Critical assessment 20: On carbon excess in bainitic ferrite

Elena V. Pereloma
University of Wollongong, elenap@uow.edu.au
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For several decades, the question of carbon supersaturation in bainitic ferrite has attracted the attention of physical metallurgists. Originally, this was associated with excess carbon due to the displacive nature of phase transformation and its subsequent trapping at defects in bainitic ferrite. The development of advanced experimental techniques, such as atom probe tomography and in situ synchrotron and neutron X-ray diffraction, has provided new insights into carbon distribution within bainitic ferrite. Possible explanations for carbon excess in solid solution are discussed, and the pathways for the future advancement of this research question are suggested.

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Critical Assessment: On the carbon excess in bainitic ferrite.

E.V. Pereloma

School of Mechanical, Materials and Mechatronic Engineering and the UOW Electron Microscopy Centre, University of Wollongong, Wollongong, Australia

Abstract

For several decades, the question of carbon supersaturation in bainitic ferrite has attracted the attention of physical metallurgists. Originally, this was associated with excess carbon due to the displacive nature of phase transformation and its subsequent trapping at defects in bainitic ferrite. The development of advanced experimental techniques, such as atom probe tomography and in-situ synchrotron and neutron X-ray diffraction, has provided new insights into carbon distribution within bainitic ferrite. Possible explanations for carbon excess in solid solution are discussed and the pathways for the future advancement of this research question are suggested.

Keywords: Bainitic ferrite; Martensite; Carbon supersaturation; Lattice structure; Atom probe tomography; Phase transformations, Diffusion, Mn-C dipoles

Introduction

There is undisputable agreement among physical metallurgists that (i) carbon concentration in the body centred cubic (bcc) lattice of ferrite formed by the diffusion-controlled mechanism\(^1\) corresponds to those of the equilibrium Fe-C phase diagram and (ii) carbon is super-saturated in the body centred tetragonal (bct) lattice of martensite formed by displacive mechanism\(^3\)\(^-\)\(^5\). Despite having carbon contents well above the equilibrium carbon concentration, the tetragonality of lattice was not experimentally observed for very low carbon martensite\(^5\)\(^-\)\(^7\) resulting in explanations being put forward as to the location of carbon at defects\(^8\)\(^-\)\(^9\) and the two-stage mechanism of martensite formation via the intermediate hexagonal close-packed lattice\(^5\)\(^,\)\(^10\). But there may, after the formation of low carbon martensite, be disordering of carbon atoms if the martensite-start temperature is below the Zener ordering temperature\(^11\). It is accepted that carbon present in austenite is locked in the martensite lattice due to the shear nature of the phase transformation mechanism. In support of this, the direct experimental evidence of uniform distribution of carbon in virgin martensite formed in Fe-Ni-C alloy in atom probe was obtained\(^12\)\(^-\)\(^14\). However if martensite forms at elevated temperatures or held for prolonged time at room temperature, the auto-tempering of martensite is manifested by segregation of carbon leading to clustering, the formation of Cottrell atmospheres at dislocations\(^15\) and even the occurrence of nanoscale carbide precipitation\(^8\)\(^,\)\(^14\)\(^,\)\(^16\)\(^,\)\(^17\). Carbon could also partition from martensite to austenite\(^17\)\(^,\)\(^18\) at elevated temperatures.
Bainitic ferrite (BF) is the ferritic component of bainite which forms at intermediate temperatures or cooling rates compared to ferrite and martensite. The mechanism of its formation remains a longstanding debate between the proponents of diffusional\textsuperscript{1, 19-21} and displacive\textsuperscript{4, 22, 23} theories. The former one considers the formation of bainite by the thermally-activated movement of atoms with ledge-wise growth (the rate of which is controlled by carbon diffusion into austenite) and resultant para-equilibrium carbon concentration. According to Aaronson\textsuperscript{1}, this carbon content is between the values defined by the $\alpha/(\text{Fe}_2\text{C}+\alpha)$ and extrapolated $\alpha/(\alpha+\gamma)$ curves (approximately 0.1-0.14 at.% depending on steel composition).

