Full length article

Atom probe tomography study of Fe-Ni-Al-Cr-Ti ferritic steels with hierarchically-structured precipitates

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A R T I C L E   I N F O

Article history:
Received 19 July 2017
Received in revised form 13 October 2017
Accepted 5 November 2017
Available online 13 November 2017

Keywords:
Ferritic steel
Precipitate strengthening
Hierarchical precipitate structure
B2-L21 phase separation
Transmission electron microscopy (TEM)
Atom-probe tomography (APT)

A B S T R A C T

The ferritic Fe-Ni-Al-Cr-Mo steel (FBB8) has good creep properties up to 700 °C due to B2-NiAl nanoscale precipitates and its creep resistance can be further improved by additions of 2 or 4 wt.% Ti, as a result of sub-precipitates within the main precipitates. Here, the hierarchical structure of the precipitates is studied in the light of phase separation via transmission electron microscopy (TEM) and atom probe tomography (APT). For FBB8-2Ti (with 2% Ti added) exhibiting B2-NiAl precipitates with L21-Ni2AlTi sub-precipitates, APT analysis shows strong partitioning of Ni, Al and Ti from the ferritic matrix into the B2/L21 precipitates and, within the precipitates, partitioning of Ti and Fe within the L21 sub-precipitates. Based on the published pseudo-binary phase-diagram between (Ni,Fe)Al and (Ni,Fe)Ti, this hierarchical precipitate microstructure is discussed based on the known miscibility gap between the B2 and L21 phases, due to partitioning of Ti into the L21 phase and ordering of Al and Ti on the Al sub-lattice of the B2 structure. For FBB8-4Ti (with 4% Ti added), by contrast, the L21 precipitates exhibit bcc sub-precipitates rich in Fe and Cr, with a composition close to that of the matrix; the absence of the B2 structure is consistent with an increase of Ti and Fe concentrations, to 18.2 and 19.3 at.% respectively, as measured via APT, in the L21 precipitates.

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1. Introduction

Precipitate-strengthened ferritic steels are an attractive alternative to austenitic steels and Ni-based superalloys for high-temperature and -stress applications due to their lower cost, lower thermal expansion, and higher thermal conductivity [1–3]. The precipitates generally consist of carbides, nitrides, and/or intermetallic compounds such as Laves, μ, η, σ phases [4–7]. However, these precipitation strengthened ferritic steels have a use temperatures limited to 600 °C, because of their weak oxidation resistance and creep strength deterioration during long-term operation [8–11]. Unlike carbide and Laves precipitates-strengthened ferritic alloys for steam-turbine applications, the present ferritic alloys are strengthened by hierarchical structured precipitates consisting of L21-Ni2AlTi sub-precipitate within B2-NiAl precipitates or bcc sub-precipitate within L21-Ni2AlTi precipitates, which are oxidation- and coarsening resistant [12,13]. The hierarchical nature of the B2/L21 precipitate increases the creep resistance by making dislocation shear of the two-phase precipitates more difficult, and by increasing the lattice misfit with the matrix, resulting in a strain field that more effectively traps dislocations on the arrival or departure sides of the precipitates [14,15]. The presence of a miscibility gap between bcc-Fe and B2-NiAl in the Fe–Ni–Al system enables precipitation hardening in the bcc-Fe matrix phase by coherent B2-ordered NiAl precipitates [16–18]. Jiang et al. [19] proposed a strategy for the design of ultra-high strength alloy via high-density B2-phase nano-precipitation with minimal lattice misfit in the coherent interface with the bcc matrix. Low lattice misfit (0.03 ± 0.04%) decreases the nucleation barrier for precipitation, which can stabilize nano-precipitates (~2.7 ± 0.2 nm) with a high number density (>1024 m–3). A high anti-phase boundary (APB) energy increases the ordering hardening of alloy by increasing dislocation shear resistance in the precipitate. However, the low misfit between precipitate and matrix is not effective in high temperature applications because the creep mechanisms in these ferritic steels strengthened by B2-ordered NiAl precipitate are not shear, but rather dislocation climb and repulsive elastic interaction between precipitates and...
matrix dislocations [20,21]. The addition of titanium to these steels significantly improves their creep resistance up to ~179 MPa from ~69 MPa at 700 °C through the creation of the L21-Ni2TiAl phase [15,20,22]. Replacing half of the Al atoms with Ti in the B2-NiAl phase results in the Heusler-phase, L21-Ni2TiAl, which provides greater creep resistance than B2-NiAl by increasing the lattice parameter mismatches between the ferritic matrix and the ordered precipitates [23,24]. The lattice parameter of ternary, stoichiometric L21-Ni2TiAl, 0.5895 nm [25] is 2% larger than twice the lattice parameter of B2-NiAl, 0.2887 nm [26]. This lattice misfit is sufficiently low to allow for a semi-coherent or coherent Heusler-phase precipitate structure within the bcc-ferritic matrix. Due to their high thermodynamic stability at temperatures [18,27] and low coarsening rate above 700 °C [28], these B2 and L21 precipitates are good substitutes for typical carbides and Laves precipitates. Furthermore, they maintain their strengthening even for long aging time, e.g., up to ~30 days at 700 °C [15]. The addition of Al (over ~2.5 at.%) in the alloy suppresses the ferrite (bcc) to austenite (fcc) phase transformation that can limit their use at an elevated temperature [29,30]. Then, coherent B2 phase and L21 sub-phase are nucleated from the stable bcc structure at elevated temperature.

