Microstructural Characteristics of a Ni₂TiAl-Precipitate-Strengthened

Ferritic Alloy

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Abstract

The microstructure of a Ni_2TiAl -strengthened ferritic alloy at room and elevated temperatures is characterized, using scanning/transmission-electron microscopy (SEM/TEM) and neutron-diffraction (ND). The SEM/TEM results revealed that this alloy contains a L_{21} -type Ni_2TiAl precipitate distributed in the Fe matrix, and the L_{21} precipitate is decorated with a high density of interfacial dislocations (semi-coherent interfaces). The TEM energy-dispersive X-ray spectroscopy (EDS) was used to derive the compositions and volume fractions of the precipitate and matrix phases, using the lever rule. The in-situ ND was conducted to investigate the evolution of the microstructures, such as lattice parameters and thermal-expansion coefficients of the Fe and L_{21} phases, and the composition and volume fraction of the precipitate, during heating to 700 °C. These in-situ ND studies revealed an increase in the intensity ratio of the $(220)_{\text{L}_{21}}$ to $(110)_{\text{Fe}}$ and the non-linear evolution of the lattice misfit between the precipitate and matrix during heating to 700 °C, which suggests a possible variation in the composition and volume fraction of the precipitate around 700 °C.

Keywords: Heusler phases; Neutron diffraction; Precipitation hardening; Transmission electron microscopy

Introduction

The NiAl-type precipitate-strengthened ferritic alloys have received considerable attention, due to their promising creep and oxidation resistance[1-5]. The body-centered-cubic (bcc) Fe matrix is reinforced by the coherent B2-ordered NiAl-type precipitate, which provides the possible strengthening and microstructural stability during creep deformation at elevated temperatures, as achieved in γ/γ' Ni-based superalloys[6-10]. The coherent interface with a small lattice mismatch between the Fe and B2 phases has been suggested to provide an excellent resistance to the coarsening behavior of the NiAl-type precipitate during the long-term exposure to elevated temperatures [11]. Investigations of the creep resistance on these alloys have been conducted in the temperature range from 600 ~ 750 °C [1, 12, 5], and revealed that these alloys have the limited creep resistance at temperatures higher than 700 °C [13]. This limited creep resistance of the NiAl-type precipitate-strengthened alloys is believed to be due to the extensive interfacial diffusion along the Fe/B2 interface [14, 10].

Figure 1. Creep curves: A plot of the applied stress versus time to rupture at 700°C on the log-log basis for the Ni₂TiAl-strengthened ferritic alloy (designated SPSFA)[15]. For comparison, the NiAl-strengthened ferritic alloy (FBB8), and commercial ferritic steels (T91, P92, T122, P122, and 12Cr) are included[16-18, 12, 19].

Recently, we have developed a new ferritic alloy consisting of a L2₁-Ni₂TiAl type precipitate in the Fe matrix [15]. This alloy was designed by adding 4.5 atomic percent (at. %) Ti into a previously-studied NiAl-strengthened ferritic alloy (Fe-12.7Al-10.2Cr-9.0Ni-1.9Mo-0.1Zr-0.024B at.%, denoted as FBB8 in the previous study) [13], in order to form a L2₁-Ni₂TiAl phase as a strengthening precipitate, which has intrinsically superior high-temperature properties [20]. The single-Ni₂TiAl-precipitate-strengthened ferritic alloy (denoted as SPSFA in this study)

