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Effects of aluminum additions to gas atomized reaction synthesis produced oxide dispersion strengthened alloys

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Effects of aluminum additions to gas atomized reaction synthesis produced oxide
dispersion strengthened alloys

by

Alexander Lee Spicher

A thesis submitted to the graduate faculty
in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

Major
Materials Science and Engineering

Program of Study Committee:
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Iowa State University
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The production of an aluminum containing ferritic oxide dispersion strengthened (ODS) alloy was investigated. The production method used in this study was gas atomization reaction synthesis (GARS). GARS was chosen over the previously commercial method of mechanical alloying (MA) process due to complications from this process. The alloy compositions was determined from three main components; corrosion resistance, dispersoid formation, and additional elements. A combination of Cr and Al were necessary in order to create a protective oxide in the steam atmosphere that the boiler tubing in the next generation of coal-fired power plants would be exposed to. Hf and Y were chosen as dispersoid forming elements due to their increased thermal stability and potential to avoid decreased strength caused by additions of Al to traditional ODS materials. W was used as an additive due to benefits as a strengthener as well as its benefits for creep rupture time. The final composition chosen for the alloy was Fe-16Cr-12Al-0.9W-0.25Hf-0.2Y at%. The aforementioned alloy, GA-1-198, was created through gas atomization with atomization gas of Ar-300ppm O2. The actual composition created was found to be Fe-15Cr-12.3Al-0.9W-0.24Hf-0.19Y at%. An additional alloy that was nominally the same without the inclusion of aluminum was created as a comparison for the effects on mechanical and corrosion properties. The actual composition of the comparison alloy, GA-1-204, was Fe-16Cr-0Al-0.9W-0.25Hf-0.24Y at%. An investigation on the processing parameters for these alloys was conducted on the GA-1-198 alloy. In order to predict the necessary amount of time for heat treatment, a diffusion study was used to find the diffusion rate of oxygen in cast alloys with similar composition. The diffusion rate was found to be similar to that of other GARS compositions that have been created without the inclusion of aluminum. The effect of heat treatment time was investigated with temperatures of 950°C, 1000°C, 1100°C, and 1200°C. A large precipitate phase, FeHf₂, was found in the 950°C and 1000°C samples through SEM. This was confirmed through XRD analysis where it was
found that the 1100°C sample may have had clusters. These clusters could act as a location for the origination of cracks during future rolling operations. For this reason, an attempt to look at the hold time and ramp rates on the formation this phase. It was found that a 1200°C hold for 5 hours was able to homogenize the sample to prevent precipitation of the FeHf₂ hₜ phase during a subsequent hold at 1000°C, the rolling temperature used in this study. For this reason a heat treatment at 1200°C for 5 hours was used in both alloys. Both alloys were rolled to 70% reduction in thickness and evaluated through microhardness, tensile testing, and corrosion testing. Microhardness showed high strength for the aluminum containing GA-1-198 and significantly more isotropic properties than mechanically alloyed ODS materials. Tensile testing showed GA-1-198 strength between MA956 and PM2000 for temperatures below 600°C and slightly lower strengths than MA856 at 800°C. GA-1-204 was not protective in either atmosphere; air at 1200°C and air with 10 vol% H₂O at 1100°C. GA-1-198 showed increased mass gains due to sub-optimal oxygen content in the alloy. GA-1-198 had spallation in the air at 1200°C atmosphere, but remained protective up to 1000 hr in the water containing atmosphere.
CHAPTER 1: Introduction

Thesis Organization

Chapter 1 of this thesis gives an overview of the layout of the thesis along with the purpose for performing this research. A literature review will talk about the energy needs of the United States as well as the carbon imprint caused by this demand (Chapter 2). Chapter 2 also includes the conditions needed to reach the goal for operating conditions in the next generation of advanced ultra-superCritical (A-USC) coal fired power plants. Chapter 3 discusses the strengthening method of oxide dispersion strengthening (ODS) as a means to meet the demands created by A-USC power plants. Previously available commercial ODS alloys produced through mechanical alloying are described in Chapter 4. Also included in Chapter 4 is a new production method, gas atomization reaction synthesis (GARS), which is under development to bypass the costly ball milling step during mechanical alloying.

