Final Scientific/Technical Report
**Computational and Experimental Design of Fe-Based Superalloys for
Elevated-Temperature Applications**

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Abstract

Analogous to nickel-based superalloys, Fe-based superalloys, which are strengthened by coherent B2-type precipitates are proposed for elevated-temperature applications. During the period of this project, a series of ferritic superalloys have been designed and fabricated by methods of vacuum-arc melting and vacuum-induction melting. Nano-scale precipitates were characterized by atom-probe tomography, ultra-small-angle X-ray scattering, and transmission-electron microscopy. A duplex distribution of precipitates was found. It seems that ferritic superalloys are susceptible to brittle fracture. Systematic endeavors have been devoted to understanding and resolving the problem. Factors, such as hot rolling, precipitate volume fractions, alloy compositions, precipitate sizes and inter-particle spacings, and hyperfine cooling precipitates, have been investigated. In order to understand the underlying relationship between the microstructure and creep behavior of ferric alloys at elevated temperatures, in-situ neutron studies have been carried out. Based on the current result, it seems that the major role of β' with a 16%-volume fraction in strengthening ferritic alloys is not load sharing but interactions with dislocations. The oxidation behavior of one ferritic alloy, FBB8 (Fe-6.5Al-10Ni-10Cr-3.4Mo-0.25Zr-0.005B, weight percent), was studied in dry air. It is found that it possesses superior oxidation resistance at 1,023 and 1,123 K, compared with other creep-resistant ferritic steels [T91 (modified 9Cr-1Mo, weight percent) and P92 (9Cr-1.8W-0.5Mo, weight percent)]. At the same time, the calculation of the interfacial energies between the α -iron and B2-type intermetallics (CoAl, FeAl, and NiAl) has been conducted.

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A. EXECUTIVE SUMMARY

Currently, ferritic steels in power plants operate under the conditions of the temperature range of 723 to 873 K and stress levels of 15 to 100 MPa due to their limited creep resistance and poor steam-corrosion resistance at higher temperatures. In order to improve the thermal efficiency of steam turbines, the Ultra-Supercritical Steam Turbines Project sponsored by the Department of Energy (DOE) Fossil Energy Program requires an increase of the steam temperature from 866 to 950 K by the year 2010 and to 1,033 K by 2020 [1].

Analogous to nickel-based superalloys, ferritic superalloys, which are strengthened by coherent NiAl precipitates, have been proposed in this project. Bulk intermetallic NiAl has good mechanical strength at high temperatures (less than 1,073 K) with a low density, high thermal conductivity, and good oxidation resistance. Specifically, the alloy design aims toward (1) a steady-state creep rate of approximately $3 \times 10^{-11} \text{ s}^{-1}$ at a temperature of 1,033 K and a stress level of 35 MPa [1], (2) a ductility of 10% at room temperature, and (3) good oxidation and corrosion resistance at 1,033 K.

During the period of the project, great efforts have been devoted to achieving these goals by the combination of computational and experimental methods. A series of ferritic alloys have been designed and prepared as listed in Table 1. According to the proposed research areas, main results are summarized in the report.

Characterizations of nano-scale precipitates have been conducted employing the methods of atom-probe tomography (APT) and ultra-small-angle X-ray scattering (USAXS). It shows that precipitates have a duplex distribution after the aging treatment at 973 K. Taking FBB8 [Fe-6.5Al-10Ni-10Cr-3.4Mo-0.25Zr-0.005B, weight percent (wt.%)] as an example, the average size of primary precipitates is around 130 nm, while the average size of hyperfine cooling precipitates is 3 nm. Their corresponding compositions are also measured. Besides, it seems that, in hot-rolled materials, precipitates coarsen quickly to 400 nm after the aging treatment. Interestingly, in these large precipitates, α -iron particles are found. Next, factors, including hot rolling, precipitates volume fractions, alloys compositions, precipitate sizes and inter-particle spacings, and hyperfine cooling precipitates, have been systematically discussed. It is found that the ductility of ferritic alloys is closely related to the precipitate volume fraction, and Al and Ni solubility in the α -iron matrix. However, it is independent of the precipitate size and inter-particle spacing in the study range. As a result, a bend ductility of more than 5% can be achieved by lowering the Al concentration to 3 wt.% in the alloy. Advanced neutron studies have been employed to explore the in-situ behavior of ferritic alloys, FBB8 and FBB3 (Fe-10Al-10Ni-10Cr-3.4Mo-0.25Zr-0.005B, wt.%), at 973 K in order to obtain an insight concerning the relationship between creep resistance and microstructures. The study shows that at low stresses (or small plastic strains), creep deformation is dominant by the dislocation-climb-controlled creep. Creep-induced intergranular lattice strains are remarkable during the primary creep regime. No interphase stress is accumulated. At high stresses (or large plastic strains), the strain rate becomes greater, and deformation shifts to a dislocation-glide-controlled plastic flow, evidenced by the texture evolution. The major role of β' with a 16%-volume fraction in strengthening is not load sharing but interactions with dislocations. At the same time, lattice constants (FBB18 [Fe-10Al-15Ni-10Cr-3.4Mo-0.25Zr-0.005B, wt.%]) of the NiAl precipitates and matrix are obtained. Oxidation behavior of heat-treated FBB8 alloys has been studied at 923, 1,023, and 1,123 K in dry air. Isothermal exposures were conducted for 100 h. Compared with other creep-resistant ferritic steels [T91 (modified

9Cr-1Mo, wt.%) and P92 (9Cr-1.8W-0.5Mo,wt.%)], FBB8 exhibits superior oxidation resistance at both 1,023 and 1,123 K. The calculation of the interfacial energies between the α -iron and B2-type intermetallics (CoAl, FeAl, and NiAl) has been performed.

B. REPORT DETAILS

B.1 Microstructure Characterizations

Generally speaking, in precipitate-strengthening alloys, the main interaction mechanisms between dislocations and precipitates include the cutting-through mechanism and Orowan bowing. In both cases, the strengthening effect is closely related to distribution parameters of precipitates, such as the average precipitate size, volume fraction, inter-particle spacing. Of course, for ferritic alloys in this project, characterization of precipitates is crucial. Two main methods, atom-probe tomography (APT) and ultra-small-angle X-ray scattering (USAXS), have been employed to accomplish these tasks. The advanced APT equipment is homed at the Oak Ridge National Laboratory (ORNL), while the USAXS study has been conducted at the Advanced Photon Source (APS) of the Argonne National Laboratory (ANL). Combinations of both methods give us a profile of precipitates in ferritic alloys.

B.1.1 Atom-Probe-Tomography Study

B.1.1.1 Experimental Methods

The based-alloy composition for the detailed study has been determined as Fe-12.7Al-9Ni-10.2Cr-1.9Mo-0.14Zr-0.024B, wt.% (FBB8). Small ingots were prepared by vacuum arc-melting and drop casting into a copper mold with a dimension of 12.7 mm $\times$ 12.7 mm $\times$ 76.2 mm. The alloys were homogenized at 1,473 K for 30 minutes, followed by aging at 973 K for 100 hours. A thin blank with a dimension of 0.25 mm $\times$ 0.25 mm $\times$ 10 mm was cut from the bulk material by electrical-discharge machining (EDM) for the micro-polishing. The electrolysis for the stage-1 micro-polishing is 75 volume percent (vol.%) acetic and 25 vol.% perchloric acid, and for the stage-2, 98 vol.% butoxyethanol and 2 vol.% perchloric acid. After a sharp needle tip was obtained by micro-polishing, it was milled by the focus-ion beam (FIB) to form a shaper needle tapering with a modest semi-angle less than 10 ° and an apex between 50 and 150 nm in radius. 12 experiments were run to collect enough ions for analyzing the area of interest. The collected counts of the ions before the sample break vary from hundreds of thousands to several millions. The APT was carried out using a pulse repetition rate of 200 kHz and a 20%-pulse fraction on the sample at a temperature of 80 K. Similar procedures have been used to characterize hot-rolled FBB8 samples.

B.1.1.2 Results and Discussion

B.1.1.2.1 Aged Alloys

The APT study revealed the formation of duplex precipitates, as shown in Figure 1(a), while nano-scale precipitates were not detected by the conventional TEM. The primary precipitates with the size of around 100 nm correspond to the precipitates observed by TEM. Figure 1(b) exhibits that most of hyperfine precipitates are spherical, while others are irregular. Their size varies from 1 nm to 5 nm. A selected atom map in Figure 1(c) of hyperfine precipitates shows that it is also an Al-rich NiAl phase. The existence of the fine precipitates is believed to be formed during air cooling, due to the fact that the solution limit of NiAl-type precipitates is significantly lower at room temperature than at high temperatures (973 K) [2].

The isoconcentration surface of 15 atomic percent (at.%) Al clearly indicated that there was a denuded zone around the equilibrium primary precipitate. It appears that nano-scale precipitates are either being dissolved into the matrix or being absorbed by larger surrounding precipitates. The compositional

analysis of the matrix, primary precipitates, and secondary hyperfine precipitates was summarized in Table 2. The APT results of Fe, Al, and Cr in primary precipitates are in good agreement with the analytical-electron microscopy (AEM). Both exhibited an Al-rich NiAl-type precipitate. Small deviation from the stoichiometry results in an increase in both the hardness and strength [3], which is beneficial to the creep resistance. The Ni and Mo concentrations detected by APT are slightly higher than those by AEM. The composition of secondary hyperfine precipitates is higher in Fe, Cr, and Mo, while lower in Al and Ni than primary precipitates. One possibility is that the interfaces of the hyperfine precipitates and matrix were hard to be defined by the same isoconcentration for all precipitates due to their irregular size and morphology, which resulted in counting some of the matrix atoms as inside hyperfine precipitates.

The Mo-atom map in Figure 1(d) clearly indicates the partitioning of Mo into primary precipitates. This feature is in disagreement with the findings in Ref. [4], which suggested that Mo formed FeMo precipitates instead of partitioning into NiAl-type precipitates. The addition of Mo reduces the lattice misfit and slows the coarsening process of NiAl-type precipitates, which results in an improved creep resistance [5]. The Cr-atom map in Figure 1(e) revealed that Cr barely partitions to precipitates. This feature proves that the formation of NiAl-type precipitates does not deplete the Cr in the matrix for the corrosion and oxidation resistance. However, the presence of about 12 at.% of Fe has a softening effect on NiAl [6]. Another feature, which should be emphasized, is that there is a significant amount of Al partitioning to the Fe matrix, which caused the ductility problems of the iron-based materials at room temperature [7].

B.1.1.2.2 Hot-Rolled Alloys

A comparison of the atom probe samples before and after rolling conditions is given in Figure 2. The NiAl precipitates appear to coarsen very fast from a diameter of 130 nm to about 400 nm during the hot-rolling process. Due to the large size of precipitates, it is difficult to obtain an area with the existence of both the precipitates and matrix. This difficulty indirectly indicates that the inter-particle spacing becomes much larger after hot rolling. Figure 3 exhibits Al-atom maps from two separate runs. Figure 3(a) represents the iron matrix, while the 15 at.% Al isoconcentration surface in Figure 3(b) reveals some particles inside the matrix. By counting the number of atoms in each phase, the compositions of the matrix and precipitates were determined and listed in Table 3. It is interesting to note that in Figure 3(b), the “matrix” is actually a coarsened NiAl precipitate, while the “particle” is the α -iron precipitates inside NiAl. This trend was also observed in nickel-based superalloys [8]. The studied alloy was hot rolled at 1,023 K, and a certain amount of NiAl precipitates were formed during this process. During the following aging process at a low temperature (973 K), the iron-matrix and initial NiAl precipitates were supersaturated with respect to each other. Not only did more NiAl precipitates form in the iron matrix, but α iron also precipitates within coarsened NiAl precipitates. Especially in our alloy, the coherent NiAl precipitates with a low interfacial energy and a small misfit provides small barriers for the precipitate nucleation.

B.1.1.3 Conclusions

Precipitates of ferritic alloys have been characterized by APT. The result shows a duplex distribution of precipitates after the aging treatment. Taking FBB8 as an example, the average size of primary precipitates is around 130 nm, while the average size of hyperfine cooling precipitates is 3 nm. Their corresponding compositions are also measured. Besides, it seems that, in hot-rolled materials, precipitates

coarsen quickly to 400 nm after the aging treatment. Interestingly, in these large precipitates, α -iron particles are found.

B.1.2 Quantification of Precipitates by Ultra-Small-Angle X-Ray Scattering for Alloys with Various Al Contents

To study the relationship between the microstructure and creep behavior, precipitate parameters have been quantitatively determined, using ex-situ ultra-small-angle X-ray scattering (USAXS) measurements coupled with a theoretical model combining the poly-dispersity and interference of the precipitates.

The variation of the precipitate parameters before and after the creep deformation has been examined. After creep deformation, a common feature for all the alloys is found, i.e., the correlation peak shifts slightly to the small Q region. A representative absolute intensity profile is displayed in Figure 4(a) for aged and crept FBB7 alloys, with correlation peaks magnified at the lower left corner. From the model fitting, it is observed that the inter-particle spacing increases, and the variance of the particle radius decreases during creep for alloys with differing Al contents. The average particle size shows either a constant or slight increment. It reveals that precipitates coarsened slightly during the 100-hour creep deformation. Nearby small precipitates coalesce and merge into large precipitates through diffusion-driven coarsening. The declined variance of the particle radius reflects a progressively more uniform distribution of precipitate sizes.

The USAXS-intensity profiles have been measured for the crept alloys with various Al additions, as displayed in Figure 4(b). These profiles show similar values of power-law slopes in the low Q range and incoherent background in the high Q range. With increasing the Al concentration, the correlation peak shifts to the high Q region, indicating that the inter-particle spacing becomes smaller.