revealed the significant improvement of the creep resistance at 700 °C [15], as compared to the FBB8 [21] and conventional ferritic steels [22, 16-18, 23-25, 19]. A plot of applied stress vs. time to rupture at 700 °C is presented in Figure 1 for the SPSFA[15], FBB8 (a NiAl-strengthened ferritic alloy)[12], and conventional ferritic steels (T91: Fe-8.7Cr, P92: Fe-9.09Cr-1.83W, T122: Fe-10.65Cr-1.87W, P122: Fe-10.15Cr-1.94W, and 12Cr: Fe-12.1Cr-1.82W in weight percent)[16-19]. This study reported that the reduced diffusion process along the L2₁-precipitate/Fe matrix interface plays an important role in the improved creep resistance[15]. However, a systematic microstructural characterization of the strengthening precipitate is necessary to obtain an in-depth understanding of the creep mechanism and further optimization in the creep properties, such as the temperature dependence of the lattice misfit between the matrix and precipitate, and the composition (volume fraction) variation of the precipitate at elevated temperatures, which are closely related to the creep-deformation mechanisms [26-28]. In the present study, the microstructure of the recently-developed Ni₂TiAl-strengthened ferritic alloy at room and elevated temperatures was characterized with the combined use of scanning/transmission-electron microscopy (SEM/TEM) and in-situ neutron diffraction (ND).

Methods

The model alloy has a nominal composition of Fe-12.6Al-10.1Cr-8.9Ni-4.5Ti-1.9Mo-0.1Zr-0.024B at. %. A rod ingot of the model alloy weighing 2 Kg with a diameter of 54.8 mm was prepared by Sophisticated Alloys, Inc., using their vacuum-induction-melting facility. Hot isostatic pressing (HIP) was applied on the ingot at 1,200 °C and 100 MPa for 4 hours. Chemical analyses were conducted on the ingot to obtain the composition. The alloy was homogenized at 1,200°C for 30 minutes, followed by air cooling and, then, aged at 700°C for 100 hours. 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 Image-J software [29] to obtain the size and the volume fraction of the precipitate, and the averaged value was estimated from about 400 particles. Transmission-electron-microscope (TEM) samples were prepared in a Zeiss Auriga 40 equipped with a dual electron and focused-ion beam (FIB). A membrane of $12 \times 6 \times 1 \mu\text{m}^3$ was cut from a heat-treated bulk sample with 30 keV Ga ions. The membrane was transferred to a Cu grid and thinned down to a thickness of about 100 nm in the FIB, followed by final polishing to remove the damaged surface and oxide layer with 5-keV-Ga ions. TEM observations were conducted, using a Zeiss Libra 200 MC TEM/STEM equipped with the energy-dispersive X-ray spectroscopy (EDS) detector, a Bruker xFlash 5030. The TEM images were taken 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 quantification [30].

The in-situ ND experiments were carried out on the Spectrometer for Materials Research at Temperature and Stress (SMARTS) diffractometer of the Los Alamos Neutron Science Center (LANSCE) facility located at the Los Alamos National Laboratory [31]. The ND instrument

utilizes time-of-flight (TOF) measurements, in which the incident beam is polychromatic with a range of wave lengths, which allows for the ND measurements with a diffraction pattern covering a wide range of dspacings without the rotation of samples or detectors. The ND measurements were conducted at room temperature, 572, and 700 °C. The samples were measured by ND at elevated temperatures after the specimen saturated within ± 1 °C of the target temperature, and the sample displacement was equilibrated. The ND data were collected for 15 minutes.

Figure 2. Representative neutron-diffraction pattern of SPSFA measured at room temperature without loading: An enlarged pattern in the inset clearly exhibits well-separated $(110)_{\text{Fe}}$ and $(220)_{\text{L21}}$ peaks. The red cross represents the measured data. The green curve is the

fitted profile, using the GeneralStructure Analysis System(GSAS) Rietveld analysis[32]. The pink curve presents the difference between the fitted profile and measured data. The peak positions of the Fe and L2₁ phases are marked as black squares and red triangles, respectively.