For the fcc structured Ni-based alloy, L12 ordered-γ′ precipitates are coherent with the fcc γ matrix. In addition, they delay the coarsening by inducing splitting of the precipitates during aging [31–33]. In this phenomenon of inverse coarsening, the γ′ precipitates serve as a matrix for γ sub-precipitates, resulting in a hierarchical microstructure consisting of γ matrix containing γ′ precipitates which themselves contain γ sub-precipitates [34]. In Ni-Al-Ti-based ferritic steels, the precipitation behavior is complicated by the presence of three phases: B2, L21, and α-bcc. The morphology and kinetic evolution of hierarchical microstructures within the precipitate of a Ni-Al-Ti ferric alloy were mainly studied by transmission electron microscopy (TEM) [13,35]. The hierarchical microstructure is, however, sensitive to the alloy Ti concentration by ordering process in B2-NiAl phase [18,31]. Three-dimensional (3D) atom probe tomography (APT) is a unique analytical instrument suited for the study of such complex nanoscale precipitates, as it allows for site-specific analysis of chemical heterogeneities of matrix and precipitates with atomic scale spatial resolution [36–39].

Here, we present a study of microstructural and chemical evolution for two types of hierarchical microstructures in ferritic Fe-Ni-Al-Cr-Mo steels modified with 2 and 4% Ti, utilizing transmission electron microscopy (TEM) and atom probe tomography (APT). Understanding the sub-precipitate formation within the main precipitates will help with a further rational alloying design of these steels to achieve higher strength and creep resistance, by tailoring the lattice parameter mismatches between matrix, precipitates and sub-precipitates, as well as the volume fraction, shape, anti-phase boundary energy and hierarchy of the precipitated phases.

2. Experimental procedures

Two ferritic steels were prepared by arc-melting, with compositions measured by direct-current plasma mass spectroscopy at ATI Wah Chang (Albany, OR): Fe-10.2Ni-5.8Al-10.4Cr-3.1Mo-0.26Zr-0.001B-2.0Ti (wt.%) labeled FBB8-2Ti and Fe-10.4Ni-5.4Al-10.0Cr-3.5Mo-0.18Zr-0.05Si-4.0Ti (wt.%) labeled FBB8-4Ti; the composition in at.% are, Fe-8.94Ni-11.39Al-10.48Cr-1.82Mo-0.25Zr-0.005B-2.21Ti and Fe-9.41Ni-10.93Al-10.31Cr-1.86Mo-0.25Zr-0.005B-4.22Ti, respectively. The cast ingots were homogenized at 1200 °C for 0.5 h in evacuated quartz tubes, air-cooled, aged at 700 °C for 100 h in air and air-cooled on a ceramic block.

TEM samples were cut using a rotary disc cutter in the polished surface. The 3 mm diameter discs were ground to ~100 μm in thickness and further thinned to electron transparency using an electrolyte of 10% perchloric acid in ethanol bath at a temperature of ~30 °C. Bright field (BF) and super-lattice dark-field (DF) TEM imaging was performed in a H8100 (Hitachi) microscopes operated at 200 kV.

Atom probe nanotips were prepared by electropolishing using 10% perchloric acid and ethanol electrolyte. Using a local electrode atom probe (LEAP) tomograph (4000X-Si), pulses of ultraviolet laser light (355 nm wavelength) were applied to the nanotips at a pulse repetition rate of 500 kHz, with 20–30 pJ per pulse, under ultrahigh vacuum (~2 × 10^-11 Torr), at a temperature at 50.0 ± 0.3 K. The times of flight of the detected ions (average detection rate of 0.01 ions per pulse) were used to produce three-dimensional (3-D) reconstructions using the program IVAS (version 3.6.8). The concentration of Al[15] is overlapped with Fe[27] at 27 Da in the APT mass spectrum, and it is corrected by extraction of isotopic ratio of Fe at 27 Da. Compositional information was obtained employing the proximity histogram methodology for APT [40].

3. Results

3.1. TEM results of hierarchical microstructure in precipitate

The precipitate structure after aging at 700 °C for 100 h was investigated utilizing bright field (BF) and dark-field (DF) transmission electron microscopy (TEM) images with selected area diffraction pattern (SADP), Fig. 1. BF and DF images are taken in the near [10T] zone axis orientation with transmitted beam, (000), for BF and (111) for DFs in the B2-ordered NiAl and L21-ordered Ni3TiAl precipitates in the FBB8-2Ti and -4Ti alloys. The SADP in Fig. 1a
results, the (020) and (222) planes of the $L_2_1$ phase overlap with the (010) and (111) planes of the $B_2$ phase in the SADP.

