Microstructural Evolution of Single Ni₂TiAl or Hierarchical NiAl/Ni₂TiAl Precipitates in Fe-Ni-Al-Cr-Ti Ferritic Alloys during Thermal Treatment for Elevated-Temperature Applications

Gian Song¹, Zhiqian Sun¹, Jonathan Poplawsky², Yanfei Gao^{1,3}, and Peter K. Liaw^{1*}

1. Department of Materials Science and Engineering, The University of Tennessee, Knoxville, TN, 37996, USA
2. Center for Nano-phase Materials Sciences, Oak Ridge National Laboratory, Oak Ridge, TN, 37831, USA
3. Materials Science and Technology Division, Oak Ridge National Laboratory, Oak Ridge, TN, 37831, USA

*Corresponding author.

Email address: pliaw@utk.edu.

Phone number: 1-865-974-6356

Abstract

Precipitate features, such as the size, morphology, and distribution, are important parameters determining the mechanical properties of semi- or fully-coherent precipitate-hardened alloys at elevated temperatures. In this study, the microstructural formation and evolution of recently-developed Fe-Ni-Al-Cr-Ti alloys with superior creep resistance have been systematically investigated using transmission-electron microscopy (TEM), scanning-electron microscopy (SEM), and atom-probe tomography (APT). These alloys were designed by adding 2 or 4 weight percent (wt. %) Ti into a NiAl-hardened ferritic alloy with a nominal composition of Fe-6.5Al-10Cr-10Ni-3.4Mo-0.25Zr-0.005B in wt. %. These alloys were, then, subjected to a homogenization treatment at 1,473 K for 0.5 hour, followed by aging treatments at 973 K for 1 ~ 500 hours. In the homogenization-treated case, both alloys contain a primary L2₁-type Ni₂TiAl precipitate, but with the distinct size and morphology of the precipitates and precipitate/matrix interface structures. In the subsequent aging treatments, the 2 wt. % Ti alloy establishes a hierarchical-precipitate structure consisting of a fine network of a B2-type NiAl phase within the parent L2₁-type Ni₂TiAl precipitate, while the 4 wt. % Ti alloy retains the single Ni₂TiAl precipitate. It was found that the hierarchical structure is more effective in remaining the coherent interface during the growth/coarsening of the precipitate. The formation of the different types of the precipitates, and their effects on the microstructural evolution are discussed, and the driving forces for these features are identified from the competition between the interface energy and elastic interactions due to the lattice misfit and misfit dislocations.

Keywords: Ferritic alloys; Precipitation; Transmission electron microscopy (TEM); Atom probe tomography (APT)

1. Introduction

The NiAl-precipitate-strengthened ferritic alloys have received increasing attention as a potential candidate for high-temperature applications, such as in fossil-fuel-power plants [1-4]. These alloys are strengthened by coherent B2-NiAl phase precipitates with a minimized elastic strain at the precipitate/matrix interfaces due to a small difference in the lattice parameters between the B2-NiAl precipitates and A2-Fe matrix phases (low lattice misfit) [5, 6], resembling the classic γ/γ' Ni-based superalloy [7-11]. The low interfacial lattice misfit provides for the excellent microstructural stability during long-term service at high temperatures [12]. However, it was reported that extensive diffusional flows occur at the interface between the precipitate and matrix (interfacial relaxation), which accelerates creep deformation [6, 13].

To improve the creep resistance of the NiAl-strengthened ferritic alloys, single-phase $L2_1$ -Ni₂TiAl and two-phase B2-NiAl/ $L2_1$ -Ni₂TiAl precipitates have been developed [14-17], which results from the excellent mechanical properties and microstructural stability of the $L2_1$ -Ni₂TiAl phase at elevated temperatures [18]. It has been reported that such microstructures can be attained by the addition of Ti to the NiAl-strengthened ferritic alloys, which can significantly improve the high-temperature mechanical properties, such as creep resistance [17]. For example, the secondary creep rates of these alloys in the range of applied stresses from 140 to 160 MPa at 973 K are significantly reduced by more than four orders of magnitude, as compared to a NiAl-strengthened ferritic alloy and conventional ferritic steels [4, 17, 19-22].

Recently, the microstructures and creep properties of single-phase $L2_1$ -Ni₂TiAl and two-phase B2-NiAl/ $L2_1$ -Ni₂TiAl precipitates [denoted as a single-precipitate-strengthened ferritic alloy (SPSFA) and a hierarchical-precipitate-strengthened ferritic alloy (HPSFA), respectively] have been systematically investigated, based on the microstructures achieved in the as-aged state

(at 973 K for 100 hours) [17]. The SPSFA containing 4 weight percent (wt. %) Ti is strengthened by a single $L2_1$ -Ni₂TiAl precipitate phase [17], while the HPSFA with 2 wt. % Ti forms a two-phase precipitate, which contains a parent $L2_1$ -Ni₂TiAl phase reinforced by a fine network of a B2-NiAl phase, the so-called hierarchical precipitate. Moreover, it was reported that the difference in the precipitate structures between these two alloys leads to distinct interface structures; e.g., semi-coherent (SPSFA) and fully-coherent (HPSFA) interfaces, which influence the elastic (coherency) strain at the interfaces, and, hence, the creep resistance [17].

During long-term exposures to elevated temperatures, the precipitates undergo morphological evolution, primarily precipitate growth and coarsening [23-27]. The morphological changes of coherent precipitates have been extensively investigated in Ni-based superalloys via experimental and theoretical approaches [28-31]. Recently, the formation and evolution of hierarchical-precipitate microstructures has been investigated by Liebscher et al. in ribbon-type Fe-Al-Cr-Ni-Ti alloys upon aging treatment at 973 K [15, 16]. Specifically, the detailed characterization of the early stages of microstructural evolution (1 ~ 10 hours at 973 K) was conducted, using transmission-electron microscopy (TEM) and atom-probe tomography (APT), which revealed the heterogeneous nucleation of B2 zones on anti-phase domain boundaries. However, the microstructural evolution of the hierarchical-precipitate-strengthened ferritic-alloys during the long-term heat-treatment has not been studied yet. Since such microstructural evolution also affects the degree of the interfacial elastic strain [32], and, thus, high-temperature deformation behavior [33], it is crucial to obtain an in-depth understanding of the microstructural evolution of the precipitate structures of both HPSFA and SPSFA, and the effect on mechanical properties for both the fundamental study and industrial applications.

