

**Alloy Design of Creep Resistant Fe₃₀Cr₃Al Alloys
Strengthened by Laves Phase**

A Dissertation Presented for the
Doctor of Philosophy
Degree

The University of Tennessee, Knoxville

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ABSTRACT

With the demand for materials at higher operation temperature for fossil energy to improve efficiency and reduce the emission of CO₂, current ferritic-martensitic steels are not comparable due to the upper temperature limit and Type IV cracking. Therefore, a carbon-free Fe-30Cr-3Al alloy system strengthened by C14 Laves phase was designed with thermodynamic calculations (ThermoCalc®) at target service temperature 700 °C for creep applications. Previous studies showed minimum creep rate decreases from 1.7×10^{-6} %/s to 1.4×10^{-7} %/s as Laves phase fraction increases from 1.5 to 3.38 mole percent. Precipitate free zones (PFZs) adjacent to grain boundaries were observed and hypothesized to be the potential creep failure mechanism. In this study, to increase the Laves phase mole percent to obtain a lower minimum creep rate, the addition of Laves phase-forming elements (e.g. Nb, Ti, W, Zr, and Ta) were considered. Alloy compositions were narrowed down based on thermodynamic and kinetic calculations and then aged at 700 °C up to 3000 hours to understand the microstructural evolution of Laves phase and PFZ. The Fe-30Cr-3Al-0.2Si-1Nb-1Ti alloy has the highest microstructural stability among all the tested alloys after 3000-hour aging. The Fe-30Cr-3Al-0.2Si-1Nb-6W alloy exhibited rapid nucleation, growth, and postponed coarsening behavior compared to the other tested alloys. Thus, a core-shell structure in Laves phase in the Fe-30Cr-3Al-0.2Si-1Nb-6W alloy was hypothesized and confirmed by atom probe tomography observation. The formation of core-shell structure was rationalized by the difference in diffusivities between Nb (1.7×10^{-16} (m²/s)) and W (5.2×10^{-18} (m²/s)) in ferritic matrix at 700 °C. Fe-30Cr-3Al-1Nb-0.2Si-5W alloy showed similar minimum creep rate (6.67×10^{-7} %/s) at 90 MPa compared to the reference Fe-30Cr-3Al-0.2Si-2Nb alloy (1.47×10^{-7} %/s) at 70 MPa at 700 °C. The minimum creep rate (9.58×10^{-7} %/s) calculated using modified Bird-Mukherjee-Dorn model based on the PFZ width characterized by TEM was similar to the experimental

minimum creep rate (6.67×10^{-7} %/s). The possibility to use metal big area additive manufacturing for Fe-30Cr-3Al was demonstrated and showed a ~66% increase in length compared to the traditionally manufactured specimen. In summary, the proposed alloy design strategy of Fe-30Cr-3Al-1Nb-based alloy system based on thermodynamic calculations was validated by microstructural characterizations and creep tests.

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CHAPTER ONE

INTRODUCTION

Background

More than 60% of the electrical power produced in the United States was generated using fossil fuels in 2018 [1]. Fossil fuel power plants are known to emit gases such as nitrogen oxides (NO_x), sulfur oxides (SO_x), and carbon dioxide (CO_2) considered as major contributors to global warming. Increasing the thermal efficiency of fossil fuel powered electricity generation can decrease the emissions of CO_2 , while maintaining the same amount of energy generation. For instance, increasing the operational condition from supercritical (SC) (540-580 °C and 22.1-25 MPa) to ultra-supercritical (USC) (580-620 °C and 22.5-25 MPa) increases the power extraction efficiency by approximately 5% [2]. For next generation fossil fuel power plants, materials need to be sustainable under the Advanced-USC (A-USC) condition (700 °C, 35 MPa). Nickel-based superalloys are one of the candidates. However, they are not economic to be implemented for the majority parts (e.g. tubing) in the power plants. Take Inconel 718 (Nickel-based superalloy) and Grade 92(ferritic-martensitic steel) for example, the costs based on alloy elements are 10.8 and 1.4 (USD/Kg), respectively¹. Approximately one-tenth in cost compared to Nickel-based superalloys makes developing ferritic-martensitic steels with creep strength which can sustain under A-USC condition attractive. The ferritic-martensitic steels containing 9-12Cr

¹ Data from December 31, 2018. Source: <http://mineralprices.com/>

(in weight percent, wt.%) are currently used in conventional SC and USC power plant applications and shows adequate component lives due to their creep strengths [3]–[8]. However, these steels are also known to suffer from an inferior oxidation resistance [9] and unexpectedly short life due to type IV cracking in the weldments. Type IV cracking is a premature failure at the fine grain heat affected zone (FGHAZ) [10], [11]. It is attributed to the formation of a weakened microstructure according to complex growth and dissolution of M_xC_y (e.g. $M_{23}C_6$) carbides during thermal cycles in the weld procedure and post-weld heat treatment. The formation of such a weakened microstructure at the FGHAZ strongly relies on the phase transformation (martensite/ferrite to austenite), so that one of the effective approaches to improve the high-temperature properties, including weldments in the scope, would be to design an alloy free from such phase transformations in a wide temperature range, from liquidus to ambient temperature. Thus, an Fe-30Cr-3Al alloy system, which has a fully ferritic (Body-centered cubic) matrix from ambient temperature to melting temperature and intermetallic Laves phase (hexagonal close packed) as strengthening phase, became the focus of current research.

Motivation

For the materials selection of tubing in fossil fuel power plants, oxidation and ash corrosion resistances are critical. Due to the formation of chromia (Cr_2O_3) and alumina (Al_2O_3), FeCrAl alloys were reported to have promising oxidation [12] and ash corrosion [13] resistances than F-M steels. As mentioned previously, Fe-30Cr-3Al alloys system has fully ferritic microstructure until melting point. The formation of weakened microstructure (e.g.

FGHAZ), which is responsible for type IV cracking, is not expected. Yet, due to the limited carbon solubility in body centered cubic (BCC) matrix, precipitate strengthening at elevated temperature by carbides and carbonitrides would not be possible. Hence, building upon the development of oxidation and ash corrosion resistances, alloy design of creep-resistant Fe-30Cr-3Al alloys system strengthened by intermetallic compound should be investigated. In this study, an alloy design methodology was proposed based on thermodynamic and kinetics calculations. The proposed methodology was later validated by characterization of microstructural evolution and creep test results.

The layout of the remaining of this dissertation is as following: Literature review of the Fe-Cr and Fe-Cr-Al alloys for creep applications and unanswered questions from the published literature were included in Chapter Two. Materials compositions and experimental details were included in Chapter Three. The alloy design and alloy down-select process based on thermodynamic calculations and manufacturing feasibility were covered in Chapter Four. The microstructural evolution of the selected alloys during isothermal aging at the target service temperature 700 °C were discussed in Chapter Five. The sub-micron level characterizations of Laves phase with 4, 24, and 3000 h aging at 700 °C were discussed in Chapter Six. The selected alloys with the expected superior creep resistance were evaluated in Chapter Seven. A potential manufacturing method for Fe-30Cr-3Al alloys via metal Big Area Additive Manufacturing (mBAAM) was demonstrated in 0. The above results and conclusions were summarized in **Error! Reference source not found..**

CHAPTER TWO

LITERATURE REVIEW

Background

The materials used in fossil fuel power plants require not only enough strength under elevated temperatures and pressures, for example 650 °C and 34.3 MPa, depend on the service condition, but also oxidation and corrosion resistance. Chromium addition enhances the oxidation and corrosion resistance in steels[14]. Therefore, Fe-Cr ferritic-martensitic alloys drew attention from researchers. Fe-Cr ferritic-martensitic alloys have been studied intensively for high temperature applications. Precipitation strengthening is one of the major strengthening mechanisms for creep resistant alloys. Strengthening effect contributed by the precipitates can be expressed by Orowan stress, which hinders the dislocation movement in material. Orowan stress is inversely proportional to interparticle spacing[15]. Therefore, with a fixed volume fraction of precipitates, alloys with the following microstructural features will potentially lead to a promising creep resistance: (1) fine particle size, usually less than 500 nm and (2) no apparent increase in particle size throughout the service time under elevated temperature. Researchers performed thermodynamic calculations and kinetic simulations to understand the microstructural evolution of the precipitates and therefore to obtain the stable microstructure by alloy design[16]–[20]. The target application in fossil fuel power plant for the materials in this study is the steam tubing between boiler and turbine with 30-60 mm diameter[21] with A-USC operating conditions(700 °C, 35 MPa). Traditional tube manufacturing process involves with hot and cold rolling to make strips. The strip would then be rolled into a

tubular form followed by a seam weld after bringing two ends of the strip to contact. Experiencing several steps of thermal and mechanical processing, intragranular and grain boundary precipitates (e.g. $M_{23}C_6$ in Grade 91 steels) are already formed before exposing to the service temperature. These pre-existing precipitates will coarsen rapidly compared to the ones formed during service and lose their strengthening effect. Therefore, solutionization treatment, to dissolve the residual precipitate into a supersaturated solid solution, is required to for the ideal ferritic microstructure with finely dispersed precipitates. Additive manufacturing is an alternative method with fewer thermal-mechanical processes. In this study, the possibility of manufacturing tube for fossil fuel applications with the one of the designed alloy compositions using metal big area additive manufacturing (mBAAM) is also investigated. Similar other additive manufacturing process, residual stress might be an issue for making large component for Fe-Cr-Al alloys due to their limited room temperature ductility. In the following paragraphs, the development of creep-resistant Fe-Cr and Fe-Cr-Al based alloys will be reviewed.

Development of Creep Resistant Alloys

Fe-Cr alloys with various Cr content and other alloying elements (e.g. Mo, W, etc.) have been investigated to enhance creep behavior under different service conditions. 9 Cr steels, a ferritic-martensitic (F-M) steels, is currently used in fossil fuel power plants. Yet, operating temperatures are indeed not good enough to increase efficiency. However, a large number of greenhouse gases, such as CO_2 and NO_x , are emitted from coal-fired power plants. The average efficiency of fossil fuel power plants in the United States is around

34% due to most of the plants are subcritical or early supercritical units. The only ultra-supercritical (USC) unit in the United States is John W Turk Jr plant in Arkansas with efficiency around 42%[22]. Increase the efficiency of the power generation by increasing the service temperature and pressure (e.g. 538 °C, 24.1 MPa to 650 °C, 34.4 MPa) can increase the efficiency by 6.5% and reduce the emission of the environmentally damaging gases. Therefore, new materials that can be used at higher temperature and pressure (700 °C, 35 MPa) must be developed. In the following paragraphs, alloy development with the increased Cr contents and their corresponding service condition will be reviewed.

9-12 Cr Steels

9-12 Cr steels are F-M steels with tempered martensite microstructure strengthened by carbides and carbon nitrides. One of the reasons for 9 wt% Cr is a balance between creep strength and low Ductile-to-Brittle Transition Temperature (DBTT) below room temperature for the ease of transportation and weldability. Abe et al [23] showed the Cr effect on DBTT and creep rupture strength after aging at 600 °C for 1000 hours from 2 to 15 wt% Cr in Cr-2W-0.1C steels (shown in Figure 2.1). With the Cr content increases from 2 to 9 wt%, the creep strength increases around 50 MPa. Although the DBTT increases, but it is still below room temperature. Increasing Cr from 9 to 12 wt% does not affect the creep strength, but a slight increase in DBTT, which is still below room temperature. Yet, if Cr content increases from 12 to 15 wt%, it not only decreases the creep strength, but increases the DBTT to around 50 °C, which would be an issue for room temperature operation and transportation.

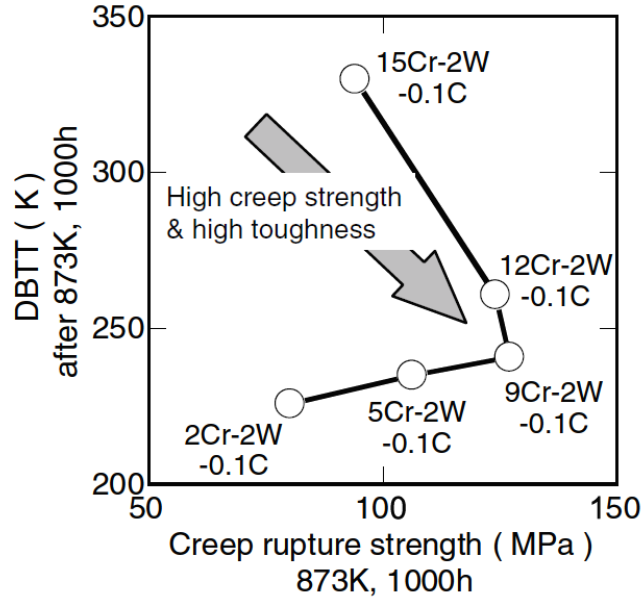


Figure 2.1 Cr effect between DBTT and creep rupture strength after aging at 600 °C for 1000 hours from 2 to 15 wt% Cr in Cr-2W-0.1C steels[7]

Strengthening Mechanism for 9-12 Cr Steels

Understanding the strengthening mechanism will help us to design and improve the creep resistance alloys. The 9-12 Cr steels are strengthened by solid-solution hardening, precipitate/dispersion hardening, and sub-boundary hardening. Solid-solution hardening is a result of lattice strain caused by the solute atoms (e.g. Mo, W) with different atomic size than the solvent iron atoms. In most cases, precipitate hardening is the dominant mechanism. For creep resistant alloys, the carbides (e.g. $M_{23}C_6$, face-centered cubic), carbonitrides (e.g. MX, face-centered cubic) and intermetallic compounds (e.g. A_2B Laves phase, hexagonal close packed) are the usual strengthening precipitates located in both

matrix and grain boundary. Also, the oxide-dispersed-strengthened (ODS) steels is another case for 9-12 Cr steels, however, it is not the focus of this study. The Orowan stress,[24], is the governing equation for precipitate strengthening as shown below,

$$\sigma_{Or} = \frac{0.8MGb}{\lambda}$$

where M is the Talyor factor, G is the shear modulus, b is the magnitude of the Burgers vector, and λ is the interparticle spacing. Orowan stress is inversely proportional to interparticle spacing, hence, to maximize the strengthening effect, finely dispersed precipitates are the ideal microstructure.

Since 9-12 Cr steels are the F-M steels, which have tempered martensitic microstructures. Tempered martensite consists of laths and blocks decorated with carbides (schematic is shown in Figure 2.2). Therefore, lath and block boundaries can be viewed as elongated subgrain boundaries for strengthening. The governing equation is shown below,

$$\sigma_{sg} = \frac{10Gb}{\lambda_{sg}}$$

where λ is the short width of the elongated subgrain. Sub-boundary strengthening is closely related to precipitates since finely distributed precipitates along the sub-boundaries have the pinning effect to suppress the boundaries coarsening. Therefore, the microstructural evolution of precipitates is critical for creep resistant steels.

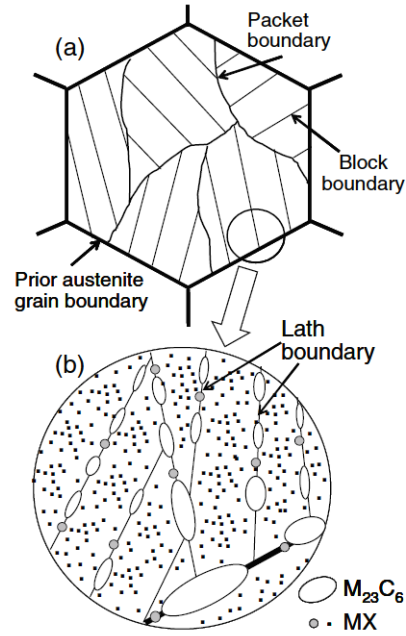


Figure 2.2 Schematics of (a) Tempered Martensite microstructure (b) the distribution of carbides in 9Cr steels[7]

Mechanism of the Loss of Creep Strength

Researchers have tried to understand the mechanism for the loss of the creep strength in 9-12 Cr steels. The loss of precipitate hardening during creep due to coarsening of carbides in both matrix and sub-boundaries is the proposed mechanism. The formation of Z phase, M_6X carbonitride, and $Fe_2(W,Mo)$ Laves phase at the expense of existing MX precipitates and solute atoms leads to the loss of creep strength[4]. For instance, Z phase number density increased, while the number density of MX carbonitrides decreased after 10000 h at 600 °C in grade 91 steels[25] (see Figure 2.3). Z phase is a nitride of $Cr(Nb,V)N$, which is a more thermodynamically stable phase than MX, that forms during service. The loss of

creep strength in T91 (9Cr-1Mo-0.2V-0.05Nb) steel (T denotes as tube) is reported due to preferential recovery of lath boundary close to PAGBs, which leads to localized creep deformation and eventually premature failure. Z phase formed at the expense of existing MX due their similarity in composition and Ostwald ripening is more prominent near PAGBs because of its enhanced diffusion[26]. This phenomenon accelerates the recovery of lath boundary near PAGBs due to lack of pinning effect of fine precipitates. Moreover, MX carbonitride (~ 50 nm) and $M_{23}C_6$ carbides (~ 200 nm) are the strengthening precipitates for grade 91 (9Cr) steels. Due to the enhanced diffusion at PAGBs, the $M_{23}C_6$ has a greater coarsening rate in vicinity of PAGBs than in the matrix during creep[27]. Therefore, controlling the microstructural stability through either thermo-mechanical treatment (TMT) or alloy design is important for 9-12 Cr steels.

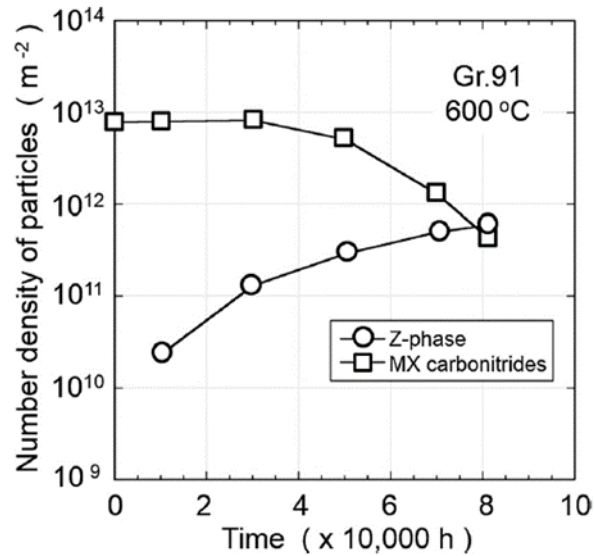


Figure 2.3 Change in number density of MX and Z-phase particles in Grade 91 during creep at 600 °C and 70 MPa[25]

Alloy Design for 9-12 Cr Steels

Controlling microstructure in 9-12 Cr steels can be conducted either through Thermo-Mechanical Treatment (TMT) or alloy design. The readers are recommended to find the detailed information about TMT for 9-12 Cr steels elsewhere [10], [11], [28]. As discussed before, coarsening of $M_{23}C_6$ along the sub-boundaries causes the loss of creep strength. 9-12 Cr steels with adequate amount of carbon will form a large amount of Cr-rich $M_{23}C_6$ carbides. Also, Wey *et al* [29] reported that the coarsening rate of Cr-rich carbides (e.g. $M_{23}C_6$) is larger than V and Nb carbides (e.g. MX, X stands for C, N). Thus, it is important to reduce the carbon concentration to eliminate the rapid coarsening of $M_{23}C_6$ carbides and promote the formation of MX carbonitrides. A thermodynamic calculation of 9Cr-3W-3Co-0.2V-0.05Nb-0.05N steel during tempering at 800 °C was reported [7]. Note that the equilibrium precipitates of this steel are Fe_2W Laves phase, MX, and $M_{23}C_6$. Due to short term tempering (1 hour), Laves phase is omitted. Also, the change in amounts of MX and $M_{23}C_6$ as a function of carbon concentration is similar in 650 °C² to 800 °C. As shown in Figure 2.4, the amount of MX remains nearly constant while $M_{23}C_6$ decreases significantly as carbon content decreases. The amount of MX is larger than $M_{23}C_6$ when carbon concentration is below 0.02 wt%. The creep behavior as a function of carbon content is shown in Figure 2.5a. The time to rupture and the minimum creep rate showed the same trend: the steel with carbon content below 0.018 wt% has the most promising creep behavior among the tested steels. Additionally,

² Calculated by author using different database (TCFE9)

Figure 2.5b shows a comparison between 0.002 wt% C and 0.078 wt% C steels. The minimum creep rate of 0.002 % is an order of magnitude lower than 0.078 % C steel. To sum up, reducing the carbon concentration, which eliminates the rapidly coarsening $M_{23}C_6$ and promotes the formation of MX carbonitride, results in a better creep behavior.

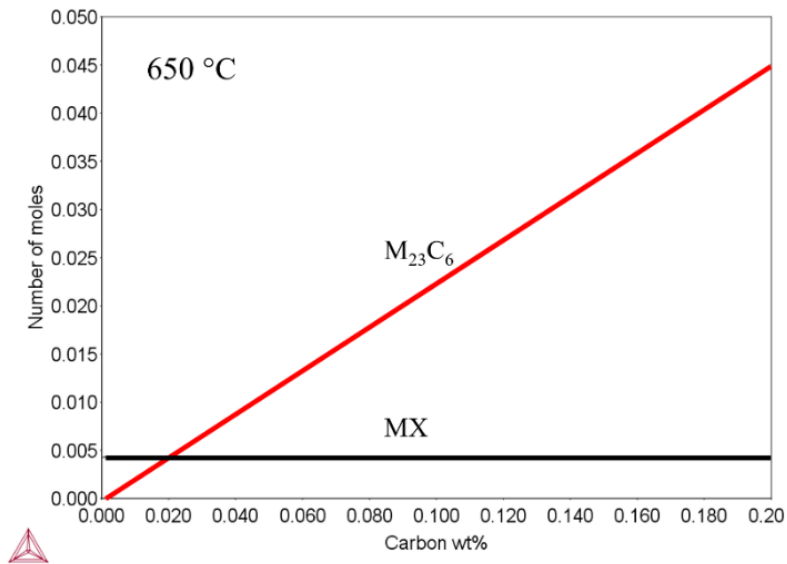
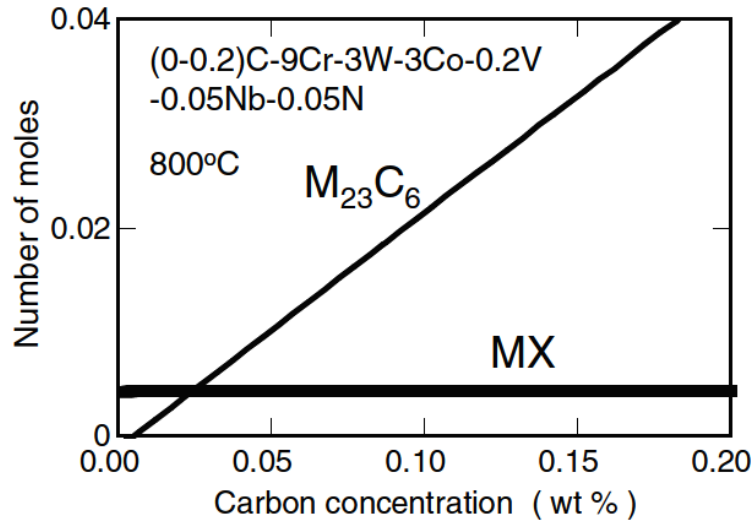


Figure 2.4 (a) The amount of MX and $M_{23}C_6$ as a function of carbon concentration at 800 °C[7], (b) at 650 °C calculated by the author with Thermocalc TCFE9 database

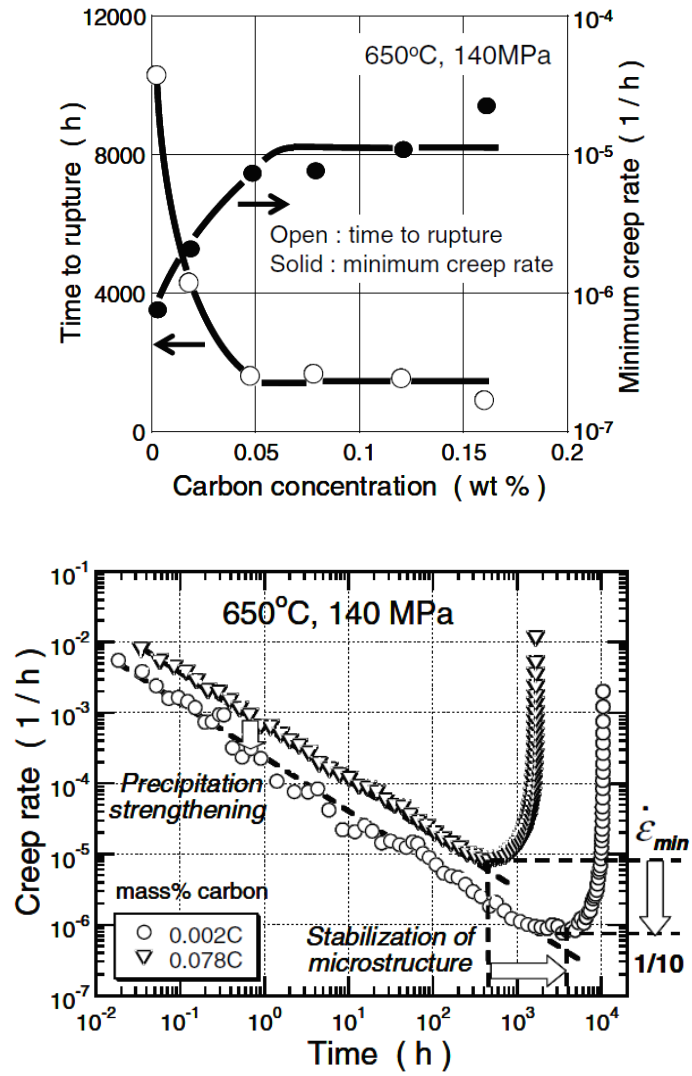


Figure 2.5 (a) Time to rupture and minimum creep rate at 650 °C, 140 MPa as a function of carbon content, (b) comparison of minimum creep rate between 0.002C and 0.078C[7]

Fe-15Cr Ferritic and Martensitic Steels

9-12 Cr steels showed adequate creep strength and are being used in convention Ultra Supercritical (USC) power plants (650° C). In order to gain a higher efficiency for the next generation fossil fuel power plants, a higher service temperature (e.g. 700° C) is required. However, 9-12 Cr steels are not suitable materials for the next generation fossil fuel power plants since the inferior oxidation resistance and the preferential recovery of sub-boundaries at the vicinity of the PAGBs due to microstructural degradation during creep. Increasing Cr content would potentially improve the oxidation behavior; however, 9-12 Cr F-M steels have a constraint of 12 Cr for maintaining fully martensitic structure. Kimura et al [30], [31] proposed a Fe-0.1C-15Cr-1Mo-3W steel system with fully annealed ferritic structure. By increasing the W and Co content with the Fe-0.1C-15Cr-1Mo-3W steel system, a comparative creep strength with Grade 92 steels is achieved. Furthermore, as shown in Figure 2.6, with the 6W-3Co added to this 15Cr steel system, not only the creep rupture time is about 100 times longer than the base 15Cr steel at 650 °C at 100 MPa, but also hardness of the as-annealed condition of 6W-3Co is about 2 times (from 168 to 351 HVN) larger than the base 15 Cr steel. It is worth mentioned that the strengthening precipitates in 15 Cr steels are carbides and intermetallic compounds such as χ phase and Laves phase due to the addition of W and Co.

Shibuya *et al* tested 15 Cr steel, a ferrite and martensite dual phase steel, at 650, 700, and 750 °C to determine the possibility of strengthening 15 Cr steel by intermetallic compounds. A 15Cr-0.05C-0.8N-2Co-6W-1Mo steel was tested at the temperatures mentioned above and compared with T92 steel[32].