In order to obtain the thermal lattice strain during heating, a whole-pattern Rietveld refinement was performed to fit the entire ND spectrum, employing the GeneralStructure Analysis System (GSAS) program developed at the Los Alamos National Laboratory[32]. Figure 2 presents a representative ND pattern measured at room temperature with the refined profile (green curve) by the Rietveld whole-peak fitting using GSAS. The average phase strain is calculated, using the following formula

$$\varepsilon = (a - a_0)/a_0 \quad (1)$$

where a is the lattice parameter of a given phase measured during heating, and a_0 is the corresponding lattice parameter at room temperature. Moreover, single-peak fitting of the (110)_{Fe} and (220)_{L21} peaks(the inset in Figure 2), using the RAWPLOT utility of the GSAS [32], was conducted to obtain the intensity ratio of I_{L21} to I_{Fe} .

Results

Figure 3. Microstructure of SPSFA: (a) Secondary-electron microscopy (SEM), (b) aselected-area-diffraction-pattern (SADP)of the $[110]$ zone axis, and (c) dark-field transmission-electron microscopy (DF-TEM) imagesof the Ni_2TiAl -strengthened ferritic alloyaged at 700 °C for 100

hours after the solution treatment at 1,200 °C for 0.5 hour, acquired along the [110] zone axis using the $\langle 111 \rangle$ superlattice reflection in (b).

Figure 3 shows the SEM and dark-field TEM images of the Ni₂TiAl-strengthened ferritic alloyed at 700 °C for 100 hours after the solution treatment at 1,200 °C for 0.5 hour. The SEM image in Figure 3(a) exhibits elliptical precipitates homogeneously distributed in the Fe matrix with an average size of $257.9 \pm 73.7 \text{ nm}$ and volume fraction of $22.2 \pm 2.2 \%$. Note that the precipitate shape is elliptical, and, thus, the average size is derived from an equivalent circle diameter. Figure 3(b) shows a selected-area-diffraction-pattern of the [110] zone, which reveals the L2₁ structure. This pattern contains two types of super-lattice reflections; $\langle 111 \rangle$ and $\langle 131 \rangle$ unique to the L2₁ structure, and $\langle 222 \rangle$ and $\langle 020 \rangle$ common to both the L2₁ and B2 structures [33]. The DF-TEM taken along the [110] zone axis, using the $\langle 111 \rangle$ super-lattice reflection, reveals the L2₁-type precipitate with misfit dislocations at the matrix/precipitate interface, as denoted by blue arrows in Figure 3(c). The DF-TEM images using the $\langle 222 \rangle$ or $\langle 020 \rangle$ reflections (not shown) revealed that there is no B2-type phase formed in the precipitate, as reported in Ref. [15]. The presence of the misfit dislocation indicates a relatively-larger difference in the lattice parameters between the Fe matrix and L2₁-type precipitate, and semi-coherent interface [15], as compared to the FBB8 [21].

Figure 4. Detailed structures of the Ni_2TiAl precipitate: (a) A high-angle annual dark-field (HAADF) scanning-transmission-electron micrograph (STEM) of the Ni_2TiAl -strengthened ferritic alloy, taken along the $[110]$ zone axis, and (b) an energy-dispersive X-ray spectroscopy (EDS) line profile of constitutive elements along the red line in Figure 4(a).

Moreover, nano-scaled zones are often observed inside the L2₁precipitate[15], as indicated by white arrows in Figures 3(a) and (c). Energy-dispersive X-ray (EDS) line scanning was conducted in order to characterize the nano-scaled zone. Figure 4 displays (a) a high-angle annual dark-field (HAADF) scanning transmission-electron micrograph (STEM) and (b) a EDS line profile of constitutive elements. The EDS line scanning was carried out along the red line in the Figure 4(a). The inclusion in the precipitate is enriched in Fe and Cr, while the amounts of other elements, such as Ni, Al, and Ti, are significantly reduced, as observed in Figure 4(b). These results support that the inclusion inside the precipitate is the Fe phase [15]. EDS measurements were conducted to derive the compositions of the Fe matrix and L2₁ precipitate [15]. Due to the presence of the Fe-rich inclusion inside the L2₁ precipitate, care was taken to avoid the Fe-rich inclusion for the EDS measurements on the L2₁ precipitate. The compositions of the bulk sample, Fe matrix, and L2₁-type precipitate are summarized in Table 1.