To gain an insight into the relationship between the amounts of Al and precipitate configurations as well as the relationship between the precipitation and creep behavior, we compile the results of the steady-state creep rate and precipitate parameters interpreted from USAXS as a function of Al contents in Figure 5. TEM results for the precipitate diameters of the aged alloys are also plotted as a reference to compare with values from USAXS fitting for crept alloys. USAXS results on the aged FBB3 (Fe-10Al-10Ni-10Cr-3.4Mo-0.25Zr-0.005B, wt.%) alloy are also plotted as a reference due to the lack of data for the crept alloy. A slight decrease of the fitted precipitate diameter and a dramatic decrease of the spacing are found as the Al contents increases. Meanwhile, the secondary creep rate first decreases and then increases with a transition at 6.5 Al wt.%. The total variation in the creep rates of all alloys was nearly two orders of magnitudes ($10^{-9} \sim 10^{-7}$ /s). Optimal compositions with minimal secondary creep rates were exhibited by the alloys with ~ 6.5 Al% (FBB8).

The volume fractions of precipitates in FBB3, 8, and 12 (Fe-4Al-10Ni-10Cr-3.4Mo-0.25Zr-0.005B, wt.%) have been determined to be 17.9%, 17.8%, and 13.5%, respectively, by analytical electron microscopy (AEM) and ATP analyses [9, 10]. Together with the trend of the precipitation diameter and spacing with Al contents, we can conclude that the volume fraction increases as Al increases to 6.5 wt.% and keeps constant with further addition of Al.

The detailed creep mechanism can be understood by investigating the dislocation-particle interactions using TEM. Figure 6 presents a typical feature of dislocation-particle interactions, which reveals the

existence of two types of interactions: dislocation loops bowing out between particles and dislocation climb around particles. Particle shearing was not observed probably due to the coarse size of precipitates. These two mechanisms both introduce a threshold stress so that the effective creep deformation is initialized if only the applied stress is higher than the threshold stress. The threshold stress could equal the Orowan stress, or a ratio of the Orowan stress for the dislocation climb, e.g., 0.4 ~ 0.7 for the local climb and 0.004 ~ 0.02 for the general climb mechanisms [11, 12]. A system with a higher volume fraction of precipitates will inhibit the dislocation motion more severely, regardless which mechanism is dominant. The Orowan stress can be calculated from the following expression [13]:

$$\sigma_{OR} = \frac{0.81Gb}{\pi\lambda_s(1-\nu)^{1/2}} \ln\left(\frac{1.63r}{b}\right) \quad (1)$$

$$\lambda_s = 0.82 \times \left[\left(\frac{\pi}{f}\right)^{1/2} - 2 \right] r \quad (2)$$

where λ_s is the square lattice spacing, r is the particle radius, f is the volume fraction, b is the Burger's vector, G is the shear modulus of the matrix, and ν is the Poissons Ratio. Using 42 GPa as the shear modulus of Fe at 973 K, ν of 0.33, and b of 0.20269 nm, we estimate the Orowan stress for FBB3, 8, and 12 to be 190, 143, and 105 MPa, respectively. Therefore, with Al ranging from 4 to 6.5 wt.%, the increased volume fraction probably leads to a higher threshold stress, and thus largely improves the creep resistance of the material. However, such correlation is not valid for alloys with Al higher than 6.5%. For FBB3 alloy, which has a similar precipitate volume fraction as FBB8, and lower inter-particle spacing, it is surprising to observe higher steady-state creep rates than FBB8. Precipitation configuration is not likely to cause the accelerated creep rates of FBB3 and 7 (Fe-8Al-10Ni-10Cr-3.4Mo-0.25Zr-0.005B, wt.%).

B.2 A Systematic Ductility Study of Ferritic Superalloys

Creep resistance at high temperatures and ductility at room temperature are two significant parts of mechanical properties of ferritic alloys. It seems that iron-based superalloys are susceptible to brittle fracture at room temperature. First of all, severe alloying in the α -iron matrix may decrease the dislocation mobility due to the solid-solution strengthening. Next, NiAl does not show any ductility at room temperature either in a single crystal or poly-crystal bulk [14, 15]. Micro-cracks may occur within brittle precipitates or along boundaries between the precipitates and matrix. Finally, elemental segregations and other minor phases, which are common in high-temperature alloys, may undermine the deformation capability of ferritic alloys at room temperature. Factors, including hot rolling, precipitate volume fractions, alloy compositions, precipitate sizes and inter-particle spacings, and hyperfine cooling precipitates, will be systematically discussed in this section. As a result, a bend ductility of more than 5% can be achieved by lowering the Al concentration to 3 mass% in the alloy [9].

B.2.1 Experimental Methods

In this part, the experimental methods for three-point-bending tests were addressed. Alloy ingots with a weight of 120 g were prepared by arc melting using commercial pure metals and then drop cast into a copper mold with the dimensions of 12.7 mm $\times$ 12.7 mm $\times$ 76.2 mm. The standard heat treatments are 30 min. at 1,473 K + air cooling + 100 hours at 973 K + air cooling. Strips with a size of 19.05 mm $\times$ 3.17 mm $\times$ 0.76 mm for three-point bending tests were cut by EDM from heat-treated alloys. Surfaces of strips were carefully polished before bending tests. The bending flexural strain can be calculated by

$$\varepsilon_f = \frac{6Dd}{L^2} \quad (3)$$

where ε_f is the strain on the outer surface, D the maximum deflection of the center of the beam, d the depth of the tested beam, and L the support span. For the B.2.2.6 Section, ingots were prepared by Sophisticated Alloys, Inc. using the method of vacuum-induction melting, and the bending strips were cut as the size of $20 \times 3.5 \times 1.5$ mm. The experimental procedures for hot rolling and tensile tests are detailed in the B.2.2.1 Section.

B.2.2 Results and Discussion

B.2.2.1 Tensile Tests of Hot-Rolled Materials

Ferritic alloys, FBB8, FBB10 (Fe-6.5Al-10Ni-10Cr-2Mo-0.25Zr-0.005B, wt.%), and FBB12, have been hot rolled in order to improve the ductility of ferritic alloys. The bulk materials were hot rolled at 1,023 K for 80%. The recrystallization temperature, T_R , of the hot-rolled materials was determined to be around 1,173 K. All the samples were annealed at 1,073 K ($< T_R$) for 1 hour, followed by aging at 973 K for 100 hours. The rectangular test pieces have the geometry of 12.7 mm in gage length, 3.18 mm in width, and 1.27 mm in thickness. The strain rate is controlled to 10^{-3} s^{-1} during tensile tests at room temperature. Figure 7 shows the tensile stress-strain curve of FBB8, which has around 10% ductility and the yield strength of approximately 917 MPa. The calculated 0.2%-offset yield strength and ductility of all hot-rolled alloys are listed in Table 4.

As can be seen, all hot-rolled alloys reach a tensile ductility of 10%. The ductility improvement can be explained by the grain-size refinement and the reduction of the casting defects, such as the porosity. Figure 8 compares the microstructures of FBB8 before and after rolling. There is less porosity observed in the as-rolled materials. In both conditions, it seems that there are two types of phases in bright-contrast areas. One is decorating along grain boundaries, the other is distributing randomly inside the grains. The EDS results in Table 5 show that they have different compositions. The phase within grains is rich in zirconium, which could explain that zirconium was not detected in precipitates either within the matrix [10]. The phase along grain boundaries is rich in molybdenum. Another issue should be noticed is that there are much more bright-contrast phases in as-rolled materials than in as-cast samples. Those phases tend to segregate to the grain boundaries and form a ribbon structure.

Electron backscatter diffraction (EBSD) was carried out to reveal the grain size after hot rolling. EBSD was obtained using a Philips XL 30 and a Camscan 2040 S, both equipped with a field emission gun (FEG) and a solid-state backscatter detector. Orientation mapping involving automatic beam scanning was used with step sizes of 0.25 μm . Data analyses were performed using the software of TSL OIM Data Collection 5.

Figure 10 presents an EBSD map of two typical grains in the hot-rolled FBB-8. The grains with thicker lines as boundaries represent that they orient at an angle larger than 15 degree to the rolling direction, and the thin lines represent the orientation angles less than 15 degree. The EBSD map illustrates clearly that most of grains with a size of 1 μm are in fact the substructures inside one grain. However, the effects of subgrains on the yield strength [16] were reported to be very similar to grains. It can be expressed by the Hall-Petch relationship with an exponent of subgrain size, m. The value of m tends to be $\frac{1}{2}$, depending on the how the recovery proceeds [16], except when their sizes are well smaller than 1 μm . As can be seen

from Figure 10, the subgrain size is about 1 μm . Thus, the subgrains are considered as grains regarding their effects on the mechanical properties in the study.

Figure 9(a) shows that the fracture surfaces consist of a mixture of ductile and cleavage fractures. The ductile areas consist of very fine grains with a size less than 1 μm . The percentage of the ductile fractures was estimated at about 40% by their areas, which is a significant improvement compared to the pure cleavage fracture of the as-cast alloys as shown in Figure 9(b).

B.2.2.2 Effects of Precipitate Volume Fraction

The volume fractions of the alloys were determined by APT results. The V_f can be calculated by the elemental partitioning data from APT according to the level rule:

$$V_f = \frac{C_0 - C_\alpha}{C_{B2} - C_\alpha} \quad (4)$$

where C_0 , C_α , and C_{B2} are the compositions of the alloy, α matrix, and B2 precipitate, respectively. The determined elemental partitioning data by APT for different alloys are listed in Table 6. Figure 11 presents that the bending ductility increases from less than 1% to more than 5% when decreasing the precipitate volume fraction from 37.5% in FBB-19 (Fe-10Al-20Ni-10Cr-3.4Mo-0.25Zr-0.005B, wt.%) to 7% in FBB-13 (Fe-3Al-10Ni-10Cr-3.4Mo-0.25Zr-0.005B, wt.%). Increasing amounts of strengthening phases reduces the ductility, which has been reported by several authors [17, 18]. Those studies focused on the materials that fractured in a ductile rupture mode, and they attributed the failures of those materials to be associated with the void nucleation and growth around the precipitates. The fracture mode of ferritic alloys was previously studied [9] and reported to be cleavage when the precipitate volume fraction is higher than 13%, and changed to a mixture of cleavage and ductile fracture when the precipitate volume fraction is lowered further. The fracture mode of the hot-rolled materials is also a mixture of cleavage and ductile fracture. Precipitates can be observed in some of the dimples on the fracture surface of the hot rolled materials, which suggests the fracture initiated with the void nucleation around the precipitates. This trend indicates that the fracture mechanism of ferritic alloys may be also explained, similar to those of ductile ruptures. Brown and Embury [19] developed a model to describe the relationship between the failure strain and the volume fraction of the strengthening precipitates for the materials that rupture in a ductile fracture mode as follows:

$$\varepsilon = \frac{1}{C} \ln \left(\sqrt{(\pi/6f)} - \sqrt{\frac{2}{3}} + \varepsilon_n \right) \quad (5)$$

where ε is the tensile failure strain, C is a constant, f the precipitate volume fraction, and ε_n the void nucleation strain. From this equation, it can be clearly seen that the tensile ductility (ε) of the material decreases as the precipitate volume fraction (f) increases, which is consistent with the results in our study. However, such a quantitative relationship has not been developed for ferritic alloys due to most of the materials exhibited a fracture mode of cleavage and the ductility measurements were conducted by three-point-bending tests.

B.2.2.3 Effects of Alloy Compositions

In the B.2.2.2 Section, we have discussed the effect of precipitate volume fraction on the ductility of ferritic alloys. As a matter of fact, as the volume fraction varies from 37.5% in FBB19 to 7% in FBB13, the elemental distribution in the α -iron matrix and precipitates is changing, especially for aluminum. The two factors intertwine with each other, and further work is needed to clarify their roles regarding the ductility of ferritic alloys.

B.2.2.3.1 Elemental Solubility in Fe

The fracture of the model alloys is believed to be initiated in the ferrite matrix. Thus, the effects of the elemental solubility in the Fe matrix will be discussed first. The compositions of both the Fe matrix and NiAl precipitates can be determined by APT. The results listed in Table 6 revealed that the solubility of Cr and Mo are very similar for all the alloys. Consequently, they are not major factors contributing to the ductility difference. The ductility as a function of the solubility of Ni and Al in the Fe matrix is plotted in Figure 12. The results clearly indicate that the addition of Ni increases the ductility. Leslie [20] reported a similar finding in the α -Fe. This ductility improvement was explained by a model developed by Pugh [21]. He proposed that the ductility of pure metals is related to the ratio of the bulk modulus to shear modulus (K/G). The rationale is that with decreasing K/G, more energy is stored as dilation rather than shear deformation. The measurement of polycrystalline elastic constants of the α -Fe solid solutions shows a marked increase in K/G when Ni is added to Fe, leading to an increase in the fracture toughness. In this study, the ductility increases from less than 1% in FBB-3 to more than 5% in FBB-13, while the solubility of Ni increases from 1.5 at.% to 3.1 at.%. This trend is consistent with Leslie's results. However, it is worth mentioning that Ni is an austenite-forming element, and its solubility has to be controlled to avoid the formation of the face-centered-cubic (FCC) Fe, as this study focuses on developing the body-centered-cubic (BCC) Fe-based alloys.

The most significant difference of the elemental solubility in the Fe matrix comes from Al, varying from 2.6 at.% in FBB-13 to 14 at.% in FBB-3 (Figure 12). The effects of Al on the ductility of a series of NiAl-strengthened ferritic steels were presented in Ref. [9]. The results showed that the alloy with the lowest Al solubility exhibits the optimal ductility, which is in good agreement with the current studies shown in Figure 12 and the research conducted by Herrmann et al [7] on the ductility of the Fe-(4 to 18) Al (at.%) solid solution at room temperature. Herrmann's study [7] indicated that Al has an ordering effect on the BCC Fe and decreases the dislocation mobility at room temperature, resulting in the low ductility in the BCC Fe with a high Al solubility. However, it should be noted that the alloy, FBB19, which contains only 4.9 at.% of Al in the matrix, still exhibited very low bending ductility (0.67%). Therefore, although increasing the Al solubility decreases the ductility of the α -Fe, it is not the sole factor in controlling the ductility of the alloys in our study. As shown in the previous section, the ductility decreases consistently, as the precipitate-volume fraction increases regardless of the elemental solubility and partitioning. This trend indicates that the ductility cannot be significantly improved, when the precipitate volume fraction is sufficiently high.