In the present study, we have investigated the microstructural evolution of the newly-

developed Fe-Ni-Al-Cr-Ti ferritic alloys with different amounts of Ti contents (2 and 4 wt. % Ti), which results in distinct reinforcing-precipitate structures during the thermal heat treatment, such as single-phase precipitates and two-phase hierarchical precipitates. Furthermore, the effect of precipitate structure on the microstructure is discussed, in terms of their size, morphology, spatial distribution, and elastic misfit. The elastic strain in the Fe matrix, caused by the mismatch between the matrix and precipitate phases, is shown to affect the morphology and spatial arrangement of the precipitate, which determines the creep resistance of the current alloys [17].

The fine hierarchical structure within the precipitate effectively reduces the lattice mismatch between the precipitate and matrix, which leads to the delay of the transition to misfit dislocations. These results provide clear insight and fundamental knowledge into further optimization of microstructures and mechanical properties of the current ferritic alloys and the novel alloy-design strategy for creep-resistant materials.

2. Experimental Methods

2.1 Materials

The model alloys have nominal compositions of Fe-6.5Al-10Cr-10Ni-xTi-3.4Mo-0.25Zr-0.005B with $x = 2$ and 4 in weight percent (wt. %). An ingot of the 2-wt. % Ti alloy with a dimension of 12.7 cm $\times$ 25.4 cm $\times$ 1.9 cm and a rod ingot of the 4-wt. % Ti alloy with 2 Kg and a diameter of 5.08 cm were prepared by the Sophisticated Alloys, Inc., using the vacuum-induction-melting facility. Hot isostatic pressing (HIP) was applied to the ingots at 1,473 K and 100 MPa for 4 hours to reduce defects forming during the casting and cooling processes. Chemical analyses were conducted on both ingots to obtain the compositions of the bulk samples. The nominal and analyzed compositions are listed in [Table 1](#). These alloys were homogenized at 1,473 K for 30 minutes, followed by air cooling and, then, aged at 973 K for different aging times (1 ~ 500 hours).

2.2 Atom-Probe Tomography

Sharp-tip specimens for atom-probe tomography (APT) were made, using standard liftout methods with an FEI Nova focused ion beam (FIB) [34, 35]. The data acquisition was performed, using a CAMECA local electrode atom probe (LEAP) 4000XHR equipped with an energy-compensated reflectron lens. The APT runs were conducted in a voltage-mode for the precipitate-density calculations and laser mode to achieve longer runs or capture large regions of interest, such as the L2₁-NiAlTi₂ precipitate phase. For the voltage-mode runs, the acquisition parameters were as follows: a 50-K base temperature, 200-kHz pulse rate, 20-% pulse fraction, and a 0.5 % detection rate. For the laser-mode runs, the acquisition parameters were shown as follows: 30 K, 200 kHz, 25-pJ laser energy, and a 0.5 ~ 2.0 % detection rate.

2.3 Scanning and Transmission Electron Microscopy

Scanning-electron microscopy (SEM) was conducted, using a Zeiss Auriga 40 equipped with an Everhart-Thornley secondary-electron detector. The SEM images were analyzed, using the ImageJ software [36] to obtain the sizes and volume fractions of the precipitates, and the average values were estimated, employing more than 200 particles. Thin foils for conventional transmission-electron-microscopy (CTEM) observations were prepared by electropolishing, followed by ion milling at an ion energy of ~ 2.5 kV and an incident angle of $\pm \sim 5$ degree. The transmission-electron-microscopy (TEM) specimens were cooled by liquid N₂ during ion milling. The TEM observations were conducted with a Zeiss Libra 200 MC TEM/STEM equipped with an energy-dispersive X-ray (EDX) detector, a Bruker xFlash 5030. The TEM images were acquired at an acceleration voltage of 200 kV. The X-ray collection time was between 300 and 500 s, and at least 10 single measurements were obtained. The Cliff-Lorimer method was used for EDX quantification [37].

3. Results

3.1 Microstructures of HPSFA in the Homogenization-Treated State

Figure 1 shows the microstructure of the HPSFA specimen subjected to the homogenization treatment at 1,473 K for 0.5 hour, followed by air cooling. The selected-area-electron-diffraction pattern (SADP) in Figure 1(a) was acquired along the [101] zone axis, with indices/d-spacings consistent with the $L2_1$ -Ni₂TiAl phase. Figure 1(b) shows a dark-field transmission-electron microscopy (DF-TEM) image obtained using a $\langle 111 \rangle$ -type superlattice reflection, which is unique to the $L2_1$ structure. The cuboidal $L2_1$ -type precipitates with an average width of 50 nm are preferentially aligned along the elastically-softest (100) direction of the Fe matrix, and the precipitates are closely spaced to each other. Moreover, the interface between the $L2_1$ -precipitate and Fe-matrix is free of misfit dislocations [Figures 1(b)-(d)].

Dark-contrast zones are observed inside the $L2_1$ precipitate by DF-TEM, as indicated by white arrows in Figure 1(b). The DF-TEM images using $\langle 111 \rangle$ - and $\langle 222 \rangle$ -type reflections, were acquired on the same precipitate region, as shown in Figures 1(c) and (d), respectively, to identify the dark zones inside the $L2_1$ precipitate. The DF-TEM image in Figure 1(c) clearly shows the presence of curved dark domains in the $L2_1$ precipitates, as denoted by white arrows. However, when imaged using the $\langle 222 \rangle$ -type reflection, common to both $L2_1$ and B2 structures, the curved dark domains are invisible [Figure 1(d)]. Following a report of a similar observation for a Fe-15.4Al-12.1Cr-1.0Mo-16.0Ni-4.3Ti [in atomic percent (at. %)] ribbon sample [15], the curved domains within the $L2_1$ -Ni₂TiAl precipitates are consistent with antiphase boundaries (APBs) with a shift vector of $R_{100} = 1/2\langle 100 \rangle$. Based on the APB extinction rule [38], APBs with $R_{100} = 1/2\langle 100 \rangle$ are visible when imaged in TEM with the $\langle 111 \rangle$ -reflection, and invisible when imaged with the $\langle 222 \rangle$ reflection, which is consistent with the present observation.

Therefore, the internal dark domains in the $L2_1$ precipitate are APBs with $R_{100} = 1/2\langle 100 \rangle$.