Chapter 5 investigates alloy design for ferritic based ODS alloys for the application in advanced ultra-superCritical coal fired power plants. Also in Chapter 5 it is demonstrate that the GARS process is still viable when aluminum additions are included in the alloys. The heat treatment of the alloy produced was investigated in Chapter 6. Physical properties such as alloy strength at various temperatures and corrosion resistance are looked at in Chapter 7, with comparison to a ferritic GARS produced ODS alloy that does not contain aluminum. Chapter 8 is a summary of the results of the thesis.

Purpose of Study

Coal power plants generate the majority of the world’s electrical energy even with current increases in renewable energy sources [1]. Even though coal is a non-renewable resource, it has the largest supply and will last approximately 250 years at the current rate of consumption [2]. With coal being the largest producer of electrical energy, coal is also the largest producer of CO₂, a substance determined to be detrimental to the
ozone. By increasing the efficiency of coal power plants a few major benefits can be seen such as; extending the coal supply and decreasing the amount of CO$_2$ produced [4,5]. Increasing the efficiency of coal power plants is highly dependent on the structural materials used to build the boilers.

Conversion of thermal energy to mechanical energy allows for coal fired power plants to function [8]. Coal is burned to produce thermal energy that heats water in tubes to supercritical steam. This steam can then be used to power generators through turbines. In order to increase the efficiency of the plants the operating temperature and pressure of the steam can be increased. Ultra-supercritical (USC) coal fired plants currently operate at 31 MPa steam with temperatures around 600°C [4,5]. The design for next generation plants, known as advanced ultra-supercritical (A-USC) plants, are currently being planned to operate under conditions with 760°C steam at 35 MPa.

In order for the components to survive at the A-USC conditions, corrosion resistance and high temperature strength are crucial [4]. Alumina scales on ferritic steels can offer increased protection in these conditions since chromium oxides will volatize [4,9]. In order to achieve a protective alumina oxide layer in ferritic stainless steels a balance of chromium and aluminum is necessary [10]. The operating conditions are greater than ~0.6 of the max melting temperature of ferritic steel alloys and require special strengthening mechanisms to maintain strength at this high temperature [25,26]. Oxide dispersion strengthening is a method that can lead to increased strength at up to 90% of the melting temperature of the alloys by utilizing high melting temperature dispersoids. The small dispersed particles act as barriers to dislocation motion and strength gains are increased by having a finer uniform distribution of particles [26, 27].

Commercial ferritic oxide dispersion strengthened (ODS) alloys were created through the process of mechanical alloying [14]. Mechanical alloying starts with the process of ball milling to homogenize the alloy and get a fine distribution of oxide particles [14, 59]. After ball milling, the powder is consolidated, usually through hot extrusion, in
order to form solid material. The ball milling portion of mechanically alloying has been known to cause some issues such as increased time of production, anisotropic properties, and contamination which led to higher costs for the material [61,64]. Commercial alloys are no longer being produced due to the high cost of making them [61]. A process is under development that will replace the ball milling portion of mechanical alloying with gas atomization and reaction of powders known as gas atomization reaction synthesis (GARS) [15,16]. The GARS process utilized rapid solidification and internal oxidation in order to achieve its dispersoid structure [51]. The size of particles can be a crucial component to the GARS process as it effects dispersoid distribution and oxygen content of the alloy [51,55].
CHAPTER 2: Advanced Ultra Super Critical Coal-Fired Power Plants