B.2.2.3.2 Elemental Partitioning in NiAl Precipitates

There is no evidence to show that the NiAl precipitates fractured during the bending and tension tests, although the NiAl intermetallic is expected to be much more brittle than the ferrite matrix. The elemental

partitioning data shown in Table 6 indicates that there is a significant amount of Fe partitioning into the NiAl precipitates, varying from 10.4 at.% in FBB-19 to 18.1 at.% in FBB-13. Several studies [22, 23] have shown that the dissolved Fe modifies the preferred slip vector of the polycrystalline NiAl, and, thus, improves the ductility. In addition, a study by Kovalev et al. [6] found that the addition of 2 at.% Fe decreases the ductile-brittle transition temperature of NiAl by ~ 200 °C. The partitioning of Fe into NiAl may be the reason contributing to the ductility improvement of the precipitates.

B.2.2.4 Fracture Mode and Crack Nucleation

The fracture mode of a series of NiAl-strengthened ferritic steels containing different volume fractions of precipitates was shown in Figure 13. The fracture mode was found to be cleavage when the precipitate volume fraction was higher than 13% (FBB-3, 8, and 9), and changed to a mixture of cleavage and ductile fracture when the precipitate volume fraction was lowered further (FBB-13). As can be seen from Figure 2(a), the fracture mode of the tensile tested hot-rolled materials is also a mixture of cleavage and ductile fracture. The average dimple size in the ductile fracture area is ~ 1 μm , which is the same as the subgrain size in the recrystallized material, indicating that the ductility improvement is due to the formation of subgrains.

A study on the tensile fracture of a NiAl-strengthened austenitic steel [24] revealed that the cracks nucleated from the NiAl precipitates. However, the morphology of those precipitates is needle-like, and their average size is ~ 1 μm in length, which are significantly different from the spherical precipitates with an average size of 100 nm in our study. Furthermore, the matrix in those studies is austenitic steel, which is much more ductile than the ferritic matrix at room temperature. In their case [24], the needle-like NiAl precipitates ruptured before the austenitic matrix. However, as presented in Figure 14(b), precipitates can be observed in some of the dimples in the ductile fracture area, as well as the surface of the cleavage fracture area. The precipitates on the fracture surface are spherical, and no evidence was observed to indicate that the NiAl precipitates were fractured. A detailed TEM study is needed to clarify if the initiation of cracks in ferritic alloys is associated with precipitates.

B.2.2.5 Effects of Primary Precipitate Size and Inter-Particle Spacing

There were two concomitant phenomena observed in the alloys after hot rolling: grain-size refinement from 100 μm to 1 μm , and coarsening of the NiAl precipitates. They were shown in Figure 15. The ductility increased from 1% to more than 10% after hot rolling. However, whether the grain size or the precipitate size contributes to the ductility improvement was unknown. The precipitate size can be controlled by the aging time at 700 °C. Therefore, the FBB8 specimen was aged for 100, 500, and 1,000 hrs, respectively, to study the effect of precipitate size on ductility.

The precipitate sizes of the as-quenched material after solution treatment, followed by aging for 100 hrs, were measured by TEM, as presented in Figure 16. The precipitate size of the samples aged for longer time is estimated by the coarsening-kinetics equation:

$$r^3 - r_0^3 = k(0)t \quad (6)$$

where r is the average particle radius after time t (hour), and $k(0)$ is the kinetics constant. $k(0)$ is calculated to be $1.5 \times 10^3 \text{ nm}^3/\text{h}$. Thus, the precipitate radius can be calculated to be 96 nm and 118 nm for the samples aged for 500 and 1,000 hrs, respectively.

The three-point-bending ductility is listed in Table 7. It shows that the ductility does not change significantly, and the materials are still very brittle after a long time of aging. It indirectly indicates that the grain-size refinement is the main reason contributing to the ductility improvement after hot rolling.

The inter-particle spacing was measured by ultra-small angle x-ray scattering (USAXS). The peaks of the USAXS intensity vs. scattering vector curves shown in Figure 17 correspond to constructive interference of inter-particle scattering. Thus, the inter-particle spacing can be calculated by 2π over peak Q [25]. For the alloy FBB-8, after aging for 100 hrs, the calculated value of λ is about 225 nm, which is consistent with the observation from TEM. As the aging time increase to 500 and 1,000 hrs, λ increases to 390 nm and 422 nm, respectively. In the alloys strengthened by spherical precipitates, the inter-particle spacing (λ) is a function of the precipitate volume fraction, V_f , and precipitate radius, r [26]:

$$\lambda = \frac{4(1-V_f)r}{3V_f} \quad (7)$$

As shown in Figure 18, the ductility is independent of the inter-particle spacing. In the precipitate-strengthened alloys, the effects of precipitate size on ductility has not been completely established nor is it clear whether or not the precipitate size dependence is related to the absolute size or the inter-particle spacing. Theoretical analyses of Ashby [27] and Gurland [28] would indicate that the ductility should increase as the precipitate size decreases. It is suggested that once the precipitate size is reduced below a certain number, the inter-particle spacing will serve to limit the length of the slip bands. Then, ductility can be achieved. As the volume fraction of B2 precipitates is fixed for FBB8, the inter-particle spacing exhibits a linear relationship with the particle size as shown in Equation (7). The effects of inter-particle spacing will be discussed here instead of precipitate size.

The results in Figure 18 show that the inter-particle spacing does not have any significant effects on the ductility of our materials. A model developed by Baker [29] may be able to explain the ductility independence of the inter-particle spacing. Baker's model [29] tried to correlate the inter-particle spacing with the ductility in the precipitate-strengthened brittle materials. He suggested that there is a critical inter-particle spacing, with which an optimal ductility can be achieved [29]. This value can be calculated by

$$\lambda_{crit} = \frac{\pi G b^2}{\gamma(1+\nu)} + 2r_s \quad (8)$$

where λ_{crit} is the critical inter-particle spacing, G is the shear modulus, b the magnitude of the Burgers' vector, γ the surface energy, ν the Poisson's ratio, and r_s the precipitate radius. For the materials in our study, the Burger's vector, b , can be calculated by:

$$b = \frac{a}{2} \sqrt{h^2 + k^2 + l^2} \quad (9)$$

where a is the lattice parameter of Fe, and $[hkl]$ is equal to $[111]$ for the body-centered-cubic(BCC) Fe, and b is calculated to be 0.248 nm. Other parameters can be obtained from the available literature data: $G = 82$ GPa [30], $\nu = 0.29$ [30], $\gamma = 15$ J/m² [31, 32], and $r_s = 65$ nm [10]. Therefore, the calculated λ_{crit} is equal to 132 nm. Baker [29] also suggested that there is a λ_{max} , which can be calculated by

$$\lambda_{max} = \frac{G}{\sigma_0} \left\{ \left[\frac{(1+\nu)\gamma}{\pi\sigma_0} \right]^{1/2} + \left[\frac{(1+\nu)\gamma}{\pi\sigma_0} - b \right]^{1/2} \right\}^2 + 2r_s \quad (10)$$

where σ_0 is the lattice resistance, and equals 70-90 MPa for ferritic steels [33]. λ_{max} is calculated to be 56 μm . As predicted by Baker's model, between λ_{crit} and λ_{max} , the ductility decreases as the inter-particle spacing increases. As the calculated results show, the inter-particle spacing, λ , of all the aging samples are larger than λ_{crit} , but much smaller than λ_{max} . Considering the inter-particle spacing range [132 nm, 56 μm] is very large, the slight increase of the inter-particle spacing from 225 nm (aged 100 h) to 422 nm (aged 1,000 h) should have very limited effects on the ductility. This trend is in good accordance with the obtained results in our study. Based on Baker's model [29], a slight increase of the ductility may be achieved by lowering the inter-particle spacing to the optimal value λ_{crit} .

B.2.2.6 Effects of Hyperfine Cooling Precipitates

From previous sections, ferritic alloys after aging treatments show a duplex precipitate distribution. For the FBB8 case, the average size of primary precipitates, which grow and coarsen during the aging treatment, is around 130 nm, and at the same time, the average size of hyperfine cooling precipitates is around 3 nm. The hyperfine cooling precipitates are believed to be formed during the cooling process following the age treatment. First let us consider the strengthening effect of primary precipitates. Assuming the main interaction mechanism between dislocations and primary precipitates is Orowan bowing, according to the Ref. [13], the estimate of the Orowan stress can be expressed as

$$\Delta\tau = \frac{0.81Gb}{2\pi(1-\nu)^{1/2}} \frac{\ln(2r_s/r_0)}{(\lambda_s - 2r_s)} \quad (11)$$

where λ_s is the mean planar separation of particles, r_s is the mean radius of intersection of a random plane with an average radius of r , and r_0 is the cutting-off radius of dislocations. According to the reference [13],

$$r_s = \sqrt{2/3}r, \text{ and } \lambda_s = 1.25r(2\pi/3f)^{1/2} \quad (12)$$

We assume $G = 82$ GPa for room temperature, $\nu = 0.32$, $b = 0.2514$ nm, $r = 65$ nm, $r_0 = b$, and $f = 0.16$ [10]. Substitute all values into (11), we get $\Delta\tau \approx 103$ MPa.

Thus, the increment of the yield strength of ferritic alloys due to primary precipitates is ~ 310 MPa, assuming that the Taylor factor is 3. According to the previous study, the yield stress of FBB8 at room temperature is $\sim 1,000$ MPa. Although currently we do not know the exact strength of the matrix, it may be around 300 MPa. Please note that the grain size of ferritic alloys is larger than 100 μm . Therefore, the strengthening effect of the grain size is negligible.

It seems that hyperfine cooling precipitates strongly interact with dislocations, and strengthen ferritic alloys, which may contribute to the high anti-phase boundary energy of NiAl. Evidence, such as the dislocations structure after deformation, is needed to verify this point. The strong dislocation-pinning effect of secondary precipitates could reduce the dislocation mobility, and therefore, cause the brittle fracture of ferritic alloys at room temperature. In order to verify this assumption, different heat treatment schedules have been employed to prevent precipitating reactions during the cooling process. Then, hardness measurements and three-point bending tests have been conducted. Please note that in this section,

all samples were fabricated by Sophisticated Alloys, Inc. using the vacuum induction melting. The results of hardness measurements are listed in Table 8.

A very interesting point is that the Vickers hardness of Alloy # 5 is much greater than those of Alloys # 3 and # 4, as shown in Table 8. Generally speaking, the hardness of samples aged at high temperatures for the same time should be lower than that aged at relative low temperatures, because the volume percentage of precipitates is smaller (according to the phase diagram) and the precipitates size is larger (due to greater diffusional coefficients) than those aged at lower temperatures. This feature would be caused by cooling precipitates during the cooling progress from the aging temperature. It is estimated that when cooling from 1,073 K, there would be more cooling precipitates than those cooled from 973 K, which could explain the above result. The hardness discrepancy between Alloys # 3 and # 4 could also be explained by cooling precipitates due to different cooling rates from 973 K. But it seems the difference between Alloys # 3 and 4 is not as obvious as the former one perhaps because there are still lots of cooling precipitates at both alloys.

Three-point bending tests on four different heat-treated samples (as-cast, 30 min. at 1,473 K + AC + 100 hours at 973 K + air cooling/ Water quenching/ furnace cooling) were conducted. The results show some scattering, and thus no decisive conclusion could be made based on the current data. As a matter of fact, elemental segregation (zirconium) along grain boundaries and within grains is found under scanning electron microscopy (SEM) after the aging treatment, which may be accounted for the poor ductility of ferritic alloys at room temperature.

B.2.3 Conclusions

In conclusion, a systematic ductility study of ferritic alloys is summarized in this B.2 section. According to the research, hot rolling can effectively improve the ductility of ferritic alloys (FBB8, FBB10, and FBB12) to around 10% at room temperature, which may be due to the fine subgrain size ($\sim 1 \mu\text{m}$), less casting defects, and coarse precipitates. It is found that the ductility of ferritic alloys is closely related to the precipitate volume fraction, and Al and Ni solubilities in the α -iron matrix. However, the ductility is independent of the precipitate size and inter-particle spacing in the study range. Please note the two factors, the precipitate volume fraction and Al and Ni solubility in the matrix, intertwine with each other. Further research is needed to clarify their separate effect. From the strengthening theory, it seems that hyperfine cooling precipitates could strongly interact with dislocations, thus decrease the dislocation mobility in ferritic alloys. The formation of cooling precipitates is also related to the Al and Ni solubility in the matrix (as a function of temperature). Further investigation will continue in order to characterize hyperfine cooling precipitates and study their effects on the ductility and creep resistance. At last, elemental segregation (mainly related to zirconium) has been found in some alloys. Future design may try to avoid this phenomenon because it could be detrimental to the ductility and creep resistance of ferritic alloys.

B.3 Neutron Study

The motivation of the work is to study the relationships among the microscopic elastic-lattice strains (both the interphase and intergranular strains), microstructure evolution, and macroscopic-creep behavior, therefore providing insights into micromechanical deformation.