The proponents of displacive theory consider the formation of bainite to be similar to martensite via the shear and diffusionless growth of bainite sub-units, which results in the absence of substitutional elements diffusion\textsuperscript{4, 24} and supersaturated carbon concentration.

Although the diffusion of carbon into neighbouring austenite takes place immediately on bainitic ferrite formation, carbon fails to reach the para-equilibrium level in the bainitic ferrite despite the availability in many cases of long times for its partitioning. Early experimental evidence on supersaturated carbon content in bainitic ferrite was obtained using field-ion atom probe microscope\textsuperscript{25, 26}, X-ray diffraction studies\textsuperscript{27}, lattice imaging\textsuperscript{28} and convergent beam Kikuchi line diffraction in the transmission electron microscope (TEM)\textsuperscript{29}. In most cases this was attributed to processes similar to martensite auto-tempering, e.g. the trapping of carbon at numerous dislocations present in the analysed BF crystals as a result of the shear mechanism. However, advances in experimental techniques in recent years have led to new experimental evidence on carbon content in defect-free bainitic ferrite, which trigged the development of new explanations for carbon supersaturation in bainitic ferrite. The aim of this critical assessment is to briefly address these recent developments and outline the difficulties and remaining open questions associated with this phenomenon.

**Recent Experimental Evidence**

Since 2007, a significant number of atom probe studies were carried out on low carbon transformation-induced plasticity (TRIP)\textsuperscript{30-34} and nanobainitic\textsuperscript{35-42} steels. Both classes of steels have high Si contents; leading to carbide-free BF formation with interlayers of retained austenite. A summary of atom probe observations on the carbon content in the BF matrix without any visible carbon segregations is given in Table 1. It is clear, that in all cases and regardless of steels composition and heat treatment, there is a supersaturation of carbon in solid solution of BF. The level of this carbon excess above the para-equilibrium value depends on the carbon content in the parent austenite and the transformation temperature. The higher the carbon concentration in
austenite and the lower the transformation temperature, the higher is the degree of supersaturation. The formation of BF by the displacive mechanism implies the inheritance of composition from austenite. Since carbon has a lower chemical potential in fcc lattice compared to the bct/bcc one, there is a driving force for its partitioning to the remaining austenite. The rate of this diffusional process is temperature-dependent. Thus, the slower diffusivity of carbon at lower temperatures may lead to higher levels of carbon remaining in BF. However, even after very prolonged heat treatments (up to several days after the completion of BF formation), BF remains supersaturated with carbon; although its concentration is reduced. This residual carbon supersaturation could not be explained by carbon segregation to defects, as Cottrell atmospheres at dislocations would have been clearly visible in atom probe maps, as was shown in several studies. Thus, other explanations need to be provided.