APT was conducted on the homogenization-treated sample to obtain the compositions of the constitutive phases. Figure 2 exhibits (a) two iso-concentration surfaces of 5 at. % Ni (green) and 5 at. % Ti (yellow), (b) one-dimension line profile (1-DLP) and atom maps of (b) Al, (c) Ni, (d) Fe, and (e) Ti. The iso-concentration surfaces clearly show two types of precipitates in the homogenization-treated HPSFA: large primary and ultra-fine precipitates (denoted as secondary precipitates in this study). Nano-scaled plate-like zones can be observed within the primary $L2_1$ - Ni_2AlTi precipitate shown in Figure 2(a), which correspond to the APBs observed in DF-TEM (Figure 1). The one-dimensional line profile (1-DLP) in Figure 2(b) reveals that the APBs exhibit slight compositional fluctuations especially for Ti, Ni, and Al elements, which could indicate that the APBs observed is not true (or thermodynamically stable) APBs, since the true APBs are atomically sharp and represent a shift of the lattice cell by less than one translational vector. Note that the 1-DLP looks like that it encompasses the matrix and the precipitate in Figure 2(a). However, the precipitate was extracted from the matrix before calculating the 1-DLP to avoid mixing of the precipitate and matrix compositions. The compositions of the Fe matrix and $L2_1$ precipitate were determined from APT and are summarized in [Table 2](#). Based on the TEM results [Figures 1(b)-(c)], which show narrow APBs inside the $L2_1$ precipitate, the plate-like zones evident in Figure 2(e) are likely the APBs.

A high density of nano-scaled secondary precipitates are distributed in the Fe matrix, as shown in Figure 2(a). Note that these secondary precipitates were not observed in the DF-TEM images of Figure 1, which indicates that the DF-TEM technique was not capable of detecting the secondary precipitates of the ultra-fine size (less than 10 nm). Thus, BF-TEM or APT were employed to capture the secondary precipitates in HPSFA samples after homogenization and/or

aging treatments. The composition of the secondary precipitates in the homogenization-treated HPSFA specimen, determined from the APT analysis is summarized in Table 2. The composition of the secondary precipitate is different from that of the primary precipitate. In particular, the amount of Ti in the secondary precipitates is very low (6.9 ± 0.58 at. %), as compared to Ti in the primary precipitate (9.75 ± 0.15 at. %). A previous APT study on the microstructure of the HPSFA sample aged at 973 K for 100 hours confirmed the formation and composition of the secondary precipitate in the Fe matrix [17]. The composition of the secondary precipitate in the homogenization-treated sample (Table 2) is close to the secondary B2 precipitate in the previous report [17], and, thus, the secondary precipitates are considered to be the B2-NiAl phase, which is also the phase identified in the core of the primary precipitates. The radius of the small precipitates, obtained from the iso-concentration surface of 7.6 at. % Ni in Figure 2(a), ranges from 1 to 5 nm.

3.2 *Microstructural Evolution of HPSFA during Aging Treatments*

Figure 3 shows the microstructures of the HPSFA (2 wt. % Ti) specimens aged at 973 K for (a)-(b) 10 hours and (c)-(d) 100 hours after the homogenization treatment at 1,473 K for 0.5 hour. The DF-TEM images acquired using the $\langle 002 \rangle$ $L2_1$ reflection in Figures 3(a) and 3(b) show the precipitates with nano-scaled bright bands, which is in contrast to the homogenization-treated sample (Figure 1). The narrow bright bands are similar in shape and size to that of the APBs observed in the homogenization-treated sample [Figures 1(b)-(c)]. Note that the superlattice reflection employed to form the DF-TEM images is common to both the B2 and $L2_1$ structures ($\langle 001 \rangle$ -B2 and $\langle 002 \rangle$ - $L2_1$). By considering the image intensity, and structure factor [15, 38], the narrow bands inside the precipitates are consistent with the B2-NiAl phase, while the surrounding regions are the $L2_1$ -Ni₂TiAl phase, which indicates that the hierarchical

precipitates exhibit a fine network of the B2-NiAl and L2₁-Ni₂TiAl phases that developed during the aging treatment at 973 K for 10 hours.

During aging for 100 hours, the well-developed hierarchical structure with a fine network inside the precipitate is observed by DF-TEM imaging [Figure 3(c)] and the average precipitate size is estimated to be 98 ± 23 nm. The DF-TEM image was acquired along the (100) zone axis using the <002> L2₁ reflection. Similar to the HPSFA aged for 10 hours, the cuboidal morphology and spatial arrangement (close separation and preferential alignment) of the hierarchical precipitates remains the same, as observed in the homogenization-treated HPSFA (Figure 1). Furthermore, the precipitate/matrix interfaces are free of misfit dislocations, which indicates the retention of coherent interfaces during the aging treatment for 100 hours [Figures 3(c) and (d)].

The SEM images in Figure 4 show the microstructures of the HPSFA specimens aged at 973 K for (a) 200, (b) 300, and (c) 500 hours. During these aging treatments, striking microstructural variations are observed, compared to the HPSFA aged for 100 hours or less (Figure 3). In particular, as the sizes of the precipitates increase, elongated- and irregular-shaped precipitates are often observed, as denoted by blue arrows in Figures 4(a)-(c). The number density of the abnormally-elongated precipitates increases with the aging time. Furthermore, the precipitates retain the alignment in certain orientations in Figures 4(a), while this alignment trend is not clearly evident in Figures 4(b)-(c).

Figures 4(d)-(f) present TEM images of the microstructure of the HPSFA specimen aged at 973 K for 500 hours. The bright-field (BF)-TEM image in Figure 4(d) shows a large precipitate with an irregular shape, consistent with those observed in Figure 4(c). In order to identify the B2 and L2₁ phases inside the precipitate, the <111> and <222> superlattice

reflections are used to form DF-TEM images shown in Figures 4(e) and (f), respectively. The hierarchical structure inside the precipitate is composed of agglomerated domains of the B2-NiAl and L2₁-Ni₂TiAl phases, rather than the fine network of the B2 phase within the L2₁ (Figure 3), which reflects coarsening of the B2-NiAl phase inside the L2₁-Ni₂TiAl precipitates. It is worth noting that misfit dislocations are often observed (blue arrows) for these large, irregular hierarchical precipitates, especially at the interface between the Fe matrix and hierarchical precipitate, which reflects the coarsening behavior of the precipitate, accompanied with the formation of the misfit dislocation [Figure 4(d)], and, thus, the semi-coherent interface.