B.3.1 Experimental Methods

FBB3 and FBB8 alloys have been studied in this section. The alloys were drop cast, and homogenized at 1,473 K for 30 minutes, followed by aging at 973 K for 100 hours. Their microstructure could be found in other sections. The ingots were machined into dog-bone-threaded tensile samples with a gage length of 40 mm and a gage diameter of 6.35 mm. The in-situ creep experiments were conducted at the Spectrometer for Materials Research at Temperature and Stress (SMARTS) diffractometer at the Los Alamos Neutron Science Center (LANSCE) facility of the Los Alamos National Laboratory. Boron nitride was sprayed outside the threads to avoid chemical reactions between threads and grips. The beam-slit size was 8 x 6 mm. In-situ creep experiments were performed in vacuum at 973 K under a constant load. The material becomes paramagnetic at this temperature and, thus, the magnetic contribution to the neutron diffraction (ND) pattern can be totally ignored. A thermal couple was attached to the sample surface, and the temperature variation was within ± 1 K during creep. A constant loading rate of 1 MPa/s was applied for loading up to 107 MPa. After the secondary creep is stabilized at 107 MPa (only for FBB8 case), the stress is increased from 107 to 150 MPa. The macroscopic strain was measured using a high-temperature extensometer over a gage length of 10 mm within a measureable strain range of 10 pct. The diffraction geometry of SMARTS, defined by the position of the detector banks at 90° and the load axis at 45° , provides the lattice-strain information parallel and perpendicular to the loading directions (both axial and transverse directions). The neutron data were collected in batches of 5 min for the first three hours of creep in order to capture any strain variation during the primary creep stage, and of 20 minutes for the rest of the creep test.

There are two categories of elastic lattice strains (or microstrains) in the studied alloys: intergranular and intragranular strains in the individual β and β' phases. The existence of intergranular strains is due to the discontinuity of the stress distributed from grain to grain, induced by the elastic and plastic anisotropy of the different oriented grains [34]. The intragranular strain in the present work refers to the interphase strains of the β and β' phases. The strains in these phases are influenced by the elastic anisotropy of each phase (the stiffness/compliance elastic constants) and plastic anisotropy due to the Schmid factor and the geometric constraint by the relative size of each phase [35]. We report the measurements of intergranular strains and average interphase strains as a function of creep time for FBB 3 and 8 alloys.

We consider the coherent β and β' phases as a single constitute and derive the intergranular strain from the composite reflections (or overlapping fundamental reflections) for subsets of grains. The diffraction peaks of [hkl]-oriented grains with the normal of the [hkl] plane along the tensile axis of the specimen were measured. The d-spacing of different hkl reflections were determined by single-peak fitting in GSAS, and, thus, the hkl-plane-specific intergranular strain is calculated by

$$\varepsilon_{hkl} = \frac{d_{hkl} - d_{hkl}^0}{d_{hkl}^0} \quad (13)$$

where ε_{hkl} is the microstrain for [hkl] oriented grains, d_{hkl}^0 is the reference lattice-plane spacing without loading at 973 K, and d_{hkl} is the d-spacing at creep time. In addition, the Rietveld whole-pattern fitting was applied to determine the of β and β' phases, and, thus, obtain the average interphase strain as

$$\varepsilon = \frac{a - a_0}{a_0} \quad (14)$$

where a_0 is the reference lattice parameter at 973 K without loading, and a is the lattice parameter at a creep time. To obtain the hkl-plane-specific interphase strains, it requires the accurate separation of the overlapping composite reflections into individual β and β' peaks, using the same method, as described in Section 1. The results will be shown in the next progress report.

B.3.2 Results and Discussion

B.3.2.1 Measurements and Modeling of the Lattice Parameters of FBB18

B.3.2.1.1 Separation of the Fundamental Reflections

Figure 19 shows a typical ND spectrum obtained from the studied alloy, with the intensity plotted vs. the d-spacing. The Rietveld refinement technique [36] is employed to analyze the neutron spectrum using the General Structures and Analysis System (GSAS) code developed by Larson and Von Dreele [37, 38] at LANSCE.

With the small lattice mismatch between the two phases, a direct separation of the fundamental peaks into the contributions from the two-phase constituents was not achieved. The determination of the accurate values of the lattice parameter involves a single-peak-fitting procedure in GSAS [37, 38]. In this approach, the superlattice reflection (100) was used to determine the d-spacing, d_{100} , for the β' phase. The lattice parameter of β' , thus, can be calculated to be $2.8752 \pm 0.0004 \text{ \AA}$. For the fundamental (110) reflection, d_{110} of β' equals $d_{100}/\sqrt{2}$. The position of the β reflection can be obtained by fitting the sum of two Gaussian peaks to the data for the composite reflections, subjected to the following constraints [39].

First, the intensity ratio of β' to β was determined from the structure factor and volume fraction, using the following equation [40]:

$$\frac{I_{hkl}^{\beta'}}{I_{hkl}^{\beta}} = \frac{|F_{hkl}^{\beta'}|^2}{|F_{hkl}^{\beta}|^2} \frac{v_f}{1-v_f} \quad (15)$$

$$F_{hkl} = b_{ce} e^{2\pi(0h+0k+0l)} + b_{co} e^{2\pi(1h+1k+1l)} \quad (16)$$

where b_{ce} and b_{co} are the scattering lengths of the corner atoms and the center atoms, respectively, F_{hkl} is the structure factor, and v_f the volume fraction of β' . For the β -matrix phase, which has a disordered BCC structure, $F_{hkl} = b_{ce} + b_{co}$ where (hkl) are all even, and $F_{hkl} = 0$ where (hkl) are of mixed character. For the β' -precipitate phase, which has an ordered BCC structure, $F_{hkl} = b_{ce} + b_{co}$ where (hkl) are all even, and $F_{hkl} = b_{ce} - b_{co}$ where (hkl) are of a mixed character. The values of scattering lengths are functions of the actual compositions of phases, expressed by:

$$b_{ce}^{\beta'} = \sum c_{i,ce}^{\beta'} b_i \quad (17)$$

$$b_{co}^{\beta'} = \sum c_{i,co}^{\beta'} b_i \quad (18)$$

$$b_{co}^{\beta} = b_{ce}^{\beta} = \sum c_i^{\beta} b_i \quad (19)$$

where $C_{i,ce}^{\beta'}$ is the atomic concentration of element, I, in the β' phase that occupies the body-centered position, $C_{i,co}^{\beta'}$ is the corresponding atomic concentration for those elements that occupy the corner position, b_i is the scattering length of neutrons by the atom of element, i, which can be obtained from the literature and C_i^{β} is the atomic concentration of element, I, in the β phase. The site preference of transition-metal elements in the NiAl phase was studied by Jiang [41]. He reported that the fractions of Fe, Cr, and Mo occupying the Al sublattice are a function of temperature and stoichiometry of NiAl. In the current study, the compositions were determined by APT and shown in Table 9. As can be observed, the NiAl precipitate phase is nearly stoichiometric in the studied alloy. Thus, the site occupancy of Fe, Cr, and Mo can be obtained from Jiang's results [41] and listed in Table 9. The precipitate volume fraction can be estimated by the lever rule. The slope of the best-fit line for all elemental compositions determined by APT shows the volume fraction (V_f) of β' phase to be ~ 0.28 . With all the parameters calculated above, the intensity ratio was determined to be 0.29 by Equation (15).

Second, assuming that the widths of the two peaks were taken to be equal, and the background was flat, the combined peak profile for the (110) reflection can be deconvoluted into two separate β and β' peaks, as shown in Figure 20. From the position of the β peak, the lattice parameter of the β phase can be calculated to be 2.8827 ± 0.0011 Å. It is clearly seen that the lattice parameter of β' is slightly smaller than that of β , resulting in a negative lattice misfit of - 0.26%, as calculated by:

$$\delta = \frac{2(a_{\beta'} - a_{\beta})}{(a_{\beta'} + a_{\beta})} \quad (20)$$

where a_{β} and $a_{\beta'}$ is the lattice parameters of β and β' , respectively.

B.3.2.1.2 X-ray Diffraction Measurement

Figure 21 shows a representative X-ray diffraction pattern of the studied alloy at room temperature. There was no peak splitting observed, indicating that the lattice misfit is very small. The intensities of the superlattice reflections are relatively low, as compared to those of the ND pattern. This trend is due to the fact that the intensity of the β' superlattice reflections depends on the difference in the scattering between Ni and Al atoms, which is quite small in the case of X-rays. Using the same single-peak-fitting procedure for the ND pattern, it yields a lattice parameter of 2.8772 ± 0.0016 Å for β' . Considering that the variance is relatively larger, this value is still in good accordance with the ND result.

B.3.2.1.3 Modeling of the Lattice Parameters of FBB18

B.3.2.1.3.1 BBC-Fe Matrix

The composition dependence of the lattice parameters of the body-centered-cubic (BCC) binary Fe-Al [42-44], Fe-Ni [45, 46], Fe-Cr [45, 46], and Fe-Mo [45, 47] alloys have been systematically investigated previously. Vegard's law can be subsequently applied to predict the lattice parameters of the alloy system consisting of these elements. However, Ghosh's study [48] revealed that the composition dependence of the lattice parameters of some Fe-X subsystems exhibited strong non-linearity with asymmetry and a

deviation from Vegard's law. After accounting for this effect, we use the model proposed by Ghosh [48] to predict the lattice parameters of the Fe-based multi-component system. For the Fe-Al-Ni-Cr-Mo system in the current study, the lattice parameter (a) of the BCC Fe matrix can be expressed as a function of the elemental concentration (x) by [48]:

$$a_{matrix} = 3.0287x_{Al} + 2.7801x_{Ni} + 2.8847x_{Cr} + 2.8665x_{Fe} + 3.147x_{Mo} + x_{Cr}x_{Fe}[0.0029496 - 0.022928(x_{Cr} - x_{Fe})] + x_{Fe}x_{Mo}0.06507 + x_{Fe}x_{Ni}[0.00778 + 0.0743(x_{Fe} - x_{Ni})] \quad (21)$$

Using the concentration values determined by APT (Table 10), the lattice parameter of the BCC Fe matrix can be calculated to be 2.8852 ± 0.0044 Å, which is in good agreement with the experimentally-determined value of 2.8827 ± 0.0011 Å by neutron diffraction. It should be mentioned that the inaccuracy of the modeled value is slightly higher than that determined experimentally, due to that the standard error (σ) of the concentration estimated by APT is $\sim 0.03\%$, given by $\sigma = \sqrt{C(1 - C/N)}$, where C is the concentration, and N is the total number of atoms in the measured volume. In order to reduce the error, hence obtaining a more accurately modeled lattice parameter, more ions are needed to collect in the APT experiments.

B.3.2.1.3.2 B2-NiAl Precipitates

The volume, V , of N unit cells of the non-stoichiometric NiAl can be given by [8]:

$$V = (N - x_{Ni}n_i)\Omega_{Ni} + (N - x_{Al}n_i)\Omega_{Al} + n_i\Omega_i = Na^3 \quad (22)$$

where x_{Ni} is the fraction of atom, i , located in the Ni sites, x_{Al} , the fraction of atom, i , located in Al sites, n_i , the number of atom, i , in the NiAl lattice, Ω_{Ni} , Ω_{Al} , and Ω_i are the atomic volumes of Ni, Al, atom i in NiAl, respectively. The atomic fraction of atom, i , is given by

$$x_i = \frac{n_i}{2N} \quad (23)$$

Differentiating V in Equation (22) and x_i in Equation (23), with respect to n_i , gives:

$$\Omega_i - x_{Al}\Omega_{Al} - x_{Ni}\Omega_{Ni} = \frac{3}{2}a^2 \frac{da}{dx_i} \quad (24)$$

Kitabjian and Nix [49] determined the values of Ω_{Al} and Ω_{Ni} to be 0.0134 nm^3 and 0.0106 nm^3 , respectively. Therefore, the atomic volume of atom, i , in NiAl can be calculated by Equation (24) from the available literature data. Table 11 listed all the calculated results. With the assumptions that the atomic volume of a constituent is independent of the site that it occupies, and there is no vacancy in the B2 phase of the Fe-Al-Ni-Cr-Mo system, the lattice parameter of B2 NiAl can be calculated to be 2.8747 ± 0.0034 Å by:

$$a^3 = 2(x_{Al}\Omega_{Al} + x_{Ni}\Omega_{Ni} + x_{Fe}\Omega_{Fe} + x_{Cr}\Omega_{Cr} + x_{Mo}\Omega_{Mo}) \quad (25)$$

The modeled result is also in good accordance with the experimentally-determined value of 2.8752 ± 0.0004 Å. Similar to the modeling of the BCC Fe matrix, the inaccuracy of the modeled parameter is also slightly higher, due to the standard error of measurements from APT.

B.3.2.2 Analyses of In-Situ Neutron-Diffraction (ND) Measurements during Creep on FBB3 and FBB8

B.3.2.2.1 In-situ Creep Behavior of FBB3 at 973 K

Figure 22 shows the macroscopic tensile creep curves for FBB-3 and -8 specimens. The primary creep is very transient in both alloys. The transition into the tertiary creep is around 200 min for FBB3 and 500 min for FBB 8. Significant macroscopic strains are cumulated during the tertiary creep in FBB3. The secondary creep rates for FBB-3 and -8 are determined to be 3×10^{-7} and 4.2×10^{-7} /s, respectively. The FBB-3 specimen ruptured around 780 min of creep with a ductility of 6%, while FBB-8 continued to deform after 900 min. of creep and finally ruptured with a ductility of 11%.

The typical ND patterns refined by the Rietveld whole pattern fitting for the two alloys are exhibited in Figure 23. Figure 24 shows the evolution of axial and transverse average interphase strains for β and β' phases, together with the macroscopic creep strain as a function of creep time for FBB3. Since the creep experiments were performed under constant load, the true stress on the sample increases as the creep strain increases. Therefore, the slight increase of lattice strain in FBB3 is probably due to the decrease of sample cross section caused by the accumulated macroscopic strain in the tertiary creep regime. The lattice misfit at 973 K can be calculated from Equation (20) using the Rietveld refined lattice parameters for β and β' phases. As shown in Figure 25, both lattice misfits are extremely low (on average -0.0002 for FBB-3 and 0.0001 for FBB-8), suggesting negligible constraints between the two phases, although the data are somewhat scattered, and the lattice misfits of the two alloys don't show an apparent change of values. Figure 26 presents the temporal evolution of intergranular microstrains along the loading direction for various grain orientations. The strains were obtained from the 110, 200, 211, and 220 reflections, assuming an average d_{hkl} for the composite $\beta + \beta'$ phases. Except the 200 reflection, the intergranular strains for the other three reflections reach a steady state immediately upon loading for both alloys. There is a gradual increase of microstrains in the 200 reflection at the beginning 100 min. of creep. After that, the 200 intergranular strain keeps a constant. A slight increase of an $\sim 1 \times 10^{-4}$ intergranular strain is observed for FBB3 at 110 and 211 reflections, during the tertiary creep.