Table 2-1 Steam temperature and pressure for fossil fuel power plants [21]

	Temperature	Pressure	Efficiency
Subcritical	540 °C	17-22 MPa	<38%
Supercritical	600 °C	25 MPa	<42%
Ultra-supercritical (USC)	620 °C	30 MPa	42-46%
Advanced ultra- supercritical (A-USC)	700 °C	35 MPa	>50%

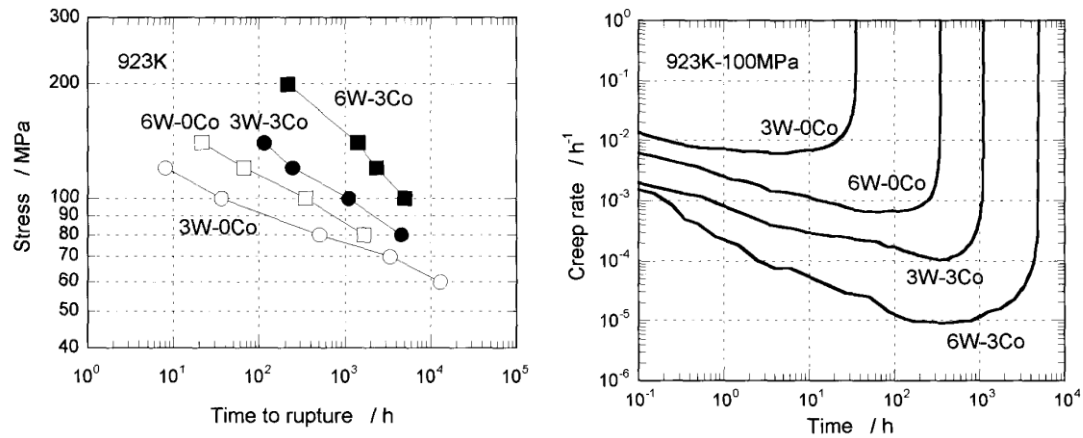


Figure 2.6 (a) Stress vs. time to rupture of steels at 650 °C, (b) Creep rate vs. time curves of the steels at 650 °C, 100 MPa[31].

Interestingly, the precipitation behavior is not identical in both ferrite and martensite grains. At 700 and 750 °C, a significant growth of precipitates along the grain boundary and an increase precipitate free zones (PFZ) were observed in ferrite grains while precipitate sizes in martensite grains are uniform and smaller than 2 µm. The intermetallic compound at 650 and 700 °C are identified by XRD as Laves phase and χ phase, whereas only Laves phase was found in 750 °C crept sample, which is consistent with the ThermoCalc® result. At 650 °C (see Figure 2.8), Laves phase only formed in ferrite grain. This can be explained by the higher solubility of W and Mo in ferrite compared to martensite, which are the elements promote the formation of Laves phase. The precipitate along the ferrite/martensite boundary was identified as $M_{23}C_6$. This can be explained by the carbon concentration difference. Higher carbon content in martensite than ferrite causes the inter-diffusion from martensite to ferrite. Moreover, by adding Ni[33], which is the austenite stabilizer, volume fraction of martensite phase increases. Increasing Ni from 0.8 to 2.1 wt%, similar microstructure (strengthened by carbides and intermetallic compounds) was observed, but the creep rupture lifetime up to 750 °C increases to 10 times more than T92 steels (see Figure 2.9). In conclusion, 15 Cr steels are dual phase steels that are strengthened by carbides and intermetallic compound. The creep strengthening mechanism is mainly precipitate hardening. However, even though 15 Cr steels showed better creep behavior than grade 92 steels, 15 Cr steels will still face similar challenge as 9 Cr F-M steels for the upper temperature limit and the rapid coarsening of $M_{23}C_6$.

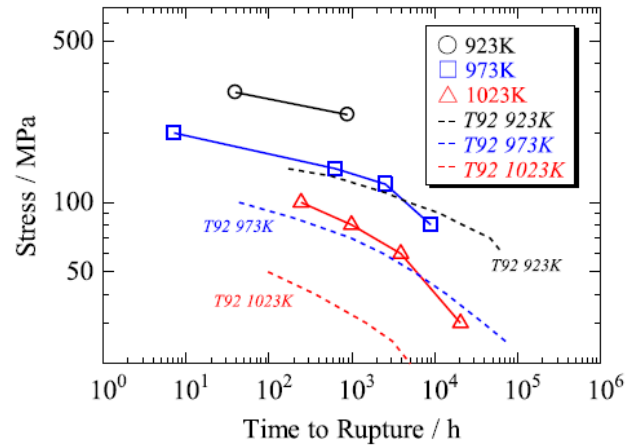


Figure 2.7 15Cr steel creep strength and rupture time compared with T92 at 650, 700, and 750 °C[32]

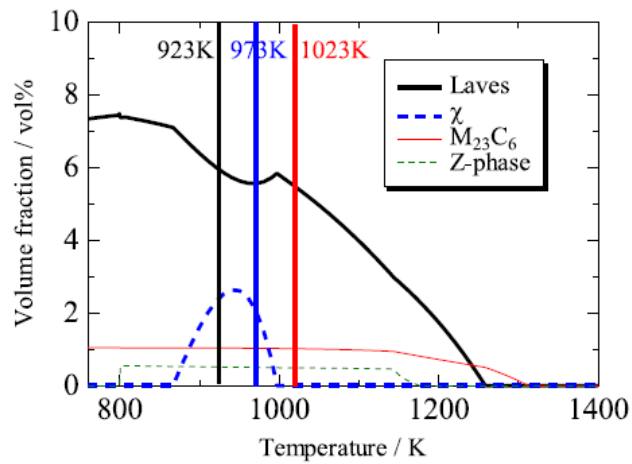


Figure 2.8 Calculation of volume fraction of precipitates as a function of temperature for 15 Cr steel[32]

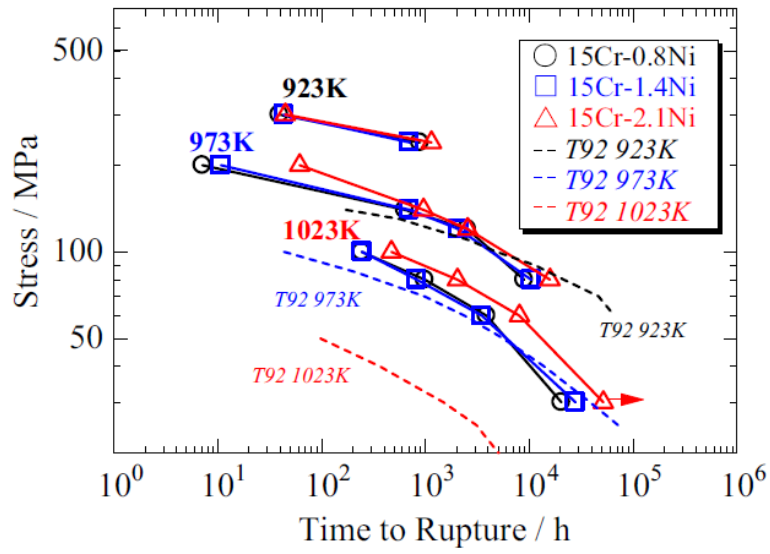


Figure 2.9 Creep strength and rupture time with various Ni concentration compared with T92 at 650, 700, and 750 °C[33]

Fully Ferritic alloys

Kuhn *et al* reported a 22 Cr steel for the application of solid oxide fuel cell(SOFC)[34]. The benefit of using ferritic steels is because ferritic steels ($12\sim13\times10^{-6} \text{ K}^{-1}$) have a lower coefficient of thermal expansion comparing to austenitic steels ($15\sim20\times10^{-6} \text{ K}^{-1}$)[35]. Therefore, ferritic steels are used for the interconnector between the electroactive ceramic components. The addition of aluminum and silicon, which are conventional deoxidants, is limited to be low since electrically insulating sub layer of alumina and silica will form. Therefore, without the deoxidants, a more expensive vacuum induction melting process is required. In addition, with low alloying elements, this 22 Cr steel showed poor creep resistance at the SOFC operating temperature range (700 to 900 °C). Hence, Laves phase, which has a higher solubility for Si, is a suitable intermetallic compound as a strengthening phase for creep resistance for SOFC application since electrically insulating silica would not form. The microstructures of different aging time were observed in this alloy at both 700 and 800 °C. PFZ was found at 500 h at 700 °C and already at 10 h at 800 °C (see Figure 2.10). Also, a steel (Crofer 22 APU) and a steel with similar composition but higher W content (Crofer 22 H) were tested. The result showed that Crofer 22 H has a superior creep resistance than Crofer 22 APU. The W content in the ferrite matrix of Crofer 22 H after creep test is still similar to the as annealed condition, which indicated the difference in creep strength is mainly due to the higher solid-solution strengthening of W atoms. Microstructure of Laves phase changed during long-term creep exposure. Laves phase was dissolved in smaller ferrite grain and only the intergranular Laves phase was observed. Yet, the formation of σ phase, and steam oxidation resistance were not addressed specifically in the previous literature.

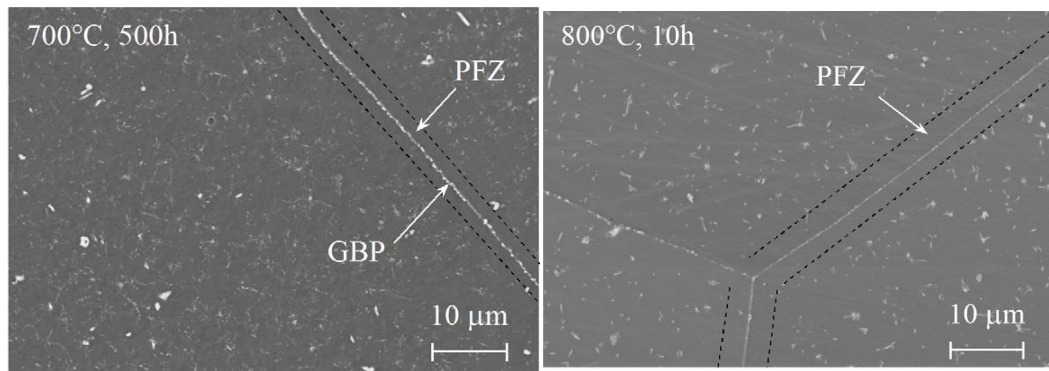


Figure 2.10 PFZ was observed at 500 h at 700 °C and 10 h at 800 °C[34]

To investigate that, steels with composition of modified Crofer 22 H with various of W, Nb, Cr and Ti contents were tested at 600 °C and microstructure characterization was conducted [9]. The creep strength and the steam oxidation resistance are compared with the most corrosion resistant commercial 9-12 Cr steel (VM12) and the most creep resistant 9-12 Cr steel (P92) (see Figure 2.11). The creep strength of the modified Crofer 22 H steels are comparable to the 9-12 Cr steel, and the weight change of modified Crofer 22 H steels are less than both P92 and VM12. The crept microstructure characterization showed the creep voids are formed along the ferrite grain boundaries (600 °C, 145 MPa) and the PFZ was also observed after long-term creep exposure (600 °C, 120 MPa). σ phase fraction was significantly reduced by decreasing the Cr content to 18 wt% without a loss in creep performance or steam oxidation resistance.

Lopez Barrilao *et al* reported the investigation of potential creep damage and failure mechanism, which is closely related to PFZ[36]. Localized deformation and dislocation

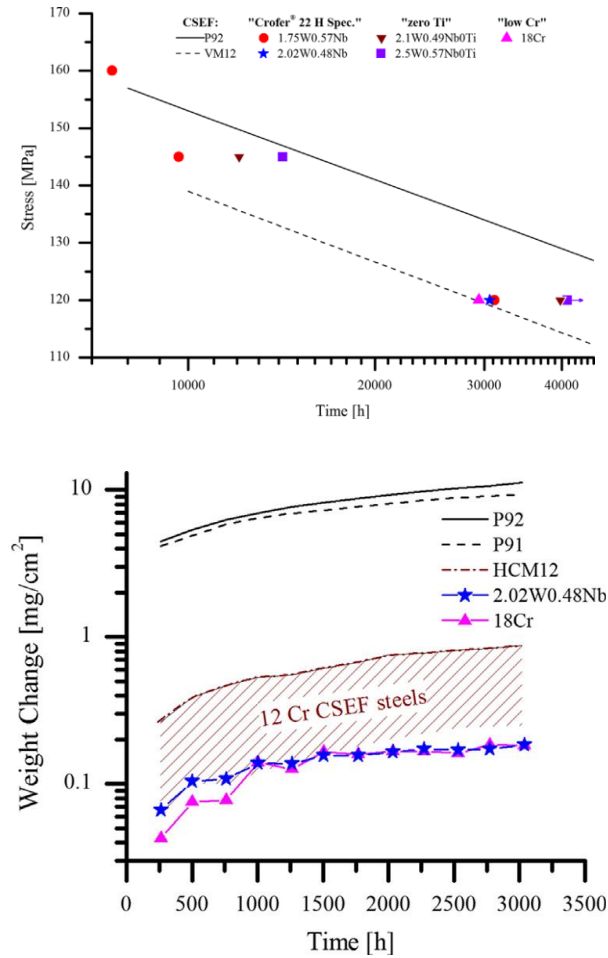


Figure 2.11 (a) Creep strength of modified Crofer 22H compared with VM12 and P92 (b) weight change of modified Crofer 22H compared with P91, P92 and HCM12

movement of PFZ and Laves phase particle size at 650 °C of a modified Crofer 22 H steel (2.5W0.57Nb) were characterized by HRSEM and STEM. The PFZ is namely a BCC region free of strengthening Laves phase precipitate and lower in solid solution strengthening elements (e.g W). The width of PFZ is proportional to the creep exposure time (see Figure 2.12). The depletion of solute atoms within PFZ due to the grain boundary precipitate coarsening is reported to be the formation mechanism of PFZ in Fe-Nb

alloy[37]. TEM EDS results showed that W concentration of the PFZ in the head section after 2425 h at 100 MPa is around 2 wt% whereas in the case of 9808 h at 70 MPa is around 1 wt%, which is in line with the reported PFZ formation mechanism. Besides, dislocations were observed to have a preferential orientation, which is parallel to grain boundaries. This phenomenon may support the hypothesis of creep void formation, by STEM bright field images (see Figure 2.13). Lopez Barrilao concluded that since the formation of PFZ is a result from Ostwald ripening of the grain boundary Laves phase, the dislocations along the grain boundaries (see Figure 2.13) hinder the diffusion towards to grain boundary Laves phase and act as heterogeneous nucleation site for smaller matrix Laves phase in vicinity of PFZ. The measurements of the width of PFZ of gauge section ($1.58 \pm 0.35 \mu\text{m}$, $2.74 \pm 1.00 \mu\text{m}$) for both 2425 h and 9808 h are smaller than the head section respectively ($1.72 \pm 0.38 \mu\text{m}$, $4.25 \pm 0.63 \mu\text{m}$), which are in line with the conclusion. Shassere *et al* showed a similar hypothesis and corresponding evidence for the potential creep void formation mechanism in a Fe₃₀Cr₃Al alloy system[38], which will be discussed in the following paragraph. In conclusion, Lopez Barrilao *et al* proposed that the formation of PFZ is due to Ostwald ripening of the grain boundary Laves phase. Also, PFZ is proposed to be the potential creep failure mechanism due to lack of both precipitate hardening and solid solution hardening, which resulted in localized deformation. The development of the fully ferritic Fe-Cr alloy showed the trend to use intermetallic compound such as Laves phase and Z phase for strengthening other than carbides (M_{23}C_6) and carbonitride (MX). The formation of PFZ was also discussed in several studies. The following paragraph will discuss the development of ferritic alloy with the addition of Aluminum.

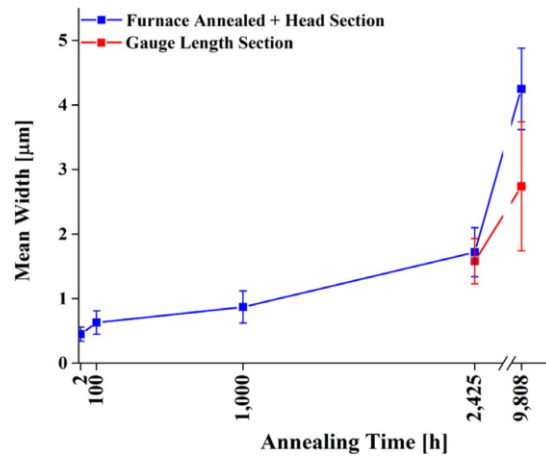


Figure 2.12 Mean width of PFZ of modified Crofer 22 H at 650 °C

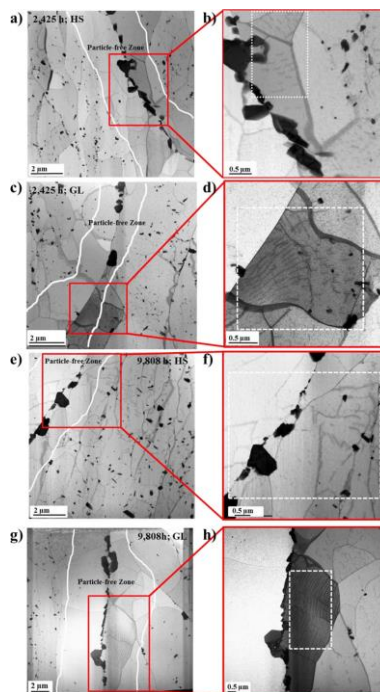


Figure 2.13 STEM bright field image of modified Crofer 22 H steel for both gauge and head section at 650 °C for 2425 h and 9808 h[36]

The Development from Low-Cr Ferritic Steels to High-Cr FeCrAl Alloys

The addition of aluminum leads to the formation of alumina, which could be beneficial for oxidation resistance. In this section, ferritic alloys with high Cr (more than 18Cr) and the addition of Al will be discussed. As mentioned before, 9-12 Cr F-M steels are the materials currently used in fossil fuel power plants. The weldment issue called Type IV cracking has been studied intensively. Yu *et al* reported that at a lower pre-weld heat-treatment (PWHT) temperature (650 °C) than the standard PWHT (750 °C) for a grade 91 steel controlled the $M_{23}C_6$ to be finely distributed along the PAGB[10]. This lower temperature PWHT reduced the steady-state creep rate at 600 °C of the welded structure for an order of magnitude compared to the standard PWHT. Shassere *et al* reported a thermomechanical treatment (TMT) on controlling the coarsening of the $M_{23}C_6$ and led to the improved creep rupture lifetime (~2700 h) compared to the samples without TMT (~1400 h) on the welded structure of grade 91 steel at 600 °C at 100 MPa. In addition, the minimum creep rate of the sample with TMT ($4.8 \times 10^{-8} \text{ s}^{-1}$) is lower than the sample without TMT ($2.04 \times 10^{-7} \text{ s}^{-1}$)[28].

To develop the materials under temperature higher than 650 °C and eliminate the Type IV cracking, carbon free/lean FeCrAl alloy was introduced. FeCrAl alloys are strengthened by intermetallic compounds, which means the coarsening or dissolution of carbides and carbonitrides would not be an issue. High Cr content enhances the oxidation and corrosion resistance by forming thin layer of chromium oxide. However, brittle σ -FeCr and α' -Cr phases are susceptible to form at high Cr content. The addition of Al can suppress the formation of the σ -FeCr and α' -Cr phases and improve oxidation resistance. Also, adding

Al suppresses the brittle σ phase formation, increases the corrosion resistance by forming alumina, and increases the Cr solubility in ferritic matrix[39]. Yet, it was reported by doubling Al content from 3 to 6 wt% in an 23 – 25 wt% Cr FeCrAl alloy system [40], the ductile to brittle transition temperature (DBTT) increased nearly 100 °C (see Figure 2.14). Therefore, a balanced Fe-30Cr-3Al alloy system was proposed with Laves phase as strengthening phase for creep applications.

In this study, an Fe-30Cr-3Al alloy system will be discussed to be the potential creep resistant alloy with a target service temperature of 700 °C in fossil fuel power plants. Shassere *et al* investigated the creep resistance and microstructural evolutions at 700 °C at 70 MPa on an Fe-30Cr-3Al-0.2Si-xNb (x = 1, 2) alloy system strengthened by Fe₂Nb Laves phase[38]. A 0.5 to 1.5 μ m PFZ was observed and quantified by a proposed grain boundary zone strength factor (GBZSF), which is a ratio of the coverage of Laves phase along the grain boundary over the mean width of PFZ, to correlate the microstructure feature with creep failure. A microstructure with GBZSF lower than 0.6 is reported to be favorable to fail based on the experimental results (see Figure 2.15). The reason may be due to the loss of Orowan strengthening with the increased interparticle spacing between grain boundary Laves phase and intragranular Laves phase on the edge of PFZ. Creep voids formed along grain boundaries and dislocation accumulation along the grain boundary region that was not covered by Laves phase indicates the PFZ (see Figure 2.16) is the potential creep failure mechanism. A core-mantle deformation model was proposed with local misorientation difference between the PFZ region and the matrix region (see Figure 2.17). The dislocation motion in the PFZ region (mantle) is not hindered by precipitates, which leads to a larger

misorientation due to the localized deformation compared to the BCC matrix with finely dispersed precipitates (core). Moreover, the Fe-30Cr-3Al-0.2Si-2Nb has a larger weight fraction of Laves phase (3.9 wt%) than the Fe-30Cr-3Al-0.2Si-1Nb alloy (1.8 wt%) at 700 °C, which is in line with the correlation Yamamoto *et al* reported the minimum creep rate at 700 °C at 70 MPa decreases as the Lave phase fraction increases [12](see Figure 2.18). To sum up, based on the literature mentioned previously, the trend showed that minimum creep rate decreased with the increased Laves phase mole percent in the Fe-30Cr-3Al-0.2Si-1Nb-xM (x = 1 to 10; M=W, Ti, Nb) alloy system. Also the formation of PFZ was proposed to be the creep failure mechanism.

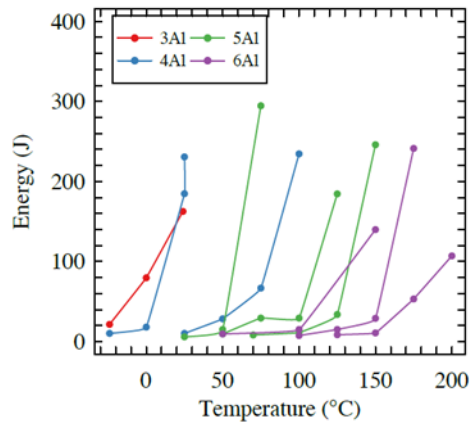


Figure 2.14 DBTT as a function of Al content (wt%) in 23-25 wt.% Cr FeCrAl alloys[40]

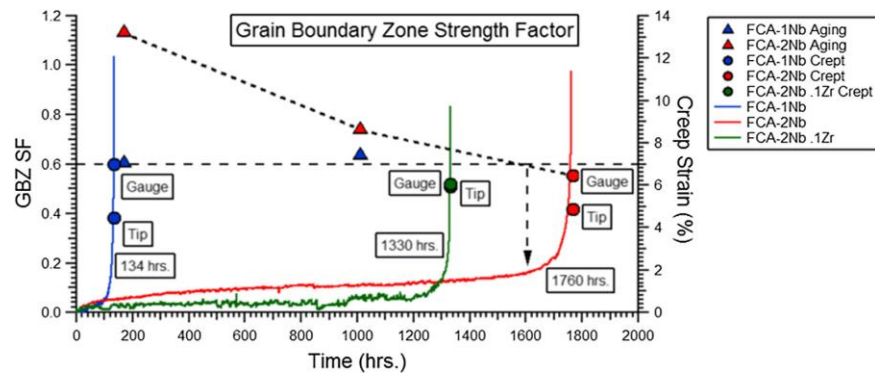


Figure 2.15 GBZSF as a function of creep exposure time[38]

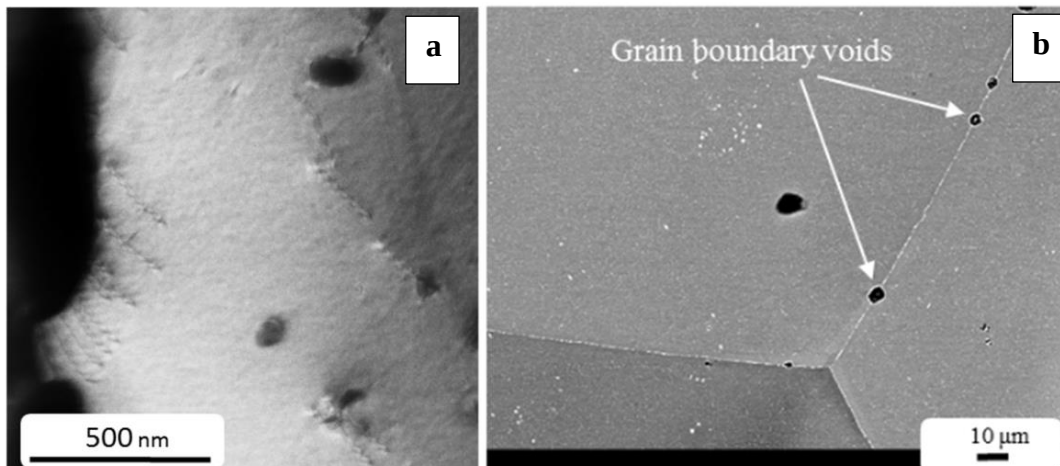


Figure 2.16 (a) dislocation accumulation along the grain boundary region without Laves phase coverage, (b) Grain boundary voids after creep at 700 °C[38]

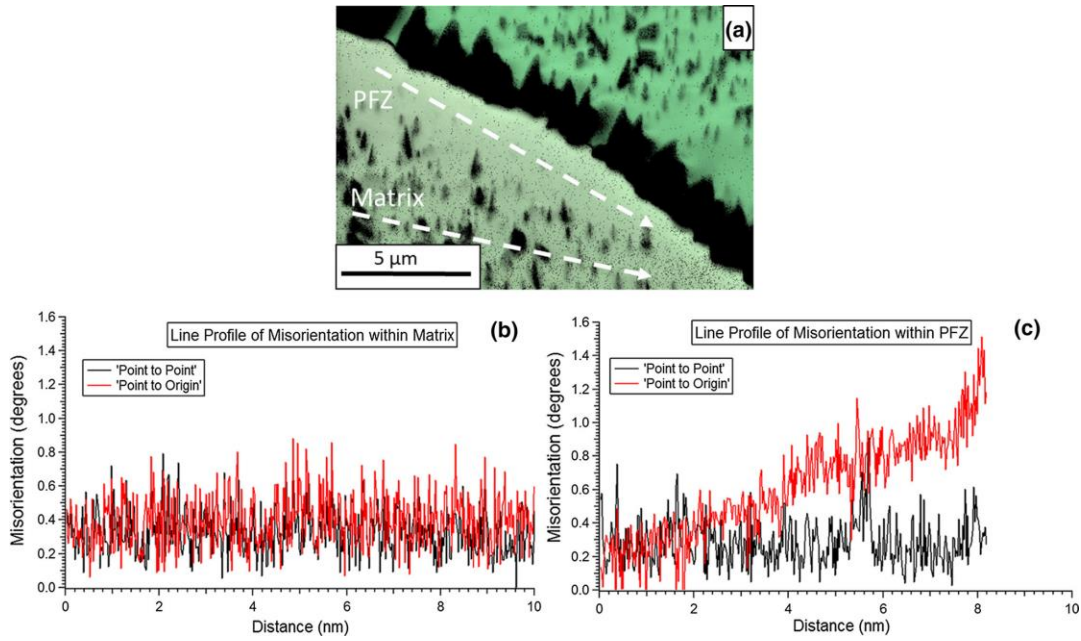


Figure 2.17 Difference of misorientation between PFZ and BCC matrix[38]

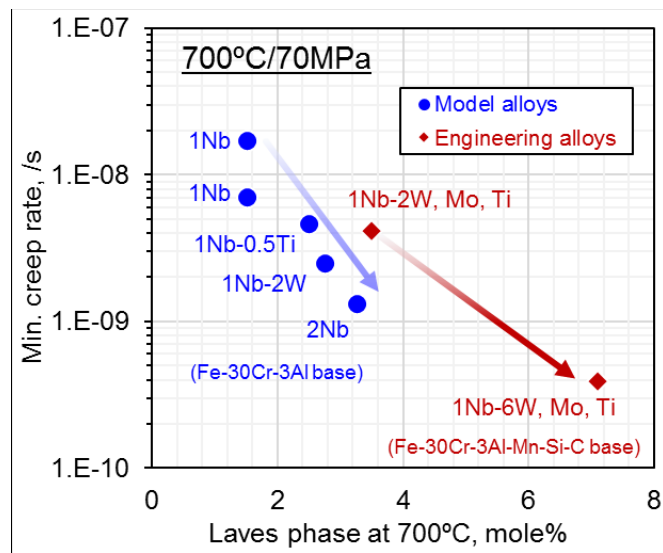


Figure 2.18 Minimum creep rate as a function of Laves phase mole percent at 700 °C[12]

Alloy Design for Ferritic Creep Resistance Alloys

Thermodynamic and kinetic calculation/simulation tools have been implemented in 9-12 Cr F-M steels to design the strengthening precipitates and understand the nucleation, growth, and coarsening of precipitates (e.g. MX, $M_{23}C_6$, Z phase, and Laves phase) at the temperature equal to or lower than 650 °C. Aghajani *et al* used the diffusion of Mo and Si to model the growth of Mo-rich Laves phase during creep test at 650 °C at 120 MPa[41], [42]. The diffusivity of Si fitted experimental measurement of the growth of Mo-rich Laves phase better than the diffusivity of Mo (see Figure 2.19). Isik *et al* reported with the increase in Si content, less Mo content is required for the Laves phase formation (see Figure 2.20). TEM EDS and Atom Probe Tomography (APT) were conducted on crept samples at 550 °C at 120 MPa to show a segregation of Si and Mo at the subgrain boundary in vicinity of $M_{23}C_6$ as a precursor of Laves phase formation since $M_{23}C_6$ has low Si solubility (see Figure 2.21, Figure 2.22, and Figure 2.23)[43], [44].