**Carbon and Lattice Tetragonality**

In the bcc lattice, interstitial carbon atoms could occupy either the octahedral or tetrahedral interstices. However, carbon atoms preferentially occupy the octahedral sites as the solution energy in this case is much lower than that for tetrahedral sites. Since octahedral site can accommodate only atoms smaller than carbon without distortion, the presence of carbon atoms lead to cube edge distortion. When ferrite is in equilibrium with austenite, carbon solubility is very low, thus resulting in the bcc lattice of ferrite. However, due to the displacive nature of martensite transformation, carbon atoms located in one octahedral interstice per iron atom in the fcc lattice of austenite are automatically transferred by the Bain strain to one out of three octahedral interstices per iron atom on one of the cubic axes in the bcc lattice of ferrite, which results in lattice tetragonality. This ordered structure of carbon in solid solution remains at temperatures below that for Zener ordering. At temperatures above that for Zener ordering, carbon atoms will tend subsequently to move to other available interstice positions and the tetragonality of lattice is gradually reduced; finally becoming the bcc lattice. However, Zener has shown that the ordered carbon atom arrangement is stable at room temperature only at carbon concentrations exceeding 0.64wt.%. This value was later corrected to 0.54wt.% in work by Kurdjumov and Khachaturyan. Moreover, the tetragonality of martensite was reported even for lower carbon levels; contrarily to Sherby et al. opinion that the martensite with carbon content below 0.6wt.% has bcc lattice. Kurdjumov and Khachaturyan showed that in the presence of austenite constraining martensite, the martensite lattice could remain tetragonal at all temperatures and for all carbon atom concentrations. This correlates with experimental data on the reduction in lattice tetragonality of tempered martensite, but which maintained a degree of tetragonality even at high temperatures.
Based on the similarities in the mechanism of martensite and BF formation, Bhadeshia\textsuperscript{50} recently suggested that BF should also exhibit the bct lattice on formation due to the described above operation of Bain strain and Zener ordering. Furthermore, in this case the observed carbon supersaturation in BF could be explained by the higher carbon solubility in a bct lattice in equilibrium with austenite compared to that of the bcc lattice\textsuperscript{51}. Although the vast majority of work carried out to-date on the crystallography of bainitic ferrite reported its bcc lattice, there have been some early reports on the tetragonal nature of BF\textsuperscript{29, 32}. Recent in-situ synchrotron studies of BF formation at 200 °C for 10 days and at 300°C for 1 day in nanobainitic steels with Fe-0.84C–2.26Mn-1.78Si-1.55Co-1.47Cr-0.25Mo-0.11V-0.106Cu\textsuperscript{53} and Fe–1.037C–3.89Si–1.97Mn–0.24Mo–1.43Al (wt-%)\textsuperscript{54} have also shown a better fit obtained for the data of the BF lattice when lattice tetragonality is assumed. Anisotropy in thermal expansion along unit cell edges of bainitic ferrite during in-situ synchrotron studies was also reported recently\textsuperscript{55}. This is consistent with BF lattice being non-cubic.

Further support for BF lattice tetragonality was reported by Garcia-Mateo\textit{ et al.}\textsuperscript{39}, based on X-ray diffraction and transmission electron microscopy studies. The latter showed a difference in the lattice spacing of BF along [001] and [010] of 0.003 nm (~1%). However, similarly to the data by Zhang and Kelly\textsuperscript{29}, these results should be treated carefully as the accuracy of crystallographic data in the TEM is at best 1% due to the presence of elliptical distortion in diffraction and imaging modes. The only way to improve this accuracy is by post- acquisition processing\textsuperscript{56}. While high dislocation density in BF affects the Kikuchi line analysis in TEM, any results of ex-situ X-ray diffraction studies of bainitic ferrite in bulk with respect to lattice tetragonality should also be considered with a caution as a small fraction of martensite is generally present in the microstructure of bainitic steels affecting peak broadening and peak shift. The above highlights the complexity of precise determination of the lattice parameters of BF even using the modern experimental techniques.

It should be pointed out that for low carbon steels there is even higher degree of an experimental difficulty in determining lattice parameters from XRD data for both martensite and bainitic ferrite due to the merged components of the X-ray pattern peaks. In addition, as both martensite and BF form at high temperatures in low carbon steels, they are subjected to auto-tempering. The first step in this process would be the diffusion of carbon to the nearest dislocation core to form an atmosphere. Kurdjumov and Khachataryan\textsuperscript{9} suggested that the excess of carbon at dislocation or irradiation defects in martensite will assist the lattice to be bcc. Bhadeshia\textsuperscript{57} calculated the maximum amount of carbon not affecting the bcc lattice parameters to be in the range 0.019-0.22 wt.% (0.089-0.101 at.%) for nanobainitic steel with dislocation density of 6.4x10\textsuperscript{15} m\textsuperscript{-2} in BF. Thus, even if the
lattice is bct during the initial stage of BF formation in low carbon steels, it may become bcc on cooling to room temperature. Based on this, only careful in-situ experiments may provide the answer on the exact lattice parameters of BF in low carbon steels. However, even assuming that the bct lattice is always formed during the formation of martensite and bainitic ferrite and remains bct, in many cases the degree of teragonality is within the instrument detection error (1-3%). This makes it nearly impossible to confirm or disprove the issue using currently available techniques, especially for low carbon phases.