The precipitates in Fig. 1b, displayed in the DF image of ($B_2$)$_{L_2_1}$ and ($B_2$)$_{L_2_1}$ super-lattice of the FBB8-2Ti alloy, show a cuboidal shape with width ranging from 50 to 100 nm. The regions of red color in the DF image, Fig. 1b, represent $L_2_1$ sub-precipitates embedded within $B_2$ precipitates with green color. The matrix-precipitate and the $B_2$-$L_2_1$ interfaces are observed to be coherent with an interfacial alignment towards a cube-on-cube orientation. The bright-field (BF) and DF images of the FBB8-4Ti alloy, Fig. 1c and d, shows $L_2_1$-ordered precipitates with a spherical and/or ellipsoidal shape with diameters between 200 and 500 nm. The dark regions in the $L_2_1$ precipitate were identified as Fe-rich bcc plates [24]. The averaged lattice misfits between bcc-Fe and $L_2_1$ phases in FBB8-4Ti, determined by neutron diffraction (ND), is 1.32% at 973 K, which is larger than that of precipitate in FBB8-2Ti (0.77%) [41]. The larger lattice misfit causes the formation of misfit dislocations at the interface between the Fe matrix and $L_2_1$ precipitate in the FBB8-4Ti alloy, Fig. 1c. The shape change from cuboidal in FBB8-2Ti to spheroidal in FBB8-4Ti is also expected to be due to loss of coherency, confirmed by the presence of a misfit dislocation network at the matrix-precipitate interface in BF image [15,27]. Precipitate alignment with the matrix along <100> occurs in FBB8-2Ti but precipitate alignment is not present in FBB8-4Ti, with its incoherent interface; this is consistent with lattice misfit driving precipitate alignment, rather than interfacial energy effects. In summary, the TEM microstructural observation confirms the prior results [15,35] that the single-phase $B_2$ precipitates present in FBB8 [20] are changed, upon Ti addition, to hierarchical $B_2/L_2_1$ for FBB8-2Ti and $L_2_1$/bcc for FBB8-4Ti.

### 3.2. Hierarchical $L_2_1$/$B_2$ precipitates

Fig. 2a displays a 3D APT reconstruction of FBB8-2Ti with 20.5 million ions showing $B_2$ and $L_2_1$ precipitates given by green Ni and red Ti iso-(concentration) surface envelopes, respectively. Iso-surface represents the average of the far-field plateau concentrations of the two phases, by employing the inflection-point methodology [42]. With iron atoms displayed as blue dots, the Fe-rich bcc matrix appears blueish despite the presence of other elements. Fig. 2b shows an extracted iso-surface image of the hierarchical precipitates with transparent green Ni and red Ti iso-surfaces. The larger $B_2$ (green iso-surface) precipitate in the upper right side of the reconstruction shows a complex hierarchical microstructure with plate-shaped $L_2_1$ sub-precipitates (red iso-surface). These $L_2_1$ sub-precipitates are crystallographically aligned (along the <001> direction, as identified in TEM experiments), which suggests a strong effect of coherency stresses on the interface [43]. It is known that the precipitate structures can be tailored via heat treatment in FBB8-2Ti. In a fast cooling process with melt-spinning technique, single-phase $B_2$ precipitates are obtained, with the hierarchical $L_2_1$...
sub-precipitates being formed within the B2 precipitates only during a subsequent aging treatment [13]. On the other hand, the L21 phase is reported as a major phase in the hierarchically-structured precipitates following homogenization at 1200 °C and air cooling [14]. The initial phase and the subsequent evolution of the precipitate substructure, which underlies the hierarchical microstructures, are strongly influenced by the B2/L21 phase equilibria in the pseudo-binary Ni(Al1-xTi)x system [13,18]. In the pseudo-binary NiAl-NiTi phase diagram, the majority phase is given by the Ti concentration and its ordering state [18]. L21-Ni5TiAl is formed by ordering of Ti, replacing half the Al atoms in the B2-NiAl phase; however, incomplete ordering with a low amount of Ti results in the two-phase decomposition (B2 and L21). This point is discussed in a later section.