Besides the large irregular precipitates, other types of smaller primary precipitates are observed. For example, one is a single L2₁-Ni₂TiAl precipitate (not shown), while another contains nano-scaled L2₁-Ni₂TiAl zones embedded in a parent B2-NiAl phase, as presented in Figures 5(a)-(b). Figures 5(a)-(b) are the DF-TEM images from the same region using (a) the $\langle 111 \rangle$ and (b) $\langle 222 \rangle$ reflections, respectively. The APT data was collected on a similar primary precipitate, as shown in Figures 5(a)-(b), which is presented in Figure 5(c). Figure 5(c) exhibits two iso-concentration surfaces of 10 at. % Ti (yellow) and 10 at. % Ni (green), which clearly show the presence of the narrow L2₁-Ni₂TiAl zones embedded in the parent B2-NiAl phase. The compositions of the B2-NiAl and L2₁-Ni₂TiAl phases were determined, using the APT analysis, and are summarized in **Table 2**. Figure 5(d) shows an iso-concentration surface of 7.5 at. % Ni (green). As observed in Figure 2, the ultra-fine secondary precipitates are present in the Fe matrix. However, the average size of the secondary precipitates is slightly smaller [1.5 nm in radius] than those observed in the homogenization-treated sample [2 nm in radius]. Although it was difficult to determine the exact composition of the secondary precipitate due to its small size, an approximate composition was obtained from the APT analysis, and is summarized in **Table 2**.

3.3 *Microstructures of SPSFA in the Homogenization-Treated State*

The microstructure of the SPSFA (4 wt. % Ti) subjected to the homogenization treatment at 1,473 K for 0.5 hour, followed by air cooling, is presented in Figure 6. The SEM image in Figure 6(a) shows the polygonal precipitates distributed in the Fe matrix. The size of the precipitates (considering the morphology to be an ellipse) was determined to be 126 ± 28 nm in diameter and 160 ± 33 nm in length, which is about two times larger than those observed in the homogenization-treated HPSFA (50 nm). As observed for the microstructures of the HPSFA aged for less than 200 hours [Figures 1 and 3], the precipitates shown in Figure 6(a) exhibit a preferential alignment and close-separation, but do not impinge on each other, as indicated by the red arrows. The SADP acquired along the (110) zone axis [Figure 6(b)] confirms the presence of the $L2_1$ - Ni_2TiAl phase. According to the electron diffraction and image contrast, all homogenization-treated and aged SPSFA contain the single-phase $L2_1$ - Ni_2TiAl in the primary precipitate. The DF-TEM image in Figure 6(c) shows the formation of primary and secondary $L2_1$ - Ni_2TiAl precipitates. The size of the secondary precipitate is about 10 ~ 30 nm, which is larger than that of the HPSFA sample homogenization-treated (1 ~ 5 nm). The primary $L2_1$ - Ni_2TiAl precipitates are decorated with misfit dislocations, denoted by white arrows in Figure 6(c). The BF-TEM image in Figure 6(d), which was obtained for the same region shown in Figure 6(c), clearly presents the misfit dislocations around the primary precipitates, suggesting a semi-coherent interface between the Fe matrix and the primary $L2_1$ - Ni_2TiAl precipitates. In contrast, the secondary precipitates are free of the misfit dislocations indicative of coherent interfaces between the Fe matrix and secondary precipitates.

3.4 *Microstructural Evolution of SPSFA during Aging Treatments*

Figure 7 shows SEM images of the microstructures of the SPSFA samples aged at 973 K

for (a) 1 hour, (b) 10 hours, (c) 50 hours, and (d) 100 hours. The size of the precipitates was measured, using the SEM-image analysis, based on an elliptical-precipitate shape. As expected, the size of the precipitate increased from 130 nm (1 hour) to 220 nm (100 hours), during the aging treatments. There are interesting microstructural variations during aging. First, the morphology of the precipitates changes from polygonal to an ellipsoidal or spherical shape, which becomes apparent in comparing Figures 7(a)-(b) and Figures 7(c)-(d). Second, the precipitates are closely spaced without impinging each other [Figure 7(a)], as denoted by blue arrows. As the precipitates coarsen (with increased aging time), irregularly-shaped precipitates, as indicated by blue arrows in Figures 7(b)-(d), are often observed, and their number density increases with the aging time. Similarly, the fine plate-like inclusions start to form within the precipitates and increase in volume and size, as the aging time increases, as denoted by red arrows in Figures 7(b)-(d). Lastly, the precipitates are preferentially aligned along certain crystallographic orientations [Figures 7(a)-(b)], while the orientation trend is not clearly observed after longer aging times [Figures 7(c)-(d)].

Figure 8 presents TEM images of the microstructures of the SPSFA aged at 973 K for (a)-(b) 1 hour and (c)-(d) 100 hours. The interfaces between the $L2_1$ - Ni_2TiAl precipitates and the Fe matrix appear to be aligned along $\langle 100 \rangle$, and the precipitates are closely spaced, but not connected, as shown in Figure 8(a). However, further aging for 100 hours leads to the decreased alignment of the precipitates and coalescence of the primary precipitates [Figure 8(c)]. These observations are consistent with the microstructures shown by the SEM images in Figures 7(a) and (d). Moreover, dark zones with different sizes and spatial distributions inside the $L2_1$ precipitate are observed in both samples, as indicated by red arrows in Figures 8(a) and (c). These dark zones correspond to the plate-like inclusions observed in Figure 7. The DF-TEM

analysis, electron diffraction, and image-contrast results revealed that the dark zones in the aged SPSFA are not the B2 phase. The SPSFA aged at 973 K for 100 hours was characterized, using the TEM-based energy-dispersive spectrometry (EDS) [17], which revealed Fe inclusions inside $L2_1$ precipitates resulting from the phase separation during the aging treatment [5]. Based on this previous finding, it can be inferred that the nano-scaled Fe-matrix inclusion inside the $L2_1$ precipitate in Figure 8(a) formed and coarsened during the aging treatment at 973 K [Figure 8(c)]. Similar to the homogenization-treated microstructure observed for SPSFA [Figure 6(d)], the precipitates are decorated with a high density of misfit dislocations at the interfaces, as reflected by the Moirée fringes caused by a slight misalignment of the matrix and the precipitate in Figures 8(b) and (d), which indicates semi-coherent interfaces between the Fe matrix and $L2_1$ - Ni_2TiAl precipitates.