**United States Energy Statistics**

With the increased awareness for a sustainable future, an increase in renewable sources for electricity generation has been demanded. From 2000 to 2010 the amount of electrical energy produced by wind energy has increased by 16.9 times while the amount of solar, thermal, and photovoltaic energy production has increased 2.5 times [1]. The total renewable sources, other than hydroelectric, have doubled the amount of electrical generation in the span of 10 years. In the year 2000 renewable sources of energy accounted for approximately 9.3% of the total electrical generation. Ten years later this fraction of electrical generation had increased to 10.3%. During this same time period, electrical generation from coal has decreased from 52% down to 45%. The surge for more renewable sources of energy has decreased the fraction of the electrical generation that coal produces, however, coal is still the leading source for production of electrical energy [2]. In the year 2000 coal accounted for 22% of the total U.S. energy production and was projected to account for 21% of the production in the year 2020.

Even though coal is a non-renewable resource the reserves for this fuel are very extensive. The United States has 275 billion short tons of coal left (approximately 250 years at current rates of consumption) [2]. Globally there are approximately 1,100 billion short tons of coal. The amount of coal left in the United States can produce approximately 6,100 exajoule (EJ) of energy. In comparison there is only 310 EJ worth of petroleum and natural gas in the U.S. and only 11,500 EJ of petroleum and natural gas globally. In an effort to limit the average temperature increase of the world to 2°C, CO₂ emissions will have to be reduced heavily [3]. Coal is the leading cause of CO₂ emissions in the year 2008 and is predicted to continue to be the largest contributor in the near future as seen in Figure 2.1 below.
The proposed ways to limit the impact of CO$_2$ produced through coal plants include increasing efficiency and creating a carbon capture and storage (CCS) system [3]. The CCS system would prevent the amount of CO$_2$ escaping to atmosphere, but would not limit the production.

**Coal Power Plants**

Coal power plants operate by converting thermal energy into mechanical energy. Coal and air are ignited in the boiler, whose thermal energy is then transferred to pipes that house water and gets turned into steam. The temperature and pressure of this steam is crucial in determining efficiency [6,7]. With temperatures greater than 374°C coupled with pressures above 22.1 MPa, steam becomes a homogenous fluid with no distinction between gas and liquid known as a supercritical steam. The first generation of supercritical steam power plants operated with conditions around 24.1 MPa steam and 565°C [5]. As the steam travels through the pipes it reaches a steam turbine where the mechanical energy can then be transferred to electrical energy. A schematic of this process can be seen below in Figure 2.2.
The efficiency of heat engines can be approximated through the Carnot cycle, which is defined as the fraction of work obtained from the system from the total heat input [6]. Equation 1 shows the efficiency of the Carnot cycle in terms of heat which can then be related to temperature.

\[
\text{efficiency} = \frac{w}{q} = \frac{q_2 - q_1}{q_2} = \frac{T_2 - T_1}{T_2}
\]

Equation 1

Efficiency is only dictated by the temperature difference between the reservoir and operation conditions. Assuming that the water for cooling the power plant comes for a large body of water approximately 30°C [11], a graph of efficiency depending on steam operation temperature can be seen below in Fig. 2.3.
At current operation conditions around 610°C the efficiency of a Carnot cycle would be 65.7%, while the new operation conditions of 760°C would result in efficiency of 70.7% or a 5% increase in efficiency. These values are much higher than efficiencies of current plants are due to the assumption of a simple Carnot cycle.

The Rankine cycle is a more accurate representation of a coal-fired steam power plant [6]. A representation of the Rankine cycle can be seen below in Figure 2.4. This is the simplest Rankine cycle involving no reheat cycles and only one turbine. More complex systems are needed to describe current coal-fired power plants that use either single or double reheat cycles, multiple turbines, and regeneration in order to increase efficiency. An example of a single reheat cycle can be seen in Figure 2.5.
In the case of a simple Rankine cycle (Figure 2.4) the thermal efficiency can be expressed through Equation 2 [7]:

\[
\text{efficiency} = \frac{W_{\text{net}}}{q_{\text{in}}} = \frac{W_{\text{turbine}} - W_{\text{pump}}}{q_{\text{in}}}
\]
While this is analogous to the form for the Carnot cycle (Equation 1), the values will be much lower due to different losses in the system [7]. The pump and the turbine will experience losses from the ideal operation and pressure drops will be experienced across the condenser and boiler.