Sanhueza *et al* and Prat *et al* simulated the mean diameter of Laves phase, $M_{23}C_6$, and Z phase of 9-12 Cr steels at 650 °C by modifying the interfacial energy and compared the results with TEM characterization to demonstrate a feasible way to use thermodynamic calculations and simulations for alloy design in 9-12 Cr steels (see Figure 2.24)[16]–[18], [45], [46]. Lu *et al* proposed an alloy design method creep resistant F-M steels with precipitate hardening (PH) factor and solid solution strengthening factor (SSS) taken into account[20]. A tremendous amount of compositions in 9-12 Cr F-M steels system could be considered based on the Lu's approach[20].

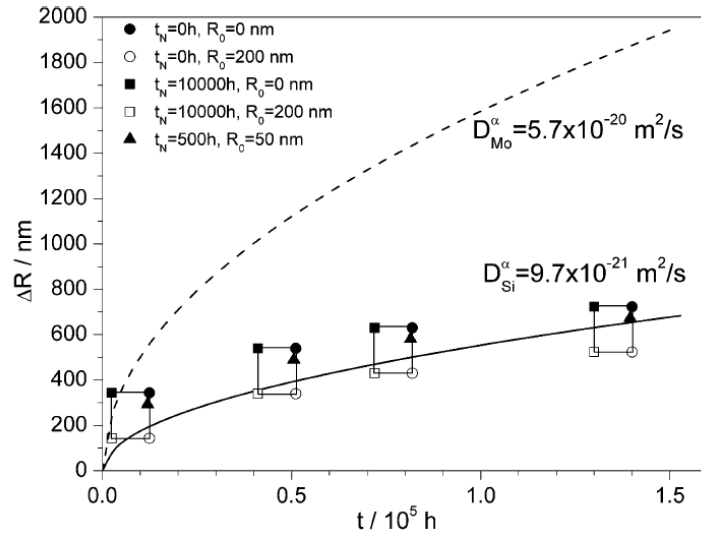


Figure 2.19 Changes of Laves phase radius as a function of creep exposure time fitted with the diffusivity of Si and Mo in BCC matrix[42]

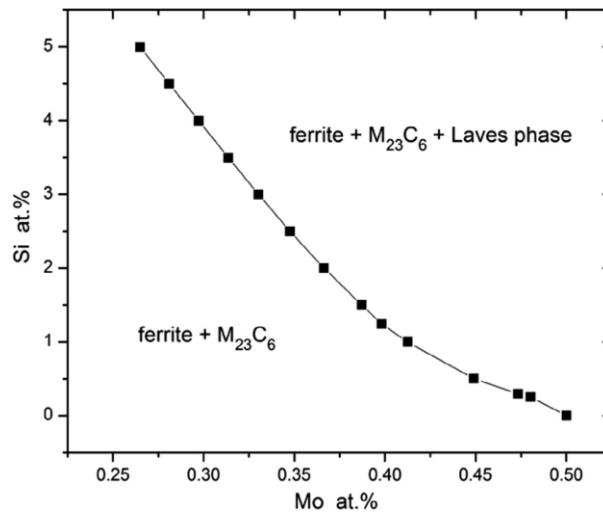


Figure 2.20 Pseudo binary phase diagram of 9-12 Cr steel with varying Si and Mo content[43]

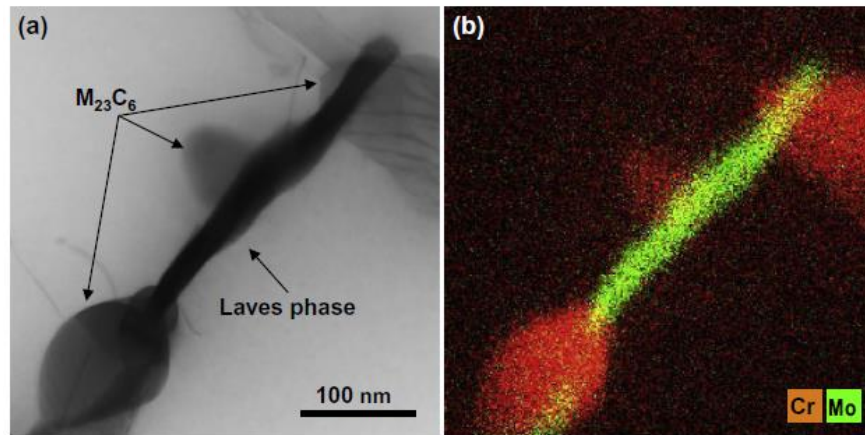


Figure 2.21 (a) Bright field image of TEM and (b) EDS showed Mo segregation and Laves phase formation at the vicinity of existed $M_{23}C_6$ [43]

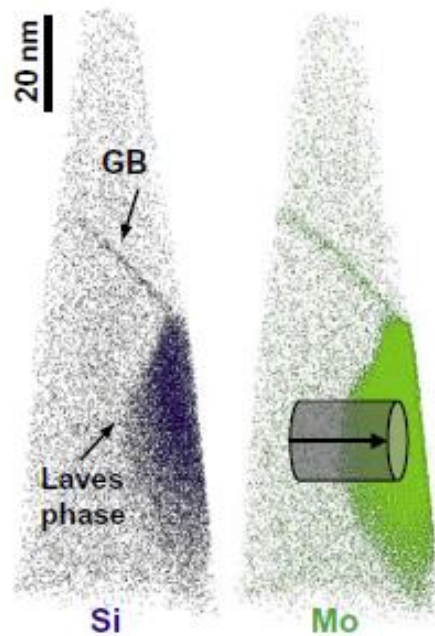


Figure 2.22 APT results of Si and Mo spatial distribution at grain boundary and inside Laves phase[43]

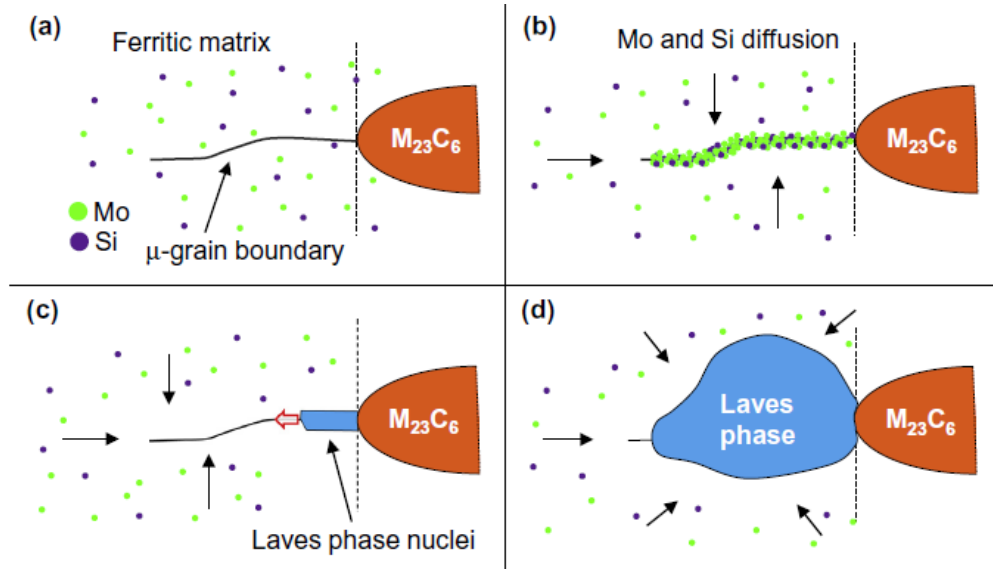


Figure 2.23 Schematic illustrations of a scenario which summarizes all stages of Laves phase nucleation. (a) Initial microstructure. (b) Segregation of Mo and Si to the micrograin boundary. (c) Nucleation and rod-like growth in the direction along the micrograin boundary (direction of the red arrow). (d) Growth into a bulky shape at later stages[43]

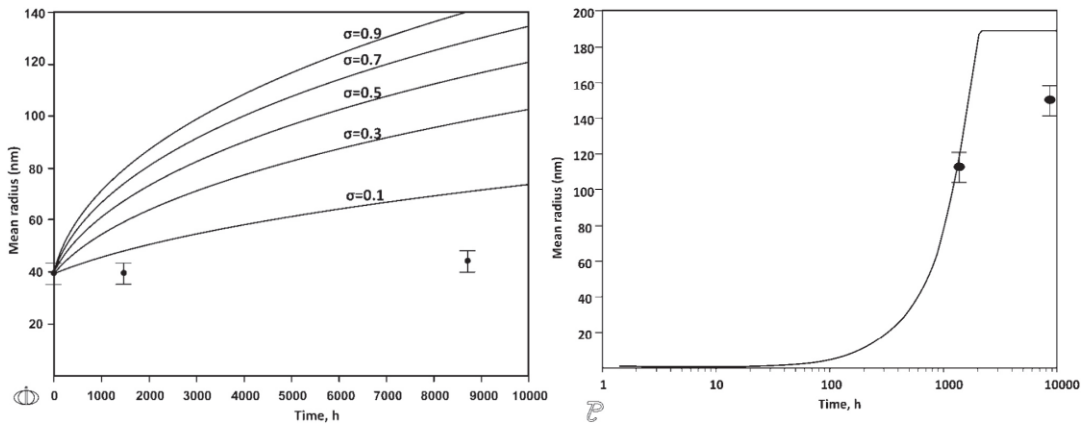


Figure 2.24 (a) Simulated mean radius with varying interfacial energy of $M_{23}C_6$ and (b) Laves phase (with interfacial energy 0.6 J/m^2) as a function of isothermal exposure time at 650°C overlaid with experimental results[17]

Therefore, target microstructural conditions were defined as following: (1) fully martensitic structure with elements could potentially provide SSS, (2) predominant volume fraction of MX and limited volume fraction of undesirable precipitate (essentially other possible precipitates other than MX, such as $M_{23}C_6$ and μ phase), (3) low calculated coarsening rate at the intended lifetime (e.g. 10000 h). For PH factor, the information of critical precipitate radius, interparticle spacing for Orowan stress, and coarsening coefficient were obtained from Thermocalc® TCFE6, MOB2 databases. Governing equations, including the Lifshitz-Slyozov-Wagner (LSW) theory for coarsening, are shown as following:

$$r_0 = \frac{2\gamma}{\Delta G_{max}}$$

$$r^3 - r_0^3 = Kt$$

$$K = 8\gamma V_m^p / \sum_{i=1}^n \frac{9(x_i^p - x_i^{mp})^2}{x_i^{mp} D_i / RT}$$

, where r_0 is the critical precipitate nucleus size, γ is matrix-precipitate interfacial energy, ΔG_{max} is the precipitate nucleation driving force, V_m^p is the molar volume of precipitate, K is the coarsening rate, t is the exposure time, x is the equilibrium interfacial concentration of the precipitate-forming elements on both matrix (m) and precipitate (p), T is the service temperature, D_i is the corresponding diffusion coefficient of precipitate-forming elements i (Ti, Nb, V, C, N) and n is the total number of the precipitate-forming elements considered. For SSS factor, Lu *et al* used the Mott and Nabarro linear dependence model[47] for SSS

and assumed the strengthening factor K_i scaled linearly at 650 °C and at room temperature. Governing equations are shown as following,

$$\sigma_{SS} = K_i C_i$$

where K is the strengthening factor and C is the atomic fraction in the ferritic matrix. Balancing the SSS and PH factor, Lu *et al* proposed a composition of Fe-11.1Cr-3.7Al-3.8Ni-0.3Nb-0.06C and compared it with existing 9-12 Cr F-M steels. The designed composition was predicted to out-perform the existing F-M steels with SSS and PH factors considered (as shown in Figure 2.25). It is worth mentioning that the results were based on only calculations, not based on experimental results. No literature about alloy design in FeCrAl alloys on Laves phase at 700 °C was published to the best of author's knowledge.

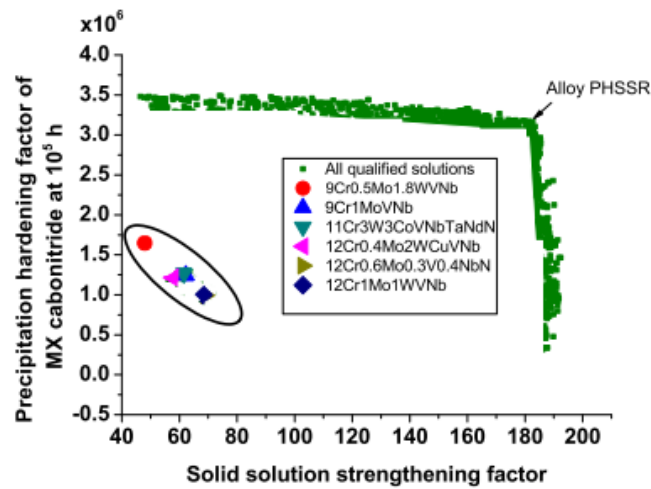


Figure 2.25 The comparison of the designed alloy based on calculations and the existing 9-12 Cr F-M steels on a SSS factor and PH factor plot with the conditions of 10000 h at 650 °C

Metal Big Area Additive Manufacturing

The development of additive manufacturing opens the opportunities for many industries to manufacture components with more flexibility in designs on both geometry and microstructure, which were challenging through the traditional subtractive approaches. Metal big area additive manufacturing (mBAAM), a wire-arc AM system, was developed at Oak Ridge National Laboratory (ORNL)[48]. The wire-arc AM system has its similarity to robotic gas metal arc welding (GMAW) system, but the major difference is the closed-loop control system developed in ORNL to ensure the geometrical homogeneity. Shassere *et al* demonstrated the ability to mBAAM system to build mild steel thin-walls (12-mm thick) with most of the build consists of polygonal ferrite and pearlite microstructure[48]. The hardness within the wall was uniform (140 – 160 HVN). The microstructural heterogeneity (as shown in the Figure 2.26) in top and interface between the vertical wall and baseplate can be explained by the local thermal history during the manufacturing process. The geometrical stability was demonstrated by using the real-time feedback sensing closed loop control system. Therefore, mBAAM could be a potential approach to fabricate near-net shaped tubes with the designed creep-resistant alloys with optimized processing parameters.

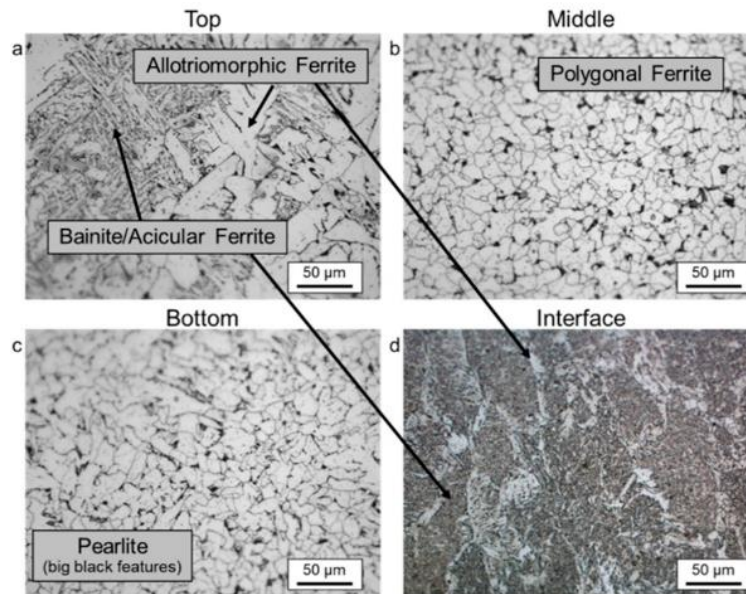


Figure 2.26 Microstructural heterogeneity observed at the (a) top and (d) interface region of the thin wall, while (b) middle and (c) bottom region of the thin wall consist of polygonal ferrite and pearlite.[48]

Research Objectives

To push the development of FeCrAl alloys further based on the review above, especially from Shassere [38] and Yamamoto [12], there are several phenomena that were still unclear. Therefore, in this study, the following unanswered questions will be addressed.

1. *Theoretically, what are the effects (e.g. phase fraction, precipitate composition, potential detrimental phases formation) from difference alloying elements that could form Laves phase other than Nb (e.g. Zr, Ta, Mo, Ti, W) based on thermodynamic calculations?*
2. *Experimentally, what are the precipitation behaviors (e.g. nucleation, growth, and coarsening) of different alloying elements during aging? Are the precipitation behaviors similar with different alloying elements? If not, why?*
3. *What is the optimal composition for creep resistance for Fe-30Cr-3Al alloy system?*
4. *Is there a threshold value for the width of PFZ that weakens the creep resistance significantly and leads to failure? If so, what is the underlying mechanism?*
5. *Could mBAAM be a potential alternative process to manufacture creep-resistant FeCrAl alloy?*

CHAPTER THREE

MATERIALS AND METHODS

Thermodynamic Calculations

The nucleation driving force of the possible precipitates in ferritic matrix at 700 °C, the equilibrium mole fraction of Laves phase at 700 °C, and the BCC solvus temperature were calculated by TCFE9 database in ThermoCalc®[49] with the addition of W, Ti, Zr, Ta, Nb in the Fe-30Cr-3Al-1Nb based FeCrAl alloys. The nucleation driving force was calculated by using the parallel tangent method to calculate the maximum difference in Gibbs free energy between the matrix and the precipitate phase[50]. BCC solvus temperature was obtained by setting the matrix BCC phase at a 99.9 mole percent in a two-phase region (BCC and secondary phase) towards the upper end of BCC single phase boundary. Diffusivity data were acquired by DicTra® using TCFE9 and MOBFE4 databases. The input for u-fraction was the atomic percentage of the alloy composition since no interstitial atoms were considered in this alloy system.

Materials Preparation and Heat-treatments

Materials Preparation

Three Fe-30Cr-3Al-1Nb base alloys were prepared in this study. Alloy compositions were quantitatively analyzed by inductively coupled plasma optical emission spectrometry (ICP-OES). Oxygen and Nitrogen contents are analyzed by inert gas fusion (IGF). Nominal and

analyzed compositions with the addition of Ti, W, and Nb were listed in Table 3-1. The analysis results indicated that the contents of major elements were close to the nominal compositions, and the amounts of impurities (C, N, O, P, and S) were mostly negligible from the viewpoint of microstructure control. Lab-scaled ingots of the selected alloys were prepared by arc-melting with pure element feedstock, followed by drop-casting into water-cooled Cu mold with a size of 12.7 mm x 25.4 mm x 127 mm. The ingots were homogenized at 1300 °C for 1 hour in an Ar cover gas, and then water-quenched. The ingots were subsequently soaked at 1200 °C in an Ar cover gas for more than 30 mins, and then hot-rolled into 2.03-millimeter-thickness sheets with 10-15% thickness reduction per pass and inter-pass annealing at 1200 °C for 10 minutes. After hot-rolling, samples were solution heat-treated at 1200 °C (for 1Nb-1Ti and 1Nb-6W) or 1275 °C (for 2Nb) for 30 mins in an Ar cover gas, followed by water quenching. Lastly, the sheet samples were mechanically ground to remove the oxide layer on the surface. Of the candidate alloys that past the processability constraint, an aging study was conducted to understand the microstructural evolution. Samples were heat-treated at 700 °C for 24, 168, 1008, and 3000 h in air, followed by air cooling.

Heat-treatments

To understand the microstructural evolution, aging study was conducted. Samples were heat-treated isothermally at 700 °C (target service temperature) for 24, 168, 1008, 3000, and 10000 hours in air to study the Laves phase precipitate behavior.

Table 3-1 Nominal and analyzed compositions of the selected alloys (1Nb-1Ti and 1Nb-6W) and the reference alloy (2Nb).

Alloys		Composition, wt. %						
		Fe	Cr	Al	Si	Nb	Ti	W
1Nb-1Ti	Nominal	64.8	30	3	0.2	1	1	-
	Analyzed*	64.96	29.96	2.9	0.19	0.98	0.98	-
1Nb-6W	Nominal	64.8	30	3	0.2	1	-	6
	Analyzed*	59.75	30.02	2.95	0.17	1	-	6.08
2Nb	Nominal	64.8	30	3	0.2	2	-	-
	Analyzed*	65.01	29.97	2.89	0.17	1.94	-	-

(*note: C <50 wppm., N <27 wppm., O <39wppm., P <60 wppm., and S <28 wppm.)

Mechanical Testing Methods

Creep Test

An ATS 2330 series® lever arm tensile testing system was used creep tests. Creep test frame was set-up with 3D digital image correlation (DIC) system (as shown in Figure 3.1). Creep specimen has a total length of 70 mm with 17.5 mm in height and ~2 mm in thickness. The total gauge length for measuring local strain using DIC covered a length of 20 mm with. The gauge surfaces of these test specimens were sandblasted for good adherence to the DIC speckle pattern paints. Random speckle patterns were created by an innovative 3-layer speckle pattern procedure [51] with randomly distributed black speckles on a white background. Two thermocouples were spot welded on the back side of the specimen to monitor temperature gradients within $\pm 1^\circ\text{C}$ during the creep test. Speckle patterned test specimens were clamped and heated inside the furnace to the test temperature of 700°C at a heating rate of 150°C/hr . A small tensile pre-load of 8lbs was applied during heating time period to avoid any buckling of the test sample due to thermal expansion. After 1 hour of soak time at 700°C , test stress of 90MPa was applied. At the onset of stress application, the VIC-Snap® software was programmed to capture images of the speckled gauge surface at every 5.25-minute interval throughout the entire duration of test. While the VIC-Snap® software was periodically collecting images of speckled sample surface during creep deformation, collected images were parallelly imported to VIC-3D® software to determine creep strain (ϵ_{yy}) distribution in the gauge surface along the loading direction. DIC image capturing was stopped after 73 days (1752 h) in the creep test to compare with the result (Fe₃₀Cr₃Al_{0.2}Si₂Nb ruptured at 1760 h, 70 MPa, 700°C) from the literature.

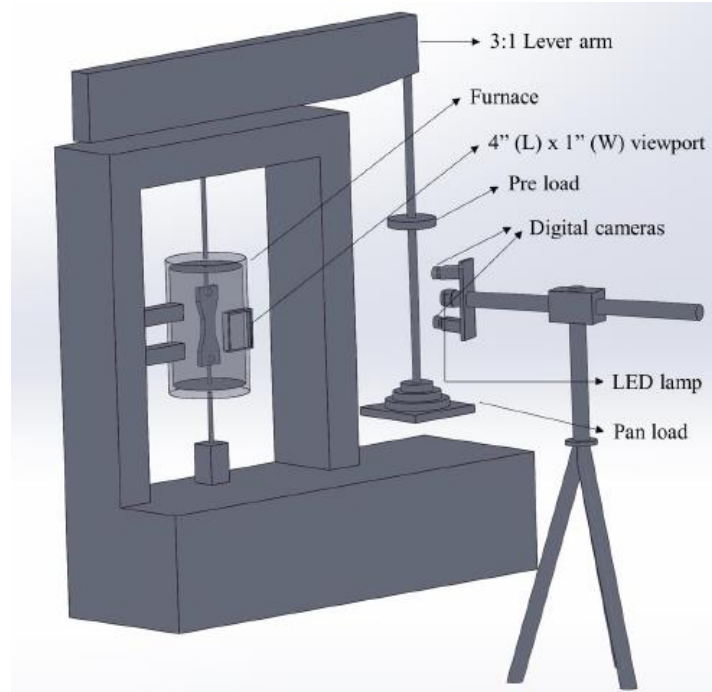


Figure 3.1 Schematic of creep testing system (ATS 2330, 3 to 1 lever arm) with DIC set-up [52]



Figure 3.2 A speckle image of the gauge section of creep specimen

Microhardness

Microhardness tests were conducted using a LECO AMH55 indenter. Force of 500 gf was used for all the tests. The reported hardness value was the average of 49 indents with 200 μm spacing with dwell time of 5 seconds.

Nanoindentation

Nanoindentation experiments were performed using a Berkovich diamond tip with an effective tip radius of 272 nm at room temperature (22°C) on a Hysitron Triboindenter.

Samples were hot-mounted and polished to 1 μm diamond suspension fluid followed by 0.03 μm colloidal silica vibration polishing on a Buehler VibroMet2 to avoid the topological artifacts for the hardness measurements. All the measurements were conducted using displacement-controlled mode with intended displacement of 125 nm to ensure the indents were located inside the PFZ. The loading rate was 10 $\mu\text{N/s}$ for both loading and unloading process with a 2-second dwell time.

Microstructure Characterization

Electron Microscopy

JEOL 6500 FEG-SEM at 20 keV with backscattered electron detector in ORNL was used to image the size and distribution of Laves phase with various aging time. Samples were hot-mounted and polished to 1 μm diamond suspension fluid followed by 0.03 μm colloidal silica vibration polishing on a Buehler VibroMet2. Particle sizes (equivalent circle diameters) of Laves phase and the width of PFZ were analyzed by using image J®. Zeiss Libra 200 TEM at 200 keV was used to observe the dislocation interaction with the Laves phase precipitate within the BCC matrix and within the PFZ. Specimen were sectioned from the gauge section of the crept sample with Allied TechCut 4™ precision low speed saw and ground down to a ~ 200 nm foil by manual polishing. The foil was then punched into discs with 3-mm diameter followed by electropolishing using perchloric acid (5%) and methanol (95%) at -40 °C at 20 V. To visualize dislocations under TEM, specimen needed to be tilted to two-beam condition (i.e. one transmission beam and one diffracted beam were the strongest in intensity under diffraction pattern). Local lattice distortion caused by dislocations changed the atomic arrangement that satisfied the Bragg's condition locally. Hence, the contrast was from the perfectly arranged atoms and locally distorted atoms (see Figure 3.3). The measurement of dislocation density was conducted by using the scanning transmission electron microscope (STEM) mode with zone axis of $[001]$ and $g = \langle 200 \rangle$ were used.