The secondary precipitates of the SPSFA aged at 973 K could be observed in Figures 8(b) and 8(d). The size of the secondary precipitate of the SPSFA aged at 973 K is smaller than that of the SPSFA homogenization-treated at 1,473 K [Figure 6(c)]. Moreover, the size of the secondary precipitates of the SPSFA remains fairly constant during the aging at 973 K. This trend is consistent with the secondary precipitate of the HPSFA. These observations suggest that the secondary precipitates of SPSFA and HPSFA are completely dissolved in the Fe matrix at 973 K (the aging-treatment temperature) and form during the cooling process [5, 39]. Sun et al. [40] investigated the effect of cooling rate on the size and volume fraction of secondary precipitates using ultra-small angle X-ray scattering, and demonstrated that the size and volume fraction of the secondary precipitate formed in a NiAl-strengthened ferritic alloy are affected by the cooling rate.

4. Discussion

- ***Evolution of Primary Precipitates and Their Effect on Strengthening Behavior***

The precipitation behavior and precipitate evolution are closely related to the alloy chemistry, in this case, the Ti content variation (2 and 4 wt. %) and composition of the constitutive phases (B2-NiAl, L2₁-Ni₂TiAl, and Fe phases). In the current study, the addition of Ti (2 and 4 wt. %) into FBB8 gives rise to the formation of the L2₁ primary precipitates after homogenization treatment at 1,473 K, which exhibits the different size and compositions. Moreover, this compositional variation between the L2₁ primary precipitates in the 2% and 4% Ti alloys is believed to result in the observed difference in the precipitate evolution during the heat-treatments, in particular, the formation of the second precipitation of the B2 phase within the primary precipitate for the 2% Ti alloy (no second precipitation of the B2 phase is observed for the 4% Ti alloy). The L2₁ precipitate compositions of the 2% and 4% Ti alloys after aging treatment (Table 2) are more or less identical to each other. These results reflect that the compositions of the constitutive phases reach the equilibrium state after aging treatment. However, the compositions of the L2₁ primary precipitates after homogenization treatment at 1,473 K are different between the 2% and 4% Ti alloys. Specifically, the 2% alloy exhibits the less Ti content than the equilibrium state, whereas the composition of the L2₁ precipitate is quite close to the equilibrated one, except for the high solubility of the Fe content. The low amount of the Ti solubility in the L2₁ phases for the 2% alloy, which reflects the incomplete ordering of the L2₁ phase, is expected to result in the two-phase decomposition (B2 and L2₁) within the primary precipitate for the 2% Ti alloy ($L2_1 \rightarrow B2 + L2_1$), whereas the ordering of the L2₁ phase has completed during the cooling after the homogenization treatment. Instead, the high Fe content in the 4% Ti alloy was reported to lead to the formation of the Fe rich inclusion inside the L2₁ precipitate during the aging treatment ($L2_1 \rightarrow Fe + L2_1$) [41], as observed in Figure 8. The

formation of the hierarchically-structured B2-NiAl/L2₁-Ni₂TiAl precipitates in the Fe matrix was also observed by Liebscher et al., [15, 16] upon aging the Fe–15.5Al–12.1Cr–1.0Mo–16.0Ni–xTi ribbon samples with x = 2 or 4 in at. % at 973 K. In particular, the as-quenched sample of the 2-at. % Ti alloy in the Liebscher et al.'s study contained primary L2₁-Ni₂TiAl precipitates with internal APBs. Further aging to 10 hours at 973 K leads to the formation of the fine network of the B2-NiAl phase on APBs [15]. The current study exhibits a qualitatively-similar phase-evolution pathway [15]. Liebscher et al. suggested possible mechanisms on the formation of the hierarchical structure in the precipitates [32, 42-44], which involves a wetting transition or heterogeneous nucleation on L2₁ APBs [15, 43, 44]. The narrow anti-phase domain boundary formed within the L2₁ precipitate is believed to be responsible for the formation of the fine lamellar-type (hierarchical) structure for the 2% Ti alloy. Note that the narrow APBs are not observed in the homogenization-treated state, and the aging treatment leads to the formation of the Fe-rich inclusion of the spherical shape in the 4% alloy.

It is important to note that a uniform distribution of smaller precipitates (primary: 50 nm, secondary 6 nm) occurs for the 2% Ti alloy subjected to the homogenization treatment followed by the air cooling, as compared to that for the 4% Ti alloy (primary: 126 nm and secondary 20 nm). The difference in size of the precipitates formed in the alloys can be understood in terms of classical nucleation theory [45]. Particularly, the formation of the precipitate after homogenization treatment can be associated with the elastic strain energy for nucleation. It is well known that the lattice mismatch plays an important role in determining the elastic strain energy and low mismatch reduces the strain energy. As a result of the decreased strain energy, the critical energy for nucleation is accordingly reduced, leading to an increased nucleation rate (a finer distribution of the precipitate). The lattice parameters and mismatch of the L2₁ and Fe

phase of the 2% and 4% Ti alloys aged at 973 K for 100 hours have been determined using neutron diffraction technique (lattice mismatch between L2₁ and Fe matrix: 2% Ti alloy; 0.7 %, 4% Ti alloy; 1.3%, respectively) [17]. Based on the classical nucleation theory, the lower mismatch of the 2% Ti alloy can lead to a smaller critical nucleation radius, and this favors a smaller dispersion of the L2₁ precipitate than the 4% Ti alloy, as observed in Figures 1 and 6.

Microstructural evolution involves various kinetic processes (such as diffusion, domain switching, or grain-boundary migration) under a driving force; i.e., the generalized functional derivative of the total free energy with respect to field parameters, such as the concentration and other order parameters [46-48]. For our alloy system that consists of second phases and lattice defects, the total free energy includes the free energy of mixing (which dictates the phase diagram), the phase-boundary energy between the matrix and the two types of precipitate phases, and the long-range elastic energy due to the presence of lattice mismatches and lattice defects. Figure 9 illustrates the microstructural evolution of the precipitates during the aging treatments at 973 K in terms of the internal structure and morphology of the precipitates and elastic strain at the interface. To further support this schematic, the dependence of the total free energy on the precipitate size, shape, and other geometric parameters will be discussed.