A one-dimensional (1-D) concentration profile across the precipitate of FBB8-2Ti is shown in Fig. 2c, using a 0.5 nm bin size along the blue arrow across the hierarchical B2/L21 precipitate shown in the 3D reconstruction image of Fig. 2b; the ±20% error is equal to the statistical variance of values from different 3-D volumes [44]. The compositions, as determined by APPTime-of-flight (TOF) analysis, of the Fe-rich bcc matrix and of the B2 and L21 precipitate are summarized in Table 1. It is apparent that Fe, Cr and Mo are strongly partitioned in the B2 and L21 phases, whereas Ni, Al, Ti and Zr are mainly concentrated in the B2 and L21 sub-precipitates. The ratios of concentrations of a solute element between two immiscible phases at equilibrium is represented as a partitioning coefficient (P) [45], also included in Table 1. The partitioning ratios of Ni (C_{\text{PP}}/C_{\text{matrix}}) are 23.2 ± 1.7 for the B2 phase and 20.2 ± 1.5 for the L21 phases. Ti partitioning ratios are also high, with values of 13.1 ± 2.5 and 37.0 ± 2.5 in the B2 and L21 phases, respectively. The partitioning of Al is much less than Ni and Ti: 6.0 ± 0.3 and 4.9 ± 0.2 in the B2 and L21 phases, respectively. Finally, the partitioning ratio of Zr between the L21 precipitates and the bcc matrix, 4.9 ± 0.2, is larger than that between the B2 precipitates and the bcc matrix. 1.4 ± 0.3. Zirconium is, however, detected at concentration lower (by a factor 0.3) than the nominal composition value, as expected from the formation of a secondary phase (identified as Fe23Zr, with space group Fm-3m) at the grain boundary region [20]. By contrast, Cr and Mo are depleted in the precipitates, with partitioning ratios below unity. From these partitioning ratios, it can be concluded that the precipitate volume fraction is controlled mainly by Ni and Ti and, to a less extent, by Al, for this concentration range of ferritic steel. On the other hand, Cr and Mo can be expected to reduce the volume fraction of precipitates.

The 1-D concentration profile in Fig. 2c shows a concentration fluctuation for the five major elements (Fe, Ni, Al, Ti, and Cr) and the two minor elements (Mo and Zr) across hierarchical B2/L21 phases in precipitate. Because the L21-Ni5TiAl phase is formed by replacing half of the Al atoms within the B2-NiAl phase, these concentration fluctuations can be matched to B2 and L21 phase separation in DF-TEM analysis, Fig. 1b, of the FBB8-2Ti alloy. Four peaks for Ti and Fe are visible, consistent with L21-Ni5TiAl sub-precipitates enriched in these elements, as compared to the B2 precipitate surrounding the sub-precipitate. By contrast, the B2 precipitate is enriched in Ni and Al as compared to the L21 sub-precipitates; Ni and Al concentrations increase to 42 and 41 at.% in the B2 phase, from 33 to 30 at.% in the L21 phase, respectively. The highest partitioning ratio between the B2 and L21 phases, among the majority elements (Fe, Ni, Al, Ti and Cr) in the precipitate, is for Ti (2.8 ± 0.2), which favors strongly the L21 phase as the transition between B2-NiAl and L21-Ni5TiAl is driven by a replacement of Ti in their sub-lattice sites. Mo, Cr and Zr also partition into the L21 phase with a value of 2.0 ± 0.4, 1.9 ± 0.4 and 3.4 ± 1.2. However, Al concentration does not drop sufficiently to compensate the increase in Ti concentration and achieve the stoichiometric equilibrium Ni5TiAl composition. The range of Al and Ti concentration variations will be discussed in the light of the (Ni,Fe)Al - (Ni,Fe)Ti pseudo-binary phase diagram later. Finally, Fe is also preferentially partitioned into the L21 phase rather than the B2 phase and the sum of Ni and Fe concentrations is nearly 50 at.% in both B2 and L21 structure which may indicate that the Fe atoms preferentially occupy the Ni sub-lattice in the L21-Ni5TiAl structure.

### 3.3. Hierarchical bcc/L21 precipitates

Fig. 3 displays a 3D APT reconstruction of the FBB8-4Ti steel with 72 million ions. The reconstructed volume shows bcc matrix, L21 precipitate and Fe-Cr-rich sub-precipitates within the L21 precipitate, assumed to have bcc crystal structure, given their composition and TEM analysis. The bcc-matrix is characterized by Fe atoms (blue dots) and is visible in the right-upper corner of the 3D reconstruction. The L21 precipitate is represented by red-colored iso-surface. The size of the L21 precipitate is ~200 nm and only part of a precipitate is represented in the lower left part of the 3D APT reconstruction. The Fe-Cr-rich sub-precipitates are represented by blue colored iso-surface within the L21 precipitate. The Fe-Cr rich precipitates appear to be aligned along specific orientation within the L21/L21 interface specifically <001> directions as shown in the TEM reconstruction, Fig. 1d.

Concentration profiles straddling the bcc-matrix/L21-precipitate interfaces and the L21-precipitate/Fe-Cr-rich sub-precipitate interfaces are presented in Fig. 3b. These concentration profiles were created utilizing the proximity histogram (proxigram) method [40,46] from the bcc-matrix to the L21 precipitate at the 10 at.% Ti iso-surface, marked “3”, and from the L21 precipitate to the Fe-Cr-rich sub-precipitate at the 20 at.% Fe iso-surface, marked “4” in Fig. 3a. It is emphasized that these concentration plots contain three-dimensional (3D) information even though this is a two-dimensional (2D) plot. The vertical dotted lines are placed at the inflection points of the measured iso-concentration (10 at.% Ti and 40 at.% Fe) profiles, and indicate the location of the matrix (bcc/L21) and L21/sub-ppts interfaces (marked zero on the abscissa axis). The concentration profile does not show segregation behavior at the interface.