B.3.2.2.2 In-Situ Behavior of FBB8 at 973 K

In this section, we continue to analyze the results of FBB8 crept at two stress levels with respect to the lattice-strain evolution, load partition, texture, peak width, and corresponding creep mechanisms, which might be utilized to compare with elastic plastic self-consistent (EPSC) or finite-element modeling of high-temperature deformation.

Macroscopic tensile creep curves at 973 K and the stress levels of 107 and 150 MPa are shown in Figures 27(a) and (b), respectively. It is evident from the plot of strain rate vs. time [Figures 27(c) and (d)] that the primary creep is transient (~ 60 minutes) followed by a short period of secondary creep (~ 200 minutes). An extended period of tertiary creep occurs afterwards. A minimal creep rate is 1.8×10^{-7} /s at 107 MPa, consistent with the measurements by a dead-load creep frame. Data analyses on the previous creep results (e.g., a stress exponent equals 4 after the threshold-stress compensation) suggest that dislocation-climb-controlled creep is the dominant deformation mechanism. However, the creep rate measured at 150 MPa is higher than what power-law creep predicts, indicating the transition of the mechanism to a dislocation-glide-controlled plastic flow [50].

The temporal evolution of axial and transverse average phase strains for β and β' phases is presented in Figures 28(a) and (b). At 107 MPa, axial-phase strains keep approximately constant during primary, secondary, and tertiary creep, while transverse-phase strains develop small amounts of compressive strains during primary creep and reach constant afterwards. Strain (or load) partitioning doesn't vary throughout secondary and tertiary creep. The magnitude of the axial β -phase strain is $\sim 100 \mu\epsilon$ higher than that of the β' phase, and in the transverse direction both strains have the same magnitude. The Young's modulus is 130.5 ± 0.2 GPa from the macroscopic stress-strain curve during loading, and yield doesn't occur when sample was loaded to 107 MPa. The diffraction elastic moduli ($E = \sigma_{\text{applied}}/\epsilon_{\text{phase}}$, where σ_{applied} is the applied stress, and ϵ_{phase} is the average phase-lattice strain) of the individual-constrained phases are roughly estimated to be 156 (β) and 219 (β') GPa, respectively, using instantaneous lattice strains upon loading to 107 MPa. Thus, the average stresses in β and β' phases after primary creep are estimated to be 107 MPa, implying that there is no load transfer. Consequently, the lattice misfit, $\delta = 2(a_{\beta'} - a_{\beta})/(a_{\beta'} + a_{\beta})$ calculated by the Rietveld refined lattice parameter essentially doesn't change during creep. The magnitude of 0.0001 for the lattice misfit is extremely low, suggesting negligible constraints between the two phases. The values are in the range of the reported room-temperature (RT) measurements of $-0.0006 \sim 0.008$ in the Fe-Ni-Al alloy systems [51, 52].

Once the applied stress is raised to 150 MPa, the difference of β and β' axial phase strains jumps to $\sim 250 \mu\epsilon$. The true-stress vs. phase-strain plot is exhibited in Figure 28(c). The true stress increases due to the accumulated macroscopic strain and reduction of the sample cross section. Features of the lattice-strain development are similar to the plastic region above the yield point during the RT tension. In the initial 15 minutes of creep (below 156 MPa), axial and transverse microstrains remain approximately the same. However, a sharp increase of the axial β' strain by a factor of 2 is observed above 156 MPa (at a macroscopic strain of 6.2%). Compared to the elastic gradient, a tensile interphase stress is generated in the β' phase along the axial direction. The phase strain along the transverse direction also shows the same trend, with β' becoming more compressive, as deformation proceeds. This is a signature of the load transfer from the plastically-deformed matrix to the elastically-deforming precipitate. Note that a 16-MPa increase in the true stress results in a lattice strain of less than $100 \mu\epsilon$ in β and β' phases, which thus cannot account for the large increase of β' strains. It is expected that the β phase deforms plastically and β' phase elastically, since the ordered β' precipitates have a high anti-phase boundary energy and relatively coarse size (~ 130 nm). Thus, dislocation shearing through particles is difficult unless pairs of superdislocations are formed. The average stresses are 148 and 140 MPa for β and β' at 150 MPa, and becomes 152 and 197 MPa when the drastic tensile-interphase strain accumulated in β' at 156 MPa. The fraction of load borne by the matrix is slightly lower than 100%, indicating that a small amount of load-transfers to the β' phase and causes the substantial average-stress increase due to the low volume fraction of β' (16%). However, such a load partition doesn't last long. It is interesting to note that the β' -phase strain in both axial and transverse directions drastically bend backwards together with a rapid increase of the β strain right before the sample rupture. Ma et al. [53] interpreted the bendback phenomenon in Ni-based superalloys as the stress on precipitates exceeds a critical resolved shear stress (CRSS), and dislocations penetrate through particles. Considering the microstructural similarity of Fe-based and Ni-based superalloys, it is possible that our observation implies the yield of β' as well. When the applied stress is further increased to 167 MPa, the average stress borne by the β phase (170 MPa) is slightly higher than the magnitude of the true stress. The lattice misfit increases from 0.0002 (156 MPa) to 0.016 (167 MPa) after the tensile strain is accumulated in the matrix. It can be concluded that the major role of

β' in strengthening with the specific volume fraction of 16% is not load sharing but resistance to the dislocation motion, while the detailed interaction mode with dislocations is hard to tell from ND measurements. The β' strengthening by dislocations interactions (reported in [54] for similar alloy systems) might also be true at applied stresses lower than 107 MPa, in the region of dislocation-creep mechanisms.

To examine the single-peak response during creep, the temporal evolution of strains for different oriented grains (hkl strains of composite peaks) is plotted in Figures 29(a) and (b). At 107 MPa, the gradual increases of 200 and 310 strains occur in the primary creep regime. Then the lattice strain reaches a constant, and the transition corresponds well with the onset of the secondary creep [see Figure 29(b)]. Similar small changes in the lattice strains during primary creep has been reported in titanium alloys [55]. Choo et al. [55] suggested that the creep-induced strain has the same trend as the strain evolution in tension at high temperatures. As expected, our observation is in agreement with the trend of hkl strains in ferritic steels during the RT tension in the elastic-plastic region caused by grain-to-grain yielding [56-58]. Specifically, the trend was reported as the 110 direction yields first with the preferred orientation for slip, while the 200 direction yields later, and the load transfers to the 200 reflection [56, 58]. At high stress levels in the initial 15 minutes of creep (below 156 MPa), hkl strains seem to saturate. After the Fe matrix has yielded at 156 MPa, and the load transfers from β to β' phases, the 110 direction continues to accumulate the lattice strain. No obvious trend is observed for other reflections. The 211, 110 [59], and 310 [60] planes of BCC steels (textured or non-textured) have been suggested to predict macroscopic strains/stresses due to their linearity response to the applied stress and the little effect of residual intergranular strains in both elastic and plastic regions. It is also found that at low stresses, 211-oriented grains mimic the elastic-lattice response of the matrix (close to the Rietveld strain) and shows a diffraction elastic constant of 158 GPa, close to 156 GPa of the matrix. However, at high stresses and large plastic deformation, 211 and 110 strains deviate from the Rietveld strains, possibly due to the plastic anisotropy.

The grain rotation (or reorientation) induced by creep deformation is manifested by the texture evolution during creep. As shown in Figure 30, the integrated intensity is normalized with respect to the initial value at an undeformed state. A preferred orientation in 220 gradually develops as a function of time at 107 MPa, and the intensity enhances by a factor of 1.1. In contrast, at 150 MPa when a large macroscopic strain develops, 220 increases sharply by a factor of 1.5, 200 and 211 decrease about 20 ~ 30%, and 310 and 321 decline slightly. Intensities vary linearly with the plastic strain. It is consistent with the fact that BCC materials form a $\langle 110 \rangle$ fiber texture in the uniaxial tension deformation [61, 62]. Due to the accelerating creep rate, the grain reorientation during creep at 150 MPa gives rise to strain softening. Such texture evolution, when interpreted in conjunction with the lattice-strain response, implies that deformation is governed by slip.

B.3.3 Conclusions

In the B.3 Section, an advanced neutron study has been conducted in order to measure the lattice constants of α -iron matrix and coherent NiAl precipitates and understand the creep behavior of ferritic alloys at 973 K. The lattice constants (FBB18) are $2.8827 \pm 0.0011 \text{ \AA}$ and $2.8752 \pm 0.0004 \text{ \AA}$ for the α -iron matrix and NiAl precipitates, respectively. A model has been used to calculate the lattice constants and the calculation show a good agreement of the experimental data. Regarding the creep behavior of

ferritic alloys, at low stresses (or small plastic strains), creep deformation is dominant by the dislocation-climb-controlled creep. Creep-induced intergranular lattice strains are remarkable during the primary creep regime. No interphase stress is accumulated. At high stresses (or large plastic strains), the strain rate becomes higher, and deformation shifts to a dislocation-glide-controlled plastic flow, evidenced by the texture evolution. There is a slight load transfer from the matrix to precipitates, shortly followed by a drastic decrease of precipitate-phase strains and a sharp increase of the matrix-phase strain, possibly implying shearing of particles by dislocations. The major role of β' in strengthening with a 16%-volume fraction is not load sharing but interactions with dislocations.

B.4 Oxidation Behavior of Alloy FBB-8 in Air

Previous creep and ductility studies indicated that the alloy for the detailed study is FBB-8, with a composition of Fe-6.5Al-10Ni-10Cr-3.4Mo-0.25Zr-0.0005B in wt.%. The alloy was solution-treated at 1,200 °C for 30 min. in evacuated and sealed quartz tubes, followed by air cooling, and then aged at 700 °C for 100 h. Oxidation behavior of this alloy was studied at 650 °C, 750 °C, and 850 °C in air. Isothermal exposures were conducted for 100 h. The oxidation test coupons were 4 mm $\times$ 2 mm $\times$ 1 mm. The oxidation data in Figure 31 illustrates that the oxidation kinetics increases as increasing the temperature. When we compare these results with other creep resistant ferritic steels [T91 (modified 9Cr-1Mo) and P92 (9Cr-1.8W-0.5Mo)], as shown in Figure 32, it is found out that FBB-8 exhibits superior oxidation resistance at both 750 °C and 850 °C.

Preliminary characterizations of the oxidation surface by SEM were conducted. The SEM image in Figure 33 shows that the grinding scratches can be clearly observed, indicating the oxidation layer is very thin. The results of the compositional analysis by energy-dispersive X-ray (EDX) are summarized in Table 12. It was found out that the oxidation surface is most likely to be Al₂O₃, as proved by X-ray diffraction (XRD) analyses in Figure 34.

B.5 Calculations of the Interfacial Energy Between the α -Fe and B2 Intermetallics

B.5.1 Computational Procedure

As a part of the computational effort relevant to this research program, we have carried out a systematic study of coherent interfacial energies between the matrix BCC-Fe and B2 precipitates by the virtue of first-principles methods. To achieve our goals, we have employed a supercell method and the first-principles code, Vienna Ab Initio Simulation Package (VASP). Intrinsic to the supercell method, it is necessary establish the convergence of the calculated interfacial energy with respect to (w.r.t.) the supercell size. Three systems relevant to our research are chosen: BCC-Fe/B2-FeAl, BCC-Fe/B2-CoAl, and BCC-Fe/B2-NiAl.

Since B2 precipitates obey a cube-on-cube orientation relationship with the bcc-Fe matrix, we have calculated the interfacial energy considering three low-index interface habits: {100}, {110}, and {111}. In all cases, the appropriate supercells were constructed by gradually increasing their sizes in a direction perpendicular to the interface habit. All supercells are considered to be symmetric w.r.t. the interface plane (i.e., one half of the supercell is a B2 phase, and the other half is a bcc-Fe), and then total energies are calculated by relaxing structural and electronic degrees of freedom, while ensuring that the interface is stress-free (i.e., in-plane stresses are negligible).

B.5.2 Calculation Results

We have computed the interfacial energies of Fe/CoAl, Fe/FeAl, and Fe/NiAl systems as a function of the supercell size. The calculated coherent interfacial energies are summarized in Figure 35.

To define the convergence of the calculated interfacial energy, we have adopted, though arbitrary, a variation of energy $\pm 5 \text{ mJ/m}^2$ with increasing the supercell size. This value represents a very small variation of the total energy (per atom). As seen in Figure 34(a) for the case of the Fe/CoAl system, this criterion is satisfied for all three habits.

Figure 34(b) presents the similar behavior for the BCC-Fe/B2-FeAl system. Here, the calculated interfacial energies continue to decrease with increasing the supercell size. Figure 34(c) presents the calculated interfacial energies for the BCC-Fe/B2-NiAl system. Here, we have achieved the converged results for both {110} and {111} habits. However, in the case of {100} habit, the results still show oscillating behavior.

The results in Figures 34(b) and (c) seem to imply a complex interplay between magnetic and structural interactions. We plan to analyze these issues further by considering the relevant densities of states and charge densities.

B.6 First-Principles Calculation of Impurity Diffusivities in α -Fe

Self- and impurity diffusivities in BCC iron have been calculated within the formalisms of harmonic transition-state theory and the Le Claire nine-frequency model for vacancy-mediated diffusion. The approach combines first-principles calculations of vacancy formation, migration, and solute-binding enthalpies and entropies in the ferromagnetic phase, with an empirical relationship for the effect of magnetic disorder on diffusion activation energies. Please refer to Ref. [63] for more details on the first-principles calculation. Calculated Fe self-diffusion [Figure 36(a)] and W [Figure 36(b)] and Mo [Figure 36(c)] impurity-diffusion coefficients are shown to agree within a factor of five with the most recent experimental measurements in both the ferromagnetic and paramagnetic phases. Calculated diffusion coefficients for Mo and W impurities are comparable to or larger than that for Fe self-diffusion [Figure 36(d)] at all temperatures below the α - γ phase transition. Calculated activation energies for Ta and Hf impurities suggest that these solutes should also display impurity-diffusion coefficients larger than that for self-diffusion in BCC Fe.