The efficiency of coal power plants has been increased with various operation temperatures and pressures [4]. The Philo 6 power plant in Columbus, OH has been operational with temperatures of 610/565/538°C double reheat cycle and steam pressure of 31Mpa. The Eddystone 1 power plant in Philadelphia, PA was designed to operate with temperatures of 650/605/565° double reheat cycle and steam conditions of 32.4 MPa. Due to metallurgical complications, mainly with austenitic steels of larger components, the Eddystone plant was usually operated at 605°C and 32.4 MPa. The development of 9-12%Cr ferritic stainless steels led to an increase in available operating conditions [4,5]. The ultra-supercritical (USC) power plants in Japan have operated with 31 MPa steam and various operation temperatures around 600°C as seen in Figure 2.6 [5].

![Figure 3: Commercial Coal Power Plant Conditions for Japan][5]

The next goal for increasing the efficiency of coal fired power plants are deemed advanced ultra-supercritical (A-USC) power plants [4]. The goals for operating conditions are 760°C and 35 MPa steam. Some critical components for being able to
reach this goal are high pressure steam piping, steam headers, and superheater tubing. Steam pipes and headers are larger components that are vulnerable to fatigue caused by thermal stress. Ferritic and martensitic steels are desired for these materials due to increased thermal conductivity and decreased thermal expansion. The desired superheater tubing has an array of required properties. These include improvements in creep strength, resistance to corrosion from the fireside of the tubing, and steam oxidation resistance. The lifetime of structural parts in these plants should be approximately 60 years or $10^5$ hours.

**Material Considerations**

Materials considered for the critical components (i.e. boiler, steam pipes and headers) are ferritic stainless steels, austenitic stainless steels, as well as nickel-based superalloys [4]. In order to obtain steam temperatures of 760°C and 35MPa, the boiler will operate at a temperature of approximately 800°C with steam piping operating around 780°C. These operating conditions are too high for conventional ferritic steels to survive in, being limited to approximately 620°C due to volatilization of the chromia oxides [21]. Both austenitic stainless steels and nickel-based superalloys offer increased high temperature strength and corrosion resistance compared to ferritic alloys (Figure 2.7), but this increase also comes with an increase in cost. The cost of potential critical component materials can be seen in Table 2.1.
Figure 2.7: Tensile and creep properties of ferritic, austenitic, and precipitation strengthened nickel-based alloys [12].

Table 2.1: Cost of potential critical component materials [18]

<table>
<thead>
<tr>
<th>Material</th>
<th>Form</th>
<th>Cost/kg (USD)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Austenitic Stainless Steel</td>
<td>316L Plate</td>
<td>~3-7</td>
</tr>
<tr>
<td>Ferritic Stainless Steel</td>
<td>446 Plate</td>
<td>~2-5</td>
</tr>
<tr>
<td>Inconel 740 alloy</td>
<td>Inconel 740 Sheet</td>
<td>~31</td>
</tr>
<tr>
<td>Ni-based alloys</td>
<td>Inconel 718 Sheet</td>
<td>~35</td>
</tr>
<tr>
<td>Ferritic ODS</td>
<td>MA956 Sheet</td>
<td>~165</td>
</tr>
</tbody>
</table>

Previously available commercial oxide dispersion strengthened (ODS) ferritic alloys (i.e. MA956 and MA957 from Inconel and PM2000 from Plansee) and experimental ODS alloys (i.e. 12Y1 and 12YWT) offered an increase in high temperature strength comparable to austenitic stainless steels and nickel-based super alloys [13]. The yield and tensile strengths of these materials can be seen in Figure 2.8.
Commercial ferritic ODS materials are no longer available due to the high cost from the processing method of mechanical alloying (See Section 4) [14]. Gas atomization reaction synthesis (GARS) is another experimental processing path that has been able to produce an ODS microstructure without the inclusion of aluminum in alloys [15,16]. By using this process the time intensive and costly step of ball milling during mechanical alloying can be eliminated or reduced significantly [17].