The classic work by Eshelby [49] investigates the strain energy of an inclusion-matrix system. For an inclusion that has a lattice-mismatch strain with the matrix phase (in general, ε_{ij}^m), a self-stress field will be induced. For example, for a spherical inclusion with a hydrostatic lattice mismatch (so that $\varepsilon_{ij}^m = \varepsilon_m \delta_{ij}$ with the Kronecker delta, δ_{ij}), the strain energy is $E_{el} = \frac{8\pi}{3} \mu \frac{1+\nu}{1-\nu} \varepsilon_m^2 a^3$, where a is the radius of the spherical inclusion, and μ and ν are the shear modulus and Poisson's ratio, respectively. The equilibrium shape of the inclusion minimizes the following

free energy:

$$\Pi = \int_r \gamma(\mathbf{n}) dA + E_{el} \quad (1)$$

where γ is the interface energy density, and $\mathbf{n}$ gives the surface normal of the inclusion. Since the first term in Eq. (1) is quadratic in a , and the second term is cubic in a , a critical size can be defined by comparing these two terms, given by

$$a_{crt} = \frac{3\gamma_0}{2\mu\varepsilon_m^2} \left(\frac{1-\nu}{1+\nu} \right) \quad (2)$$

where γ_0 denotes the magnitude of the surface energy. When the inclusion size is smaller than a_{crt} , the surface energy dominates, and the shape of the inclusion is governed by the interface-energy anisotropy in $\gamma(\mathbf{n})$. Experimental observations of the precipitate morphology in coherent systems, such as Ni-based superalloys [26, 28, 32, 50, 51], can be qualitatively explained from the above thermodynamic formulation. For example, a lower lattice misfit between the precipitate and matrix decreases the ratio of the elastic-strain energy to interface energy. Thus, the equilibrium shape of the precipitate is governed by the interface-energy anisotropy. Usually, the degree of this type of anisotropy is weak. Hence, small precipitates are spherical, as observed in low-misfit Ni-based superalloys and NiAl-strengthened ferritic alloys [3, 11, 24, 52, 53]. In contrast, with a higher lattice misfit or a lower interface energy (i.e., equivalent to the situation, when the inclusion size is larger than a_{crt}), the elastic-strain energy dominates, which leads to the cuboidal shape of the precipitate [31, 54] in crystals with the cubic symmetry. Moreover, the elastic strain influences the spatial distribution of the coherent precipitates, such as the alignment of the interfaces and close inter-precipitate separations. In order to minimize the elastic interaction, the inclusions will align in the compliant directions or assume a cuboidal shape that resembles the dependence of the direction modulus on the crystallographic orientation [50, 55,

56]. It has been reported that the elastic-strain energy at the interface leads to an elastic interaction between coherent precipitates, which is attractive at long distances and repulsive at short distances [32, 55]. The microstructure of the SPSFA subjected to the homogenization treatment [Figure 9(a)] shows the alignment of the interface and close inter-precipitate separation, which indirectly reflects the presence of the elastic strain and interaction (the short-range repulsive force between precipitates).

Johnson and Cahn [57] further point out that when $a \gg a_{crt}$, the spherical inclusion will transform into needle-like ellipsoidal ones, which further reduces the elastic-strain energy. **In the SPSFA case, this trend is not observed because of the large precipitate size leading to the formation of misfit dislocations, as shown in Figure 9(a).** For the HPSFA case and moderate precipitate sizes, such as shown in Figures 9(b) and (d), the overall shape is still cuboidal. The elongated shape in Figure 9(e), however, is not due to the elastic interaction, as discussed by Johnson and Cahn [57]. The shape in Figure 9(e) forms because of the coarsening and agglomeration behavior of two neighboring precipitates, and the corresponding elastic interaction is relaxed because of misfit dislocations at the precipitate-matrix interface.

With the appearance of misfit dislocations, the misfit strain will be reduced accordingly, as given by $\varepsilon_m^{eff} = \varepsilon_m - b/\lambda$ where the line density of dislocations is $1/\lambda$. For simplicity, considering again a spherical inclusion, the total strain energy will be

$$E_{el} = \frac{8\pi}{3} \mu \frac{1+\nu}{1-\nu} a^3 \left(\varepsilon_m - \frac{b}{\lambda} \right)^2 + \frac{2\pi a}{\lambda} \frac{\mu a b^2}{2(1-\nu)} \left[\ln \left(\frac{4a}{\rho_0} \right) - 1 \right] \quad (3)$$

with a dislocation-core cutoff radius, ρ_0 [58]. Since $a^3 > a^2 \ln a$, a comparison between Eqs. (1) and (3) suggests that the misfit dislocation will be preferable at large inclusion sizes. **We note that misfit dislocations appear even in the homogenization treated sample of SPSFA, whereas**

HPSFA exhibits the formation of the misfit dislocations in later stage during the growth and coalescence of these precipitates. This is because the hierarchical precipitate structure in HPSFA effectively reduces the lattice mismatch between the precipitate and the matrix. Noting that $a_{crt} \propto \gamma_0/\mu\epsilon_m^2$, the critical precipitate size in HPSFA is much larger such that misfit dislocations appear in the later stage during the growth and coalescence of these precipitates. Thus SPSFA precipitates are all shown to have misfit dislocations in our case.

Due to the presence of the misfit dislocations, which releases the elastic strain, it is expected that the degree of the elastic strain for SPSFA is lower than that for HPSFA. Furthermore, the elastic strain at the semi-coherent interfaces seems to be relaxed on the aging by the formation of more misfit dislocations [Figures 6 and 8]. Once the precipitates become larger in size, the elastic strain will be further relaxed, which reduces the elastic strain/interaction, and induces the agglomeration of neighboring precipitates and the disappearance of the preferential crystallographic alignment, as illustrated in Figure 9(e).

The coherent and hierarchically-structured precipitates formed in HPSFA are sustained until aging times between 100 and 200 hours. Moreover, further aging to 100 hours results in the well-developed hierarchical precipitate structure [Figure 3(c)], as compared to the microstructure formed when aged for 10 hours [Figures 3(a)-(b)]. As mentioned above, since the hierarchical structure is effective in retaining the coherent interfaces [Figure 9(d)], the spatial distributions (the alignment of the interface and close inter-precipitate separation) are retained. Further aging to 500 hours leads to the agglomeration of the B2-NiAl phase within the L2₁-Ni₂TiAl precipitates, as illustrated in Figure 9(f). Once the primary precipitates lose the fine network hierarchy, the misfit dislocations start to form to release the elastic-strain energy, which is similar to that observed for SPSFA (Figure 8).