Similar partitioning trends as those reported above for FBB8-2Ti sample are found in these concentration profiles across the bcc-matrix/L21-precipitate interface. Fe, Cr and Mo are strongly partitioned to the matrix, whereas Ni, Al, Ti and Zr are partitioned to the L21 precipitate. The elemental concentrations and partitioning ratios are summarized in Table 2. The partitioning ratio of Ti, 50.2 ± 5.3 is much higher than for the matrix/L21 precipitate in the FBB8-2Ti, 37.0 ± 2.5. The Al concentration also does not reach the stoichiometric concentration of Ni5TiAl-L21 structure. Both Ti and Fe concentrations, 18.2 ± 0.26 and 19.25 ± 0.27 at.%, in the L21 precipitates of FBB8-4Ti are somewhat higher than those found in the L21 phase of FBB8-2Ti, 13.13 ± 0.38 and 17.42 ± 0.46 at.% respectively. As also seen in the FBB8-2Ti sample, the Fe and Ti concentrations are nearly identical in the L21 phase. Also, the sum of Ni and Fe concentrations is nearly 50 at.%, which is consistent with the preferential occupation of Fe atoms in the Ni sub-lattice of the L21 structure.

The concentration profile straddling the interface between the L21 precipitates and the Fe-Cr rich sub-precipitate along the arrow “4” show that, even though the Cr concentration does not quite reach the value found in the matrix (11.55 ± 0.49 vs. 13.08 ± 0.21 at.%), all other elements show nearly the same values of concentration as those of the bcc matrix. This means the hierarchical Fe-Cr rich sub-precipitate within the L21 precipitate are matrix-like in terms of concentration and thus crystal structure. The intermediate B2 structure with high Ni and Al and...
FeCr-rich sub-precipitate at the 20 at% Fe iso-surface, marked
interpreting the references to colour in this
utilizing a proximity histogram (proxigram) method [40] from the bcc-matrix to L21
precipitate to its imbedded sub-precipitates. The concentration pro-
surfaces. (b) Concentration pro-
sub-precipitates within the L21 precipitate. The L21 phase is de-
during aging, they may eventually split the L21 precipitate in a
portion of L21 precipitate has not occurred yet; however the growth of
superalloy [34]. For the present again condition, the full separa-
process known as “inverse coarsening” observed in a Ni-based
alloy [34]. For the present again condition, the full separa-
ration between precipitate and matrix (C_b-C_a)
gram, shown in Fig. 4. The slopes of the best-fit lines for all
elemental compositions give the volume fraction of the precipitate
phases in the two alloys: 17.6 ± 1.7% for B2 and 20.5 ± 1.6% for L21
in FBB8-2Ti and 22.1 ± 1.0% for L21 in FBB8-4Ti (the error is a standard
deviation (σ) from the value in the fitted line). This lever rule dia-
gram is an estimation assuming a single phase precipitate. In the
mixture of B2 and L21 phases for FBB8-2Ti, the precipitate volume
fraction is positioned between the two phases’ volume fraction. In
the lever rule diagram, Fig. 4, the points for Ti and Al deviate from
the best-fit line. This represents the progression of Ti and Al
separating into their eventual equilibrium concentrations in the B2
and L21 phases as the transition from the B2 to the L21 structure
involves ordering of the Al and Ti atoms on the Al sub-lattice of the
B2 structure. After homogenization at 1200 °C for 0.5 h, the pre-
cipitate has 36.8Ni-33.9Al-18.3Fe-9.75Ti-0.37Mo-0.65Cr (at.%)
composition as measured by APT [35]. The initial Ti concentration
of the precipitate, 9.75 at.%, in the homogenized sample is inter-
mediate between the two compositions of the B2 and L21 phases,
6.76 and 13.13 at.%. The Al concentration also evolves from 33.9% in
the homogenized structure to 37.5 and 32.2% in the B2 and L21
phases, respectively. This means that the precipitate volume
fraction (V_f) increases as the phases present in the matrix evolve
fraction (V_f) increases as the phases present in the matrix evolve
where C_a, C_b, and C_s are the compositions of the overall alloy, the
matrix and the precipitates, respectively. For each element, the difference between the overall alloy concentration and the matrix
concentration (C_s - C_b) is plotted against the difference in composition
between precipitate and matrix (C_p - C_b) in a lever rule dia-
gram, shown in Fig. 4. The points for Ti and Al deviate from the
best-fit line. This represents the progression of Ti and Al
separating into their eventual equilibrium concentrations in the B2
and L21 phases as the transition from the B2 to the L21 structure
involves ordering of the Al and Ti atoms on the Al sub-lattice of the
B2 structure. After homogenization at 1200 °C for 0.5 h, the pre-
Table 2
Composition (at. %) of FBB8-4Ti alloy (measured by direct-current plasma mass spectroscopy after casting) and of constitutive phases, matrix, B2 and L21 (after aging treatment
at 700 °C for 100 h, as determined by atom probe tomography, all in at. %). Uncertainties are represented by the standard deviation (σ) from the counting statistics mea-
surement series (1σ). Partitioning ratios and their errors (sum of relative errors of concentration) are also given.