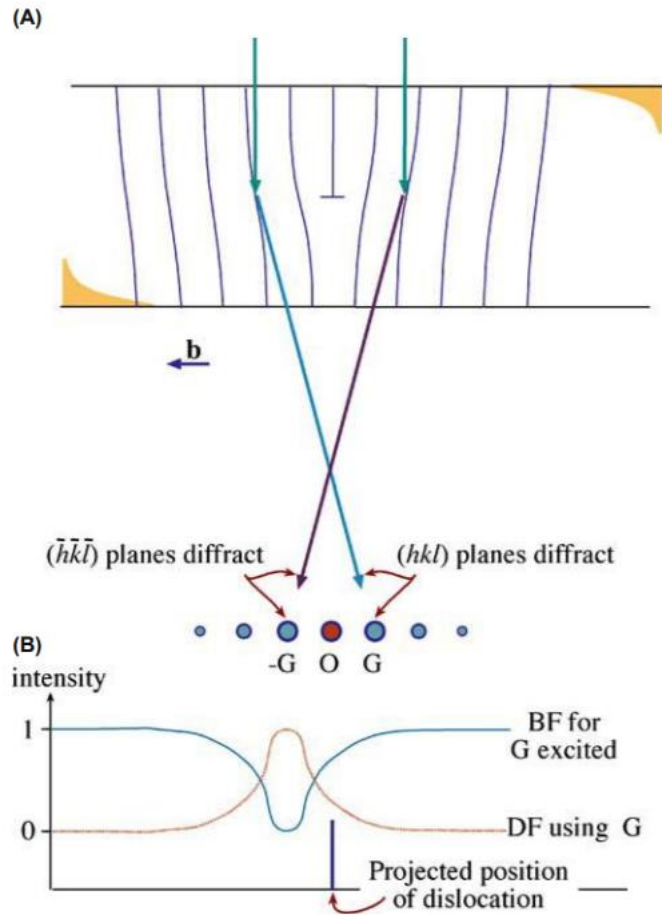


Figure 3.3 Imaging strain field in TEM. (a) Distorted lattice by an edge dislocation (b) Change in intensity due to the strain field created by the dislocation [53]

Atom Probe Tomography

Atom Probe Tomography (APT) was used to analyze and visualize the composition of the Laves phase precipitates in the aged samples. Traditional APT focused ion beam (FIB) sample preparation techniques were used, and the details can be found elsewhere [54]. An FEI Nova 200 dual beam focused ion beam (FIB)/SEM was used to trench and lift out site selective regions of interest inside the grain interiors. The subsequent lift-outs were

transferred and mounted to Si posts on a Si micro-post array. Annular milling followed by a 2 kV cleaning step were used to create needle shapes with a ~50 nm apex radius suitable for APT field evaporation. The micro-post array was inserted into a CAMECA® local electrode atom probe (LEAP 4000XHR) and run in laser mode using 10 ps, 60-80 pJ laser pulses at a pulse repetition rate to allow for all ions to be collected in the mass spectrum and a detection rate of 1 atom for every 50-200 pulses. The measurements were conducted at 30 K. The reconstruction was analyzed by using CAMECA's Integrated Visualization and Analysis Software (IVAS 3.8.0).

X-ray Diffraction

X-ray diffraction (XRD) was used to obtain lattice parameters of BCC matrix. The measurements were conducted using Panalytical Empyrean instrument with Cobalt K-alpha X-ray source (0.178 nm wavelength). Cobalt K-alpha was chosen to avoid the high background noise generated by fluorescence from Copper K-alpha X-ray source and Iron containing materials. The XRD measurements were collected at the angles from 35 to 140 degrees in 2 theta with 0.013 degree per step.

CHAPTER FOUR

ALLOY DESIGN FOR CREEP-RESISTANT FECRAL ALLOYS

Background

The Fe-30Cr-3Al-1Nb based alloys are consisting of a fully ferritic matrix with the formation of Fe_2Nb type C14 Laves phase at around 700°C. Based on the results from the literature (see Figure 2.18), the Fe-30Cr-3Al-1Nb based alloys with higher Laves phase mole percent are expected to have smaller minimum creep rate. It is due to that fact that precipitation strengthening is the dominant strengthening mechanism for this alloy system. Furthermore, to obtain the finely dispersed precipitate to maximize the Orowan stress for strengthening purpose, solutionization treatment is needed. Therefore, BCC solvus temperature should be considered. Also, to ensure Laves phase is the only expected precipitate and to prevent other phases (e.g. sigma phase, mu phase, etc.) that could be detrimental to creep performance to form, nucleation driving force should be taken into account. After the alloy compositions met the criteria mentioned above, manufacturing feasibility also need to be considered. The compositions with apparent cracks after the rolling process would be ruled out. Thus, thermodynamic calculations were conducted to design alloys within Fe-30Cr-3Al-1Nb alloy system to have anticipated superior creep resistance.

Thermodynamic Calculation Results

Total 57 alloy compositions containing Laves phase forming elements were evaluated, in the range of Fe-30Cr-3Al-0.2Si-1Nb+XM (X=0-9 wt.% (with 0.5 or 1 at.% per step),

M=Nb, Ti, Ta, Zr, W, Mo). The alloy design down-selection process (see Figure 4.1) is described as follows. First, the alloys needed to meet three conditions to be candidates for fabrication: a high Laves phase nucleation driving force (Figure 4.2), a high Laves phase mol % (Figure 4.3), and a low BCC solvus temperature (Figure 4.4). The nucleation driving force needs to be higher than all other secondary phases in the alloy system (e.g. χ phase, μ phase, σ phase, etc.), which implies the most thermodynamically favorable phase to nucleate. In this alloy system, the driving forces of Laves phase nucleation should be larger than 7000 J/mol which was sufficiently higher than the driving forces of any other second-phase precipitation (e.g. Mu-phase with ~ 5000 J/mol, Chi-phase with ~ 1200 J/mol, or Sigma phase with ~ 800 J/mol), to ensure that Laves phase is the only secondary phase. For the improved creep behavior, only the alloys with more than 3.38 mole% of Laves phase were considered as the potential candidates to be down-selected (see Figure 4.3), based on the correlation between Laves phase mole percent and the minimum creep rate in the literature [12], targeting the expected minimum creep rate lower than that of the reference alloy ($6.91 \times 10^{-9} \text{ s}^{-1}$), Fe-30Cr-3Al-0.2Si-2Nb) [38]. For a finely dispersed Laves phase distribution and modest grain growth, solutionization heat-treatment was needed. Thus, the BCC solvus temperature was taken into account (see Figure 4.4). The alloys containing more than 3 wt.% of Ta were excluded because the BCC solvus temperature was at or above 1308 °C, even though the calculated amount of Laves phase was more than 4.54 mole%. Also, the addition of Nb larger than 2 wt.% (total 3 wt.% Nb) and Ti more than 4 wt.% had the BCC solvus temperatures exceeding 1,300 °C and were therefore ruled out. A total of 22 samples met the requirements, and several alloys with Ti, W, and Mo additions were selected for experimental validation. After applying thermomechanical

treatments, some alloys containing Ti and Mo were found to be very susceptible to cracking even at high-temperature process. This was possibly due to an unexpected partial melt or the formation of a brittle secondary phase during processing. Detailed evaluation of the embrittlement mechanism of these alloys was out of the scope of the present study, so that no further investigation was made. After taking the BCC solvus temperatures into account, three final compositions (1 wt.% Ti, 5 wt.%W and 6 wt.% W) were selected (Table 4-1) for experimental validation. In order to provide a base-line comparison, the reference alloy (Fe-30Cr-3Al-0.2Si-2Nb) was also evaluated. The summary of the nucleation driving forces and BCC solvus temperatures of the selected alloys and the reference alloy are listed in Table 4-1

Table 4-1 Selected alloy composition for experiment

wt%	Laves Phase Mole Percent at 700 °C	BCC Solvus Temperature (°C)
1Nb-1Nb	3.38	1251.4
1Nb-1Ti	4.19	1150.4
1Nb-5W	5.49	1143.4
1Nb-6W	6.28	1155.8

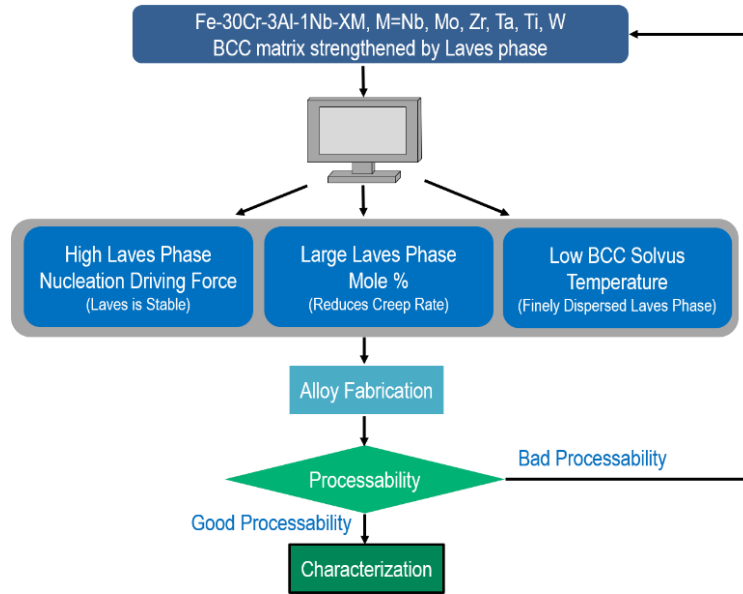


Figure 4.1 Schematic flowchart of the alloy design thought process based on thermodynamic calculations and processabilities on Fe-30Cr-3Al-1Nb based alloy system

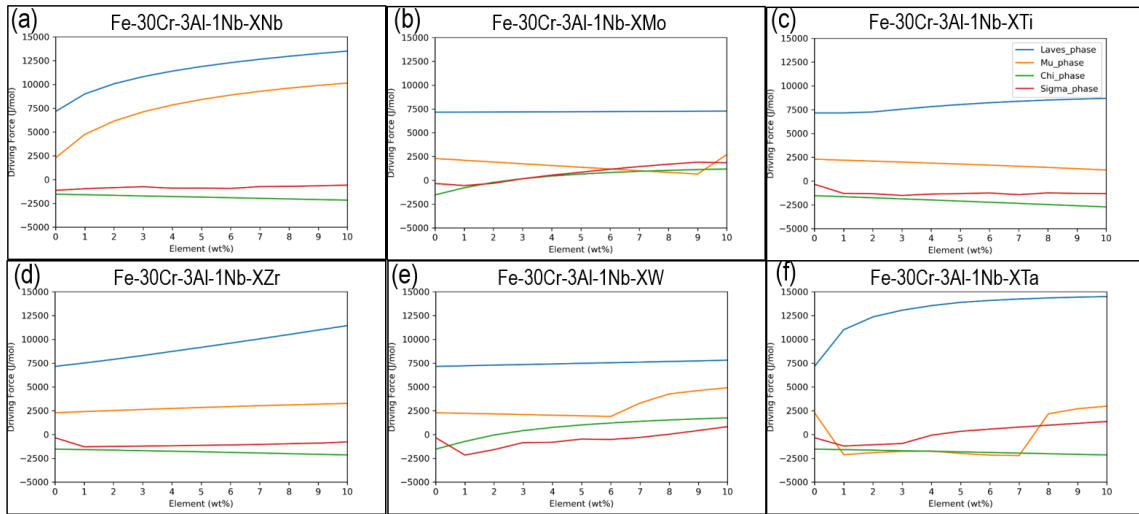


Figure 4.2 Calculated nucleation driving force at 700 °C as a function of weight percent of the additional elements (a)Nb (b)Mo (c)Ti (d)Zr (e)W (f)Ta. (X: element addition (wt%), Y: driving force (J/mol))

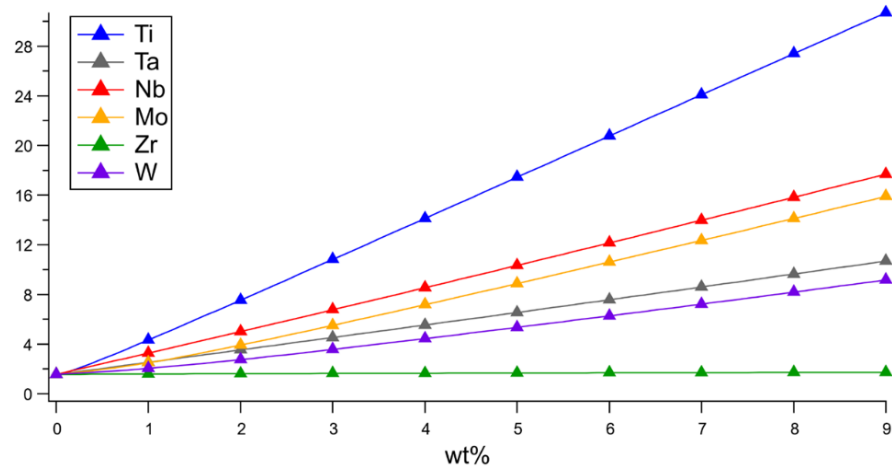


Figure 4.3 Calculated Laves phase mole percent (y axis) as a function of additional elements in weight percent (x axis) at 700 °C

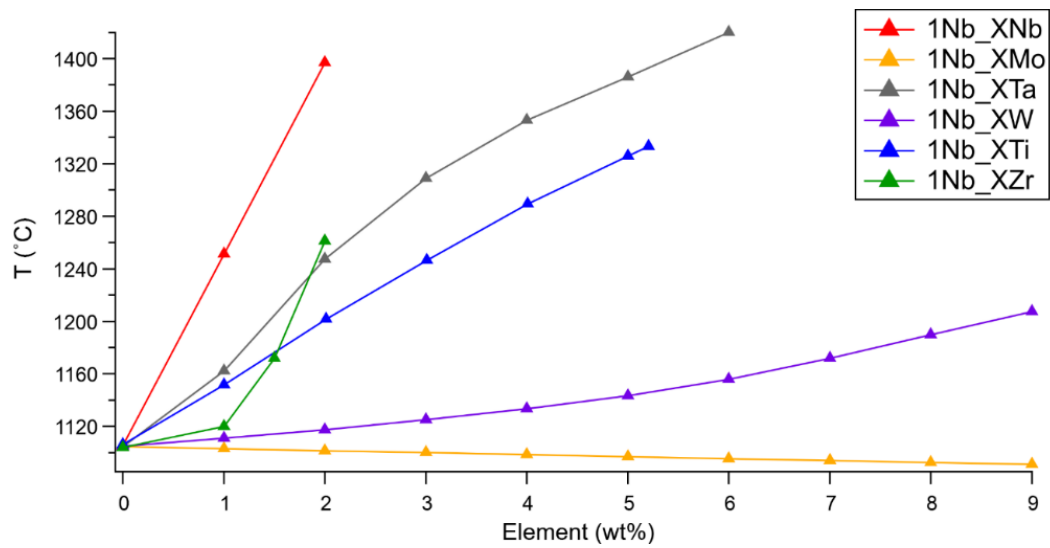


Figure 4.4 BCC solvus temperature as a function of additional elements

Discussion

Discussion on Alloy Design Criteria for Precipitate Hardening Creep-Resistant

Materials

There are three stages for precipitation behavior: nucleation, growth, and coarsening. Nucleation behavior was predicted by the calculated results above. Growth and coarsening will be investigated experimentally by the isothermal aging studies in the following chapter. Moreover, coarsening behavior of Laves phase could also be evaluated via thermodynamic calculated before obtaining the isothermal aging experimental results.

Coarsening of the precipitates in ferritic creep-resistant alloys were studied intensively in the literature (see Chapter Two). Coarsening or Ostwald ripening, is a thermodynamic and kinetic process to minimize the surface energy between precipitate and the matrix, which is mainly due the to the curvature difference. The driving force of Ostwald ripening can be described by the equation below:

$$\Delta G = \frac{2\gamma V_m}{r}$$

, where γ is surface energy between precipitate and the matrix, V_m is molar volume of precipitate, and r is the curvature of the precipitate. Smaller precipitates with higher curvature are more thermodynamically unstable than the larger precipitates. Therefore, the atoms at the boundary of smaller precipitates tend to diffuse away to the larger precipitates. As a result, smaller precipitates shrink, while larger precipitates continue to increase in size. To predict the coarsening behavior of the selected alloys listed in Table 4-1 to evaluate

the long-term precipitation behavior, the LSW model (equations listed below) was used with diffusivity database from Thermocalc (TCFE9 and MOBFE4).

$$r_0 = \frac{2\gamma}{\Delta G_{max}}$$

$$r^3 - r_0^3 = Kt$$

$$K = 8\gamma V_m^p / \sum_{i=1}^n \frac{9(x_i^p - x_i^{mp})^2}{x_i^{mp} D_i / RT}$$

, where r_0 is the critical precipitate nucleus size, γ is matrix-precipitate interfacial energy, ΔG_{max} is the precipitate nucleation driving force, V_m^p is the molar volume of precipitate, K is the coarsening rate, t is the exposure time, x is the equilibrium interfacial concentration of the precipitate-forming elements on both matrix (m) and precipitate (p), T is the service temperature, D_i is the corresponding diffusion coefficient of precipitate-forming elements i (Ti, Nb, W) and n is the total number of the precipitate-forming elements considered. As shown in Figure 4.5, Laves phase in 1Nb6W alloy had the least increase in diameter, which was still below 100 nm, while 2Nb and 1Nb1Ti had precipitate diameter of more than 400 nm after 10,000 hours at 700 °C. This result indicated that 1Nb6W alloy would have superior creep resistance than 2Nb and 1Nb1Ti based on its Laves phase stability. The microstructural evolution will be investigated and discussed in the following chapter to validate this design criteria.

Table 4-2 Parameters used for LSW coarsening calculations

	2Nb	1Nb1Ti	1Nb6W
Volume Fraction	3.8×10^{-2}	4.8×10^{-2}	7.0×10^{-2}
Initial Radius (m)	2.2×10^{-8}	2.4×10^{-8}	2.9×10^{-8}
Coarsening Coefficient (m³/s)	3.0×10^{-28}	4.4×10^{-28}	5.3×10^{-31}

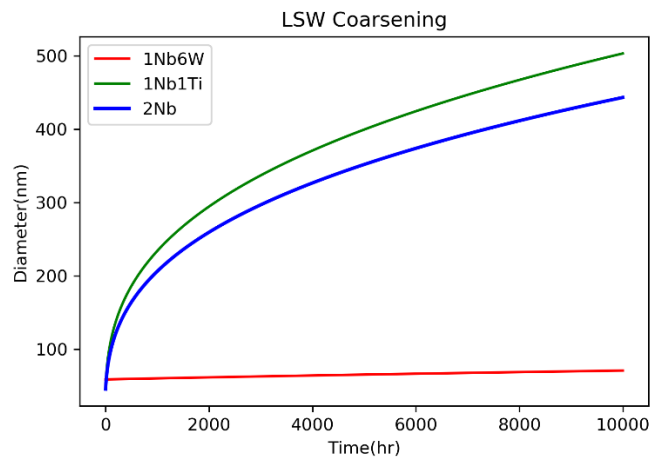


Figure 4.5 Calculated Laves phase diameter using LSW coarsening model at 700 °C

Summary

3 out of the total 57 alloy compositions containing Laves phase forming elements were selected for experiments with 2Nb as a reference alloy based on the thermodynamic calculations. Three constraints (1) Laves phase nucleation driving force, (2) Laves phase mole percent, and (3) the BCC solvus temperature for solutionization treatments were

considered for alloy design process. W containing alloys were expected to have superior creep resistance than the other alloys based on the calculated results. Further isothermal aging studies at target service temperature and the actual creep tests will be conducted and discussed in the following chapters.

CHAPTER FIVE

MICROSTRUCTURAL EVOLUTION OF ISOTHERMAL AGED FECRAL ALLOYS

Background

Alloys selected based on thermodynamic calculations in Fe-30Cr-3Al-1Nb alloy system were isothermally aged at 700 °C for 24, 168, 1008, and 3000 hours for microstructural evolution. There were microstructural features that need to be considered. Key features include the size and number density for Laves phase inside the matrix, the width of PFZ, and GBZSF. Even though the results from isothermal aging were stress free and would be arguable to represent the microstructure of the actual creep tests, it would be a decent indication to validate alloy design process based on the microstructural stability and a reference to the post-Mortem microstructure characterization after creep tests, which will be discussed in Chapter Seven.

Results

SEM Characterization

The microstructural characterization was conducted by using SEM backscattered electron (BSE) images. As-solution heat-treated alloys revealed no clear evidence of second-phase formation in the BCC-Fe matrix. This indicates that the BCC solvus temperatures of the alloys are lower than the solution treatment temperatures, which is consistent with the predicted results. The SEM-BSE images in Figure 5.1 to Figure 5.4 provide an overview

of the precipitate characterization on both inside the ferritic matrix and PFZ in the alloys after aging at 700 °C for 24 h (Figure 5.1 and Figure 5.3) and 3,000 h (Figure 5.2 and Figure 5.4). The observed microstructure consisted of a single-phase matrix (BCC-Fe) with single type of second-phase precipitates, based on the morphology and the contrast, suggesting that only Laves phase formed during aging as expected. The size and number density of the Laves phase precipitates are quantified by using the equivalent circle diameter (ECD)[55] approach.

To analyze the evolution of the precipitate coarsening process, the median ECD of each alloy is plotted as a function of aging time in Figure 5.5. In the early stage of aging up to 1,008 h, the median ECD in 1Nb-6W indicates a modest growth compared to 1Nb-1Ti and 2Nb alloys. On the other hand, the trend in ECD as a function of time are different with increasing time from 1,008 to 3,000 h; the median ECD in 1Nb-6W alloy increased significantly compared to 1Nb-1Ti, and the ECD of the 2Nb alloy increased at a rate intermediate to that of the 1Nb-6W and 1Nb-1Ti alloys. The number density of Laves phase precipitates in 1Nb-6W decreased during aging from 168 to 3,000 h (from 5.6×10^{19} to $0.9 \times 10^{19} \text{ m}^{-3}$), as shown in Figure 5.6, while that for 1Nb-1Ti remains almost unchanged (from 1.6×10^{19} to $1.4 \times 10^{19} \text{ m}^{-3}$). In Figure 5.7, the volume fraction of all the alloys remained almost unchanged, which means all the alloys are already in coarsening stage after 24 h at 700 °C. These results imply that 1Ti-1Nb and 2Nb alloys exhibit relatively simple, monotonic characteristic of precipitate coarsening, whereas 1Nb-6W alloy shows possibly two different coarsening modes, with one active up to 1,008 h of aging and a second active after 1,008 h of aging.

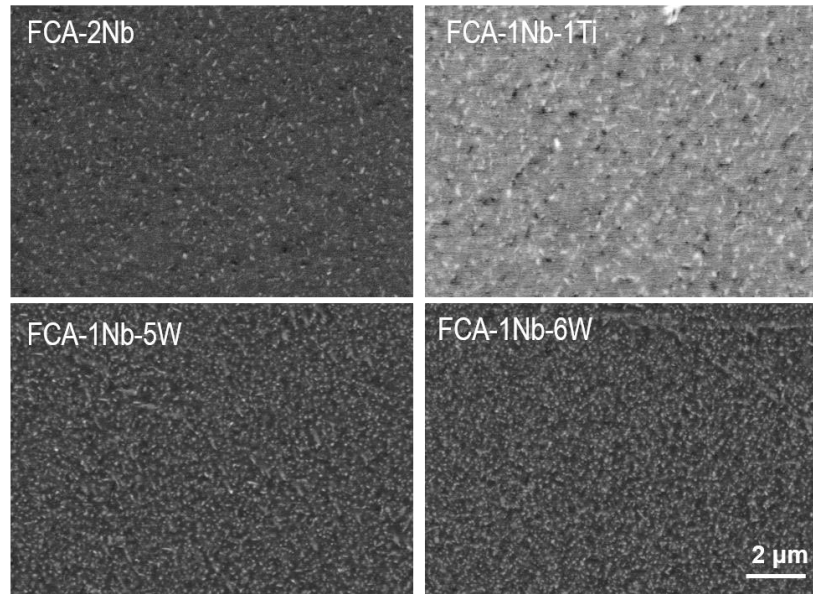


Figure 5.1 SEM images of Laves phase in BCC matrix after 24 h aging

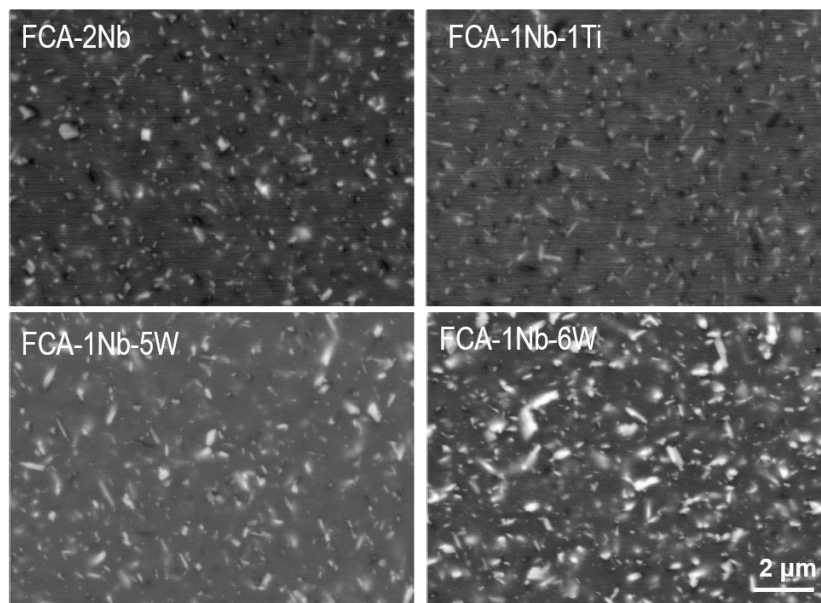


Figure 5.2 SEM images of Laves phase in BCC matrix after 3000 h aging

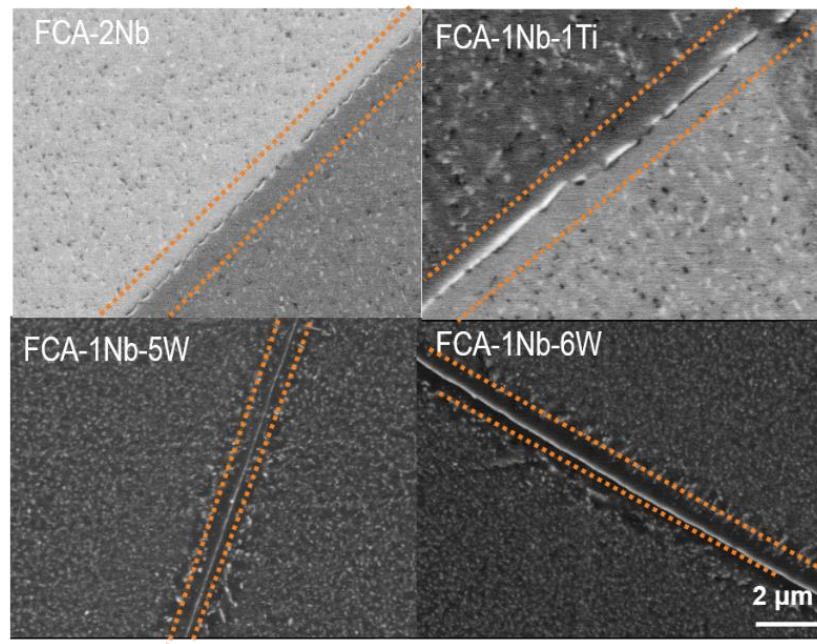


Figure 5.3 SEM images of PFZ after 24 h aging

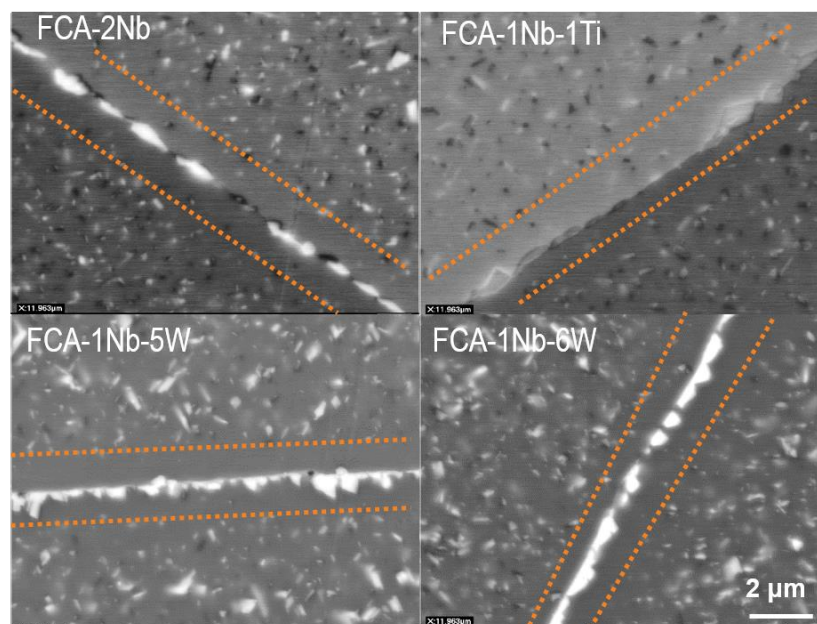


Figure 5.4 SEM images of PFZ after 3000 h aging

The PFZ measurements reveal similar and invert trends of the number density, as shown in Figure 5.8. The 1Nb-6W has the narrowest mean PFZ width ($0.69 \pm 0.03 \mu\text{m}$) at 1,008 h, while 1Nb-1Ti has the largest mean PFZ width ($1.1 \pm 0.05 \mu\text{m}$) among all the tested alloys. However, the mean PFZ width of 1Nb-6W ($1.24 \pm 0.06 \mu\text{m}$) slightly exceeds that of 1Nb-1Ti ($1.17 \pm 0.05 \mu\text{m}$) at 3,000 h, which presumably represents a constant PFZ growth rate in the W containing alloy compared to a leveled off growth rate in the 2Nb and 1 Ti alloys. The underlying PFZ evolution in 1Nb-6W seems to be strongly correlated to the two-step coarsening mode of the precipitates described above, and it needs to be further investigated.