For high-temperature engineering materials reinforced by coherent and misfitting precipitates, the creep resistance is known to be dependent upon the elastic-strain field in the matrix created by the lattice mismatch between the matrix and precipitate [59]. Moreover, for a harder precipitate, the strain at the outer surface corresponds constantly to the lattice mismatch (ϵ_m) in both lateral directions for all particle sizes, and the larger size leads to the spatial extension of the strain field and thus the total elastic energy, which scales with a^3 , which could lead to the more enhanced elastic interaction between the precipitate and mobile dislocations. [60-62]. Therefore, in terms of the optimization of the creep resistance, it would be beneficial to have coherent precipitates with the high level of elastic strains, which can be controlled by the size of the precipitate. However, a transition from the coherent to semi-coherent interface occurs by forming misfit dislocations when the precipitate is larger than the critical size. The formation of the misfit dislocations relaxes the elastic-strain field, and reduces the elastic interactions [17, 63]. In the current study, the transition from the coherent to semi-coherent precipitates happens for both alloys, but the hierarchical structure inside the precipitate of HPSFA will effectively reduce the lattice mismatch. Therefore, the transition to misfit dislocations will be significantly delayed, as shown in Fig. 9. Hence, based on the current study, it is believed that the hierarchical precipitate could provide more possibilities to optimize microstructures and creep properties, which is ideal for the high-temperature structural applications, such as fossil-energy power plants. A systematic study of the effect of precipitate size upon the creep resistance of the present hierarchical-precipitate-strengthened ferritic alloy would be of high scientific and engineering interest.

5. Conclusions

The microstructural formation and evolution of Fe-Ni-Al-Cr-Ti alloys with different amounts of Ti contents (2 or 4 weight percent, wt. %) were investigated during aging treatments at 973 K following homogenization treatment at 1,473 K. The detailed microstructures were characterized using transmission-electron microscopy (TEM), scanning-electron microscopy (SEM), and atom-probe tomography (APT). Both alloys consist of a single $L2_1$ -Ni₂TiAl phase as a primary precipitate with different morphology, size, and inter-phase structure in the homogenization-treated state. The 2 wt. % Ti alloy is composed of a coherent and cuboidal precipitate with an average edge length of 50 nm, and narrow anti-phase boundaries are present inside the precipitate. In contrast, the addition of 4% Ti content leads to a semi-coherent and irregular/polygonal-shaped precipitate with a size range of 130 ~ 160 nm, and the precipitate is observed to be decorated with misfit dislocations at the interfaces. In the subsequent aging treatments at 973 K, both alloys exhibit distinct microstructural evolutions in terms of the internal structure, interface structure, and spatial arrangements of the precipitates (the alignment of the interface and close inter-separation of the precipitates), which are closely associated with the coherency strain, and can be summarized as follows.

1. Fe-Ni-Al-Cr-Ti alloy with 4 wt. % Ti

[Single-precipitate-strengthened ferritic alloy (SPSFA)]

- All the microstructures aged at 973 K only contain a semi-coherent single $L2_1$ -Ni₂TiAl precipitate with a high density of misfit dislocations and no B2-NiAl phase inside the $L2_1$ -precipitate is observed (single precipitate structure).

- During aging at 973 K, the primary $L2_1$ precipitates gradually coarsen and changes their morphology from polygonal to spherical.
- The spatial arrangements gradually disappear as the precipitates coarsen.

2. Fe-Ni-Al-Cr-Ti alloy with 2 wt. % Ti

[Hierarchical-precipitate-strengthened ferritic alloy (HPSFA)]

- The early stage of aging treatments (≤ 100 hours) establishes a fine network of a B2-NiAl phase along the anti-phase boundaries within the primary $L2_1$ -Ni₂TiAl precipitate (hierarchical precipitate structure).
- The hierarchical precipitate retains the coherent interfaces and the spatial arrangements.
- Longer aging treatments (> 100 hours) lead to the disappearance of the hierarchical structure and coalescence of the B2 phase within the precipitate.
- The disappearance of the hierarchical structure is accompanied with the occurrence of the coalescence of the primary precipitates and transition from the coherent to semi-coherent interfaces.

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Table Legends

Table 1   **Chemical compositions of bulk alloys.** Nominal and analyzed compositions (in wt. %) of bulk materials of HPSFA and SPSFA.

Table 2.   **APT compositions of HPSFA and SPSFA.** Chemical compositions (in at. %) of constitutive phases in the HPSFA SPSFA after homogenization and aging treatment, followed by air cooling, determined using APT and TEM-EDS. The uncertainties for the EDS results are represented by the standard deviation from the measurement series, while those of APT represent the statistical counting scatter [64].

Figure Legends

Figure 1. TEM characterization of HPSFA in the homogenization-treated state.

Microstructure of the 2-wt. %-Ti-alloy (HPSFA) subjected to the homogenization treatment at 1,473 K for 0.5 hour, followed by air cooling. (a) Selected-area-electron-diffraction pattern (SADP) acquired along the (101) zone axis, (b)-(d) dark-field (DF) transmission-electron microscopy (TEM) images acquired using (b)-(c) the $\langle 111 \rangle$ reflection and (d) the $\langle 222 \rangle$ reflection.

Figure 2. APT characterization of HPSFA in the homogenization-treated state.

APT reconstructions of the homogenization-treated 2-wt. %-Ti-alloy (HPSFA). (a) Iso-concentration surface of 5-at.-% Ni (green) and 5-at.-% Ti (yellow), (b) An one-dimension line profile (1-DLP) along the red arrow in (a), and atom maps of (c) Al, (d) Ni, (e) Fe, and (f) Ti, which are acquired from the red square region in (a).

Figure 3. TEM characterization of HPSFA after aging treatments.

The microstructure of HPSFA aged at 973 K for (a)-(b) 10 hours and (c)-(d) 100 hours. [(a)-(c)] DF-TEM images are acquired along the [100] zone axis using the $\langle 002 \rangle$ reflection, and (d) bright-field (BF) TEM image.

Figure 4. SEM and TEM characterization of HPSFA after longer aging treatments.

SEM images of HPSFA subjected to the homogenization treatment at 1,473 K for 0.5 hour, followed by aging at 973 K for (a) 200 hours, (b) 300 hours, and (c) 500 hours. (d) BF-TEM, (e) and (f) DF-TEM images acquired at the same region for HPSFA subjected to the aging treatment at 973 K for 500 hours. (e) and (f) DF-TEM images

acquired using the $\langle 111 \rangle$ and $\langle 222 \rangle$ reflections, respectively. White dotted lines indicate the irregular morphology of the precipitate, and white and red arrows denote the B2 and L2₁ phases in (e) and (f), respectively.