B.7 Descriptions of the Phase Stability in the Fe-Al-Ni-Cr System by First-Principles Calculations and Integrated Design of the Alloy Using Thermo-Calc and DICTRA

The goals of this task, “Integrated design of the alloy using Thermo-Calc and DICTRA”, were to integrate results of first-principles calculations within the framework of computational thermodynamics and kinetics, using Thermo-Calc and DICTRA software. It is important to recognize that the accuracy and reliability of the predicted results derived from this approach depend critically on the accuracy of the relevant thermodynamic and kinetic databases (e.g., Thermo-Calc and DICTRA databases). This is particularly important given that we are concerned with multi-component and multi-phase alloys in this research program, and the experimental data available in the literature is insufficient to develop reliable databases, for reasons that are explained in detail below. Thus, our main accomplishment was to

undertake a very extensive literature review and pinpoint the key areas where further work is needed to develop reliable databases for computational design. This principle guided the work under this task, “Descriptions of the phase stability in the Fe-Al-Ni-Cr system by first-principles calculations”, in the present project, and has influenced work being done with the aid of the new Co-PIs in the recently started project of DE-FE0005868.

To elaborate, we conducted a literature survey of relevant diffusion data and realized important shortcomings of the DICTRA database, which relies heavily on the accuracy of the experimental data. It turns out that diffusivity of Cr and Mo show a large scatter (as shown in Figure 37). The DICTRA code cannot be used as a stand-alone software, as it requires the relevant thermodynamic parameters in addition to the mobility databases. We fully realized this issue in the course of our research during this project. To overcome important shortcomings of relevant databases, recently we have undertaken calculations of both thermodynamic and kinetic properties under the same footing, i.e., using the same computational tools with an emphasis on first-principles methods. This effort is being continued under the current grant (DE-FE0005868) where we leverage our work performed under this project.

Below is a brief summary of our effort in the areas of Milestones 3 and 5, “Description of the phase stability in the Fe-Al-Ni-Cr system by first-principles calculations” and “Integrated design of the alloy using Thermo-Calc and DICTRA,” respectively. These two tasks are tightly coupled and the progress in Milestone 3 was key to progress made in Milestone 5. Our major accomplishments may be summarized as follows:

- (i) Cluster expansion of BCC-(Al, Ni) and (Fe, Ni) alloys to calculate bulk thermodynamic properties
- (ii) An extensive literature review of the available data on diffusivities
- (iii) Publication of a paper presenting a new protocol for calculating impurity diffusivity in α -Fe: S. Huang, D.L. Worthington, M. Asta, V. Ozolins, G. Ghosh, and P.K. Liaw (2010), “Calculation of Impurity Diffusivities in α -Fe Using First-principles Methods”, *Acta Mater.*, vol. 58, p 1982-1993, 2010. The work that was presented in this manuscript was started under a previous grant, but the efforts under DE-09NT0008089 were critical to completing the work, which is why this grant was cited in the acknowledgements in the manuscript.

Further details of the progress made under Milestones 3 and 5 are given below. Due to the tightly inter-related nature of the tasks, we will group the accomplishments together. We acknowledge that our final goal of using Thermo-Calc and DICTRA to optimize the design of a new alloy was not met under the funding of DE-09NT0008089. However, important progress towards this goal was reached, as summarized below.

B.7.1 Computation of Bulk Thermodynamic Properties of Solid Solutions

The first-principles calculation of finite-temperature thermodynamic properties for bulk alloy phases makes use of the well-developed cluster-expansion approach. In this approach, the configurational energy of a substitutional alloy is parameterized in the form of a lattice model, with pair and multibody effective cluster-interaction parameters that are derived from fits to the energies of ordered intermetallic compounds calculated from first-principles methods based on the electronic density-functional theory. To perform these fits, we employ an automated software tool known as the Automated Alloy-Theoretic Alloy

Toolkit (ATAT). This is an important and critical issue when conventional experiments cannot be performed to measure thermodynamic properties.

B.7.1.1 Case 1: BCC Al-Ni alloys

Experimentally, the Al-Ni binary phase diagram is well established. There is no BCC phase field in the equilibrium diagram. Therefore, thermodynamic properties of BCC Al-Ni solid solutions cannot be measured by conventional experimental methods, such as calorimetry, etc.

On the other hand, the state-of-the-art computational method, such as cluster expansion, allows us to establish the effective-cluster-interaction (ECI) parameters of the Al-Ni system with the underlying BCC lattice. Once the ECIs are established, they can be used in large-scale Monte-Carlo simulations to compute mixing thermodynamic properties, such as mixing energy. The results of cluster expansion of (BCC)-Al-Ni are summarized in Figure 38.

As seen in Figure 38(a), a large number of ordered structures (green diamonds) are used in the cluster expansion to derive the mean field parameters (ECIs) that embody alloy energetics. Figure 38(b) shows the ECIs as a function of the size of clusters, such as pair, three-body, and four-body interactions. Considering the relative magnitudes of pair, three-body, and four-body interactions, it is obvious that the contribution of the latter to alloy energetics is not negligible, which could not be guessed without actually doing such calculations. A key advantage in this approach is that the ECIs enable us to calculate thermodynamic properties in the entire composition range without resorting to interpolation and extrapolation.

B.7.1.2 Case II: BCC Fe-Ni alloys

Experimentally, the Fe-Ni binary phase diagram is also well established, but the BCC phase field is stable only up to about 6 atomic percent (at.%) of Ni in the equilibrium diagram. As it is an important binary system for the alloys of interest, we have carried out cluster expansion of (BCC)-Fe-Ni alloys, and the results are summarized in Figure 39. As seen in Figure 39(a), like the (BCC)-Al-Ni system, a large number of ordered structures (green diamonds) are used in the cluster expansion to derive the mean field parameters (ECIs) that embody Fe-Ni BCC alloy energetics. Figure 39(b) shows the ECIs as a function of the size of clusters, such as pair, three-body, and four-body interactions. Once again, considering the relative magnitudes of pair, three-body, and four-body interactions, it is obvious that the contribution of the latter to alloy energetics is not negligible, which, once again, could not be guessed without actually doing such calculations.

All results based on first-principles calculations, summarized in Figures 38(a) and 39(a), require significant computational resources.

B.7.2 Computation of Kinetic Properties

Like bulk thermodynamics, we have undertaken a similar effort in the area of computational kinetics. The goal is to facilitate the design of alloys with optimal creep and coarsening properties. Therefore, it is imperative to undertake the development and validation of first-principles methods for calculating diffusivities in pure Fe and in representative binary alloys. For the purposes of alloy design, this information can be integrated with available experimental data in the development of the predictive

kinetic databases for the DICTRA-based calculations of diffusion-limited processes in multicomponent systems.

Critical assessments of thermo-kinetic data, combining experimental and ab initio results, and building relevant databases (Thermo-Calc and DICTRA) remain a major task as we seek to develop/design new and better materials with improved performance. Notwithstanding the associated optimizer sub-routine, the PARROT module, Thermo-Calc and DICTRA databases are not developed automatically, nor there is any built-in artificial intelligence. Rather, this task (developing Thermo-Kinetic databases) is largely a human effort requiring significant knowledge and expertise in areas of Physics, Chemistry, and Materials Science, and their integration into modern computational techniques and tools. In our current effort, a goal is to capture the underlying physics and mechanisms, as much as possible, within empirical models employed in Thermo-Calc and DICTRA formalisms.

Figure 39 illustrates the need for computational methods to augment the experimental data in the development of accurate kinetic databases. The figure shows a compilation of the available experimental data on impurity-diffusion coefficients in BCC Fe, plotted as a function of the solute-species electron-to-atom ratio. It can be seen that for several species (e.g., Cr and Mo), the measured values from the literature differ by as much as an order of magnitude. Further, diffusivities for several solute species, including most of the 5d elements, have yet to be measured. Clearly, an independent computational methodology capable of resolving discrepancies between measured values, which can also be used to derive estimates for species where data is not available, is critical to the development of the accurate kinetic databases required for alloy design where it is necessary to identify slow diffusing species.

In an effort to search for slow diffuser(s) in BCC Fe, our current effort includes a systematic study of calculating the impurity diffusion coefficients for all 5d solute atoms in Fe. To impart the reliability of calculated parameters governing diffusion kinetics, it is necessary to capture underlying physics and mechanism(s). This effort may further help build up the database for numerical diffusion calculations on multi-component Fe-based alloys within the DICTRA simulation formalism.

C. DEVELOPED PRODUCTS AND TECHNOLOGY-TRANSFER ACTIVITIES

C.1 Publications

1. Z.K. Teng, M.K. Miller, G. Ghosh, C.T. Liu, S. Huang, K.F. Russel, M.E. Fine, and P.K. Liaw, "Precipitate Characterization in a NiAl Strengthened Ferritic Steel," *Scripta Materialia*, 2010;63:61.
2. Z.K. Teng, C.T. Liu, G. Ghosh, P.K. Liaw, and M.E. Fine, "Effects of Al on the microstructure and ductility of NiAl-strengthened Ferritic Steels at Room Temperature," *Intermetallics*, 2010;18:1437.
3. S. Huang, D.L. Worthington, M. Asta, V. Ozolins, G. Ghosh, and P.K. Liaw, "Calculation of Impurity Diffusivities in α -Fe using First-principles Methods," *Acta Materialia*, 2010;58:1982.
4. S. Huang, B. Clausen, D. Brown, Z.K. Teng, Y.F. Gao, and P.K. Liaw, "Study of Microstrain Evolution during Creep of a Ferritic Superalloy," *Metallurgical and Materials Transactions A*, 2012;43:1497.
5. Z.K. Teng, F. Zhang, M.K. Miller, C.T. Liu, S. Huang, Y.T. Chou, R.H. Tien, Y.A. Chang, and P.K. Liaw, "Thermodynamic Modeling and Experimental Validation of the Fe-Al-Ni-Cr-Mo Alloy system," *Materials Letters*, 2012;71:36.
6. Z.K. Teng, C.T. Liu, M.K. Miller, G. Ghosh, E.A. Kenik, S. Huang, and P.K. Liaw, "Room Temperature Ductility of NiAl-strengthened Ferritic Steels: Effects of Precipitate Microstructure," *Materials Science and Engineering A*, 2012;541:22.
7. H. Ding, S. Huang, G. Ghosh, P.K. Liaw, and M. Asta, "A Computational Study of Impurity Diffusivities for 5d Transition Metal Slutes in α -Fe," *Scripta Mater.*, accepted.
8. S. Huang, G. Ghosh, X. Li, J. Ilavsky, Z.K. Teng, and P.K. Liaw, "Effect of Al on the NiAl-type B2 Precipitates in Ferritic Superalloys," *Metallurgical and Materials Transactions A*, accepted.
9. Z.K. Teng, G. Ghosh, M.K. Miller, S. Huang, B. Clausen, D.W. Brown, and P.K. Liaw, "Neutron-Diffraction Study and Modeling of the Lattice parameters on a NiAl Precipitate Strengthened Fe-Based Alloy," *Acta Materialia*, accepted.
10. S. Huang, Y.F. Gao, K. An, W. Wu, L. Zheng, M. Rawlings, D.C. Dunand, and P.K. Liaw, "In-situ Neutron-Diffraction Study of a Ferritic Superalloy during Tensile Deformation at Room and Elevated Temperatures," in preparation for *Acta Materialia*.

C.2 Presentations

1. S. Huang, Y.F. Gao, K. An, W. Wu, L. Zheng, M. Rawlings, D. Dunand, and P.K. Liaw, "In-situ Neutron-Diffraction Study of a Ferritic Superalloy during Tensile Deformation at Room and Elevated Temperatures," TMS 141th Annual Meeting, Orlando, FL, Mar., 2012.
2. S. Huang, B. Clausen, D. Brown, Z.K. Teng, G. Ghosh, M.E. Fine, and P.K. Liaw, "Study of Microstrain Evolution during Creep of a ferritic Superalloy by In-Situ Neutron Diffraction," TMS 140th Annual Meeting, San Diego, CA, Mar., 2011.
3. Z.K. Teng, F. Zhang, M. Miller, C.T. Liu, A.Y. Chuang, S. Huang, R.H. Tien, Y.T. Chou, and P.K. Liaw, "New Ferritic Steels with Combined Optimal Creep Resistance and Ductility

Designed by Coupling Thermodynamic Calculations with Focused Experiments,” 140th Annual Meeting, San Diego, CA, Mar., 2011.

4. S. Huang, X. Li, G. Ghosh, E. Kenik, J. Ilavsky, Z. K. Teng, G.Y. Wang, M.E. Fine, L. Liu, and P.K. Liaw, “Investigation of the Nano-Scale NiAl Precipitates in the Ferritic Superalloys by USAXS,” TMS 139th Meeting, Seattle, WA, 2010.
5. Z.K. Teng, P.K. Liaw, C.T. Liu, G. Ghosh, M.E. Fine, S. Huang, and G.Y. Wang, “The Ductility of NiAl-Strengthened Ferritic Superalloys at Room Temperature,” TMS 138th Meeting, San Francisco, CA, 2009.
6. P.K. Liaw, C.T. Liu, M.E. Fine, G. Ghosh, M. Asta, M. Miller, S. Huang, Z.K. Teng, and G.Y. Wang, “Computational Design and Prototype Evaluation of Aluminide-Strengthened Ferritic Superalloys for Power-Generating Turbine Application up to 1,033 K,” International Conference on Advanced High-Temperature and High-Strength Structure Materials (HTHSSM), The Hong Kong Polytechnic University, Hong Kong from October 4-8, 2009 (Invited).