It is also worth noting that in the case of martensite tetragonality, a question was raised by Kurdjumov and Khachaturyan\textsuperscript{9} as to whether it is the result of Bain transformation only or whether the ordered carbon distribution is additionally more thermodynamically favourable than the disordered one at room temperature. Probably the same question should be considered for bainitic ferrite.

**Other Possible Explanations of Carbon Supersaturation in Bainitic Ferrite**

Although the displacive theory of BF formation states no diffusion of substitutional alloying elements from BF to austenite\textsuperscript{6,24}, recent theoretical and experimental work by H. Chen et al.\textsuperscript{58} predicts the migration of Mn and Si into austenite/BF interfaces. They proposed the new Gibbs Energy Balance (GEB) model explaining that the significantly slowed down rate of this interface migration due to the diffusion of alloying elements inside interfaces at a later stage of transformation results in the well-known phenomenon of transformation stasis or incomplete bainite transformation. The GEB model showed a good agreement with experimental data in respect to the effect of Mn content on the BF transformation behavior. It also led to conclusion that any alloying elements having a significant segregation tendency will have a similar effect. This was further confirmed by the modelling of Mo and Ni behavior.\textsuperscript{59} Interrupted cooling experiments also provided clear evidence of the local chemical enrichment at the interface during bainite transformation\textsuperscript{60}. The GEB model also predicts spikes of substitutional elements, such as Mn, in front of bainitic ferrite/austenite interfaces due to its very slow velocity at a later stage of isothermal bainite transformation. However, it should be highlighted that to-date all atom probe data on solute distribution across the austenite/BF interface did not show any segregation of substitutional elements at or in the vicinity of the interface.\textsuperscript{32, 35, 38, 39, 41} There is only one recent APT study on bainitic Fe-0.2C-1.5Mn-1.2Si-0.3Mo-0.6Al-0.036Nb wt.% (Fe-0.95C-1.5Mn-2.29Si-0.16Mo-1.15Al-0.02Nb at.%) steel after 4% pre-straining and 30 minutes holding at 200 °C\textsuperscript{33}, clearly showing the segregated layers of Mn and C (and to a small extent of Mo) in austenite at approximately 1.5-2 nm distance from the bainitic ferrite/austenite interface.
However, this segregation occurred on ageing most probably after completion of bainite transformation. It is well known that due to their high binding energy, Mn and C atoms form dipoles both in the fcc and bcc lattices of iron alloys and that the formed in austenite dipoles are quenched in. It was suggested that high Si content may increase the interaction between Mn and C atoms. In addition, it was shown by Massardier that while the solubility of carbon in ferrite is not affected by the presence of Mn at high temperatures (550-700 °C, 823-973 K), the solubility limit of carbon increases with increase in Mn content at temperatures below 550 °C(823 K). It is also interesting to note, that experimental data on the tempering of steel at 120°C(393K) after quenching from 680 °C(953 K) showed that the majority of single carbon atoms left the solid solution to form precipitates, whereas a significant amount of carbon atoms bound to Mn atoms remained in solid solution. It was also reported that Mn-C binding energy in austenite increases with increasing Mn content and that the presence of Mn-C dipoles reduces the diffusion rate of carbon. Thus, it could be speculated that the presence of Mn-C dipoles in the BF lattice could also be a contributing factor to the observed carbon supersaturation. Furthermore, the segregation of Mn to austenite/BF interface and/or higher Mn content in austenite in front of the austenite/BF interface could slow down the diffusion of carbon and significantly increase the time required to achieve the para-equilibrium concentration in BF.

**Future Experimental and Theoretical Work**

There is a convincing experimental evidence of carbon supersaturation in defect-free BF, which could be explained by higher solubility of carbon due to the (i) non-cubic, tetragonal nature of BF lattice and (ii) formation of Mn-C dipoles. Thus, more theoretical and experimental work is required to provide proof for the operation of one or both of these mechanisms. Some of the questions that require exploring are:

(i) Is it thermodynamically favourable for carbon to be located in ordered interstices at room temperature?