<table>
<thead>
<tr>
<th>Phase</th>
<th>Fe</th>
<th>Ni</th>
<th>Al</th>
<th>Ti</th>
<th>Mo</th>
<th>Cr</th>
<th>Zr</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nominal composition</td>
<td>63.11</td>
<td>9.41</td>
<td>10.93</td>
<td>4.22</td>
<td>1.86</td>
<td>10.32</td>
<td>0.15</td>
</tr>
<tr>
<td>Matrix (bcc)</td>
<td>75.56 ±0.30</td>
<td>2.03 ±0.09</td>
<td>6.83 ±0.17</td>
<td>0.36 ±0.04</td>
<td>2.09 ±0.09</td>
<td>13.06 ±0.21</td>
<td>0.02 ±0.01</td>
</tr>
<tr>
<td>Precipitates (L21)</td>
<td>19.25 ±0.27</td>
<td>33.51 ±0.31</td>
<td>27.48 ±0.28</td>
<td>18.21 ±0.26</td>
<td>0.88 ±0.06</td>
<td>0.58 ±0.05</td>
<td>0.05 ±0.02</td>
</tr>
<tr>
<td>Partitioning ratio (L21/bcc)</td>
<td>0.2 ±0.01</td>
<td>16.0 ±1.53</td>
<td>4.0 ±0.11</td>
<td>50.1 ±5.25</td>
<td>0.4 ±0.03</td>
<td>0.1 ±0.01</td>
<td>3.3 ±0.9</td>
</tr>
<tr>
<td>Sub-precipitates</td>
<td>76.15 ±0.75</td>
<td>2.84 ±0.27</td>
<td>7.02 ±0.44</td>
<td>0.37 ±0.10</td>
<td>2.0 ±0.2</td>
<td>11.6 ±0.5</td>
<td>0.02 ±0.01</td>
</tr>
</tbody>
</table>
4.2. Thermodynamic evaluation for hierarchical sub-precipitate formation in precipitate

The heretical structure B2/L21 phase in the precipitates can be discussed from the pseudo-binary phase-diagram between (Ni,Fe)Al and (Ni,Fe)Ti [18,47], as shown in Fig. 5. It should be noted that the composition of matrix of FBB8-2Ti after homogenization at 1200 °C for 0.5 h is 77.2Fe-1.34Ni-6.3Al-0.33Ti-2.26Mo-12.5Cr at.% [35]. This is nearly identical to its matrix composition after aging at 1200 °C [35]. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

In the pseudo-binary phase-diagram between (Ni,Fe)Al and (Ni,Fe)Ti, Fig. 5, miscibility gaps exist on both the B2-NiAl and the B2-NiTi sides of the diagram and the two resulting B2-L21 two-phase regions are widening with decreasing temperature. The dotted lines represents the critical temperature (Tc), for a given composition, at which the ordering reaction from B2 to L21 phase takes place. In this system, the transition is achieved by ordering of the Al and Ti atoms on the Al sub-lattice of the B2 structure. The tricritical temperature (Tt) point in the Ni-Al-Ti system corresponds to the B2-NiAl and L21-Ni2AlTi reaction at the intersection of the miscibility gap and the continuous ordering line. The Tc and Tt for 0 at.% Fe for the B2-NiAl and L21-Ni2AlTi reactions are marked as Tc^{0Fe} and Tt^{0Fe} in Fig. 5 and they decrease when adding Fe. During cooling from the 1200 °C homogenization temperature of the FBB8-2Ti and 4Ti steels, the Ti concentration within the precipitates determines which majority phase is created in the precipitates. If the initial concentration of Ti is higher than the Tt concentration, it forms a L21 structure; otherwise, a B2 structure first forms, and then evolves into a hierarchical B2/L21 microstructure. However, Fe additions to the alloy change the phase equilibrium and miscibility-gaps between the B2-NiAl and L21-Ni2AlTi phases. With increasing Fe concentration, as shown in the phase diagram of Fig. 5, the stability region of the L21 phase shrinks as do the B2-L21 two-phase regions on both the Al- and Ti-rich sides of the diagram. It is indicated by the decrease of both maxima given by Tc and Tt (marked on Fig. 5 for 0% Fe). For 20 at.% Fe, the B2-L21 two-phase regions disappear at homogenization temperature of 1200 °C, i.e. the Tt temperature sinks below 1200 °C. At the aging temperature of 700 °C, the volume fraction and Ti concentration of B2 and L21 phases are delineated by the dotted red line in Fig. 5. The equilibrium concentrations of Ti in the phase diagram are ~6% in the B2 phase and ~17% in L21 phase at the aging temperature of 700 °C with 20 at.% Fe, as shown with vertical lines in Fig. 5. These equilibrium Ti concentrations are in general agreement with the APT values measured for the precipitates of FBB8-2Ti (see Table 1): 6.7 and 13 at.% in the B2 and L21 (sub-)precipitates, respectively. The discrepancy may be due to the presence of other alloying elements in the precipitates (i.e., Zr, Mo and Cr) and the possibility that equilibrium has not yet been fully reached.