**Oxidation Resistance**

In order for a superheater tubing component to survive for the expected lifetime of 60 years there are two different regions that the component must be able to survive in [4]. The first region is the fireside of the tubing. This region has an environment that consists of reaction products from burning coal. This leads to exposure to combinations of oxygen, carbon dioxide, and sulfur. The main causes of corrosion on the fireside are sodium-potassium-iron trisulfates. It has been shown that 9 to 12% Cr ferritic steels are protective in current operating conditions and that increasing the chromium content results in better corrosion properties.
A second region exists on the inside tube that is exposed to the steam. This area will be exposed to the supercritical steam that is planned to be kept at 760°C and 35 MPa [4]. It has been shown that corrosion rates in steam are usually greater than from being performed containing dry air [9]. The type of oxide scale formed is critical for different corrosion properties.

Ferritic steels form different oxide scales depending on the concentration of elements such as chromium and aluminum. In dry air the formation based upon temperature has been documented and created into an oxide map as seen in Figure 2.9 [10]. Three different regions can be seen labeled I, II, III, and IV. Region I is confines alloys which contain less than 2 wt% (4 at%) aluminum and less than approximately 12 wt% chromium. Region II is defined by alloys that contain less than 2 wt% (4 at%) aluminum while also containing greater than approximately 12 wt% chromium. Alloys found in Region III three contain at least 2 wt% (4 at%) aluminum. The upper bound of this region depends on chromium content; increasing chromium content decreases the upper bound. Region IV transitions out of region three as aluminum content is increased. The oxides formed in 200 torr O₂ at 800°C are as follows: Region I forms Fe₃O₄, Region II forms Cr₂O₃ (chromia), Region III forms Al₂O₃ (alumina) with Fe₃O₄ nodules, and Region IV forms Al₂O₃.

![Figure 2.9: Oxide map for FeCrAl alloys at 800° C](image-url)
A comprehensive oxidation map has not been made for Fe-Cr-Al alloys with the presence of saturated water vapor like the conditions that would be seen on the inside of boiler tubing. Figure 2.10 shows various composition dependent Fe-Al corrosion rates in 10 vol% water at 700°C. Some data points contain differing levels of chromium, which lowers the amount of mass loss during the testing [19]. The inclusion of hafnium in the sample greatly lowered the amount of corrosion during testing.

![Figure 2.10: Mass loss for Fe-Al alloys with alloying effects [19]](image)

The parabolic scaling constants for different oxides can be seen in Figure 2.11. Alumina (Al₂O₃) has a slower growth rate than chromia (Cr₂O₃) for all temperatures [22]. The slower scale coarsening rate along with prevention of volatilization of chromium is beneficial to the life of the part in steam containing atmospheres [21]. Alumina is also considered one of the best defenses against sulfidizing environments. A high surface content of aluminum is necessary for protection in sulfidizing environments (upwards of 20 at%) [23]. In order to obtain adequate protection, surface coatings may be necessary. Coatings on alloys that do not contain aluminum will fail before the required time due to the speed at which aluminum is depleted from the surface due to the concentration gradient from the coating and base alloy [23].
Figure 2.11: Parabolic Scaling Constant for various oxides as a function of temperature [22]
CHAPTER 3: Oxide Dispersion Strengthening (ODS)

Dispersion Strengthening

With the majority of ferritic ODS alloys being composed of Fe-Cr-Al with varying contents the melting temperature will be approximately 1500°C (1773K) [24]. With the proposed operation temperature of approximately 800°C (1073K) tubing temperatures, these alloys will be operating at ~0.6T_m. Table 3.1 below shows the maximum effective temperature as a fraction of melting temperature for different strengthening mechanisms. The operation temperature is on the threshold of loss of most precipitation strengthening and will require oxide dispersion strengthening in order to increase high temperature strength [25,26]