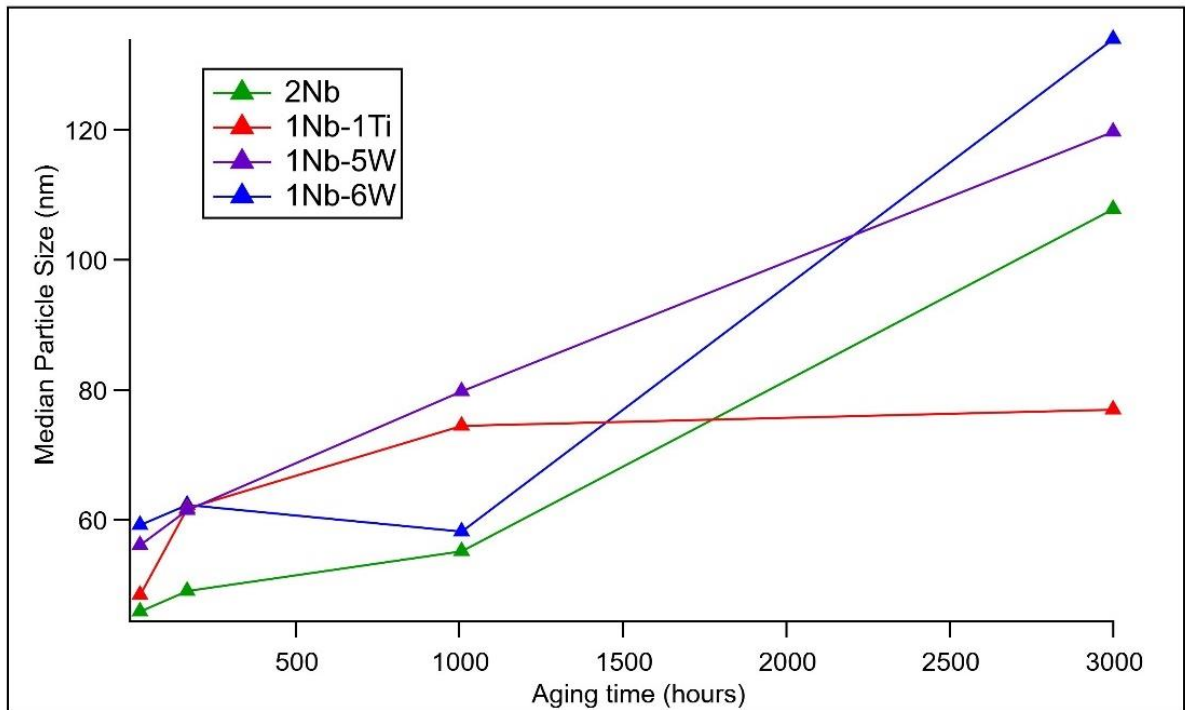


Figure 5.5 Equivalent circle diameter (ECD) as a function of aging time

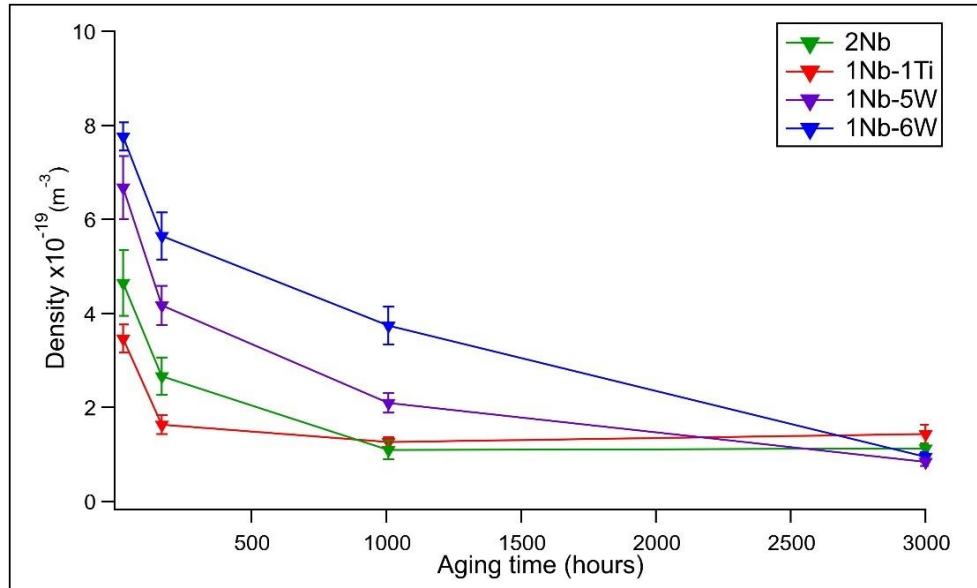


Figure 5.6 Number density of Laves phase in BCC matrix as a function of aging time

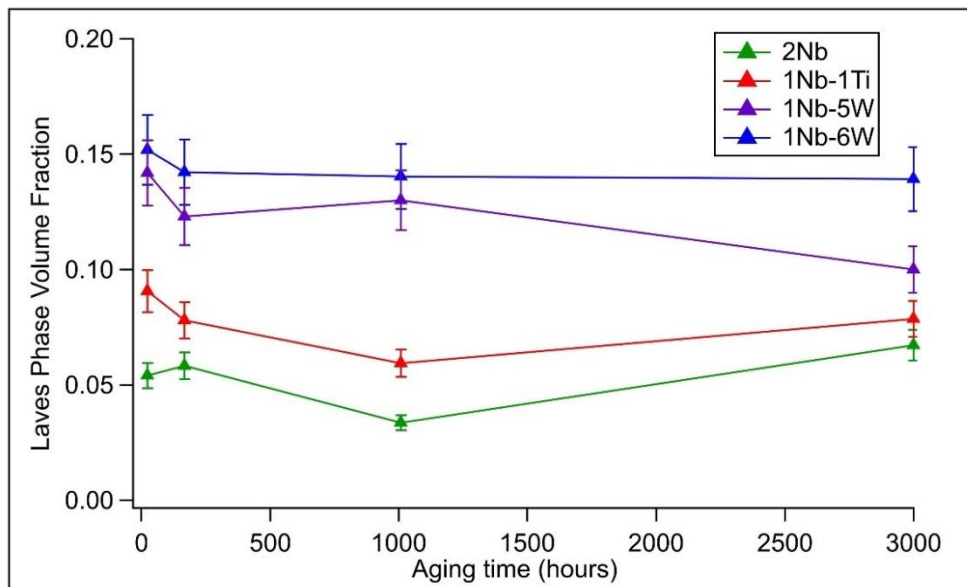


Figure 5.7 Laves phase volume fraction as a function of time

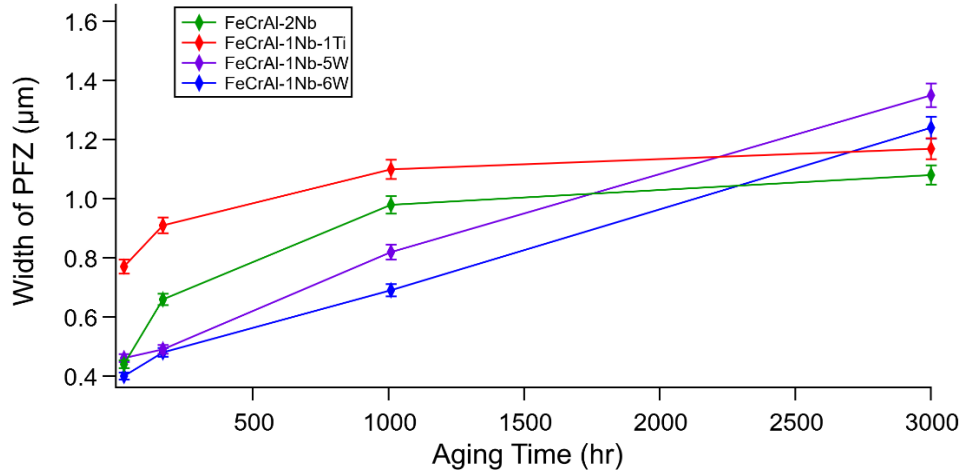


Figure 5.8 Mean width of PFZ as a function of aging time

Shassere *et al.* [38] proposed the grain boundary zone strength factor (GBZSF) as a correlation between the mean PFZ width and the amount of the grain boundary Laves phase for both aged and crept samples. GBZSF is defined as the following:

$$GBZSF = \frac{f_{GB}^{Laves}}{\delta_{PFZ}}$$

, where the numerator is the linear coverage of the Laves phase on the grain boundary and the denominator is the mean width of the PFZ. Although the GBZSF is an empirical equation, it was reported that [38] all the creep ruptured samples of the Fe-30Cr-3Al-xNb alloys had a GBZSF below 0.6 and the aged samples, with aging time close to rupture times, also had a value close to 0.6. Therefore, GBZSF has been used as a scale to comment on the creep resistance of the alloys. GBZSF of all the aged samples and the data points from the literature[38] are plotted in Figure 5.9 The aging time dependence of GBZSF showed a very similar trend to that of the number density of Laves phase precipitates

(Figure 5.6). At 1,008 h, the 1Nb-6W alloy has a larger GBZSF (1.42) than that in 2Nb (0.78) and 1Nb-1Ti (0.74). However, the GBZSF of all the samples approach a similar value around 0.7 after 3,000 h aging, which indicates the microstructure of all the alloys are not favorable for creep-failure after 3,000 h aging.

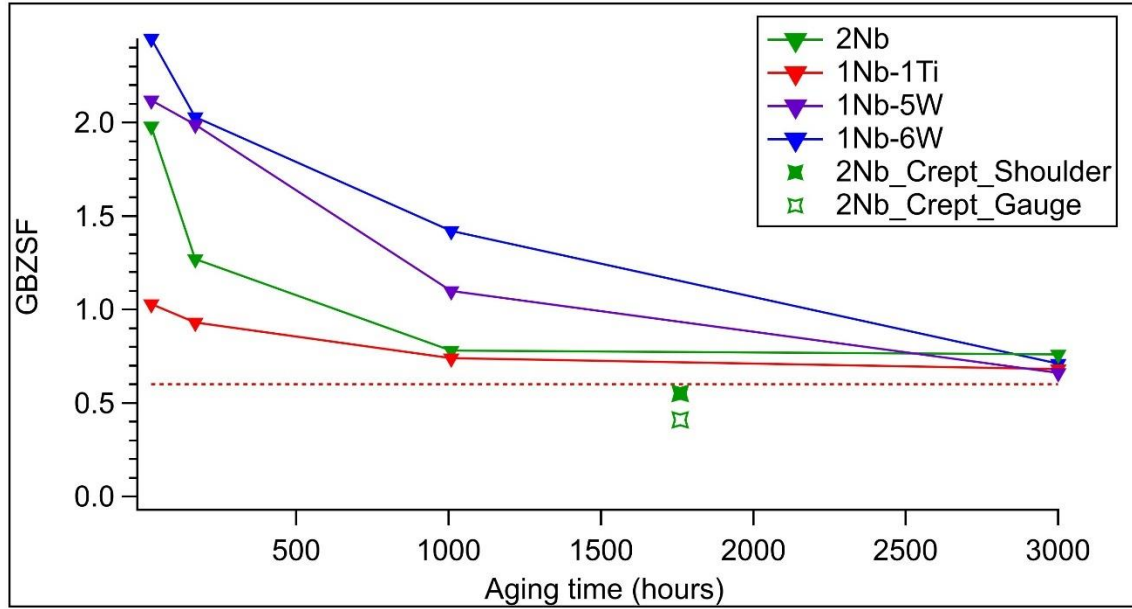


Figure 5.9 GBZSF of aged samples overlaid with crept 2Nb sample

Discussion

Discussion on Validation of the Proposed Design Strategy

1Nb-1Ti and 1Nb-6W were down-selected by the alloy design process (Chapter Four) based on the 3 constraints: (1) the highest Laves phase nucleation driving force among the other second phases, (2) higher Laves phase mole percent at 700°C than that of the

reference alloy, and (3) lower BCC solvus temperature than 1300°C. For constraint (1), based on the precipitate morphology in the SEM BSE images, no second-phase other than Laves phase was observed from all the aged condition for both alloys. For constraint (2), Laves phase mole percent reflects the volume fraction of Laves phase formed as a second-phase precipitates in the BCC-Fe matrix. The volume fractions of Laves phase was measured by using the area ratio of Laves phase precipitates to the field of view in the SEM images. As shown in Figure 5.7, 1Nb-6W (0.14) and 1Nb-1Ti (~0.08) have volume fractions larger than 2Nb (~0.05) alloy in most of the aging periods in the present study. For constraint (3), no precipitate was observed inside the ferritic matrix for the as-solution heat-treated condition for all three alloys. Thus, it is experimentally validated that the expected, controlled microstructure can be obtained by the proposed computational based design methodology with guide from thermodynamic calculations.

Summary

The isothermal aging studies at 700 °C validated by SEM characterizations three constraints (1) the highest Laves phase nucleation driving force among the other second phases, (2) higher Laves phase mole percent at 700°C than that of the reference alloy, and (3) lower BCC solvus temperature than 1300°C that were proposed in the design strategy from the previous chapter. Interestingly, the significant increase in median ECD and decrease in number density of W-containing alloys compared to the Ti-containing alloy required further investigation, which will be discussed in the following chapter.

CHAPTER SIX

ROLE OF CORE-SHELL STRUCTURE IN W-CONTAINING LAVES PHASE

Background

While the selected alloys suggest potentially a “good” creep performance from the calculated Laves phase mole fraction, the underlying precipitation kinetics in these alloys need to be rationalized. To capture the chemical effect on the precipitation kinetics, atom probe tomography (APT) was used to probe the details near the interfaces between the Laves phase precipitate and the ferrite matrix. The 1Nb-1Ti and 1Nb-6W alloys aged for 4, 24, and 3,000 h were characterized by APT to measure the compositional evolution of the Laves phase precipitates with respect to aging time.

Results

APT Characterization

Figure 6.1a represents a part of the APT atom map showing Nb, Si, and W atoms along with a 4 at. % W iso-concentration surface (iso-surface) for the 4 h-aged 1Nb-6W sample. The map indicates that at least four of the Nb- and W-enriched Laves phase precipitates appeared in the area. Figure 6.1b illustrates 1D concentration profiles obtained from one of the Laves phase precipitates in the same sample with the region of interest shown in Figure 6.1a (a colored box). The 1D concentration profile clearly reveal that Si and Nb are

enriched inside of the precipitates, while a sharp W peak appears near the precipitate-matrix interface, indicating a formation of “core-shell” structure.

Concentration profiles from the precipitate-matrix interfaces were compared for the 1Nb-1Ti and 1Nb-6W alloys as a function of aging time, as summarized in Figure 6.2. Unlike the 1Nb-6W samples, the 1Nb-Ti containing alloy does not show a core-shell structure in the Laves phase precipitates for any aging time periods. By focusing on the 1Nb-1Ti precipitate-matrix interface concentration profiles, there is a drastic change in the Ti concentration of the precipitate from the 4 h compared to the 24 h aged samples (Figure 6.2a and Figure 6.2b, respectively), while there is a slight change in the concentration profiles between the samples after aging for 24 and 3,000 h (Figure 6.2b and Figure 6.2c, respectively). In fact, the Ti and Nb concentration profile at the precipitate-matrix interface after 3,000 h (Figure 6.2c) show constant Ti and Nb contents within the Laves phase precipitate. This observation confirms that the precipitate has reached an equilibrium composition. The changes in the Ti and Nb concentrations can be directly related to the precipitate coarsening rates between these aging steps, such that the microstructure remains relatively stable after aging for 24 h.

The W containing sample, on the other hand, does not show an equilibrium precipitate composition for all aging time periods in the range of the present study. To understand the supersaturation inside the ferritic matrix, the concentration profiles of Nb, Si, Ti or W inside the ferritic matrix of 1Nb-1Ti and 1Nb-6W measured by atom probe are plotted as

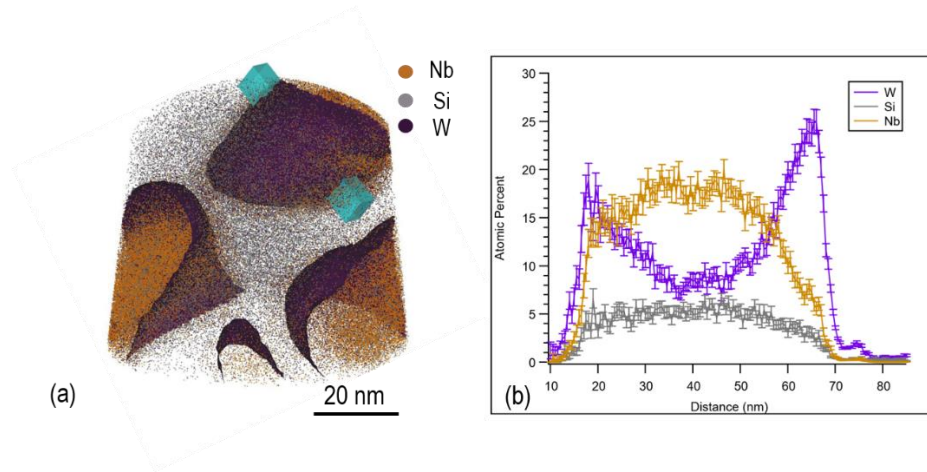


Figure 6.1 (a) corresponding atom maps with a 4 at.% W iso-surface and the 1D line profile region of interest and (b) a characteristic core-shell concentration profile of Nb/Si core and W shell in Laves phase in 1Nb-6W sample after 4 h aging

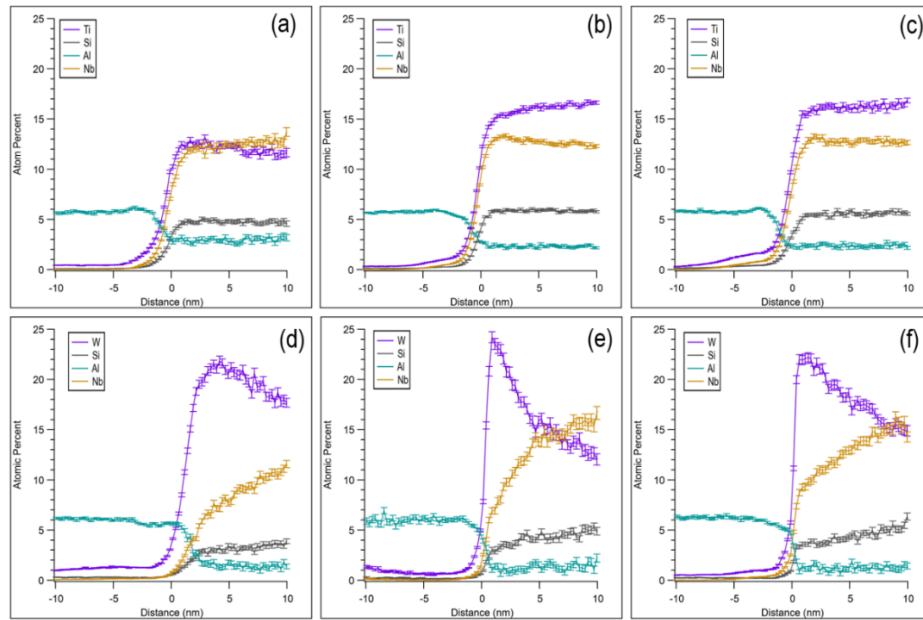


Figure 6.2 Composition profiles of the matrix/precipitate interface for the 1Nb-1Ti samples aged after (a) 4 h, (b) 24 h, and (c) 3,000 h and the 1Nb-6W samples aged after (d) 4 h, (e) 24 h, and (f) 3,000 h measured by atom probe.

a function of aged time in Figure 6.3. In Figure 6.3a, the drop in Ti content and the increase in Si content from 4 to 24 h could be explained by the slightly faster diffusivity of Si than that of Ti (Table 6-1) which might affect to the initial partitioning in the Laves phase nucleation before 24 h. Also, as shown in Figure 6.2a and Figure 6.2b, the Laves phase in 24 h aged sample contains ~ 3 at.% more Ti than the Laves phase in 4 h aged sample, which is consistent with the observation in Figure 6.3a. From 24 to 3,000 h, the Ti content remained almost unchanged, which indicates 1Nb-1Ti has already exhausted the supersaturation of Laves phase composing elements in the ferritic matrix after 24 h. On the other hand, in Figure 6.3b, the continuous decrease in W content from 24 to 3,000 indicates that the transportation of W from the matrix to the precipitates continues after 24h aging. Nb contents in both Figure 6.3a and Figure 6.3b present similar behavior: A slight drop from 4 to 24 h followed by a nearly flat profile from 24 to 3,000 h, which indicates the supersaturations of Nb in both alloys have already been exhausted after 24 h. It should be emphasized that a closer inspection of one of the Laves phase precipitates in the 3,000 h-aged 1Nb-6W sample (shown in Figure 6.4) revealed a plateau of approximately 25 at. % W on the right-hand side of the plot in Figure 6.4b, which is close to the calculated equilibrium concentration of W (24.1 at.%, in Table 6-2), indicating that the precipitate in the 3,000 h-aged sample could be in the transition stage from meta-stable to stable conditions. In addition to the Ti, W, and Nb profiles, the lower solubility of Al and higher solubility of Si were also detected inside the Laves phase precipitate, which is consistent with the calculated Thermo-Calc[®] results (Table 6-2).

Table 6-1 Calculated diffusivity (m²/s) of major elements in Laves phase at 700 °C

	Cr	Al	Si	Nb	Ti	W
1Nb-1Ti	1.10E-17	1.17E-16	1.33E-16	3.63E-16	9.04E-17	-
1Nb-6W	4.29E-18	1.35E-16	1.56E-16	1.75E-16	-	5.27E-18

Table 6-2 Calculated Laves phase nucleus and equilibrium composition of 1Nb-1Ti and 1Nb-6W in at. %

		Fe	Cr	Al	Si	Nb	Ti	W
Nucleus	1Nb-1Ti	32.85	23.68	3.38E-5	10.13	32.53	0.79	-
	1Nb-6W	31.34	25.26	4.92E-5	10.05	28.38	-	4.94
Equilibrium	1Nb-1Ti	60.37	2.26	2.39E-4	4.07	12.59	20.69	-
	1Nb-6W	42.99	21.09	2.86E-4	2.59	9.16	-	24.14

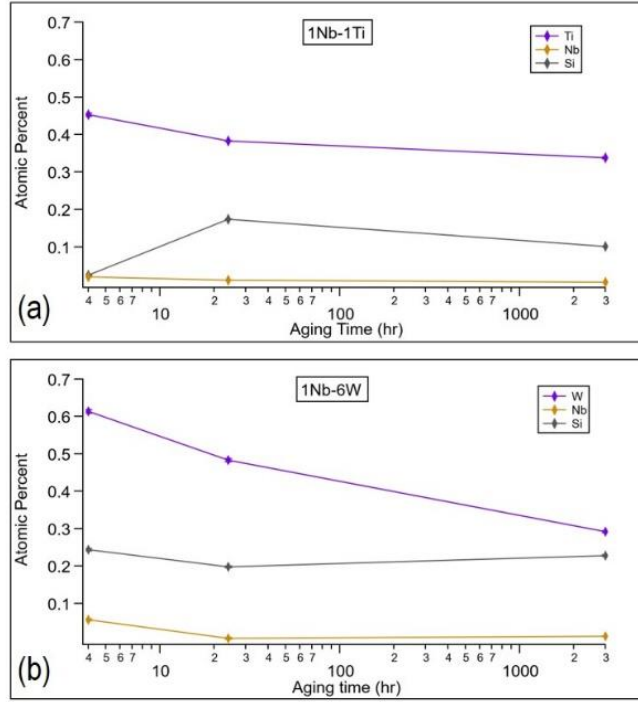


Figure 6.3 (a) Mole fraction of Nb, Si, Ti in the BCC-Fe matrix for the 1Nb-1Ti samples aged after 4 h, 24 h, and 3,000 h and (b) Mole fraction of Nb, Si, W in the BCC-Fe matrix for the 1Nb-6W samples aged after 4 h, 24 h, and 3,000 h measured by atom probe

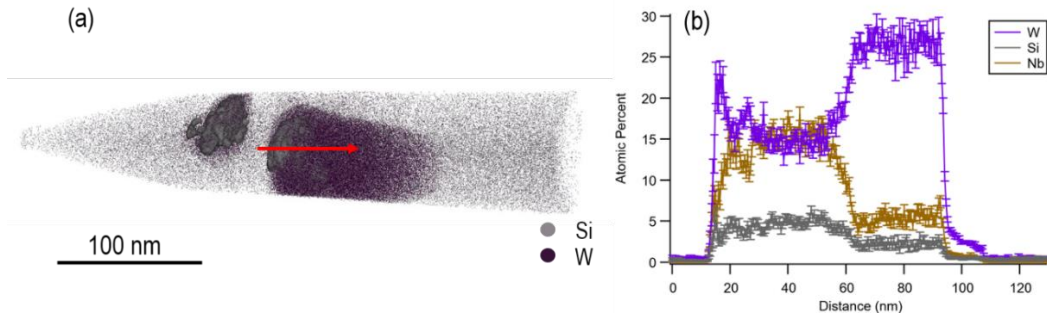


Figure 6.4 (a) atom map with a 4.2 at.% Si iso-surface for the 3,000 h aged 1Nb-6W sample. (b) A 1D composition profile highlighted by the red arrow in (a).

Discussion

Discussion on Core-shell Structure and Precipitate Kinetics

Based on literature[56], the difference in diffusivity between Nb, Si and W in the ferritic matrix calculated by DICTRA[®]TM are hypothesized to be the main reason for the formation of a core-shell structure in the W containing alloy. The calculated diffusivities of Nb and Si (Table 6-1) were almost 2 orders of magnitude faster than W at 700 °C. Therefore, Laves phase precipitates' initial nucleation and growth starts with Nb and Si because these elements have move to the precipitate with a higher flux than W. At later stages, the Nb and Si are depleted from the matrix and W becomes the main element to diffuse to the precipitate. Several literature have reported that Si promotes the formation of Laves phase[41], [42], [57], [58].

Isik *et al.* reported that with an increase in Si content, less Mo content is required for the Laves phase formation in a 12Cr-1Mo Ferritic-Martensitic steel for the same Laves phase fraction [43], [44]. The researchers used Transmission Electron Microscopy (TEM) based Energy Dispersive X-ray Spectroscopy (EDS) and APT for characterizing the crept samples at 550 °C at 120 MPa which showed a bulk segregation of Si and Mo at ferrite sub-grain boundaries. Si has very little solubility in $M_{23}C_6$ carbides, and therefore, Si atoms partition into the sub-grain boundary in the vicinity of $M_{23}C_6$ carbides as $M_{23}C_6$ grows. Both the bulk segregation of Si and Mo at sub-grain boundaries and the continuous rejection of Si atoms at the carbide-ferritic interface from growth of $M_{23}C_6$ act as a

precursor to Laves phase formation at the sub-grain boundaries and in the vicinity of $M_{23}C_6$ carbides.