Figure 5. TEM and APT characterization of HPSFA aged for 500 hours. (a)-(b) DF-TEM images and (c) Two iso-concentration surfaces of 10 at. % Ti (yellow) and 10 at. % Ni (green). The DF-TEM images (a) and (b) were acquired for the same region along the (101) zone axis using the $\langle 111 \rangle$ and $\langle 222 \rangle$ reflections, respectively. (d) An iso-concentration surface of 7.6 at. % Ni.

Figure 6. SEM and TEM characterization of SPSFA in the homogenization-treated state. (a) SEM image, (b) SADP acquired along the (101) zone axis, (c) DF-TEM image acquired using the $\langle 111 \rangle$ reflection, and (d) BF-TEM image for SPSFA homogenization-treated at 1,473 K for 0.5 hour, followed by air cooling.

Figure 7. SEM characterization of SPSFA after the aging treatments. SEM images of SPSFA subjected to the homogenization treatment at 1,473 K for 0.5 hour, followed by aging at 973 K for (a) 1 hour, (b) 10 hours, (c) 50 hours, and (d) 100 hours.

Figure 8. TEM characterization of SPSFA after aging treatments. (a) and (c) DF-TEM and (b) and (d) BF-TEM images of homogenization-treated HPSFA at 1,473 K for 0.5 hour, followed by aging at 973 K for 1 hour (a)-(b), and 100 hours (c)-(d). DF-TEM images in (a) and (c) acquired along the $\langle 101 \rangle$ zone axis using the $\langle 111 \rangle$ reflection.

Figure 9. Schematic illustration of microstructural evolution. Schematic illustrations showing the microstructural evolution of SPSFA [(a), (c), and (e)] and HPSFA [(b),

(d), and (f)] during aging treatments: (a)-(b) homogenization-treated, (c)-(d) short-term aging-treated, (e)-(f) long-term aging-treated conditions. The gray and orange colors of the interface lines between the Fe matrix and precipitate phases represent the semi-coherent and coherent states, respectively. The thickness of the interface lines indicates the magnitude of the elastic strain.

2% Ti alloy, Solution treated at 1,473 K

(a)

(b)

(c)

(d)

2% Ti alloy, Solution treated at 1,473 K

2% Ti alloy, aged at 973 K

10 hr

10 hr

(a)

(b)

100 hr

100 hr

(c)

(d)

2% Ti alloy, aged at 973 K

(a)

(b)

(c)

(d)

(e)

(f)

2% Ti alloy, aged at 973 K for 500 hrs

4% Ti alloy, solution-treated at 1,473 K

(a)

(b)

(c)

(d)

4% Ti alloy, aged at 973 K

(a)

(b)

(c)

(d)

4% Ti alloy, aged at 973 K

1 hr

(a)

1 hr

(b)

100 hr

(c)

100 hr

(d)

SPSFA (4% Ti)

Fe-6.5Al-10Cr-10Ni-4Ti-3.4Mo-0.25Zr-
0.005B (wt. %)

Single-precipitate-
strengthened ferritic alloy

(a)

HPSFA (2% Ti)

Fe-6.5Al-10Cr-10Ni-2Ti-3.4Mo-0.25Zr-
0.005B (wt. %)

Hierachical-precipitate-
strengthened ferritic alloy

(b)

(c)

(d)

(e)

(f)

Primary Precipitate Evolution During Thermal Treatment at 973 K

Hierarchical-Precipitate-Strengthened Ferritic Alloy (HPSFA)

Single-Precipitate-Strengthened Ferritic Alloy (SPSFA)

Secondary Precipitate

Table 1

Alloy		Fe	Al	Cr	Ni	Ti	Mo	Zr	B
HPSFA	Nominal	Bal.	6.5	10	10	2	3.4	0.25	0.005
	Analysis	Bal.	6.56	10.04	9.92	2.01	3.23	0.28	0.004
SPSFA	Nominal	Bal.	6.5	10	10	4	3.4	0.25	0.005
	Analysis	Bal.	6.60	10.08	10.09	4.08	3.41	0.25	0.006

Table 2

Alloy	Heat-treatment	Phase	Al	Fe	Ni	Ti	Mo	Cr
2% Ti	H [@]	L2 ₁	33.95±0.20	18.26±0.20	36.81±0.23	9.75±0.15	0.37±0.01	0.65±0.04
		Fe	6.34±0.06	77.20±0.18	1.34±0.04	0.33±0.02	2.26±0.04	12.49±0.12
		SP [*]	36.84 ± 0.91	13.34 ± 0.77	42.45 ± 1.08	6.90 ± 0.58	0.09 ± 0.05	0.35 ± 0.13
	100 ^h	L2 ₁	29.25±0.23	18.05±0.18	36.23±0.20	15.39±0.18	0.46±0.03	0.59±0.04
		B2	38.20±0.03	14.03±0.02	42.82±0.03	4.42±0.01	0.07±0.01	0.43±0.01
		Fe	7.096±0.018	75.85±0.03	1.54±0.01	0.40±0.01	2.28±0.01	12.80±0.02
		SP [*]	34.44±1.109	17.78±0.93	41.58±1.26	3.10±0.43	0.69±0.24	2.37±0.37
	500 ^h	L2 ₁	30.46±0.37	18.33±0.34	35.25±0.41	14.71±0.31	0.40±0.02	0.55±0.06
		B2	39.88±1.31	14.16±1.00	41.53±1.43	3.59±0.53	0.30±0.09	0.49±0.19
		Fe	6.94±0.07	76.00±0.17	2.16±0.05	0.43±0.02	1.65±0.03	12.78±0.12
		SP [*]	25.61 ± 1.72	42.83 ± 2.26	22.57 ± 1.85	3.09 ± 0.79	0.43 ± 0.06	6.51 ± 1.08
4% Ti	H [@]	L2 ₁	19.5±2.0	27.9±1.8	34.6±0.9	15.3±0.9	0.3±0.1	0.8±0.1
		Fe	6.3±1.5	77.7±2.1	5.0±0.9	1.6±0.3	2.5±0.3	6.5±2.2

	100 ^h	L2 ₁	25.0±2.0	22.9±3.7	33.8±1.9	16.5±0.9	0.1±0.1	1.0±0.7
		Fe	7.0±0.4	74.9±0.5	2.1±0.2	1.0±0.1	2.0±0.2	12.8±0.2

- H[@]: Homogenization at 1,473K.
- 100^h and 500^h: Aging treatment at 973 K for 100 and 500 hours, respectively.
- SP^{*}: Secondary precipitate.