C.3 Awards

1. P.K. Liaw, Engineering Research Fellow Award, The University of Tennessee, 2012.
2. S.Y. Huang, University of Tennessee Citation for Extraordinary Professional Promise. 2011.
3. S.Y. Huang, 1st Award, 2011 TMS Outstanding Student Paper Contest, TMS 2011 Annual Meeting & Exhibition.
4. S.Y. Huang, 1st Award, Student Poster Contest, Oak Ridge Chapter ASM Educational Symposium, 2011.
5. Z.K. Teng, University of Tennessee Chancellor’s Award for Extraordinary Professional Promise, 2011.
6. Z.K. Teng, Graduate Student Award for Excellence in Research, Department of Materials Science and Engineering, University of Tennessee, 2011.
7. S.Y. Huang, TMS Best Paper - Graduate Level Award, 2010.
8. S.Y. Huang, 1st Award, UT Chapter Sigma Xi Student Competition, The University of Tennessee, 2010.
9. Z.K. Teng, 2nd Award, ASM student poster competition, Knoxville, TN, November 2010.
10. Z.K. Teng, 1st Award, 2010 TMS Outstanding Student Paper Contest, TMS 2010 Annual Meeting & Exhibition.
11. Z.K. Teng, 2nd Award, UT Chapter Sigma Xi Student Competition, The University of Tennessee, 2010.
12. P. K. Liaw, L. R. Hesler Award, The University of Tennessee, 2010.
13. M.E. Fine, University of Minnesota Alumni Outstanding Achievement Award, 2010.
14. S.Y. Huang, 2nd Award, UT Chapter Sigma Xi Student Competition, The University of Tennessee, 2009.
15. S.Y. Huang, 3rd Award, Student Poster Contest, Oak Ridge Chapter ASM Educational Symposium, 2009.
16. Z.K. Teng, 1st Award, UT Chapter Sigma Xi Student Competition, The University of Tennessee, 2009.
17. Z.K. Teng, 3rd Award, Student Poster Contest, Oak Ridge Chapter ASM Educational Symposium, 2009.

C.4 Networks and Collaborations

1. National Ocean University, Taiwan: Dr. Kai Wu.
2. Oak Ridge National Laboratory: Dr. Michael Miller.

3. Advanced Photon Source at the Argonne National Laboratory: Dr. Jan Ilavsky.
4. Los Alamos Neutron Science Center, Los Alamos National Laboratory: Drs. Donald Brown and Bjorn Clausen.

D. LIST OF TABLES AND FIGUERES

Table 1 Compositions [weight percent (wt.%)] of FBB series alloys designed and fabricated until now.

Alloys #	Fe	Al	Cr	Ni	Mo	Hf	Zr	B	Nb	V	C	W	Ti
FBB-1	70	10	10	10	-	-	-	-	-	-	-	-	-
FBB-2	66.3	10	10	10	3.4	0.25	-	0.005	-	-	-	-	-
FBB-3	66.3	10	10	10	3.4	-	0.25	0.005	-	-	-	-	-
FBB-4	66.1	10	10	10	3.4	-	0.25	0.005	0.1	0.1	0.05	-	-
FBB-5	63.2	10	10	10	3.3	-	-	0.005	-	-	-	3.5	-
FBB-6	65.6	10	10	10	1.7	-	0.25	0.02	-	-	-	2.5	-
FBB-7	68.3	8	10	10	3.4	-	0.25	0.005	-	-	-	-	-
FBB-8	69.8	6.5	10	10	3.4	-	0.25	0.005	-	-	-	-	-
FBB-8W1	67.8	6.3	9.7	9.7	-	-	0.23	0.005	-	-	-	6.3	-
FBB-8W2	68.8	6.4	9.8	9.8	1.7	-	0.24	-	-	-	-	3.2	-
FBB-9	71.3	5	10	10	3.4	-	0.25	0.005	-	-	-	-	-
FBB-10	71.2	6.5	10	10	2.0	-	0.25	0.005	-	-	-	-	-
FBB-11	72.7	5	10	10	2.0	-	0.25	0.005	-	-	-	-	-
FBB-12	72.3	4	10	10	3.4	-	0.25	0.005	-	-	-	-	-
FBB-13	73.3	3	10	10	3.4	-	0.25	0.005	-	-	-	-	-
FBB-14	69.6	6.5	10	10	3.4	-	0.5	0.005	-	-	-	-	-
FBB-15	69.1	6.5	10	10	3.4	-	1	0.005	-	-	-	-	-
FBB-16	68.8	6.5	10	10	3.4	-	0.25	0.005	-	-	-	-	1
FBB-17	70.3	6	10	10	3.4	-	0.25	0.005	-	-	-	-	-
FBB-18	61.3	10	10	15	3.4	-	0.25	0.005	-	-	-	-	-

FBB-19	56.3	10	10	20	3.4	-	0.25	0.005	-	-	-	-	-
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Table 2 Composition [atomic percent (at.%)] of the phases in FBB8, determined by APT and AEM (in parenthesis).

	Fe	Al	Ni	Cr	Mo
Nominal	66.1	12.7	9.0	10.2	1.9
Matrix	71.9 (75.7)	8.9 (8.2)	4.5 (2.1)	11.7 (11.9)	3.0 (2.1)
NiAl Precipitates	12.7 (14.3)	43.6 (44.8)	41.2 (39.2)	0.8 (1.5)	1.4 (0.2)
Hyperfine precipitates	26.9 $\pm$ 2.1	41.6 $\pm$ 3.4	26.3 $\pm$ 3.7	3.3 $\pm$ 0.3	1.7 $\pm$ 0.6

Table 3 Compositions of the matrix and precipitates of the hot-rolled FBB8 (at.%).

FBB8 HR	Fe	Al	Ni	Cr	Mo
Figure 3 (a)	73.39	8.18	3.20	12.25	2.85
Figure 3 (b) precipitates	73.11	8.12	4.20	11.38	2.55
Figure 3 (b) matrix	14.47	41.94	40.71	1.07	1.38

Table 4 Tensile yield strength and ductility of hot-rolled ferritic alloys.

	Yield Strength (MPa)	Ductility (%)
FBB8	917	10
FBB10	898	9.6
FBB12	880	10.1

Table 5 Compositions (at.%) of the bright contrast phases

Phases	Fe	Al	Ni	Cr	Mo	Zr	B
Within grains	43.3	6.0	18.2	4.3	2.1	26.3	0.15
Along grain boundaries	60.8	6.3	11.1	6.1	8.0	4.2	0.22

Table 6 Elemental partitioning (at.%) and precipitate volume fractions of studied alloys. The standard error (σ) of the concentration estimate by APT is $\sim 0.03\%$, given by $\sigma = \sqrt{C(1 - C)/N}$, where C is the concentration, and N is the total number of atoms in the measured volume.

(α -Fe)-Matrix	Fe	Al	Ni	Cr	Mo	V _f
FBB3	69.0	14.5	2.2	11.7	2.5	82
FBB8	75.1	7.2	3.0	11.9	3.1	84
FBB12	79.3	3	3.1	12.1	2.4	86.4
FBB13	80.6	2.6	3	12	1.8	92.7
FBB18	73.5	9.3	1.7	12.4	3	72.5
FBB19	77	4.9	1.5	14	2.5	62.5
NiAl Precipitate	Fe	Al	Ni	Cr	Mo	V _f
FBB3	12.2	45.2	40.3	1.5	0.8	18
FBB8	12.7	43.6	41.2	0.8	1.4	16
FBB12	12	38.5	48.2	0.6	0.2	13.6
FBB13	18.1	36.5	43.1	1.7	0.3	7.3
FBB18	10.6	43.6	43.6	1.2	0.6	27.5
FBB19	10.4	43.2	44.1	0.8	1.1	37.5

Table 7 Bending ductility of FBB8 after aging for different time periods.

Aging Time (hrs)	Precipitate Radius (nm)	Bending Ductility (%)
100	65	0.94
500	96	0.91
1,000	118	0.91

Table 8 List of the Vickers hardness of FBB8 alloys before and after heat treatments (AC: air cooling; WQ: water quenching).

Alloy #	HV0.5	Description of heat treatment
1	383 $\pm$ 5	As-cast alloy delivered from Sophisticated Alloys, Inc.
2	474 $\pm$ 9	30 min. at 1,473 K+ AC
3	406 $\pm$ 6	30 min. at 1,473 K + AC + 100 hours at 973 K + AC
4	383 $\pm$ 9	30 min. at 1,473 K+ AC + 100 hours at 973 K + WQ
5	473 $\pm$ 7	30 min. at 1,473 K + AC + 100 hours at 1,073 K+ WQ

Table 9 The elemental concentrations in the β/β' phases, and the equivalent scattering lengths

Element	c_i^β	$c_i^{\beta'}$	$c_{i,ce}^{\beta'}$	$c_{i,co}^{\beta'}$	b_i (10^{-15} m)	$b_{i,ce}^{\beta'}$ (10^{-15} m)	$b_{i,co}^{\beta'}$ (10^{-15} m)	b_i^β (10^{-15} m)
Fe	0.735	0.106	0.045	0.16	9.45	0.4253	1.512	6.9458
Al	0.093	0.436	0.933	0	3.45	3.2188	0	0.3209
Ni	0.017	0.436	0	0.826	10.3	0	8.5078	0.1751
Cr	0.124	0.012	0.016	0.008	3.64	0.0582	0.0291	0.4507
Mo	0.030	0.0056	0.006	0.006	6.72	0.0403	0.0403	0.2015
Σ	0.999	0.996	1	1	-	3.7426	10.0892	8.0939

Table 10 Elemental partitioning by both experimental and thermodynamic predictions (at.%).

FBB18	Fe	Al	Ni	Cr	Mo
BCC-Fe Matrix	71.72	9.86	2.23	13.00	2.82
B2-NiAl Precipitates	10.63	43.56	43.64	1.17	0.56

Table 11 Atomic volumes of alloying elements in B2-NiAl precipitate.

Atom	x_{Al} [41]	x_{Ni} [41]	da/dx_i (nm)	Ω_i (nm ³)
Fe	0.20	0.80	-0.00267 [64]	0.01080
Cr	0.69	0.31	-0.0115 [65]	0.01091
Mo	0.46	0.54	0.0547 [66]	0.01873

Table 12 Composition of the selected area 1 shown in Figure 32.

Element (at. %)	Fe	Al	Cr	O
1	6.7	32.80	2.28	58.22

Figure 1 APT characterization of precipitates: (a) corresponding 15 at. % Al isoconcentration surface, (b) morphology of secondary hyperfine β' precipitates, (c) selected atom map of one hyperfine β' precipitate, (d) Mo-atom map, and (e) Cr-atom map. The total number of atoms analyzed is 3,532,698.

Figure 2 Atom probe samples by scanning electron microscopy (a) before rolling and (b) after rolling.

Figure 3 Two APT runs of the hot-rolled FBB8 sample: (a) Al-atom map of the matrix and (b) 15 at.% Al isoconcentration surface showing α -iron precipitates within the NiAl particles.

(a)

(b)

Figure 4 (a) Measured and fitted absolute intensity profiles for aged and crept FBB7 alloys, and (b) measured and fitted absolute intensity profiles for crept ferritic alloys with different Al contents.

Figure 5 Secondary creep rate, predicted precipitate parameters for the crept specimen, and measured precipitate diameter for aged alloys by TEM as a function of Al content. Spacing and diameter of precipitates for aged FBB3 alloy are denoted by orange closed and open circles, respectively.

Figure 6 Bright-field (BF) micrograph of dislocation-particle interactions identified as the Orowan bowing (dislocation loop) and dislocation climb in the compressively crept FBB7.

Figure 7 Tensile stress-strain curve of hot rolled and annealed FBB8.

Figure 8 A comparison of the microstructures of FBB8 in (a) before rolling, and (b) after rolling conditions.

Figure 9 Fracture surfaces of FBB8 in (a) after rolling and (b) before rolling conditions.

Figure 10 EBSD mapping of the hot-rolled FBB8 after annealing at 1,173 K for 1 hour, showing that many subgrains with a size of about $1\ \mu m$.

Figure 11 Bending ductility vs. precipitate-volume fraction (V_f) curve showing that the ductility decreases as V_f increases.

Figure 12 Elemental solubility in the α -Fe matrix showing that the low Al and high Ni solubility contributes to the ductility improvement.

Figure 13 Fracture surfaces of bending-tested samples (a) FBB-3, (b) FBB-8, (c) FBB-9, and (d) FBB-13, the representative ductile fracture is shown as an inset.

Figure 14 Fracture surface showing a mixture fracture mode of cleavage and ductile fractures, and (b) high magnification micrograph of the fracture surface in both ductile and cleavage areas.

Figure 15 The average grain size of FBB8 is about 100 μm before rolling (a) and 1 μm after rolling (b); the precipitate size grows to around 400 nm after rolling (c).

Figure 16 The precipitates radii of the as-quenched material after solution treatment and aging for 100 hrs were determined to be 50 nm (a) and 65 nm (b), respectively, by TEM.

Figure 17 USAXS intensity vs. scattering-vector plot of FBB8 aged for different time. The inter-particle spacing can be roughly calculated by 2π over the peak Q .

Figure 18 Bending ductility of the alloy FBB8 aged for different times showing independence of the inter-particle spacing and precipitate size on aging time.

Figure 19 Representative neutron-diffraction pattern and the single-peak-fitting result of the β' (100) superlattice reflection.

Figure 20 The separation of a fundamental reflection (100).

Figure 21 Representative X-ray diffraction pattern and the single-peak-fitting result of the β' (100) superlattice reflection.

Figure 22 Macroscopic creep curves of FBB-3 and -8 alloys during tensile creep at 973 K and 107 MPa. The FBB-3 ruptured around 780 min. of creep with a ductility of 6%, while FBB-8 continued to deform after 900 min. of creep.