Table 1. Chemical composition: Chemical compositions (in atomic percent) of the bulk sample, derived from chemical analyses, and the constitutive phases in the Ni₂TiAl-strengthened ferritic alloy, obtained from the transmission-electron-microscopy energy-dispersive X-ray spectroscopy (TEM-EDS) analysis [15]. The uncertainties for the EDS results are represented by the standard deviation from the measurement series.

Phase	Fe	Cr	Al	Ni	Ti	Mo	Zr
Bulk	61.6	10.1	12.8	8.9	4.5	1.9	0.1
Fe	74.9 ± 0.5	12.8 ± 0.2	7.0 ± 0.4	2.1 ± 0.2	1.0 ± 0.1	2.0 ± 0.2	0.2 ± 0.1

L2 ₁	22.9 ± 3.7	1.0 ± 0.7	25.0 ± 2.0	33.8 ± 1.9	16.5 ± 0.9	0.1 ± 0.1	0.5 ± 0.3

The L2₁-Ni₂TiAl phase has an off-stoichiometric composition with an Al/Ti ratio of 5/3 rather than 1/1. The composition of the L2₁-Ni₂TiAl phase was derived from calculating structure factors by Liebscher et al., which demonstrates the formation of the off-stoichiometric L2₁-Ni₂TiAl phase with an approximate composition of (Ni₃₅Fe₁₅)(Al₃₇Ti₁₃) in a Fe-15.4Al-12.1Cr-1.0Mo-16.0Ni-4.3Ti (atomic percent, at. %) alloy [33]. Assuming that the Ni sublattice is only occupied by Ni and Fe in the Ni₂TiAl phase [33], this process gives rise to a composition of (Ni₃₅Fe₂₃)(Al₂₅Ti₁₇) (at. %) in the L2₁ phase in the present study. In this investigation, the L2₁-type precipitate has a higher amount of Fe and the lower amount of Al than a previous report [33]. The difference in the L2₁ composition reflects the suggestion that the Fe atoms not only occupy the Ni sublattice but also the Ti sublattice, which leads to an approximate composition of (Ni₃₅Fe₁₅)(Al₂₅)(Ti₁₇Fe₈) (at. %) of the L2₁ phase in this study.

Figure 5. Volume fraction calculation of the Ni_2TiAl precipitate: A plot of $(C_{bulk} - C_{matrix})$ vs. $(C_{L21} - C_{matrix})$ to calculate the volume fraction of the $L2_1$ -type precipitate, based on the transmission-electron-microscopy energy-dispersive X-ray spectroscopy (TEM-EDS) analysis in Table 1.

The precipitate volume fraction (V_p) can be estimated using the lever rule;

$$V_p = \frac{C_{bulk} - C_{matrix}}{C_{L21} - C_{matrix}} \quad (2)$$

where C_{bulk} , C_{matrix} , and C_{L21} are the compositions of the bulk alloy, Fe matrix, and $L2_1$ -type precipitate, respectively. Figure 5 shows a plot of $(C_{bulk} - C_{matrix})$ vs. $(C_{L21} - C_{matrix})$ for 6 elements (Fe, Cr, Al, Ni, Ti, and Mo), which gives rise to a reasonable linear fit. The volume fraction of

the L2₁ phase is determined from the slope and found to be about $24.8 \pm 2.1\%$, which is in reasonable agreement with the SEM-image analysis (22.2 %) in Fig. 3(a).

Figure 6. Evolution of the lattice parameters during heating: Plots of (a) lattice parameters and (b) thermallattice strains of the Fe matrix and Ni₂TiAl precipitate as a function of temperature.

Table 2. Lattice parameter and misfit: Average lattice parameters of the Fe and L₂₁ phases and corresponding misfits as a function of temperature.