Niewolak *et al.* observed the formation of Nb-rich Laves phase surrounded by W-rich Laves phase in Crofer 22 H after annealed at 700 °C for 1,000 h by SEM and APT [59]. Niewolak *et al.* hypothesized that equilibrium had not been reached after annealing for 1,000 h at 700 °C and the two regions of Laves phases might transform into a single Laves phase after a longer exposure time. Similarly, Lopez Barrilao *et al.* [56] observed a metastable core/shell dual composition precipitate at the grain boundaries in an 18-22Cr ferritic steel system with a Nb/Si-rich core surrounded by a W-rich shell, both of which are Laves phase. The dual phase feature was present in short-term aging (up to 1,000 h at 600 °C) and only the W-rich Laves phase remained after long-term aging (30,000 h at 600 °C). These authors also concluded that the Nb/Si-rich Laves phase may be more kinetically favorable due to supersaturation of Nb in the matrix and a faster diffusivity of Nb and Si than W in BCC-Fe. Based on the Si enhanced Laves phase formation found in the literature,[44], [57], [60] it is clear that the Nb/Si rich core-W rich shell structure found in this study is indeed expected in the W-containing alloy. In order to confirm the generality of the core-shell structure, further analyses were performed on the data from 1Nb-6W samples. The measured concentration profile of the 1Nb-6W sample (Figure 6.2d-f) showed a characteristic core-shell structure in all the measured conditions. The core-shell structure was still observed in the 3,000 h aged 1Nb-6W sample as can be seen in Figure 6.2f, whereas the rapid coarsening of the Laves phase precipitates was also observed in the

same aged condition. These incompatible phenomena can be explained by the two-step coarsening, as discussed in the following section.

Discussion on Phase Transformation Kinetics and PFZ in W- and Ti-containing FeCrAl Alloys

After 1,008 h aging, (see Figure 5.5, Figure 5.6, and Figure 5.8), the 1Nb-6W sample exhibited a modest growth in precipitate size, the narrowest PFZ, and the highest number density among the alloy studied. The observed microstructural feature and consideration of the GBZSF indicate that the 1Nb-6W sample is expected to exhibit the highest creep resistant microstructure among all present alloys up to 1,008 h. However, the results after 3,000 h aging demonstrate a significant change in the precipitate size and the number density of the 1Nb-6W sample which indicates relatively rapid coarsening of the Laves phase precipitates. Comparing Figure 6.2a and Table 6-2, the measured concentrations of Nb (~18 at.%) and Si (~5 at.%) of 1Nb-6W alloy in the Laves phase precipitate after 4 h aging are closer to the calculated equilibrium concentrations of Nb (9.1 at.%) and Si (2.5 at.%), rather than the nucleus concentrations of Nb (28.3 at.%) and Si (10 at.%), respectively. This indicates that the precipitates after 4h aging are not in the nucleus state anymore but in the transition to the equilibrated condition. On the other hand, the measured W concentration at the core (~8 at.%) is closer to the calculated nucleus concentration (4.9 at.%) than the equilibrate concentration (24.1 at.%), suggesting the transportation of W from the matrix to the precipitate is slower than the growth the Laves phase precipitate. The observed enrichment of Nb and Si in the precipitates clearly indicates that the fast

diffusion of Nb and Si in the BCC-Fe matrix contribute to forming the Nb/Si rich nucleus at the beginning of the Laves phase precipitation, which is similar to mechanism of the core-shell structure formation in Al-Zr-Sc alloys [61]. However, the slow diffusion of the W atoms from the ferritic matrix into the Laves phase causes insufficient transportation of Laves phase composing element (tungsten in this case) and decelerates the coarsening of Laves phase precipitates in the early stages of aging (up to 1,008 h). This matches with the SEM characterization of the Laves phase precipitate size distribution from 24 h to 1,008 h aging (Figure 5.5). However, the precipitate size increases drastically after 1,008 h, and a partial loss of the core-shell structure in the precipitates can be found in the 3,000 h aged sample as shown in Figure 6.4a. These observations suggest that the formation of the core-shell structure affects the coarsening behavior of 1Nb-6W alloy in two different ways, before and after 1,008 aging.

A closer look at the Laves phase with core-shell structure after 3,000 h aging, a 1-D atomic profile shown in Figure 6.4b along the long axis of a lenticular Laves phase showed a core-shell structure followed by a near-equilibrium composition (see Table 6-2). The Fe_2W Laves phase is reported to grow faster on the incoherent interface than the semi-coherent interface between the Laves phase and the BCC matrix with the crystallography orientation relationship of $(110)_{\alpha\text{-Fe}} // (0\bar{1}13)_{\text{Laves}}$ [16], [62], [63]. Although the crystallographic relationship between the Laves phase precipitate and the BCC-Fe matrix has not been identified in the present study, it can be postulated that the interface has reached the near-equilibrium composition. This statement is based on the observation of a significant amount of W (24.1 at.%) compared to Nb (9.1 at.%) at the interface. These concentration

variations in the precipitate-matrix interfaces could explain the reversal in the trends of PFZ between 1Nb-1Ti and 1Nb-6W samples after 1,008 h. The coarsening of the grain boundary Laves phase was hypothesized to be the reason for PFZ broadening[36], [38]. W-containing grain boundary Laves phase would not start the second step of coarsening until the precipitate-matrix interface reaches equilibrium composition, and therefore, the 1Nb-6W alloy shows a continuously increasing PFZ with aging time. As mentioned before, the nearly unchanged volume fractions of all the alloys (Figure 5.7), combined with the increase in median ECD (Figure 5.5) and decrease in number density (Figure 5.6), indicate that all aged alloys observed in the present study completed the “nucleation” stage and are now in the “coarsening” stage.

Based on the discussion above, it is hypothetically considered that the changes in both precipitate size and number density of 1Nb-6W (in Figure 5.5 and Figure 5.6, respectively) exhibit at least two different modes with a transition occurring between 1,008 and 3,000 h, as schematically illustrated in Figure 6.5 This can be explained by the formation of core-shell in 1Nb-6W alloy. At the early stage (before 1,008 h), the precipitate-matrix interface has not reached the equilibrium composition due to insufficient W transportation which is attributed to slow W diffusion in the ferritic matrix. Precipitation coarsening would not be promoted until the inter-phase boundary reaches to the equilibrated W concentration. In other words, the precipitate coarsening stays temporarily unchanged until the matrix composition reaches to the equilibrated condition. During this period, the precipitate nucleation mode has already been completed because of sufficiently fast diffusion of Nb and Si in the matrix, whereas the slow delivery of W atoms from the BCC-Fe matrix to the

Laves phase precipitates is still continued. Once the equilibrium composition at precipitate-matrix interface has been reached and supersaturation of W has been consumed by Laves phase precipitation (Figure 6.3), the second step of the precipitate coarsening is to be initiated which is now driven by the reduction of total surface energy between the precipitates and the matrix (e.g. Ostwald ripening). On the other hand, there is no core-shell structure in 1Nb-1Ti alloy due to the fast transportation of Nb and Ti. Thus, there is no second-step coarsening during aging.

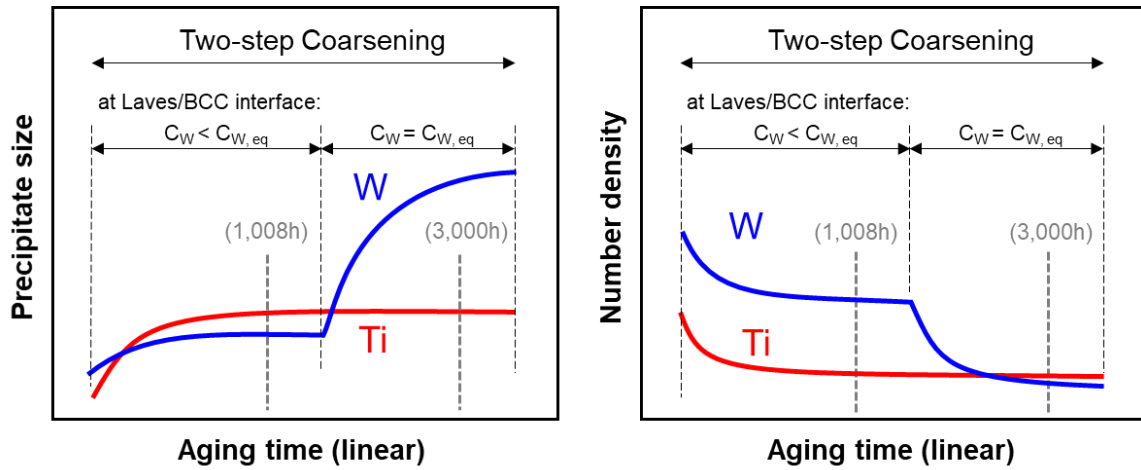


Figure 6.5 Schematics of two-step coarsening in 1Nb-6W alloys due to the formation of Nb-rich core and W-rich shell structure

Although no specific inter-diffusion coefficients inside Laves phase were discussed in the present study, a sluggish W diffusion rate inside the Laves phase could explain the existence of the core-shell structure up to 3,000 h aging. In Figure 6.2, the flat concentration profiles of the 1Nb-1Ti sample with all three aging time periods show the absence of a core-shell structure in the Laves phase, and the flat Ti and Nb profile within

the Laves phase at 3,000 h aging suggests this alloy has reached an equilibrium condition. The changes in the concentration profiles between 24 h and 3,000 h were very little, which indicates the contents in the Laves phase particles were mostly equilibrated before 24 h of aging. The measured concentration of Nb (~13 at.%) in Figure 6.2 matched the calculated concentration of Nb (12.5 at.%) in Table 6-2, whereas the measured Si (~6 at.%) and Ti (~16 at.%) concentration were deviated from the calculated equilibrium concentration of Si (4 at.%) and Ti (20.6 at.%). Such nuances in changes in the growth rate of product phase into parent phases and concurrent shift of local equilibrium concentrations have been proven before in stainless steels (δ - γ equilibrium) welds. The net flux of the solutes (in this case, Ni and Cr) at the interface between ferrite and austenite, which determines the growth rate of the ferrite, depends on both concentration gradient and diffusion coefficient across the interface [64]. To obtain a reliable calculation of local equilibrium during the precipitate coarsening, a new boundary condition including diffusion inside the Laves phase precipitates as well as updated thermodynamic database based on the present study would be required. This approach may help visualizing the two-step coarsening more generically, and the effort is currently in progress. In summary, the formation of core-shell structure in the 1Nb-6W sample explains the accelerated Laves phase precipitate coarsening in the 1Nb-6W sample after 1,008 h aging compared to a stable growth trend in the 1Nb-1Ti sample.

Summary

The delayed increase in precipitate size and the drop in number density of 1Nb-6W alloy from the SEM results were rationalized by the formation of core-shell structure. A Nb/Si-rich core and W-rich shell was observed in 1Nb-6W alloy by APT. The core-shell structure only observed in 1Nb-6W while not in 1Nb-1Ti was explained by the comparatively larger diffusivity difference between Nb($1.75 \times 10^{-16} \text{ m}^2/\text{s}$) and W($5.27 \times 10^{-18} \text{ m}^2/\text{s}$) at 700 °C calculated by DiCTra. Equilibrium concentrations were mostly reached at the Laves phase/BCC interfaces for the three different aging time periods, while the W and Nb concentration inside the core of the Laves phase did not reach equilibrium even after 3,000 h. A precipitate partially reached the equilibrium composition was also found, which explained a potential mechanism of two-step coarsening behavior in the 1Nb-6W sample after 1,008 h aging.

CHAPTER SEVEN

CREEP TEST OF THE DESIGNED FECRAL ALLOYS AND POST-MORTEM CHARACTERIZATIONS

Background

The proposed alloy design strategy was validated by electron microscopy and APT on the microstructural evolution aspect during isothermal aging in the previous chapters. To evaluate the creep resistance of the designed alloys (1Nb-1Ti, 1Nb-5W, and 1Nb-6W), creep tests need to be conducted. Sub-sized ASTM-E8 specimens (see Figure 7.1) were used for creep test at the target service temperature 700 °C. However, the length of the as-rolled 1Nb-6W sheet was not enough to make a total 70 mm specimen. Therefore, the total length of the 1Nb-6W specimen was then shorten to 50 mm, which was unfortunately not sufficient in length to be assembled on both sides of the loading grips. Thus, creep tests were only conducted with 1Nb-1Ti and 1Nb-5W specimens. The creep tests were conducted on an ATS 2330 series® lever arm tensile testing system with DIC to capture the creep rate. The detailed creep testing procedure was described in the chapter of Mechanical Testing Methods (page 42). Stress level of 90 MPa was chosen to compare with the literature [38] for minimum creep rate and the time to rupture. As shown in Figure 2.18, 1Nb-1Ti and 1Nb-5W were expected to have superior creep resistance than 2Nb since these two designed alloys have higher mole percent of Laves phase (see Table 4-1). In other words, assuming similar precipitation behavior, higher mole percent of Laves phase would lead to smaller interparticle spacing, which resulted in higher Orowan-Ashby stress to pin

the dislocations. The Orowan-Ashby stress and interparticle spacing on the designed alloys will be discussed later in this chapter.

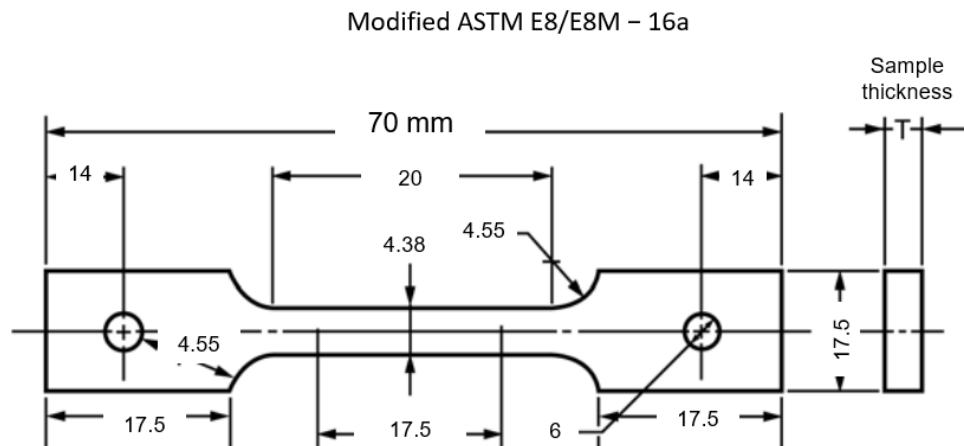


Figure 7.1 Sub-sized ASTM E8 specimen for creep test

Creep Testing Results

Creep Test for 1Nb-1Ti

The 1Nb-1Ti specimen was failed prematurely within 48 h. The fracture surface of the 1Nb-1Ti sample showed predominantly ductile dimples (see Figure 7.2), which indicated that the rupture could be due to stress overloading. The remaining materials of the as-rolled 1Nb-1Ti sheet was not able to machine one more 70 mm sub-sized ASTM E8 specimen, therefore, no creep data could be obtained for 1Nb-1Ti.

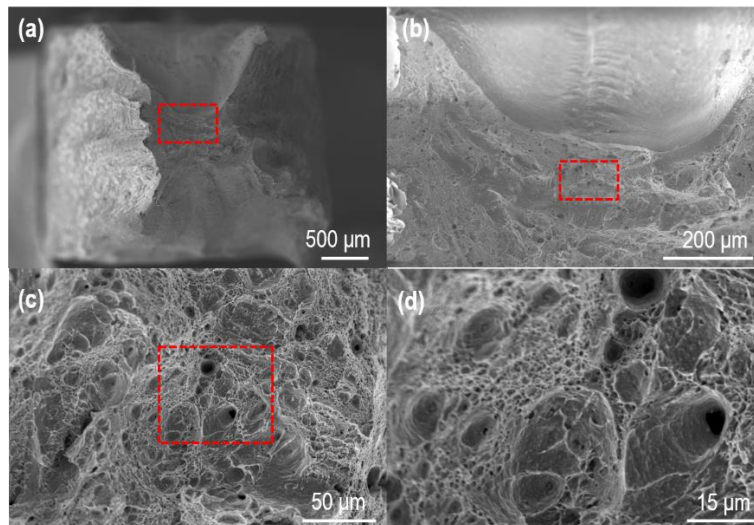


Figure 7.2 The fracture surface of 1Nb-1Ti specimen with various magnitudes. The red dotted boxes in (a)-(c) showed the corresponding region on interest with different magnitudes.

Creep Test of 1Nb-5W

The creep strain as a function of time of 1Nb-5W was shown in Figure 7.3. The 1Nb-5W specimen crept for 1728 h (~98% of the 2Nb rupture time—1760 h) without rupture at

stress level that was 20 MPa higher than 2Nb. The minimum creep rate of 1Nb-5W was $6.67 \times 10^{-7} (\%/s)$, which was comparable to the reported minimum creep rate ($1.47 \times 10^{-7} (\%/s)$) of 2Nb at 70 MPa. The above results validated the proposed alloy design strategy for creep resistance. The creep test of 1Nb-5W was then interrupted to preserve the microstructure during the steady state to understand the underlying deformation mechanism and the role of PFZ. SEM images from the gauge section of the 1Nb-5W sample showed creep voids nucleated within the PFZ (see Figure 7.4). The nucleation of creep voids predominantly within the PFZ reflected that the accelerated deformation concentrated within PFZ compared to the matrix away from the grain boundaries.

The stress exponent (n) reflects the bulk creep deformation mechanism. Monkman-Grant relationship is one of the methods to obtain the stress exponent from the relationship between steady state strain rate (minimum strain rate) and rupture time[7]. The Monkman-Grant relationship can be expressed as following:

$$\dot{\varepsilon}_{ss} t_{rupture} = K_{MG}$$

, where $\dot{\varepsilon}_{ss}$ is strain rate in steady state (minimum strain rate), $t_{rupture}$ is the rupture time, and K_{MG} is the Monkman-Grant constant. The equation above expressed that the steady state dominates the creep life, and hence K_{MG} is a close approximation of rupture strain. For power law creep,

$$\dot{\varepsilon}_{ss} = A\sigma^n$$

, where σ is the applied stress, n is the stress exponent, and A is a fitting constant. The Monkman-Grant relationship can be rewritten as:

$$\sigma^n t_{rupture} = \frac{K_{MG}}{A} = K'_{MG}$$

Or

$$n \ln \sigma + \ln t_{rupture} = K''_{MG}$$

Rearrange the equation:

$$\ln t_{rupture} = K''_{MG} - n \ln \sigma$$

Thus, the stress exponent can be obtained from slope of the plot of rupture time as a function of stress in nature log scale.

The assumption of Monkman-Grant relationship is that creep rupture time and steady-state creep rate (minimum creep rate) is approximately linear. To verify whether the Monkman-Grant relationship is applicable for Fe-30Cr-3Al-1Nb based alloys, the creep tests conducted at Oak Ridge National Laboratory confirmed that creep rupture time increased linearly as minimum creep rate decreased (see Figure 7.5).

As mentioned previously, 1Nb5W specimen was not ruptured. However, results of rupture times and stress levels at 700 °C were reported by Yamamoto *et al* on Fe-30Cr-3Al-1Nb-6W based alloy[12], which was a closely similar composition and could be used for a reasonable approximation to obtain the stress exponent. The acquired data from the literature[12] were plotted in Figure 7.6 to get the stress exponent. The stress exponent was 5.37 ± 0.76 , which suggested the bulk creep deformation mechanism was dislocation climb. Further advance characterization is needed to provide evidence for this bulk creep deformation mechanism.

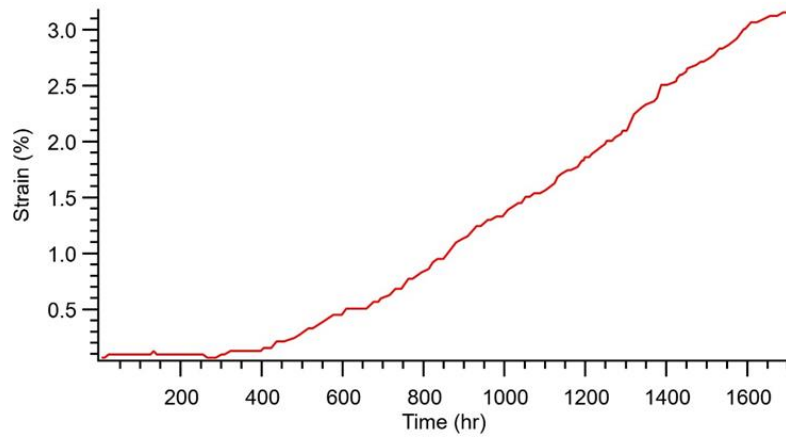


Figure 7.3 Creep strain as a function of time of 1Nb-5W

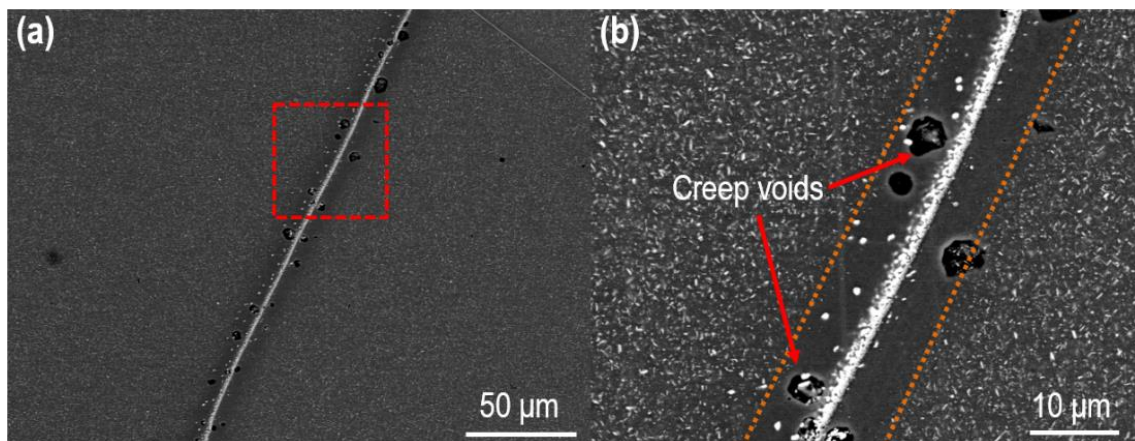
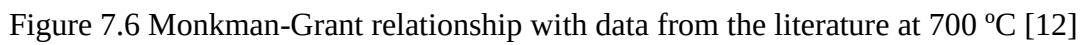
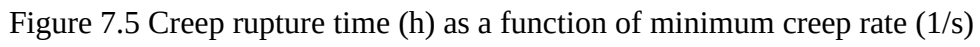


Figure 7.4 SEM-BSE image of the gauge section of the crept 1Nb-5W specimen. The red dotted box in (a) is the region of interest magnified in (b). The orange dotted lines in (b) outlined the region of PFZ.



Post-Mortem Characterization Results

To further understand the (1) Laves phase precipitation behavior under stress and (2) interaction between dislocation and Laves phase in the matrix and within PFZ, several characterizations on the gauge section of the 1Nb-5W crept specimen were conducted. SEM-BSE images were taken in both shoulder and gauge section to compare the precipitation behavior under stress (700 °C, 90MPa) to that of isothermal aging (700 °C) condition. GBZSFs of the crept 1Nb-5W specimen were overlaid on Figure 2.15 for comparison. X-ray diffraction (XRD) was used to obtain an estimated bulk dislocation density of crept 1Nb-5W specimen through modified Williamson-Hall plot [65]–[68]. TEM was used to investigate the local dislocation distribution and the dislocation interaction with Laves phase. Furthermore, PFZ was hypothesized to be responsible for creep deformation mechanism, it is reasonable to assume the hardness within PFZ would be smaller comparing to the matrix even at room temperature. Therefore, nanoindentation was conducted to acquire the local hardness within PFZ and matrix.

Influence of the Stress on Microstructure

To understand the stress effect on microstructure, the difference in strain in gauge and shoulder section of the crept 1Nb5W needed to be assured. With similar grain size, The wider peak width of the XRD results of the gauge section compared to the shoulder section of the crept specimen (see Figure 7.7) indicated higher strain in the gauge section. The strain can be evaluated more quantitatively through the slope of modified Williamson-Hall

plot[65]–[68]. As shown in Figure 7.8, the slope in the gauge section was larger than that in the shoulder section.

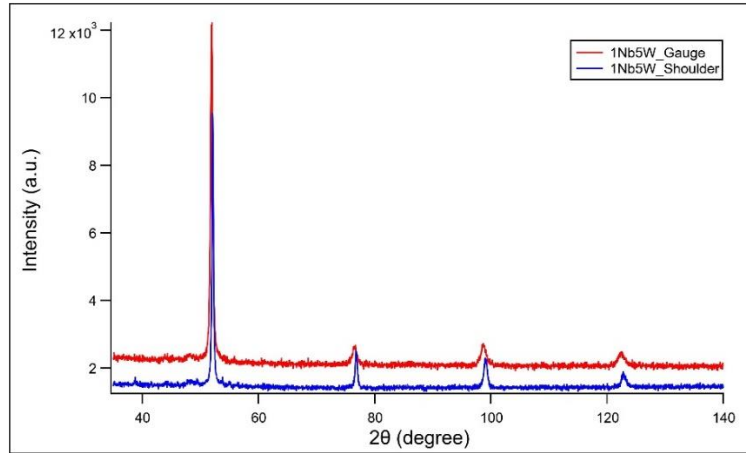


Figure 7.7 XRD of gauge and shoulder section of the crept 1Nb5W specimen

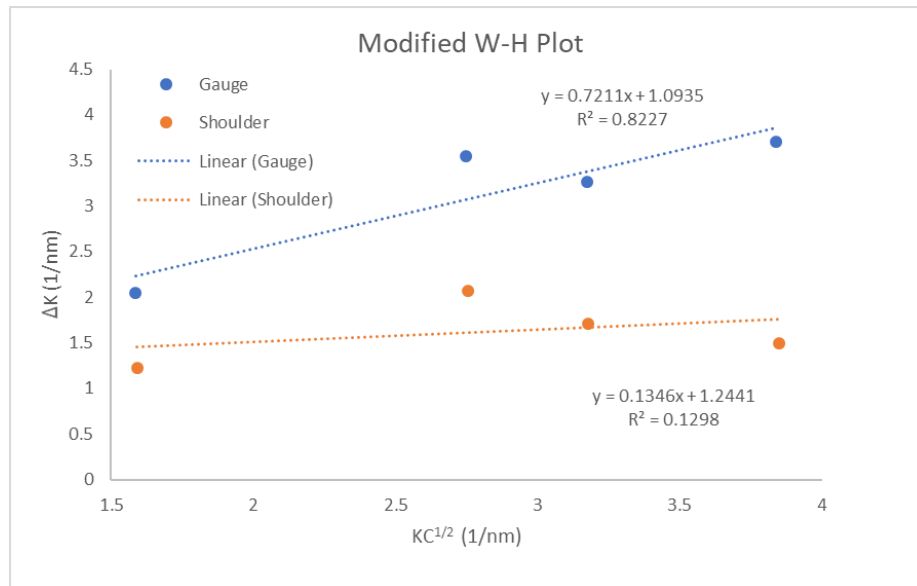


Figure 7.8 Modified Williamson-Hall plot of gauge and shoulder section of the crept 1Nb5W specimen

To investigate microstructure with stress effect, the median equivalent circular diameter (ECD) of gauge section and shoulder section of the crept 1Nb5W specimen were overlaid on the plot of isothermal aged 1Nb5W samples as a function of aging time (see Figure 7.9). The median ECD in gauge section (119.4 nm) was larger than that in the shoulder section (92.3 nm). The dislocations generated inside the gauge section due to plastic deformation from creep could be responsible for the enhanced diffusion that accelerated the growth and coarsening of Laves phase. The GBZSF of both gauge and shoulder sections were overlaid on the plot with aged samples (see Figure 7.10). The GBZSF of the gauge section of crept 1Nb5W specimen was still slightly above 0.6, which was the value hypothesized from the literature[38] that indicated the microstructure would be favorable for fracture. This suggested that even at 90 MPa, which was 20 MPa higher than literature[38], the designed 1Nb5W alloy had a more stable and creep-resistant microstructure than 2Nb.