Table 3.1: Strengthening Mechanisms in Metals as seen in [18], adapted from [25,26]

<table>
<thead>
<tr>
<th>Strengthening Mechanism</th>
<th>Effective Temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>Work Hardening</td>
<td>~0.3T_m</td>
</tr>
<tr>
<td>Grain Size</td>
<td>~0.3T_m</td>
</tr>
<tr>
<td>Solid Solution Strengthening</td>
<td>~0.4T_m</td>
</tr>
<tr>
<td>Precipitation Strengthening</td>
<td>~0.6T_m</td>
</tr>
<tr>
<td>Oxide Dispersion Strengthening</td>
<td>~0.9T_m</td>
</tr>
</tbody>
</table>

Dispersion strengthening occurs when there is a fine distribution of particles in a matrix material. When a dislocation approaches an array of particles the dislocation will bow until it bypasses the particle [27]. The conditions in which dislocations bypass a particle lead to two categories of dispersion strengthened alloys based upon the type of obstacle the particles form, strong or weak [26,27]. The angle at which a dislocation will break is determined by the particle strength, F, and the line tension of the dislocation, T [26,27]. If the particle can provide a strong enough force that \( F \geq 2T \), then the dislocation will bypass the particle which can be called a strong obstacle. If \( F < 2T \), then the particle will
shear and $F$ is determined by multiple mechanisms. In oxide dispersion strengthened alloys, the particles are often strong obstacles [51]

![Dislocation/particle interaction schematic](image)

**Figure 3.1: Dislocation/particle interaction schematic [26]**

**Strong Obstacles**

Assuming a simple array of particles the bypass criteria can be shown below in Figure 3.3. By having an applied shear stress the dislocation will bow as seen, where $R$ is the radius of curvature of the dislocation bowing, $\lambda$ is the separation of particles in an equally spaced linear array, $T$ is the line tension of the dislocation, $F$ is the obstacle strength, and $\phi$ is the angle at which dislocations will breakaway (0 when the obstacle is strong) [26].

![Linear array of dislocation impeding particles](image)

**Figure 3.2: Linear array of dislocation impeding particles [26]**

When this case is applied the shear stress will cause bowing according to equation 3.
Figure 3.2 shows that the relationship between the radius of curvature and inter-particle spacing is:

Equation 3

\[ \tau b = \frac{T}{R} \]

By substituting the \( R \) in equation 3 with the relationship in equation 4, equation 5 can be created. It can also be seen that the relationship between \( \Theta \) and \( \phi \) is \( \Theta = 90^\circ - \frac{1}{2} \phi \), or \( \sin(\Theta) = \cos(\frac{1}{2} \phi) \).

Equation 4

\[ 2R \sin(\theta) = \lambda \]

Equation 5

\[
\tau b = \frac{2 T \sin(\theta)}{\lambda} = \frac{2 T \cos(\frac{1}{2} \phi)}{\lambda}
\]

In the case of strong obstacles the equation can be simplified by removing the \( \cos(\frac{1}{2} \phi) \) term since it will be equal to 1. A simple relationship of \( T = \frac{1}{2} G b^2 \) can be used to approximate the relationship between the line tension, \( T \), and material properties [26]. In this relationship \( G \) is the shear modulus of the matrix material, and \( b \) is the burger’s vector of the dislocation. This substitution leads to a theoretical shear stress increase of:

Equation 6

\[ \tau = \frac{G b}{\lambda} \]

Equation 6 gives an order of magnitude approximation of strength increase obtained from varying the spacing of dispersoids. Equation 6 is commonly referred to as the Orowan equation in which dislocation bypass occurs through a uniform array of impenetrable particles. Figure 3.3 shows a schematic of a dislocation as it bows, when approaching the array of particles (a), dislocation loops left surrounding the particles after dislocation bypass (b), as well as different aspects of dislocation bowing when
screw (c) or edge (d) character dislocations approach an array of particles. Improvements upon equation 6 can be made in order to obtain more accurate predictions.