The Ti concentration in the L21, precipitates of FBB8-4Ti is 18.2 at.% and falls in the L21-stabilized region in the pseudo-binary (Ni,Fe)Al-(Ni,Fe)2AlTi phase-diagram from the homogenization temperature of 1200 °C. Thus, L21 precipitates are fully formed after homogenization and the phase separation during aging of FBB8-4Ti.
is different from that of FBB8-2Ti as Fe-Cr-rich, bcc sub-precipitates, with composition nearly identical to that of the matrix, form within the L21 precipitates. This may be due to (i) Ti concentration is in the L21 stabilized region in the Ni-Al-Ti ternary diagram, (ii) Fe concentration being higher (19.3 at.% in the L21 precipitates of the FBB8-4Ti) than in those of FBB8-2Ti (17.4 at.%). As shown above in the APT experiments, the Fe concentration increases along with Ti concentration in the L21 structure; the Fe decreases the stability of both the L21 and B2 structures, as possibly do other bcc partitioning alloying elements such as Cr and Mo. Thus, it appears that the bcc-structure is more stable than the B2 structure when forming within the L21 precipitates for FBB8-4Ti, resulting in the observed different hierarchical microstructure for the precipitates than in FBB8-2Ti. The excess of Fe, Cr and Mo in L21 out-diffuses to bcc matrix or forms a bcc phase inside L21 phase precipitate.

4.3. Kinetic path of hierarchical microstructure

In this section, we discuss the nucleation and growth of hierarchical precipitate in the FBB8-Ti ferritic alloy. In the as-homogenized alloy at 1200 °C, the microstructure is that of a typical precipitation-strengthened ferritic alloy [20,52,53], where single-phase B2 or L21 precipitates are coherently or semi-coherently embedded in the bcc-Fe matrix. The presence of Al in the matrix, 6.5 at.% in 2Ti and 6.8 at.% in 4Ti-FBB8 alloy, stabilizes the bcc-phase, and the initial microstructure of precipitates and bcc-Fe matrix is created during cooling from the liquid phase [17,54]. This also occurs in very fast cooling experiments from the solidus, via the melt-spinning method, where B2 or L21 precipitates are obtained in the Fe bcc-matrix [13,55], implying that the B2 or L21 phases are already stable from the liquidus line [56,57]. When the Ti concentration is < 15 at.% Ti in the Ni-Al-Ti phase diagram, Fig. 5, rapid solidification from the liquid shows that the B2 phase is more stable than the L21 phase and that the L21 phase is nucleated from the B2 phase.

In early-stage aging at 700 °C, the B2-phase precipitate of FBB8-2Ti contains supersaturated Ti, and the L21-Ni2TiAl phase is nucleated by Ti ordering and replacing half of the Al atoms in the B2 lattice. The nucleation of L21/B2 hierarchical structure in the precipitates occurs by wetting or heterogeneous nucleation on B2 anti-phase domain boundaries (APBs) because the high APB energy of the B2 structure, 0.5 J/m² [58], can reduce the energy barrier between B2 and L21 phases for nucleation [13,56]. Furthermore, the decrease in interface energies between B2 and L21 for temperatures above 350 °C plays a role in the development of hierarchical microstructures within the precipitates, which varies from 50 mJ/m² at 0 K to 11 mJ/m² at 973 K, as determined from canonical Monte-Carlo simulations [13]. By reducing the interface energy between the B2 and L21 phases, the nucleation and growth of sub-precipitates in the main precipitates can be promoted. The coarsening of sub-precipitate is not well represented in this single aging time study [13,35]. The hierarchical structure is, however, already well developed in a sample aged at 700 °C for 100 h and the compositions are similar to B2 and L21—alloys in the Ni-Al-Ti phase diagram [18]. The precipitation of L21-Ni2AlTi in B2-NiAl requires not only segregation of Ti to localized regions of high concentration but also arrangement of Ti on specific lattice sites. The nucleation at APB and further development of L21 phase in the B2 phase are consistent with the homogenous nucleation growth, which is also supported by canonical Monte-Carlo simulations [13]. The bcc sub-precipitate in L21 precipitate is similar to the formation of L21 sub-precipitates in the B2 phase [55]. The L21 precipitates in the FBB8-4Ti alloy are fully formed after homogenization, and the bcc/L21 phase separation takes place within the L21 precipitates during aging at 700 °C. As shown above in the APT experiments, Fe, Cr and Mo supersaturated in the L21 phase out-diffuse to the bcc matrix or forms a bcc phase within the L21 precipitates.