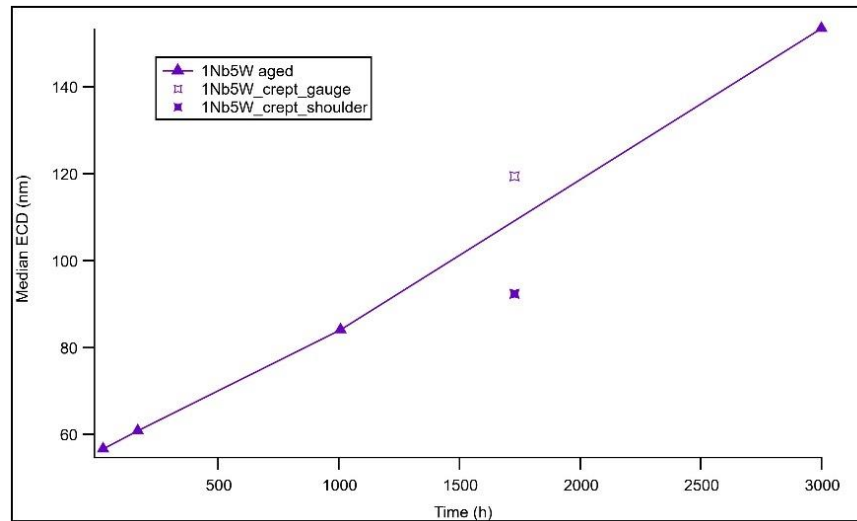


Figure 7.9 Median ECD of the aged and crept 1Nb5W samples as a function of aging time

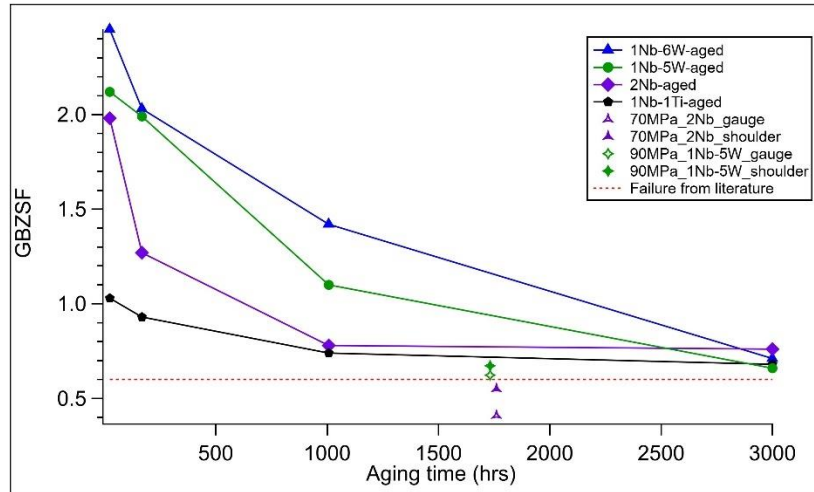


Figure 7.10 GBZSF of the designed alloys for aged and crept conditions

Characterization of Precipitate Free Zone (PFZ)

From the literature [36], [38] suggested that PFZs were critical for creep rupture due to its lacking of Orowan-Ashby stress to pin dislocations. In this study, as shown in Figure 7.4, creep voids were observed within the PFZ, which was consistent with the literature. Hence, to quantify the relatively soft PFZ and the matrix, hardness measurements were conducted using nanoindentation. It could be argued that the nanoindentation was conducted under room temperature, which was not the same condition as 700 °C for creep testing. However, there were no testing device that could be operated at 700 °C that author had access to. The vibration at elevated temperature could also induce a significant amount of noise, which would make the measurement less accurate.

By using displacement-controlled mode, the indent size could be controlled to be less than 1 μm , which was smaller than the width of PFZ ($\sim 1.4 \mu\text{m}$). Based on the literature[69], with Berkovich indenter (Centerline-to-face angle of 65.3°), the area of contact has a relationship with depth of contact:

$$A = 24.5 h_c^2$$

, where A is the area of indent and h_c is the depth of contact. By using displacement of 125 nm, the length of one side of the equal-lateral triangular indent would be 940.2 nm, which could be located inside the PFZ entirely. For comparison, 10 indents were measured inside the PFZ and 10 indents were measured inside the matrix for both gauge and shoulder sections. The load and displacement curves were shown in Figure 7.11, in both sections, the matrix required more load to reach the same displacement compared to that in the PFZ. Furthermore, the hardness value for all the tested conditions were summarized in Table 7-1. For both sections, the hardness inside the PFZ dropped $\sim 10\%$ compared to the matrix.

Table 7-1 Summary of nanoindentation results of matrix and PFZ for both gauge and shoulder sections

	Matrix Hardness (GPa)	PFZ Hardness (GPa)
Shoulder	5.41 ± 0.16	4.75 ± 0.07
Gauge	4.89 ± 0.08	4.44 ± 0.18

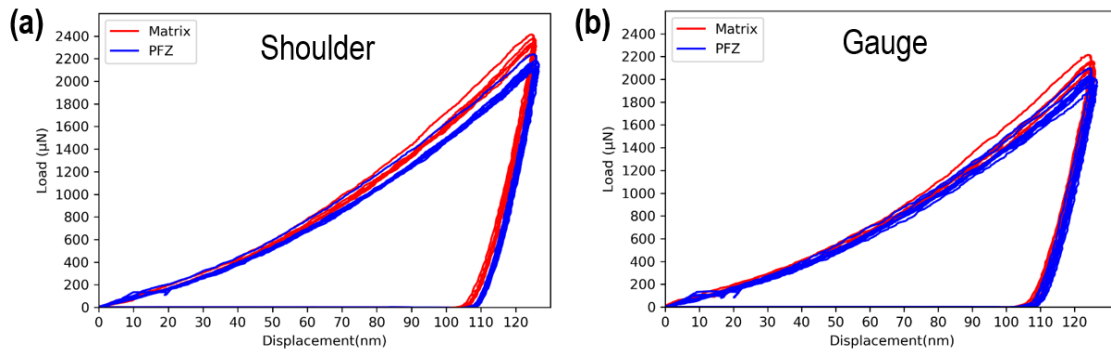


Figure 7.11 Nanoindentation results of matrix and PFZ for both gauge and shoulder sections of 1Nb5W crept specimen at room temperature

To further understand the interaction between Laves phase and dislocation inside the matrix and the dislocation motion inside the PFZ, TEM characterization was conducted. Dislocations were visualized both within the PFZ and the matrix (see Figure 7.12). Namely, inside the PFZ, there were no obstacles (i.e. precipitates) to pin the dislocation movement. Whereas dislocations were pinned by the Laves phases inside the matrix, which increased the stress that would be needed to move the dislocation for further deformation. To quantify the dislocation densities in both matrix and inside the PFZ, bright field image from STEM mode with field of view of more than 8 μm away from the grain boundary was shown in Figure 7.13. Most of the dislocations in Figure 7.13 were pinned by the Laves phase. Furthermore, as shown in Figure 7.14, the dislocation density ($1.87 \times 10^{13} \text{ m}^{-2}$) inside the matrix (8 μm away from the grain boundary) was more than two times higher than the dislocation density ($7.85 \times 10^{12} \text{ m}^{-2}$) inside the PFZ (2 μm away from the grain boundary). The precipitate number density showed the same trend that the precipitate number density inside the matrix ($13.1 \times 10^{19} \text{ m}^{-3}$) was more than two times higher than that of inside the

PFZ ($5.79 \times 10^{18} \text{ m}^{-3}$). For comparison of the Laves phase size, the median ECD inside the PFZ (66.9 nm) was more one and half times larger than that inside the matrix (38.3 nm). The above results suggested that PFZ had a weaker microstructure than the matrix.

Identifying the Burger's vectors and habit planes of observed dislocations inside the PFZ would be beneficial to understand the what slip system was operating inside the PFZ. To identify the Burger's vectors(**b**) of the dislocations, tilting the specimen to different zone axes and different reciprocal lattice vectors (**g**) would provide different invisible criteria [53]. As mentioned in Chapter Three(p.45), The contrast from the bright field TEM images of dislocation came from the strain field generated by the distorted atomic planes (see Figure 3.3). When the specimen was tilted to an angle that the distorted atomic planes would not affect the local Bragg's condition, no contrast would be observed. This tilting condition satisfied the invisible criterion where $\mathbf{g} \cdot \mathbf{b} = 0$. By comparing different invisible criteria under different zone axes and **g** vectors, Burger's vectors and habit planes of dislocations could be identified. Figure 7.15 showed the same region of interest inside the PFZ with different zone axes and **g** vectors. Zone axes and **g** vectors and Burger's vectors of Figure 7.15 were summarized in Table 7-2 and . The results from Figure 7.15 showed that the dislocations inside the PFZ of 1Nb5W crept specimen were predominantly $a/2\langle 111 \rangle$ type dislocations. Interestingly, the majority of the dislocations had a Burger's vector of $a/2[11\bar{1}]$, which could be influenced by the loading direction. To have a thorough understanding of the deformation inside the PFZ, for instance, the critical resolved shear stress and the slip directions, a site-specific specimen prepared by focus ion beam (FIB) along the loading direction is recommended as a future direction.

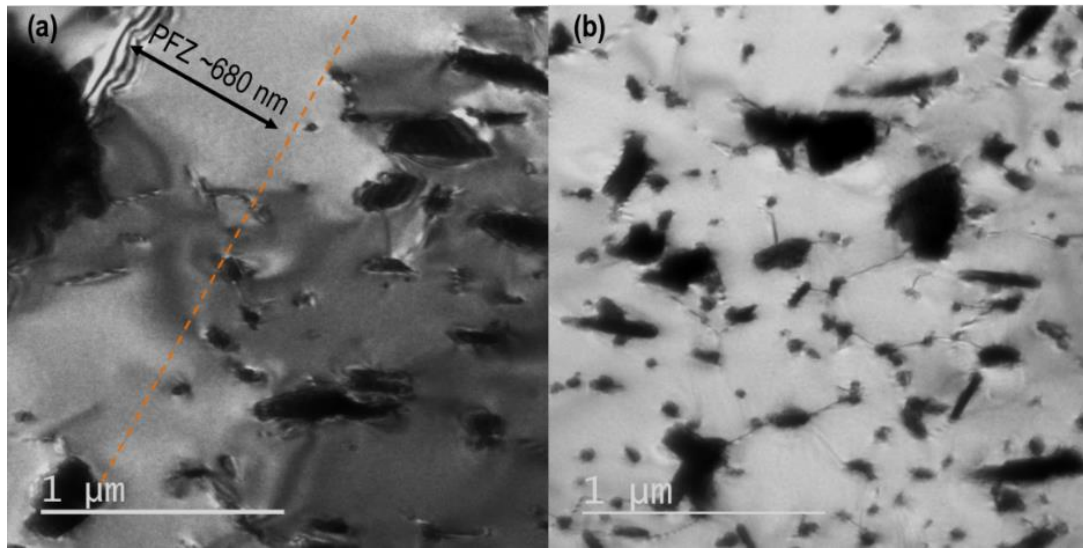


Figure 7.12 Bright field TEM images showing dislocations in the (a) PFZ and (b) matrix of 1Nb5W crept specimen.

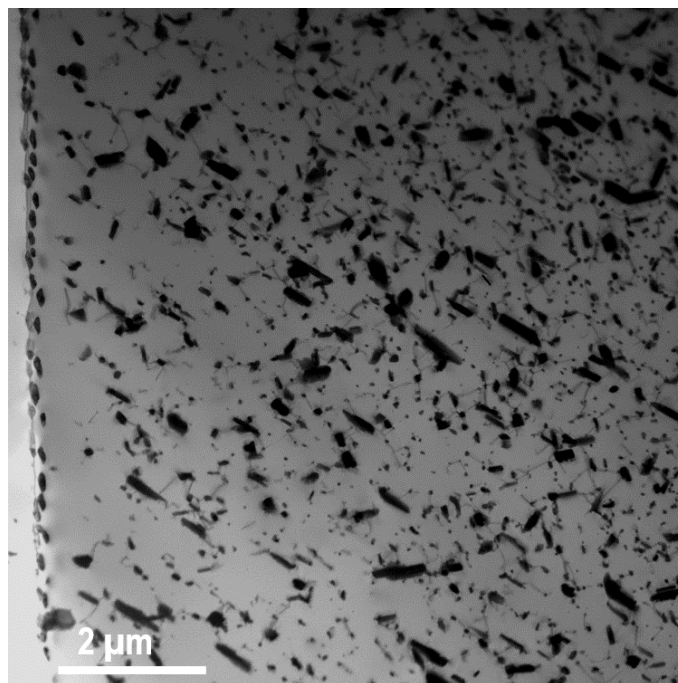


Figure 7.13 STEM bright field image of crept 1Nb5W sample near grain boundary

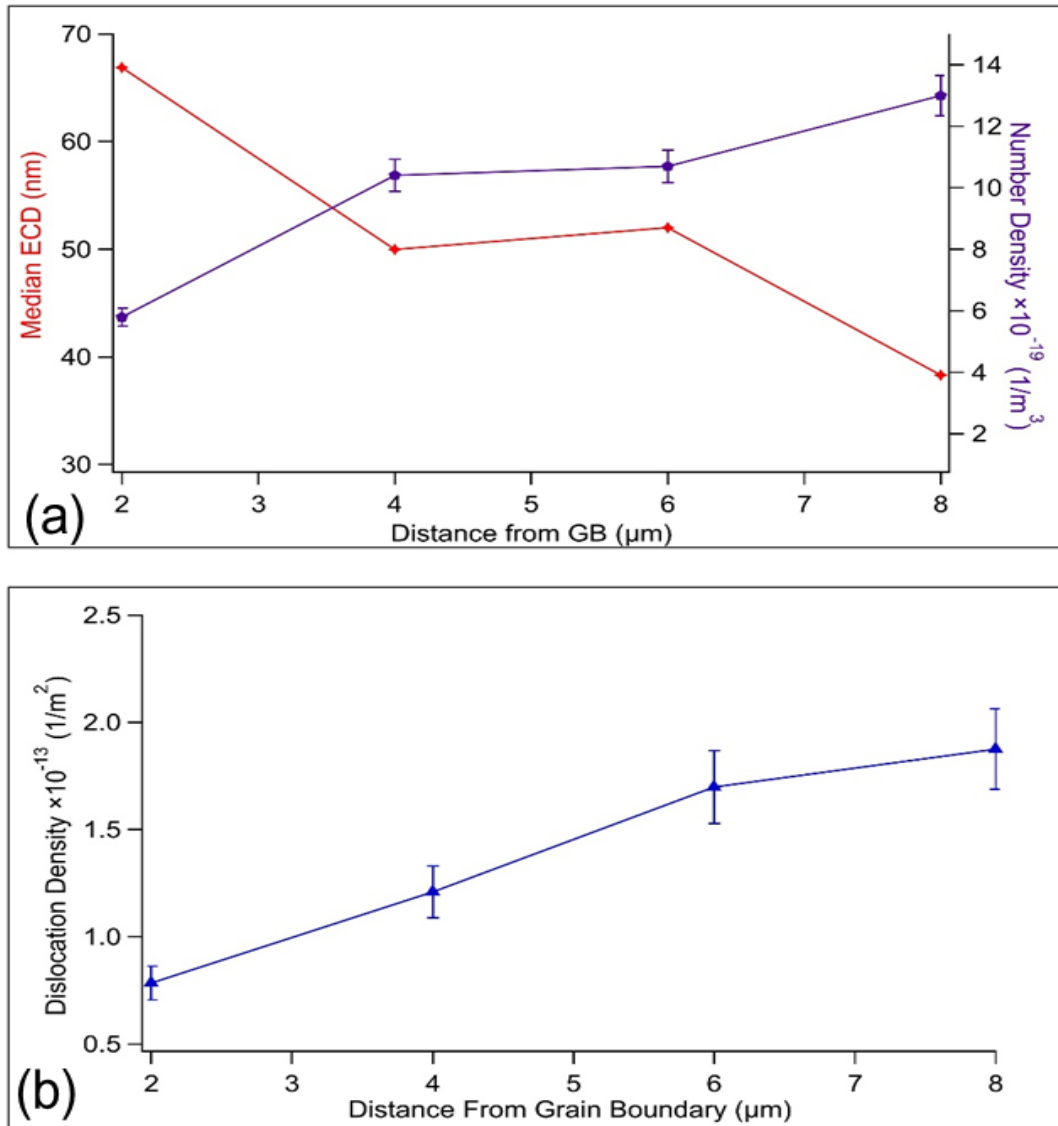


Figure 7.14 (a) Median ECD and precipitate number density (b) dislocation number density as function of distance from the grain boundary in Figure 7.13

Table 7-2 Summary of visible (V) and invisible (I) criteria for Figure 7.15

	Zone [001]		Zone [110]		
	$g=002$	$g=011$	$g=002$	$g=\bar{1}10$	
$b=a/2[111]$	V	V	V	I	12.5%
$b=a/2[\bar{1}11]$	V	V	V	V	12.5%
$b=a/2[1\bar{1}1]$	V	I	V	V	12.5%
$b=a/2[11\bar{1}]$	V	I	V	I	62.5%

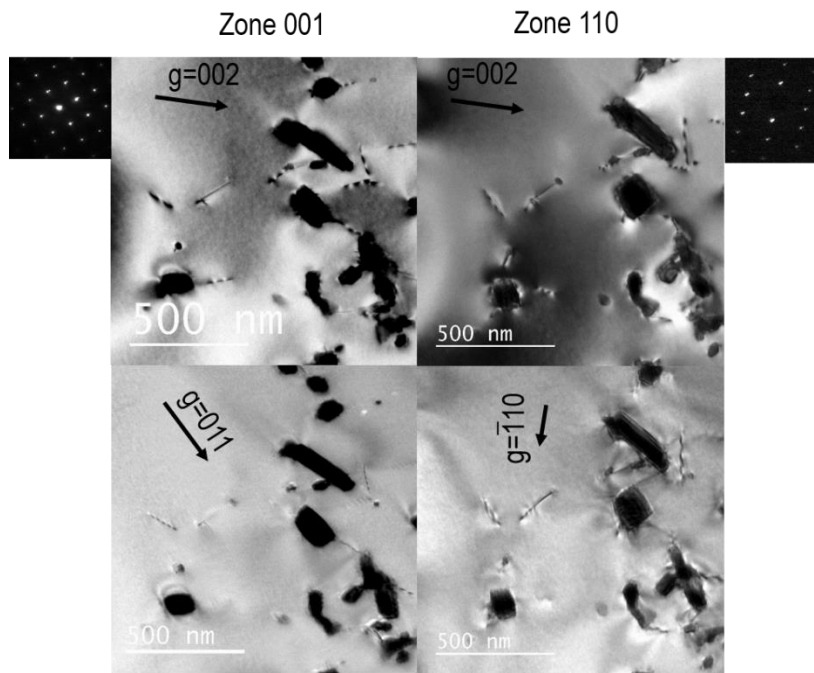


Figure 7.15 Dislocations within PFZ of 1Nb5W crept specimen with different zone axes and g vectors

Characterization of Dislocations inside the Ferritic Matrix

This Fe-30Cr-3Al-0.2Si-1Nb-5W alloy was designed to be strengthened by Laves phase precipitates during creep deformation. Therefore, it is necessary to investigate the dislocation interaction with Laves phase at the target service temperature 700 °C. Same method as mentioned in the previous paragraph to identify the Burger's vector was used (see Table 7-3). Figure 7.16 showed the region of interest inside the ferritic matrix with different zone axes and ***g*** vectors. Similarly, results from Figure 7.16 showed that the dislocations inside the ferritic matrix were predominantly $a/2\langle 111 \rangle$ type dislocations.

Table 7-3 Summary of visible (V) and invisible (I) criteria for Figure 7.16

	Zone [001]		Zone [110]		
	$g=002$	$g=011$	$g=002$	$g=\bar{1}10$	
$b=a/2[111]$	V	V	V	I	23.1%
$b=a/2[\bar{1}11]$	V	V	V	V	46.1%
$b=a/2[1\bar{1}1]$	V	I	V	V	15.4%
$b=a/2[11\bar{1}]$	V	I	V	I	15.4%

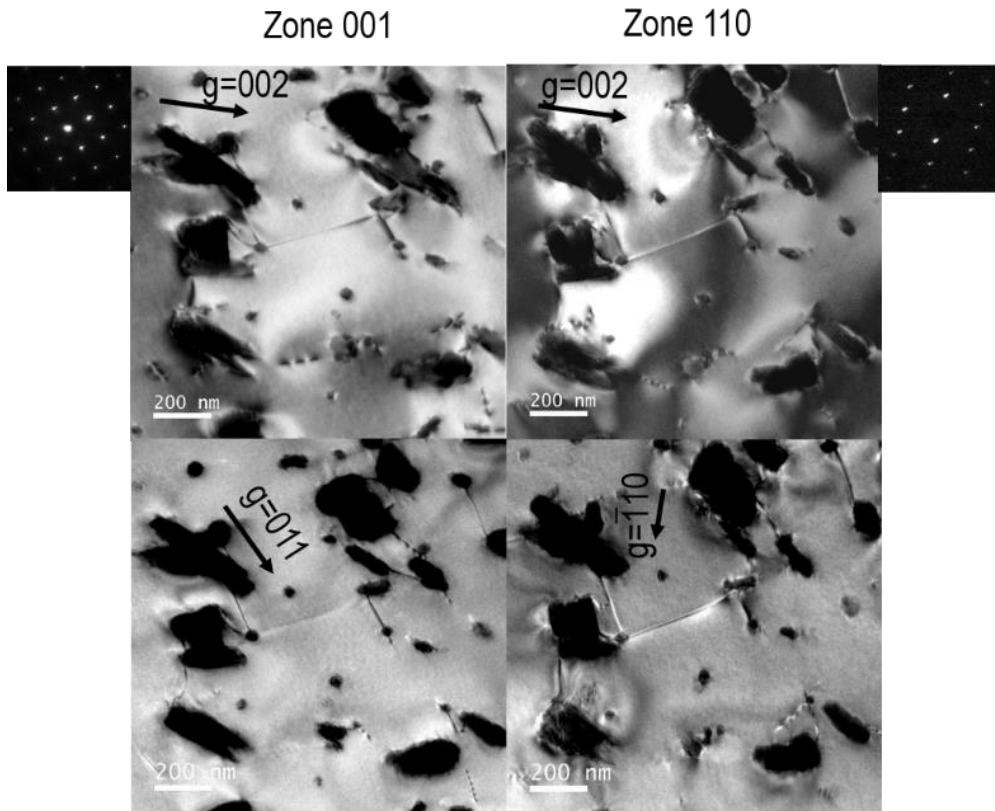


Figure 7.16 Dislocations within ferritic matrix of 1Nb5W crept specimen with different zone axes and g vectors

Discussion

Discussion on Minimum Creep Rate of 1Nb5W

1Nb5W alloy was based on the design strategy that was discussed in Chapter Four to have an expected lower minimum creep rate. However, due to the instrumental constraint, the creep test of 1Nb5W specimen could not be conducted at 70 MPa and was tested at 90 MPa at 700 °C. The 1Nb5W specimen crept at 20 MPa higher than the 2Nb from the literature for the similar duration without rupture. Furthermore, to compare the minimum creep rate, the creep rate as a function of creep time with overlaid 2Nb data from the literature was shown in Figure 7.17. 1Nb5W specimen showed similar minimum creep rate (6.67×10^{-7} (%/s)) at 90 MPa compared to 2Nb (1.47×10^{-7} (%/s)) at 70 MPa. The above results suggested that the designed 1Nb5W alloy has a superior creep resistance than 2Nb alloy at 700 °C.

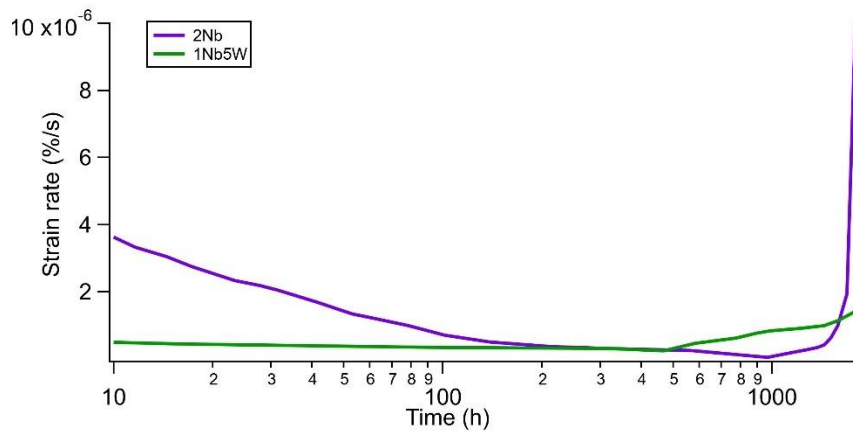


Figure 7.17 Minimum creep rate comparison of 1Nb5W and 2Nb [38]

Discussion on the Influence of PFZ in Creep

PFZs are namely weaker zones near the grain boundaries that do not have the pinning effect from the precipitate to hinder the dislocation motion. The 10% hardness drop inside the PFZ compared to the ferritic matrix from the nanoindentation of the crept 1Nb5W specimen (Figure 7.11) and the drop of dislocation density close to the grain boundary from Figure 7.14(b) supported the statement. The formation of PFZ was explained to be the coarsening from the grain boundary precipitate with the enhanced grain boundary diffusion, which was supported by the results from Figure 7.14(a) with decreased precipitate number density ($13.1 \times 10^{19} \text{ m}^{-3}$ to $5.79 \times 10^{18} \text{ m}^{-3}$) and increased median ECD (38.3 nm to 66.9 nm) from 8 μm away from the grain boundary to PFZ.

Several studies[36], [38], including the results from 1Nb5W crept specimen in this study that creep voids were concentrated within the PFZ (Figure 7.4), showed that the PFZ played an important role in creep deformation. GBZSF was proposed based on experimental results to correlate the width of PFZ to creep failure. The definition of GBZSF is a ratio of the percentage of grain boundary covered by precipitate to the width of PFZ, and the critical GBZSF value is 0.6 since that all the failed specimen in the Fe-30Cr-3Al alloy system were below this value[38]. Based on the above, the critical PFZ width should be 1.67 μm assuming the ideal 100% precipitate coverage on the grain boundary. However, how much of a difference in creep rate could that be for inside the PFZ compared to inside the ferritic matrix has not been addressed yet. The stress exponent of 5.37 from the 1Nb6W alloy was obtained through Monkman-Grant relationship (Figure 7.6), which indicated the

underlying creep mechanism should be dislocation climb. The modified Bird-Mukherjee-Dorn (BMD) model described by Shrestha[70] and Shassere[38] to relate the minimum creep rate and microstructure could be used for explaining the difference in minimum creep rate between the matrix and the PFZ. The modified BMD model is listed below:

$$\dot{\epsilon}_{min} = A_{Dis} \left(\frac{\sigma - \sigma_{th}}{E} \right)^n \left(\frac{Eb}{kT} \right) \left(D_0 \exp \left(\frac{-Q}{RT} \right) \right)$$

, where A_{Dis} is the dimensionless constant, k is Boltzmann's constant ($m^2 \cdot Kg \cdot s^{-2} \cdot K^{-1}$), T is the creep temperature (K), n is the stress exponent, b is the burger vector, E is the elastic modulus, σ_{th} is the threshold stress required for dislocations to overcome pinning effect from the precipitates, D_0 is the self-diffusion coefficient (m^2/s), Q is the activation energy, and R is the gas constant ($J \cdot mol^{-1} \cdot K^{-1}$). The threshold stress was taken as 30% of the Orowan-Ashby stress [71], [72] listed below.

$$\sigma_{O-A} = M \frac{Gb}{2\pi\lambda} \ln \left(\frac{2r}{b} \right)$$

, where, M is average Taylor factor (2.5), G is the shear modulus of BCC matrix, b is the burger vector, r is the radius of the particles, and λ is the interparticle spacing. The calculated minimum creep rate map with the modified BMD model using stress exponent from the experimental data of 1Nb6W was shown in Figure 7.18. As shown in Figure 7.14, the median ECDs of the 1Nb5W specimen from both matrix and PFZ observed were in the range between 50 to 100 nm and the width of PFZ in the crept 1Nb5W in Figure 7.15 was approximately 500 nm. Take 50 nm for the radius and 500 nm for interparticle spacing to calculate the minimum creep rate inside the PFZ. The calculated minimum creep rate based on modified BMD model was 9.58×10^{-7} (%/s), which was close to the measured minimum creep rate (6.67×10^{-7} (%/s)) from creep test. Furthermore, if taking 50 nm for the radius

and 1600 nm for interparticle spacing (the critical width of PFZ based on GBZSF), the minimum creep rate would be 5.86×10^{-6} (%/s), which was almost an order of magnitude faster than when the width of PFZ was 500 nm. Thus, the accelerated creep rate with increased width of PFZ could be responsible for creep voids concentration and eventual failure of Fe-30Cr-3Al alloy system.