Temperature (°C)	Rietveld refinement		
	Fe (Å)	L ₂₁ (Å)	Misfit (%)
23	2.88643 ± 0.00002	5.85376 ± 0.00023	1.391 ± 0.288
572	2.90663 ± 0.00003	5.89786 ± 0.00027	1.445 ± 0.326
700	2.91322 ± 0.00003	5.91085 ± 0.00024	1.436 ± 0.293

The Rietveld-refinement technique was used to obtain average lattice parameters of the Fe and L₂₁-type phases, using the GSAS code developed by Larson and Von Dreele[32] at the Los Alamos Neutron Science Center (LANSCE). The average lattice parameters of the Fe matrix and L₂₁-type precipitate at room temperature are 2.8864 and 5.8537 Å, respectively, and gradually increase with temperature, as shown in Figure 6(a). The lattice mismatch between the lattice parameters of the Fe and L₂₁ phases is calculated, using the following equation;

$$\delta = \frac{2(a_{L21} - a_{Fe})}{(a_{L21} + a_{Fe})} \quad (3)$$

where δ is the lattice misfit, and a_{Fe} and a_{L21} are the lattice parameters of the Fe and L₂₁ phases, respectively. Since the L₂₁ structure consists of eight sub-lattices of a B2 structure[20], the lattice

parameter of the Fe was multiplied by a factor of two for the corresponding structural comparison[15]. The average lattice parameters of the Fe and L2₁ phases, and corresponding lattice misfits at room and elevated temperatures are summarized in Table 2. The lattice misfit at room temperature is 1.39 %, and no clear temperature dependence of the lattice misfit is observed. The thermal strains of both phases were estimated, using Equation (1), and Figure 6(b) shows the thermal strains of the Fe and L2₁ phases as a function of temperature. Thermal strains determined, using ND, have been employed to obtain the coefficients of thermal expansion (CTEs) of constitutive phases in composite materials [34, 2]. Similarly, the average CTEs were determined from the slopes of linear fits to the data in Figure 6(b) and found to be $1.34 \times 10^{-5} / ^\circ\text{C}$ and $1.42 \times 10^{-5} / ^\circ\text{C}$ for the Fe and Ni₂TiAl phases, respectively. The reported CTE of α Fe is $1.18 \times 10^{-5} / ^\circ\text{C}$ [35], which is slightly lower than the CTE of the Fe matrix in the current alloy. The slight difference of CTEs could be caused by the presence of 7 at. % of Al in the Fe matrix, which has a higher CTE of $2.31 \times 10^{-5} / ^\circ\text{C}$ than Fe[35]. The measured CTE of the Fe matrix is still in good agreement with the reported CTEs of different steels in the range from 1.1 to $1.7 \times 10^{-5} / ^\circ\text{C}$ [35]. In contrast, there is no available experimental value of the CTE of the Ni₂TiAl with a high amount of Fe elements. An experimental CTE of a Fe₂TiAl alloy with the L2₁ structure has been determined by neutron diffraction (ND) [36], and was found to be $1.45 \times 10^{-5} / ^\circ\text{C}$, which is close to that of the Ni₂TiAl phase in the current alloy. The CTEs of the Fe matrix and Ni₂TiAl phases, acquired from the ND results in the present study, are listed in Table 3.

Table 3. Thermal expansion: Coefficients of thermal expansion (CTEs) of the Fe and Ni₂TiAl phases in the Ni₂TiAl-strengthened ferritic alloy. For comparison, the CTEs of the Fe and Fe₂TiAl phases from the previous reports are included.