5. Conclusions

The ferritic steel FBB8 (Fe−10.0Cr−9.9-10.5Ni−5.4-5.8Al−3.1-3.5Mo−0.18-0.31Zr−0.0-0.005B, wt.%) shows, after aging at 700 °C, single-phase B2 precipitates. The precipitates, upon addition of 2 and 4 wt% of Ti, remain B2 or become L21, respectively, but both display sub-precipitates. These hierarchical precipitates are studied here, utilizing transmission electron microscopy (TEM) and atom probe tomography (APT), leading to the following conclusions:

- Dark-field (DF) TEM images reveal, in both FBB8-2Ti and -4Ti, the hierarchical microstructure of the precipitate. FBB8-2Ti exhibits cuboidal (50−100 nm in size), coherent B2 precipitates, with an interfacial alignment towards a cube-on-cube orientation, containing L21-Ni2TiAl sub-precipitates. By contrast, FBB8-4Ti shows L21-ordered precipitates (200−500 nm in size) containing plate-like sub-precipitate. Thus, these relatively small Ti additions to FBB8 have a strong effect on the microstructure of the precipitates.

- 3D APT analysis of FBB8-2Ti further clarifies the B2/L21 hierarchical microstructure of the precipitates. Fe, Cr and Mo are strongly partitioned to the matrix phase, whereas Ni, Al, Ti and Zr are mainly concentrated in the B2 and L21 (sub-)precipitates. Between the B2 and L21 precipitates, Ti, Fe, Mo, Cr and Zr are enriched in the L21 sub-precipitates (and consequently Ni and Al are depleted). Fe is also preferentially partitioned into the L21 phase rather than the B2 phase and the sum of the Ni and Fe concentrations is nearly 50 at.% in both B2 and L21 structure. This may reflect that Fe, occupying the Ni sub-lattice in the L21-Ni2TiAl structure, has higher affinity for Ti than for Al.

- 3D APT analysis of FBB8-4Ti shows L21 precipitate containing sub-precipitates whose composition is nearly identical to that of the bcc matrix of the steel. These Fe- and Cr-rich sub-precipitates within the L21 precipitates are thus likely disordered (with the same bcc structure as the matrix), unlike the ordered sub-precipitates in FBB8-2Ti. As they grow during aging, these matrix-like sub-precipitates may be able to split the L21 precipitates, effectively decreasing their size, which may prevent the loss of mechanical strength associated with long-term coarsening in alloys with single-phase precipitates.

- The volume fraction of precipitates is estimated by the lever rule using the measured compositions in the APT experiment. When ignoring the secondary precipitates and assuming that the alloying elements evenly partition to every precipitate, the volume fraction of the B2 precipitates in FBB8-2Ti is 17.6 ± 1.7%, and that of the L21 precipitates is 20.5 ± 1.6%. The volume fraction of L21 precipitates in FBB8-4Ti is 22.1 ± 1.0%. The deviation of Ti and Al concentration from the best fit lines in the lever rule diagram, Fig. 4, represents the progression of Ti and Al partitioning into the equilibrium concentration between B2 and L21 phases.

- The hierarchical structure of the B2-L21 and L21-bcc precipitates is discussed in the light of Ti ordering and phase separation using a published pseudo-binary phase-diagram between (Ni,Fe)Al and (Ni,Fe)Ti, Fig. 5. The volume fraction and Ti concentration of B2 and L21 phases in FBB8-2Ti is determined by the iso-temperature intersection of the misibility gap at 700 °C from this diagram, and the predicted Ti concentration of both phases is in reasonable agreement with APT measurements. In FBB8-4Ti, the appearance of Fe-Cr rich bcc sub-precipitates may be due to the high Fe concentration in the
L21 main precipitates, which can decrease the stability of both L21 and B2 phases.

Acknowledgements

This research was supported financially by the US Department of Energy (DoE), Office of Fossil Energy, under Grant DE-FE0005868 (Dr. V. Cedro, monitor). The authors gratefully acknowledge Prof. P.K. Liaw, Mr. Z. Sun and Mr. G. Song (University of Tennessee) for providing the alloys and useful discussions. We also thank these researchers and Dr. Gautam Ghosh (Northwestern University) for numerous helpful discussions. APT measurements were performed at the Northwestern University Center for Atom-Probe Tomography (NUCAPT). The LEAP at NUCAPT was acquired and upgraded with equipment grants from the MRI program of the National Science Foundation (NUCAPT). The LEAP at NUCAPT was acquired and upgraded with equipment grants from the MRI program of the National Science Foundation (SHyNE) Resource (NSF ECCS-1542205). Additional instrumentation at NUCAPT was supported by the Initiative for Sustainability and Energy at Northwestern (ISEN).

Appendix A. Supplementary data

Supplementary data related to this article can be found at https://doi.org/10.1016/j.actamat.2017.11.013.

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