to three possible scenarios, as described in the main body of the text.

Figure 2. Examples of X-ray spectra for Alloy 2 in the as-quenched condition and after bainitic transformation at 350 and 220 °C, (a) general and (b) detail.

Figure 3. APT measurements on Alloy 2 treated at 300 °C showing (a) carbon atom map, (b) carbon iso concentration surface at 4 at. % superimposed with the carbon atom map, and (c) proximity histograms across the bainitic ferrite/austenite interfaces indicated by arrows, the carbon concentration reported has been measured in austenite and ferrite regions far away from any defect and interface [1], indicated by boxes.

Figure 4. APT measurements on carbon supersaturation in ferrite as a function of (a) transformation temperature, (b) transformation time indicating the fraction of bainitic ferrite at 200 °C for Alloy 1, and (c) different tempering conditions applied to the 200 °C bainitic microstructure of Alloy 1. The para-equilibrium (PE) phase boundary between ferrite (BCC) and austenite were calculated from [26] and the para-equilibrium (PE) phase boundary between ferrite (BCT) and austenite using [10]. The tempering parameter is defined as $T(20 + \log(t))$ where T is expressed in K and t in h.

Figure 5. For Alloy 2 and Alloy 3 transformed at 250 °C comparison of the observed (blue open circles) and calculated (red solid line) XRD pattern obtained after Rietveld refinement using beside a FCC austenite, the crystal structure of (a) a BCC ferrite (b two BCC ferrites and (c) a BCT ferrite. The differences between experimental data and the fitted simulated pattern is plotted as a continuous grey line at the bottom, and the contribution of the component phases in different colours (orange for ferrite and green for austenite).

Figure 6. (a) Alloy 2 and (b) Alloy 3, lattice parameters and a/c ratio evolution as a function of the bainitic transformation temperature measured by X-ray. Dotted lines represents the corresponding values for the as-quenched condition.

Figure 7. (a) Alloy 2 and (b) Alloy 3, C content of bainitic ferrite (α_b) and retained austenite (γ) as a function of the bainitic transformation temperature. Dotted lines represents the corresponding values for the as-quenched condition. Carbon deficit represent the difference between mass balance and the Alloy C content, as described in the main body of the text.

Figure 8. Nanostructured bainite in Alloy 1 treated at 200 °C (a) TEM micrograph showing thin film of retained austenite (γ) between two nanostructured bainitic ferrites plates (α_b), (b) HRTEM image showing the interface between bainitic ferrite (α_b) and retained austenite (γ), (c) the corresponding FFT diffractogram indicating the Nishiyama-Wassermann (NW) orientation relationship (OR), and (d) the contrast profiles respectively along the $[0\ 1\ 0]$ and $[0\ 0\ 1]$ directions in the region of interests (the black square in (b)).

Figure_1

Figure_2a

Figure_2b

Figure_3

Figure_4a

Figure_4b

Figure_4c

Figure_5a

Figure_5b

Figure_5c

Figure_6a

Figure_6b

Figure_7a

Figure_7b

Figure_8