Phase	CTE ($\times 10^{-5} \text{ }^{\circ}\text{C}^{-1}$)	
Fe	1.34 ± 0.08	Present study
Fe	1.18	[35]
Ni ₂ TiAl	1.42 ± 0.04	Present study
Fe ₂ TiAl	1.45	[36]

Discussion

The volume fraction of the L_{21} precipitate derived from the EDS composition analysis (24.8 %) is in reasonable agreement with the value obtained from the SEM-image analysis (22.2 %) [15]. The EDS measurements reveal that the L_{21} phase has an off-stoichiometric composition with the enrichment of Fe, as observed in the previous report [33]. However, the presence of the nano-sized Fe-rich inclusion inside the precipitate could contribute to the EDS measurements on the composition of the L_{21} phase. For example, the high amounts of Fe and Cr in the precipitate indicate the possible effect of the Fe-rich inclusion on the EDS measurement. To verify this hypothesis, the neutron-intensity ratio from the matrix and precipitate was used.

Figure 7. Single-peak-fitting (SPF) result on a partially-overlapped $(110)_{Fe}/(220)_{L21}$ peaks at room temperature: The redcross represents the measured data. The green curve is the fitted

profile, using the GSAS[32]. The pink curve presents the difference between the fitted profile and measured data.

A direct separation of the fundamental peaks can be made, using GSAS single-peak fitting (SPF) [32], due to the reasonable intensity of the L2₁ phase and well-separated fundamental reflections, as shown in Fig. 2. In this study, fundamental reflections (110)_{Fe}/(220)_{L2₁} were selected to determine the intensity ratio, as shown in Figure 7. The intensity ratio of L2₁ to Fe can be determined from the structure factor and volume fraction, using the following equations[37]:

$$\frac{I_{hkl}^{L21}}{I_{hkl}^{Fe}} = \frac{(F_{hkl}^{L21})^2}{(F_{hkl}^{Fe})^2} \frac{v_f}{(1-v_f)} \quad (4)$$

$$F_{hkl}^{Fe} = b_{co}e^{2\pi i(0h+0k+0l)} + b_{ce}e^{2\pi i(0.5h+0.5k+0.5l)} \quad (5)$$

$$F_{hkl}^{L21} = b_{co}e^{2\pi i(0h+0k+0l)} + b_{ce}e^{2\pi i(0.5h+0.5k+0.5l)} + b_{h.ce}e^{2\pi i(0.25h+0.25k+0.25l)} \quad (6)$$

where I_{hkl}^{L21} and I_{hkl}^{Fe} are the intensities of the (hkl) peaks in the L2₁ and Fe phases, respectively, F_{hkl}^{L21} and F_{hkl}^{Fe} are the structure factors of the (hkl) peaks in the L2₁ and Fe phases, respectively, b_{co} , b_{ce} , and $b_{h.ce}$ are the scattering lengths of the corner, center, and half center atoms, respectively, and V_f is the volume fraction of the L2₁-type precipitate. The values of scattering lengths are functions of the actual compositions of phases, expressed by:

$$b_{co,ce}^{Fe} = \sum c_{i,co,ce}^{Fe} b_i \quad (7)$$

$$b_{co,ce,h.ce}^{L21} = \sum c_{i,co,ce,h.ce}^{L21} b_i \quad (8)$$

where $c_{i,co,ce}^{Fe}$ and $c_{i,co,ce,h.ce}^{L21}$ are the atomic concentrations of the element, i, in the Fe and L2₁ phases, respectively, b_i is the scattering length of neutrons by the atom of the element, i, which can be obtained from the literature [38]. The EDS analysis revealed the considerable amount of

Fe dissolved in the L2₁-type precipitate, which alters the structure factor, and, thus, intensity. Assuming that 15 at. % of Fe in the L2₁-type precipitate occupies on the Ni sublattice site, while the rest on the Ti sublattice site, the structure factors were calculated for four (Ni₃₅Fe₁₅)(Al₂₅)(Ti_{25-x}Fe_x) (at. %) compounds with x = 0 ~ 7.5 using Eqs. (5) ~ (8), and the resulting volume fractions were estimated employing Eq. (4). The compositions, corresponding ratios of structure factors, and volume fractions of the L2₁ phase are summarized in Table 4.