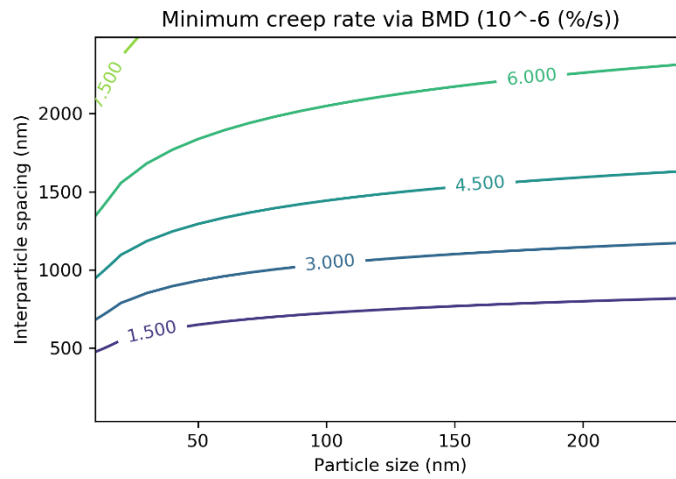


Figure 7.18 Calculated minimum creep rate map via BMD model with various interparticle spacings and particle sizes

Summary

The creep test of the designed 1Nb5W alloy was conducted at 90 MPa at 700 °C. The measured minimum creep rate was similar to the 2Nb alloy at 70 MPa at 700 °C and the 1Nb5W underwent similar creep lifetime of 2Nb alloy without failure at 90 MPa at 700 °C without failure. The above results validated the designed 1Nb5W had superior creep resistance than the 2Nb alloy. Creep voids concentrated inside the PFZ from SEM images

suggested that PFZ could be responsible for potential failure. The results from nanoindentation and TEM/STEM showed the weaker nature of PFZ, which supported the finding in SEM. Calculations based on modified BMD showed similar minimum creep rate compared to the experimental results. Also, the calculations based on the modified BMD model showed that the increase in PFZ width would increase the minimum creep rate significantly, which could be the reason for the critical PFZ of $\sim 1.6 \mu\text{m}$ based on GBZSF.

CHAPTER EIGHT

METAL BIG AREA ADDITIVE MANUFACTURING FOR FE-30CR-3AL-BASED ALLOYS

Motivation

This Fe-30Cr-3Al-1Nb alloy system has been developed for the tubing in fossil fuel power plants to be operated at A-USC conditions for the next generation fossil fuel power plants due to their superior oxidation and corrosion resistance (Chapter One and Chapter Two). Previous chapters discussed the alloy design (Chapter Four), microstructural evolution for both aged (Chapter Five and Chapter Six) and crept conditions (Chapter Seven). Yet, there were two challenges on the manufacturing aspect that needed to be addressed – formability and weldability. For formability, the size limit as mentioned in the previous chapter that ASTM E8 sample cannot be manufactured due to the size of the as-rolled sheet. Also, the cracking occurred after rolling process would be challenging for manufacturing larger parts (see Figure 8.1). For weldability, Gas Tungsten Arc Welding (GTAW) with preheat temperature of 400 °C of Fe-30Cr-3Al-1Nb based alloy was attempted at ORNL. Cracks were observed across the weld metal to the base metal after the sample was cooled to room temperature. The reason for this cracking is due to the comparatively high DBTT (above room temperature) and the residual stress. Finer grain structure could accommodate more uniform deformation near the crack front, and larger amount of grain boundaries could hinder crack propagations. Therefore, grain refinement was attempted at ORNL and resulted in a decrease in DBTT[73]. The weldability and formability issues could be circumvented by using the mBAAM system. As mentioned in Chapter Two (p.36),

mBAAM is a wire-arc AM system that is similar to a robotic gas metal arc welding (GMAW) system, but it is operating with the closed-loop control system developed in ORNL to ensure the geometrical homogeneity. Refined equiaxed grains should be expected due to its rapid processing ability comparing to the traditional hot rolling process. The purpose of this work is to demonstrate the ability of manufacturing Fe-30Cr-3Al alloys in a larger scale for potential applications in fossil fuel power plants.



Figure 8.1 As-rolled FeCrAl sheet with visible cracks

Experiments and Characterizations

Fe-30Cr-3Al mBAAM Process

A spool of 12 pounds (net weight), 1/16" Fe-30Cr-3Al-0.2Si-1Nb-6W based metal cored wire was used to manufacture a wall (300×150×~12 mm³). Two beads of mild steel were added on both top and the bottom to absorb the deformation during cooling to minimize the crack initiation (see Figure 8.2). Creep specimen and cubes for microstructure characterization were machined out from the regions marked on Figure 8.2.

Figure 8.3 showed that mBAAM successfully fabricated a creep specimen that was ~66% larger in length.

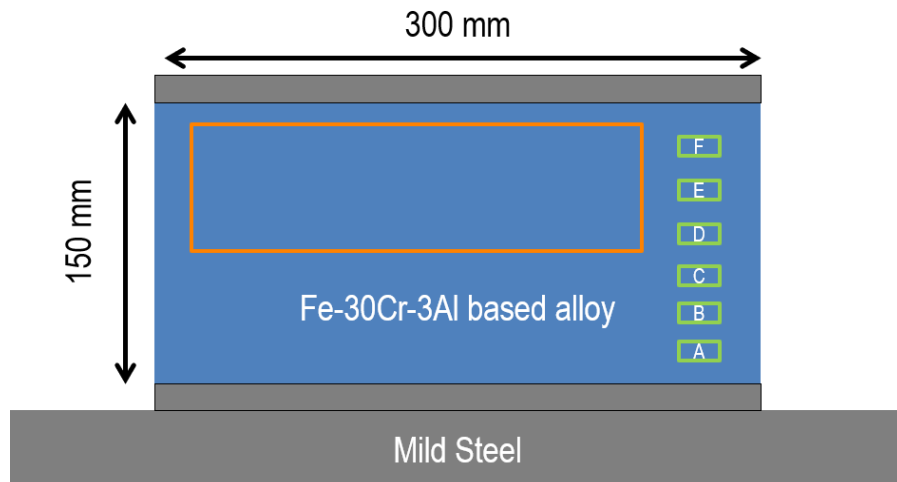


Figure 8.2 Schematic of the wall built by mBAAM with marked region for creep specimen (orange) and microstructure characterization (green).



Figure 8.3 Photo of traditional manufactured creep specimen (top) and mBAAMed creep specimen (bottom)

Microstructure Characterization

For precipitate strengthened creep-resistant alloys, finely dispersed precipitate is ideal to have higher Orowan-Ashby stress. Therefore, solutionization treatment after the hot rolling process is usually needed to dissolve all the existing precipitates back to matrix. For mBAAMed specimen, the exposure time at elevated temperature was significantly lower comparing to multi-pass hot-rolling process. Therefore, the as-fabricated microstructure might not have existing Laves phases, hence, solutionization treatment might not be needed. Cube E in Figure 8.2 was chosen since its microstructure could be representative for the creep specimen due to the similar height in building direction. Figure 8.4(a) and (d) showed that the precipitation of Laves phase within the matrix and on the grain boundaries for the as-fabricated condition. Thus, solutionization was required. It is worth mentioning that the Fe-30Cr-3Al-0.2Si-1Nb-6W based metal core wire has a slightly different chemical composition than the designed alloys. The actual composition is not disclosable at this point due to it is under development.

Thus, the BCC solvus temperature was calculated to determine to temperature for solutionization treatment (same method as mentioned in Chapter Four). The BCC solvus temperature calculated by Thermocalc TCFE9 database was 1175.08 °C (see Figure 8.5). Solutionization treatment temperature was then determined at 1200 °C for both 30 min and 1 h. As shown in Figure 8.4 (c) and (f), no Laves phase inside the matrix was observed and the size of Laves phase along the grain boundary decreased after solutionization for 1 h comparing to Figure 8.4 (b) and (e) for 30 min. The creep specimen was then solutionized at 1200 °C for 1h before the creep test.

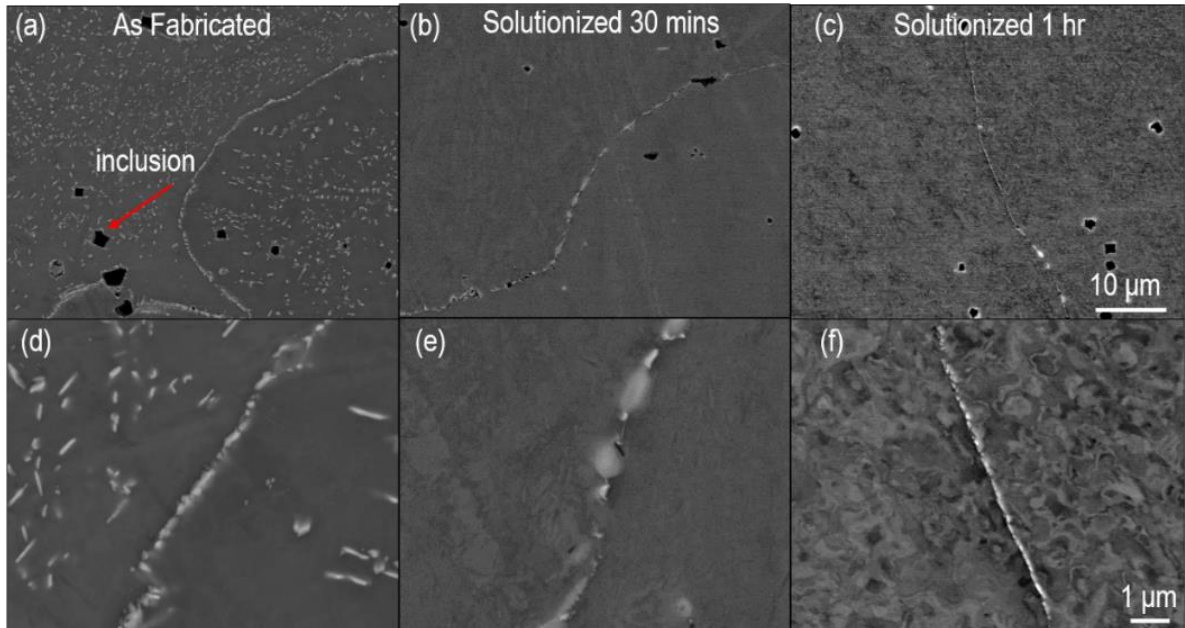


Figure 8.4 SEM backscattered images of cube E from the mBAAMed wall for (a) as-fabricated (b) solutionized for 30 min (c) solutionized for 1 h. (d) – (f) are the sample conditions with larger magnifications

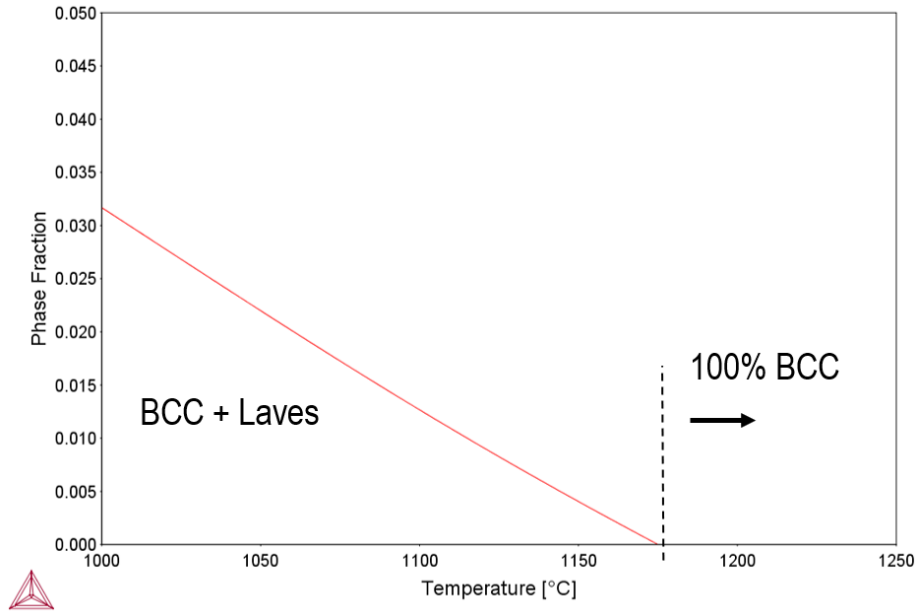


Figure 8.5 BCC solvus temperature calculated by Thermocalc using TCFE9 database for the Fe-30Cr-3Al-0.2Si-1Nb-6W based metal core wire for mBAAM

Hardness Tests

To investigate the microstructural homogeneity along the building direction, hardness was measured on cube A to F in Figure 8.2. The hardness value slightly decreased with increased distance away from the baseplate along the building direction (Figure 8.6(a)). To evaluate the microstructural homogeneity, grain size, Laves phase number density and Laves phase median ECD were measured. Grain size measurements were conducted via optical microscope, Laves phase number density and Laves phase median ECD were characterized by SEM. The measured grain size (see Figure 8.6(a)) was $\sim 30 \mu\text{m}$ with insignificant deviation for different locations. The number densities (see Figure 8.6(b)) of Laves phase with different locations were $\sim 1.5 \times 10^{18} \text{ (1/m}^3\text{)}$. The median ECD (Figure 8.6(b)) of different locations were ranging from 300 nm to $\sim 370 \text{ nm}$. However, the trend

of median ECD was not aligned with hardness values as a function of distance away from the baseplate along the building direction.

Creep Test

The creep test was setup with the same method as mentioned in Chapter Seven with DIC for the consistency. The strain and strain rate curves could be found in Figure 8.7. Minimum creep rate was acquired while the test is still uninterrupted to get the rupture time. Minimum creep rate at 90 MPa at 700 °C of mBAAMed specimen (2.8×10^{-6} (%/s)) was an order of magnitude higher than that of the traditionally manufactured 1Nb5W specimen (6.67×10^{-7} (%/s)).

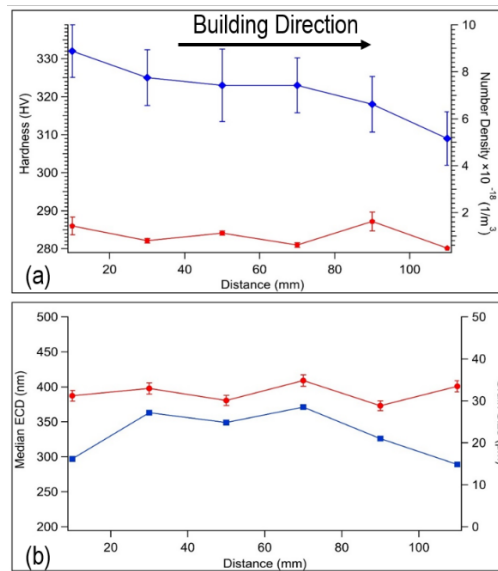


Figure 8.6 Hardness as a function on distance away from the baseplate along the building direction

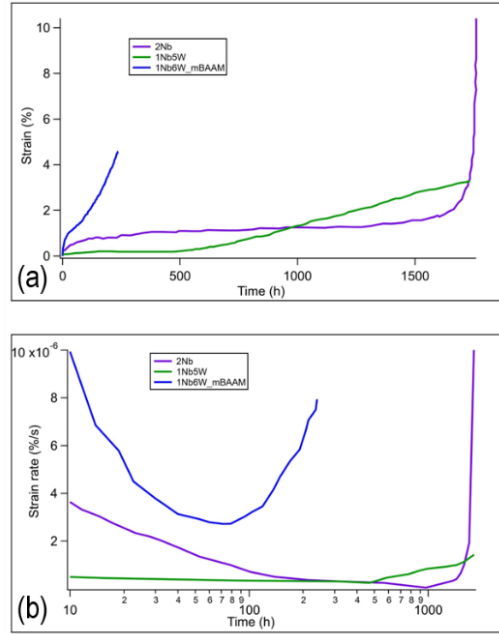


Figure 8.7 Comparison of (a) creep strain and (b) creep strain rate as a function of time for 2Nb[38], 1Nb5W, and mBAAMed 1Nb6W

Discussion

Discussion on the Potential of using mBAAM for Creep Resistant FeCrAl Alloys

The 1Nb6W based creep specimen was successfully manufactured by mBAAM using metal core wire with a ~66% increase in length comparing to the hot-rolled 1Nb6W specimen. Lack of correlation between hardness value and Laves phase precipitate could be due to microstructural heterogeneity resulted from complex thermal history. Layer by layer thermal history monitoring is recommended for future research direction. The grain size of the as-solutionized mBAAM specimen was still less than 100 μm , which could be beneficial to improve the room temperature ductility[73]. Moreover, most of the Laves phase was dissolved into the supersaturated ferritic matrix after solutionization treatment at 1200 °C for 1 h. The premature failure due to the rapid coarsening of existing Laves phase was not expected.

The minimum creep rate of the mBAAMed specimen was more than four times faster than the 1Nb5W traditionally manufactured specimen. This could be due to the grain size difference that resulted in difference dominant creep deformation mechanism. Grain size of the traditionally manufactured 1Nb5W specimen was ranging from 300 to 500 μm , while that of the mBAAMed specimen was less than 100 μm . The creep deformation, as shown in Figure 7.4, was concentrated within the PFZ near the grain boundaries. Therefore, decrease in grain size resulted in increase in the amount of grain boundaries, which could potentially alter the dominant creep deformation mechanism. The balancing the grain size between room temperature ductility and creep resistance is recommended to explore the

availability to use mBAAM to fabricate creep resistant FeCrAl alloys as a future research direction.

Summary

The results shown in this chapter demonstrated the potential of using mBAAM to fabricate Fe-30Cr-3Al for larger component for fossil fuel power plant applications. The as-fabricated grain size was $\sim 30\text{ }\mu\text{m}$, which could be beneficial for the enhancement of room temperature ductility for Fe-30Cr-3Al alloys. The solutionization treatment at $1200\text{ }^{\circ}\text{C}$, determined by thermodynamic calculation for BCC solvus temperature, for 1 h dissolved most of the Laves phase inside the ferritic matrix, which could prevent premature failure due to the rapid coarsening of the existing Laves phase. An order of magnitude faster minimum creep rate of the mBAAMed 1Nb6W specimen compared to the traditionally manufactured 1Nb5W specimen could be due to different dominant creep deformation mechanism. The grain size difference between mBAAMed 1Nb6W specimen (less than $100\text{ }\mu\text{m}$) and traditionally manufactured 1Nb5W specimen ($300\text{ to }500\text{ }\mu\text{m}$) could be responsible to the change in dominant creep deformation mechanism. Optimizing the mBAAM parameter to fabricate creep specimen to control the microstructure to obtain comparable minimum creep rate with traditionally manufactured specimen needs further investigation in the future.

CHAPTER NINE

SUMMARY AND CONCLUSION

Summary

A Fe-30Cr-3Al based ferritic alloy system with additions of Nb, Ti, and W was designed by using Thermo-Calc[®] to increase the amount of Laves phase precipitates in the ferrite matrix with certain processing constraints to improve creep resistance at target service temperature 700 °C. Three alloys, Fe-30Cr-3Al-0.2Si-1Nb-1Ti, Fe-30Cr-3Al-0.2Si-1Nb-5W, and Fe-30Cr-3Al-0.2Si-1Nb-6W (wt.%), were selected for experimental validation of the proposed alloy design methodology, and then compared with a reference alloy, Fe-30Cr-3Al-0.2Si-2Nb. The selected alloys met with the required constraints including high nucleation driving force of Laves phase precipitates, a larger amount of predicted Laves phase in BCC-Fe matrix at 700°C than that of the reference alloy, and sufficiently low BCC solvus temperature (below 1,300°C).

The microstructural evolutions of this alloy system were investigated up to 3,000 h aging at 700 °C. The Laves phase precipitate size distribution and PFZ width were characterized by SEM and the nano-scale alloying element partitioning between the ferrite and Laves phases was characterized by APT. The 1Nb-1Ti alloy has a rapid growth kinetics in the early aging stage (up to 168 h), followed by a stable plateau, in both the median ECD (61.7 nm) and PFZ width (0.91 µm). On the contrary, the Laves phase precipitates in the 1Nb-6W alloy had slow coarsening kinetics in the early stage of aging up to 1,008 h, followed by an acceleration of the coarsening rate after 1,008h up to 3,000 h, with a concurrent

increase in the PFZ. A Nb/Si-rich core and W-rich shell was observed in the 1Nb-6W alloy by APT. The formation of the Nb/Si-rich core and W-rich shell was rationalized by the relatively large difference in calculated diffusivity between Nb($1.75 \times 10^{-16} \text{ (m}^2/\text{s)}$) and W($5.27 \times 10^{-18} \text{ (m}^2/\text{s)}$) at 700°C by DicTra. Equilibrium concentrations were mostly reached at the Laves phase/BCC-Fe interfaces for the three different aging time periods, while the W and Nb concentration inside the core of the Laves phase did not reach equilibrium even after 3,000 h. A precipitate partially reached the equilibrium composition was also found, which explained a potential mechanism of two-step coarsening behavior in the 1Nb-6W sample after 1,008 h aging.

The sub-sized ASTM E8 creep specimen of the designed alloys (1Nb-1Ti and 1Nb-5W, 1Nb-6W) were machined out from the sheet. The dimension for 1Nb6W did not fit the requirement of the creep test instrument. Thus, creep tests of 1Nb-1Ti and 1Nb-5W were conducted at 90 MPa at 700°C. The 1Nb-1Ti specimen experienced stress overloading and failed prematurely. The 1Nb-5W had a similar creep lifetime without rupture and had a similar minimum creep rate ($6.67 \times 10^{-7} \text{ (%/s)}$) at 90 MPa compared to the 2Nb ($1.47 \times 10^{-7} \text{ (%/s)}$) at 70 MPa. The above results validated that the designed 1Nb-5W alloy had a superior creep resistance than the reference alloy 2Nb.

Post-Mortem characterization of the 1Nb-5W alloy from SEM showed that creep voids concentrated within the PFZ indicating that PFZ played an important role for creep rupture in Fe-30Cr-3Al alloy system. Nanoindentation results showed that the hardness values inside PFZ were 10% less than that inside the ferritic matrix. The decrease in the number

density of Laves phase ($13.1 \times 10^{19} \text{ m}^{-3}$ to $5.79 \times 10^{18} \text{ m}^{-3}$) and dislocation density ($1.87 \times 10^{13} \text{ m}^{-2}$ to $7.85 \times 10^{12} \text{ m}^{-2}$) in PFZ compared to that in the ferritic matrix supported the statement of the weaker nature of PFZ. The stress exponent of the 1Nb6W alloy was 5.37, which suggested the creep mechanism was dislocation climb. The critical width of PFZ based on the proposed GBZSF was 1.6 μm could be rationalized by the calculated minimum creep rate via BMD model that above 1.6 μm , minimum creep rate increased to $5.86 \times 10^{-6} (\%/s)$, which was almost five times faster than the calculated creep rate of 500 nm PFZ ($9.58 \times 10^{-7} (\%/s)$).

Due to the size limit of the 1Nb6W creep specimen, the potential of using mBAAM to manufacture larger components with 1Nb6W alloy was evaluated. The creep specimen of mBAAMed 1Nb6W was ~66% larger than the traditionally manufactured 1Nb6W specimen. The grain size of the mBAAMed 1Nb6W was ~30 μm , which was significantly smaller than the traditionally manufactured sample (300 to 500 μm) and could be beneficial for the improvement of room temperature ductility. The minimum creep rate of the mBAAMed 1Nb6W ($2.8 \times 10^{-6} (\%/s)$) conducted at 90 MPa at 700 °C was an order of magnitude faster than the traditionally manufactured 1Nb5W specimen ($6.67 \times 10^{-7} (\%/s)$). The reason for the accelerated minimum creep rate could be the change in the dominant creep deformation mechanism due to the significant grain size difference. The balance between room temperature ductility and minimum creep rate based on the grain size control was recommended for future research direction.

Conclusions

Based on this study, the answers to the questions proposed in the research objectives are listed below.

- 1. Theoretically, what are the effects (e.g. phase fraction, precipitate composition, potential detrimental phases formation) from difference alloying elements that could form Laves phase other than Nb (e.g. Zr, Ta, Mo, Ti, W) based on thermodynamic calculations?*

Based on the calculations, Zr does not affect the Laves phase mole percent significantly and has limited solubility in Fe-30Cr-3Al-1Nb alloy system, therefore, compositions with Zr were ruled out. Mo and Ta showed promising increments of Laves phase mole percent with increased weight percent addition. Yet, the BCC solvus temperature for Ta increased significantly (over 1300 °C) with only 3 wt% addition, which would not be ideal for solutionization treatment. Also, alloys with Mo showed cracking after the hot-rolling process, hence, both of them were ruled out. Ti and W containing alloys met the three proposed design constraints, which are (1) the highest Laves phase nucleation driving force among the other second phases, (2) higher Laves phase mole percent at 700°C than that of the reference alloy, and (3) lower BCC solvus temperature than 1300°C. Thus, Ti and W containing alloys were selected for microstructural evolution and creep tests.

2. *Experimentally, what are the precipitation behaviors (e.g. nucleation, coarsening) of different alloying elements during aging? Are the precipitation behaviors similar with different alloying elements? If not, why?*

The precipitation behavior of Ti and W containing alloys were not similar. The formation of Nb/Si-rich core and W-rich shell observed by APT in Chapter Six was responsible for the two-step coarsening of the 1Nb6W alloy compared to the typical coarsening behavior of 1Nb1Ti. The reason for the formation of core-shell structure was rationalized by the relatively huge diffusivity difference between Nb and W calculated by DicTra.

3. *What is the optimal composition for creep resistance for Fe-30Cr-3Al alloy system?*

Based on the proposed design strategy, 1Nb6W was expected to be the optimal composition for creep resistant Fe-30Cr-3Al-1Nb based alloy. Yet, due to the limitation of the creep specimen dimension, 1Nb5W was tested to be the optimal creep resistant Fe-30Cr-3Al-1Nb based alloy.

4. *Is there a threshold value for the width of PFZ that weakens the creep resistance significantly and leads to failure? If so, what is the underlying mechanism?*

The weaker nature of PFZ was suggested by the experimental results from SEM, nanoindentation and TEM/STEM. The threshold/critical width of PFZ that would lead

to creep failure was 1.6 μm based on the GBZSF. The critical width of PFZ was rationalized by the calculated minimum creep rate via BMD model that above 1.6 μm , minimum creep rate increased to 5.86×10^{-6} (%/s), which was almost five times faster than the calculated creep rate of 500 nm PFZ (9.58×10^{-7} (%/s)). The underlying mechanism is the loss of pinning effect for dislocations to move for further deformation from the precipitate, which was evident by the quantification of precipitate number density and dislocation number density using STEM.

5. *Could mBAAM be a potential alternative process to manufacture creep-resistant FeCrAl alloy?*

A $300 \times 150 \times 12 \text{ mm}^3$ wall was manufactured via mBAAM system using Fe-30Cr-3Al-0.2Si-1Nb-6W based metal core wire and a creep specimen that was 66% larger in length than the traditionally manufactured Fe-30Cr-3Al-0.2Si-1Nb-6W creep specimen was machined out from the wall. Besides, the grain size of the solutionized mBAAM sample was significantly smaller (less than 100 μm) than the solutionized traditionally manufactured sample (300 to 500 μm), which was beneficial for room temperature ductility. Even though the minimum creep rate of the mBAAMed specimen was an order of magnitude higher than the traditionally manufactured creep specimen, there is still potential to manufacture Fe-30Cr-3Al based creep resistant alloy with mBAAM system with optimal processing parameters to control and balance the grain size between room temperature ductility and creep resistance.

To sum up, in this study, a Fe-30Cr-3Al-1Nb alloy system was intensively investigated for creep resistance at 700 °C for potential applications in A-USC fossil fuel power plants. The composition of Fe-30Cr-3Al-0.2Si-1Nb-5W alloy was the optimal alloy with the most promising creep resistance based on the (1) thermodynamic calculation (2) microstructure characterization and (3) actual creep test among all the alloys that were investigated in the Fe-30Cr-3Al-1Nb alloy system.

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