(ii) What is the effect of other alloying elements on BF lattice tetragonality? It was suggested recently by Kremnev for low carbon martensite that non-carbide forming elements increase the tetragonality, whereas carbide-formers decrease it. So what is the exact mechanism behind this and how does one go about obtaining direct experimental evidence?
(iii) Could core-linkage\textsuperscript{66} approach or other methodologies for atom probe data analysis provide the answer to the presence of Mn-C dipoles in bainitic ferrite and retained austenite?

(iv) Can more precise XRD (or other) techniques/methodologies be developed for the determination of lattice parameters and carbon content in order to take into account fine details of martensite or bainite substructure, e.g. effect of transformation strain, effect of Cottrell atmospheres on the strain from dislocations, shift in peak positions, etc.?

<table>
<thead>
<tr>
<th>Steel grade and nominal C content, at%</th>
<th>Mean C content in BF matrix free of any segregation, at.%</th>
<th>BF isothermal formation temperature and holding time</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>TRIP, 0.95</td>
<td>0.25 ± 0.03</td>
<td>450 °C/0.2 h</td>
<td>30</td>
</tr>
<tr>
<td>TRIP, 0.953</td>
<td>0.4 ± 0.02</td>
<td>470 °C/0.3 h</td>
<td>34</td>
</tr>
<tr>
<td>TRIP, 0.55</td>
<td>0.2 ± 0.03</td>
<td>400 °C/0.08 h</td>
<td>31</td>
</tr>
<tr>
<td>Nanobain, 4.3</td>
<td>1.36 ± 0.07</td>
<td>200 °C/48 h</td>
<td>38</td>
</tr>
<tr>
<td>Nanobain, 4.3</td>
<td>0.92 ± 0.32</td>
<td>200 °C/96 h</td>
<td>38</td>
</tr>
<tr>
<td>Nanobain, 4.3</td>
<td>0.78 ± 0.18</td>
<td>200 °C/144 h</td>
<td>38</td>
</tr>
<tr>
<td>Nanobain, 4.3</td>
<td>0.57 ± 0.5</td>
<td>200 °C/240 h</td>
<td>38</td>
</tr>
<tr>
<td>Nanobain, 3.48</td>
<td>0.56 ± 0.09</td>
<td>250 °C/120 h</td>
<td>32</td>
</tr>
<tr>
<td>Nanobain, 3.48</td>
<td>0.3 ± 0.05 (when carbides present) 0.7 ± 0.1</td>
<td>200 °C/240 h</td>
<td>41, 42</td>
</tr>
<tr>
<td>Nanobain, 3.48</td>
<td>0.35 ± 0.05</td>
<td>350 °C/24 h</td>
<td>40, 41</td>
</tr>
<tr>
<td>Multiphase, 1.2</td>
<td>0.4 ± 0.08</td>
<td>300 °C/2 h</td>
<td>32</td>
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<tr>
<td>Nanobain, 4.4</td>
<td>0.78 ± 0.18*</td>
<td>200 °C/144 h</td>
<td>37, 39</td>
</tr>
<tr>
<td>Nanobain, 4.4</td>
<td>0.6 ± 0.1*</td>
<td>300 °C/12 h</td>
<td>39</td>
</tr>
<tr>
<td>Nanobain, 3.1</td>
<td>0.75 ± 0.3*</td>
<td>220 °C/24 h</td>
<td>39</td>
</tr>
<tr>
<td>Nanobain, 3.1</td>
<td>0.92 ± 0.23*</td>
<td>250 °C/14 h</td>
<td>39</td>
</tr>
<tr>
<td>Nanobain, 3.1</td>
<td>(0.7-1.2) ± 0.1</td>
<td>300 °C/5 h</td>
<td>39</td>
</tr>
<tr>
<td>Nanobain, 4.34</td>
<td>0.62 ± 0.1</td>
<td>300 °C/8 h</td>
<td>37</td>
</tr>
</tbody>
</table>

*Estimated from Fig. 4a in Garcia et al.\textsuperscript{39}
References