Table 4. Composition estimation by structure factor: Ratio of the square of the structure factor (F) and intensity (I) between different L2₁ compounds with varying Ti and Fe contents, and the resulting volume fraction (V_f) of the L2₁ phase.

Composition (at. %)	$(F_{L21})^2/(F_{Fe})^2$	I_{L21}/I_{Fe}	$V_f(\%)$
	$(220)_{L21}/(110)_{Fe}$		
(Ni ₃₅ Fe ₁₅)(Al ₂₅)(Ti _{17.5} Fe _{7.5})	0.738 ±	0.178±	19.471 ±
	9.3×10^{-5}	0.009	0.007
(Ni ₃₅ Fe ₁₅)(Al ₂₅)(Ti ₂₀ Fe ₅)	0.608 ±	0.178±	22.698 ±
	9.3×10^{-5}	0.009	0.011
(Ni ₃₅ Fe ₁₅)(Al ₂₅)(Ti _{22.5} Fe _{2.5})	0.490 ±	0.178±	26.693 ±
	9.3×10^{-5}	0.009	0.015
(Ni ₃₅ Fe ₁₅)(Al ₂₅)(Ti ₂₅)	0.385 ±	0.178±	31.668 ±

	9.3×10^{-5}	0.009	0.023

The volume fraction of the L2₁ phase determined from the SEM-image analysis (22.2 %) is in better agreement with the value (22.7 %) calculated, based on an approximate composition of (Ni₃₅Fe₁₅)(Al₂₅)(Ti₂₀Fe₅) (at. %) in Table 4, which supports that the L2₁-Ni₂TiAl phase is enriched in Fe. Based on the composition of the L2₁-Ni₂TiAl phase [(Ni₃₅Fe₁₅)(Al₂₅)(Ti₂₀Fe₅)] (at. %), the volume fraction of the L2₁-Ni₂TiAl phase was recalculated, using Equation (2), and found to be $23.5 \pm 2.1\%$, which is in better agreement with the volume fractions derived from the SEM-image (22.2 %) and ND (22.7 %) analyses. Assuming that the compositions of the Fe and L2₁ phases do not vary at higher temperatures, the volume fractions are calculated at 572 °C and 700 °C, and are given in Table 5. The calculated volume fraction at 572 °C remains fairly similar to that at room temperature, but increases to 23.4 % at 700 °C. In general, it is known that as the temperature increases, the volume fraction of precipitates decreases. Thus, the increase in the volume fraction is unlikely to happen at 700 °C. This trend reflects that the compositions of the matrix and L2₁ phases could vary at 700 °C. The intensity ratio of L2₁ to Fe (I_{L21}/I_{Fe}) in Table 5 remains fairly constant (0.178 ~ 0.179) at room temperature and 572 °C. However, the intensity ratio increases to 0.184 at 700 °C. With a decrease in the volume fraction at high temperatures, it would be expected that the intensity ratio decreases accordingly (Equation 4). However, structure factors can also contribute to the intensity magnitude, which depends on the compositions of the constitutive phases (Equations 5 ~ 8). First, more elements from the precipitate, such as Al, Ni, and Ti, could be dissolved into the matrix, which results in a reduction of the intensity of the Fe matrix. This is because Fe has the higher solubility of Al, Ni, and Ti at high temperatures [39], and all these solute elements have smaller scattering lengths than Fe [38]. Second, since the

TEM and ND analyses reveal the enrichment of Fe in the L2₁-type phase, it can be inferred that more amounts of Fe could be dissolved into the L2₁ precipitate at 700 °C, which results in an increase in the intensity of the L2₁ phase.

Table 5. Volume fraction calculation: Intensity ratio of (220)_{L21}/(110)_{Fe} as a function of temperature with a composition of (Ni₃₅Fe₁₅)(Al₂₅)(Ti₂₀Fe₅) of the L2₁ phase, and the resulting volume fraction (V_f) of the L2₁ phase.