(a)

(b)

Figure 23 Typical neutron-diffraction patterns for (a) FBB-3 and (b) FBB-8 alloys at 973 K. The red cross represents neutron-diffraction data. The green curve is the fitted profile using the Rietveld refinement. The pink curve is the difference between the fitted curve and measured data. The red toggle indicates the peak position of the β' phase, and the black toggle indicates the peak position of the β phase.

Figure 24 Longitudinal and transverse average interphase microstrains for β and β' phases in FBB-at 973 K under tensile stress of 107 MPa, together with the macroscopic creep strain as a function of time. Error bars from the GSAS Rietveld refinement are plotted.

Figure 25 Lattice misfit determined by the lattice parameters from Rietveld refinement for FBB-3 and -8 alloys.

Figure 26 Intergranular microstrains along the loading direction for [110], [200], [211], and [220] oriented grains.

Figure 27 Macroscopic-creep curves of strain vs. time at (a) 107 and (b) 150 MPa measured at the spectrometer for materials research at SMARTS. Strain rate vs. time is plotted in (c) and (d), respectively. Two dashed lines characterize primary, secondary, and tertiary creep regimes.

(a)

(b)

(c)

Figure 28 Temporal evolution of axial and transverse average phase strain for β and β' phases at (a) 107 and (b) 150 MPa. Error bars from the the GSAS Rietveld refinement are plotted. The average phase strain as a function of true stress along axial and transverse directions at 973 K is plotted in (c). Selected data points for the phase strains are shown at 107 MPa.

Figure 29 Temporal evolution of (a) hkl plane-specific strain in the axial direction; (b) true stress vs. hkl strain (dash curves representing the Rietveld-refined matrix-phase strain). T represents transverse, and A represents axial. Inset enlarging the high-stress region are inserted in (b). Errors bars from the GSAS Rietveld refinement and single-peak fitting are plotted.

Figure 30 Intensity evolution of the single peak as a function of (a) creep time and (b) plastic strain. The integrated intensity is normalized with respect to the initial integrated peak intensity at 18 MPa.

Figure 31 Oxidation data at 650 °C, 750 °C, and 850 °C in air for alloy FBB-8.

Figure 32 Comparisons between the oxidation kinetics of FBB-8 and other creep-resistant ferritic steels: (a) 1,023 K and (b) 1,123 K.

Figure 33 SEM images of the oxidation surface at 850 °C.

Figure 34 XRD analyses of FBB-8 after oxidation at 1,173 K for 100h.

(a)

(b)

(c)

Figure 35 Coherent interfacial energies of bcc-Fe and B₂ precipitates with different habits calculated from first principles: (a) BCC-Fe/B₂-CoAl, (b) BCC-Fe/B₂-FeAl, and (c) BCC-Fe/B₂-NiAl system.

(a)

(b)

(c)

(d)

Figure 36 (a) Predicted temperature dependence of the calculated α -Fe self-diffusion coefficient (red line) vs. published experimental data [67-76]; (b) Predicted temperature dependence of the calculated impurity-diffusion coefficient for W in α -Fe (red line) vs. published experimental data [77-81]; (c) Predicted temperature dependence of the calculated impurity-diffusion coefficient for Mo in α -Fe (red line) vs. published experimental data [80-84]; (d) Predicted temperature dependence of the diffusion coefficient for W and Mo-impurity diffusion, compared with that for self-diffusion in α -Fe.

Figure 37 Ratio of diffusivities for impurity diffusion relative to self-diffusion in the BCC Fe, which is plotted for a variety of solutes as a function of electron to atom ratio. The results correspond to a temperature of $T = 1,050$ K and are obtained from the published measurements.

Figure 38 Cluster expansion of a BCC Al-Ni system: (a) calculated formation energy, from first-principles, of ordered structures (in green diamond), and (b) the corresponding fitted ECIs versus cluster diameter (normalized by the nearest neighbor distance) in BCC Al-Ni alloys.

Figure 39 Cluster expansion of a BCC Fe-Ni system: (a) calculated formation energy, from first-principles, of ordered structures (in green diamond), and (b) the corresponding fitted ECIs versus cluster diameter (normalized by the nearest neighbor distance) in BCC Fe-Ni alloys.

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F. REFERENCES

1. H.K.D.H. Bhadeshia. ISIJ International 2001; **41**: 626.
2. C. Stallybrass and G. Sauthoff. Materials Science and Engineering A 2004; **387-389**: 985.
3. J.H. Westbrook. J. electrochem. Soc. 1956; **103**: 54.
4. M.K. Miller and M.G. Hetherington. Journal de physique 1989; **50**: 8425.
5. H.A. Calderon-Bonavides, *Oswald ripening of NiAl precipitates in Fe base Ni-Al-Mo alloys*. 1986, Northwestern University
6. A.I. Kovalev, R.A. Barskaya, and D.L. Wainstein. Surface Science 2003; **35-40**: 532.
7. J. Herrmann, G. Inden, and G. Sauthoff. Acta Materialia 2003; **51**: 2847.
8. J.M. Oblak, J.E. Doherty, A.F. Giamei, and B.H. Kear. Metallurgical Transactions 1974; **5**: 1252.
9. Z.K. Teng, C.T. Liu, G. Ghosh, P.K. Liaw, and M.E. Fine. Intermetallics 2010; **18**: 1437.
10. Z.K. Teng, M.K. Miller, G. Ghosh, C.T. Liu, S. Huang, K.F. Russell, M.E. Fine, and P.K. Liaw. Scripta Materialia 2010; **63**: 61.
11. L.M. Brown and R.K. Ham, eds. Strengthening Methods in Crystals, ed. A. Kelly and R.B. Nicholson. 1971, Elsevier: Amsterdam.
12. M.E. Kassner, *Fundamentals of creep in metals and alloys*. 2004: Elsevier.
13. J.W. Martin, *Micromechanisms in Particle-Hardened Alloys*. 1980, Cambridge, U.K.: Cambridge University Press. 62.
14. R. Darolia. JOM 1991; **43**: 44.
15. D.B. Miracle. Acta Metall. Mater. 1993; **41**: 649.
16. A.W. Thompson. Metall. Trans. A 1977; **8A**: 833.
17. P. Mummery and B. Derby. Mater. Sci. Eng. A 1991; **135**: 221.
18. V. Amigo, J.L. Ortiz, and M.D. Salvador. Scr. Mater. 2000; **42**: 383.
19. L.M. Brown and J.F. Embury. *The microstructure and design of alloys*. in *The third international conference on the strength of metals and alloys*. 1973.
20. W.C. Leslie. Metall. Trans. A 1972; **3**: 5.
21. S.F. Pugh. Phil. Mag. 1954; **45**: 823.
22. R. Darolia, K.M. Chang, and H.A. Lipsitt. Intermetallics 1993; **1**: 65.
23. R. Darolia, D. Lahrman, and R.D. Field. Scripta Metall. Mater. 1992; **26**: 1007.
24. H. Bei, Y. Yamamoto, M.P. Brady, and M.L. Santella. Mater. Sci. Eng. A 2010; **527**: 2079.
25. B. Ingham, S. Dickie, H. Nanjo, and M.F. Toney. Journal of Colloid and Interface Science 2009; **336**: 612.
26. C.W. Corti, P. Cotterill, and G. Fitzpatrick. Int. Met. Rev. 1974; **19**: 77.
27. M.F. Ashby. Phil. Mag. 1966; **14**: 1157.
28. J. Gurland. Trans AIME 1963; **227**: 1146.
29. I. Baker. Scr. Mater. 1999; **41**: 409.
30. H. Kuhn and D. Medlin, *Mechanical Testing and Evaluation*, in *ASM Handbook*. 2000.
31. D.A. Curry and J.F. Knott. Metal Science 1978; **12**: 511.
32. G. Oates. JISI 1969; **207**: 353.
33. R.C. Sharma, *Principles of heat treatment of steels*. 2003: New Age International.
34. Y.D. Wang, H.B. Tian, A.D. Stoica, X.L. Wang, P.K. Liaw, and J.W. Richardson. Nat. Mater. 2003; **2**: 101.
35. S. Ma, D. Brown, M. Bourke, M.R. Daymond, and B.S. Majumdar. Mater. Sci. Eng. A 2005; **399**: 141.
36. H.M. Rietveld. J. Appl. Crystallogr. 1969; **2**: 65.
37. A.C. Larson and R.B. Von Dreele, *General Structure analysis system (GSAS)*. 1994, Los Alamos National Laboratory Report LAUR. p. 86.

38. R.B. Von Dreele. J. Appl. Crystallogr. 1997; **30**: 517.
39. H.J. Stone, T.M. Holden, and R.C. Reed. Acta Materialia 1999; **47**: 4435.
40. S. Ma, P. Rangaswamy, and B.S. Majumdar. Scr. Mater. 2003; **48**: 525.
41. C. Jiang. Acta Materialia 2007; **55**: 4799.
42. Z.A. Basinski, W. Hume-Rothery, and A.L. Sutton. Proc. Roy. Soc. (London) A 1955; **229**: 459.
43. A.J. Bradley and A.H. Jay. Proc. Roy. Soc. (London) A 1932; **136**: 210.
44. A. Taylor and R.M. Jones. J. Phys. Chem. Solids 1958; **6**: 16.
45. E.P. Abrahamson and S.L. Lopata. Trans AIME 1966; **236**: 76.
46. A.L. Sutton and W. Hume-Rothery. Phil. Mag. 1955; **46**: 1295.
47. A.P. Gulyaev and E.F. Trusova. Zh. Tech. Fiz 1950; **20**: 66.
48. G. Ghosh, *EPRI Report, Part I*. 1999.
49. P.H. Kitabjian and W.D. Nix. Acta Materialia 1998; **46**: 701.
50. H.J. Frost and M.F. Ashby, *The plasticity and creep of metals and ceramics*. 1982, UK: Cambridge University.
51. H. Calderon and M.E. Fine. Mater. Sci. Eng. 1984; **63**: 197.
52. R. Taillard, A. Pineau, and B.J. Thomas. Mater. Sci. Eng. 1982; **54**: 209.
53. S. Ma, V. Seetharaman, and B.S. Majumdar. Acta Materialia 2008; **56**: 4102.
54. S.M. Zhu, S.C. Tjong, and J.K.L. Lai. Acta Materialia 1998; **46**: 2969.
55. H. Choo, D. Seo, J. Beddoes, M. Bourke, and D. Brown. Appl. Phys. Lett. 2004; **85**: 4654.
56. M.R. Daymond and H.G. Priesmeyer. Acta Materialia 2002; **50**: 1613.
57. E.C. Oliver, M.R. Daymond, and P.J. Withers. Acta Materialia 2004; **52**: 1937.
58. Y. Tomota, P. Lukas, S. Harjo, J.H. Park, N. Tsuchida, and D. Neov. Acta Materialia 2003; **51**: 819.
59. M.T. Hutchings, P.J. Withers, T.M. Holden, and T. Lorentzen, *Introduction to the characterization of residual stress by neutron diffraction*. 2005: CRC Press.
60. S.J. Lewis and C.E. Truman. J. Phys. D-Appl. Phys. 2010; **43**.
61. O. Engler and V. Randle, *Introduction to texture analysis: macrotexture, microtexture, and orientation mapping*. 2009: CRC press.
62. J.W.L. Pang, T.M. Holden, and T.E. Mason. J. Strain Anal. Eng. Des. 1998; **33**: 373.
63. S. Huang, D.L. Worthington, M. Asta, V. Ozolins, G. Ghosh, and P.K. Liaw. Acta Materialia 2010; **58**: 1982.
64. H. Lipson and A. Taylor. Proc. Roy. Soc. A 1939; **173**: 232.
65. G. Frommeyer, R. Fischer, J. Deges, R. Rablbauer, and A. Schneider. Ultramicroscopy 2004; **101**: 139.
66. H. Latreche, G. Bozzolo, P. Masset, T. Weber, and M. Schutze. Mater. Sci. Eng. A 2010; **527**: 5837.
67. R.J. Borg and C.E. Birchenall. AIME 1960; **218**: 980.
68. F.S. Buffington, K. Hirano, and M. Cohen. Acta Metall. 1961; **9**: 434.
69. J. Geise and C. Herzig. Z. Metallk. 1987; **78**: 291.
70. D. Graham and D.H. Tomlin. Phil. Mag. 1963; **8**: 1581.
71. G. Hettich, H. Mehrer, and K. Maier. Scr. Metall. 1977; **11**: 795.
72. Y. Iijima, K. Kimura, and K. Hirano. Acta Metall. 1988; **36**: 2811.
73. D.W. James and L.G. M. Phil. Mag. 1966; **14**: 701.
74. J. Kucera, B. Millien, J. Ruzickova, V. Foldyna, and A. Jakobova. Acta Metall. 1974; **22**: 135.
75. M. Lubbehusen and H. Mehrer. Acta Metall. Mater. 1990; **38**: 283.
76. C.M. Walter and N.L. Peterson. Phys. Rev. 1969; **178**: 922.
77. P.L. Gruzin. Dokl Akad Nauk SSSR 1954; **94**: 681.
78. S. Takemoto, H. Nitta, Y. Iijima, and Y. Yamazaki. Phil. Mag. 2007; **87**: 1619.
79. J. Kieszniowski. Prace Inst. Hutniczych 1967; **19**: 253.
80. J. Kucera, B. Millien, and K. Ciha. Koveve Mater. 1969; **7**: 97.

81. P.J. Alberry and C.W. Haworth. *Met. Sci.* 1974; **8**: 407.
82. V.T. Borisov, V.M. Golikov, and G.V. Sherbedinskiy. *Phys. Met. Metall.* 1966; **22**: 175.
83. H. Nitta, T. Yamamoto, R. Kanno, K. Takasawa, T. Lida, Y. Yamazaki, S. Ogu, and Y. Iijima. *Acta Materialia* 2002; **50**: 4117.
84. K. Nohara and K. Hirano. *J Jpn Inst. Met.* 1976; **40**: 1053.