Phase	Room temperature		572 °C		700 °C	
	Neutron intensities	I_{L21}/I_{Fe}	Neutron intensities	I_{L21}/I_{Fe}	Neutron intensities	I_{L21}/I_{Fe}
(220) _{L21} /(110) _{Fe}						
Fe	188.2 ± 0.5	0.178 ± 0.009	128.0 ± 0.3	0.179 ± 0.009	151.7 ± 0.4	0.184 ± 0.010
L2 ₁	33.6 ± 0.3		22.9 ± 0.2		28.3 ± 0.3	
V_f	22.69 ± 0.03		22.73 ±0.03		23.47 ±0.05	

The difference in the CTEs between constitutive phases contributes to the temperature dependence of the lattice misfit [28]. The linear CTE of the L2₁ phase is slightly higher than that of the Fe matrix [Figure 6(b)], and, thus, the slight increase of the misfit at 572 °C is observed (Table 2). However, the misfit at 700 °C is smaller than that at 572 °C (Table 2). Another feasible influence on the temperature dependence of the misfit is the compositional variation of

the two phases. As the temperature increases, the compositional variation starts to occur, which is supported by the increase in the intensity ratio of L2₁ to Fe (I_{L21}/I_{Fe}) (Table 5). As mentioned above, it is believed that the Fe matrix has the higher solubility of Al, Ni, and Ti, while the L2₁ precipitate contains a greater amount of Fe at 700 °C, as compared to the room and 573 °C. Since the atomic size of Fe is smaller than that of Al and Ti[40], it can be inferred that the increase in the solubility of Al and Ti in the Fe matrix leads to an increase of the lattice parameter of the Fe matrix, whereas the enrichment of Fe in the L2₁ precipitate results in a reduction of the lattice parameter of the L2₁ phase. Hence, the changes in the lattice parameters of the Fe and L2₁ phases result in the decrease of the lattice misfit at 700 °C (Equation 3), as compared to 572 °C (Table 2). Based on the misfit evolution (Table 2) and the change of the intensity ratio (I_{L21}/I_{Fe}) (Table 5), it is suggested that the compositional change accompanied with the variation in the volume fraction of the precipitate appears to become significant at temperatures near 700 °C.

Conclusions

The microstructures of a Ni_2TiAl -precipitate-strengthened ferritic alloy at room and elevated temperatures have been studied, using scanning-electron microscopy (SEM), transmission-electron microscopy (TEM), and neutron-diffraction (ND). The SEM and TEM observations reveal that this alloy consists of a L_{21} -type Ni_2TiAl precipitate homogeneously embedded in the Fe matrix with an elliptical shape of 257 nm diameter and a volume fraction of 22.2 %. The TEM energy-dispersive X-ray spectroscopy (EDS) and ND results revealed that the L_{21} -type Ni_2TiAl phase has an off-stoichiometric composition with Fe enrichment (about 20 at. %). The volume fraction of the Ni_2TiAl phase is determined, based on the EDS and ND analyses and is found to be 22.7 ~ 23.5 %, which is in agreement with the value derived from the SEM result (22.2 %). The average lattice parameters of the Fe and L_{21} phases and the lattice misfits between them at room and elevated temperatures were determined by the Rietveld refinement, using the General Structural Analysis System (GSAS). The lattice parameters of the Fe and L_{21} phases gradually increase with temperature, whereas the lattice misfit exhibits no clear temperature dependence. The intensity ratio of $(110)_{\text{Fe}}/(220)_{\text{L}_{21}}$, obtained from the single peak fitting technique, increases at 700 °C, as compared to room temperature and 572 °C. This trend indicates the occurrence of compositional variations of the L_{21} and Fe phases, and feasible changes of the lattice parameters, and, thus, the misfit around 700 °C, which is also related to the volume-fraction change.

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