![Figure 3.3: Orowan process of dislocation bypass: (a) bowing as dislocation approaches array, (b) bypassing of the particles, (c) screw and (d) edge dislocation bowing characteristics [26]](image)

The first assumption that was made that can be improved upon is the square array of particles. By assuming a random array of particles equation 7 can be made for the average spacing given a volume fraction, \( f \), and radius, \( r \), of the particles [26, 37].

**Equation 7**

\[
\lambda_{\text{average}} = 1.25 \, r \left( \frac{2\pi}{3f} \right)^{\frac{1}{2}}
\]

Equation 7 will hold true if the spacing is much less than the radius of the particles (i.e. \( \lambda \gg r \)). If the radius is not much less than the spacing than then \( \lambda_{\text{average}} \) must be reduced by
20

\[ \sqrt[3]{\frac{2}{3}} r, \text{ for spherical particles [26].} \] Equation 7 leads to a reduction in the flow stress by a factor of 1/1.25 or 0.8.

A second factor that can be added to equation 6 is a reduction caused by the dislocation dipole effect [38, 26]. The dislocation dipole effect is a phenomenon that occurs as the dislocation bows around the particle and the interaction between these segments reduces the amount of stress needed to bypass the particle. A schematic representation of this can be seen in Figure 3.4. When dislocation segment 1 is near segment 2, the energy of segment 2 is lower which makes it more flexible and easier to bypass the obstacle [38]. The reduction of caused by this affect is \( \ln(2r/r_o) \) where \( r \) is the particle radius and \( r_o \) is the size of the dislocation core.

![Figure 3.4: Schematic representation of dislocation dipole effect [38]](image)

A different value for the line tension of the dislocation can be used in equation 5 that will lead to a more accurate prediction of strength increase [26]. As an edge dislocation approaches the array of particles the majority of dislocations comprising the increase in length due to bowing are of screw character. As a screw dislocation approaches the majority formed are of edge character. Edge dislocations have a higher line tension (by a factor of \((1-v)^{-1}\)) compared to screw dislocations. Even though the values for the line tension differ, as either dislocation approaches the array, the value for \( T/\lambda \) remains
constant. This effect leads to a \( T \) that is the geometric mean of the due different line tension values, or \( Gb/(2\pi(1-v)^{\frac{1}{2}}) \).

The spacing should be changed from \( \lambda \) to \( \lambda - 2r \) to account for the surface to surface distance compared to center to center of the particle. These changes to equation 6 lead to a more accurate form model in equation 8.

**Equation 8**

\[
\tau = \frac{(0.8)Gb}{2\pi(1-v)^{\frac{1}{2}}} \ln\left(\frac{2r}{r_0}\right) \frac{\lambda - 2r}{\lambda - 2r}
\]

The validity of equation 8 has been tested in a few different alloys. Figure 3.5 shows two different cases in which the model has excellent correlation. The alloy on the left is a Co-Ni-Cr alloy strengthened through a \( \gamma' \) precipitation, while the alloy on the right is a Cr-Mo-V alloy strengthened by carbides MC carbides with slightly large M\(_7\)C\(_3\) and M\(_{23}\)C\(_6\) carbides enriched in V.

Figure 3.5: Verification of accuracy of model in Co-Ni-Cr superalloys (left) [26,39] as well as Cr-Mo-V alloy (right) [26]
Weak Obstacles

When the force required to bypass the particle is less than twice the line tension of the dislocation the obstacles are considered weak since they will shear (see figure 3.1) [26,27]. The strength increase related to the force, $F$, which is required in order to bypass can be related through equation 9 [26]:

\begin{equation}
\tau_x \approx \frac{3}{2} \frac{F^2}{b} \left( \frac{2\pi r^2}{3f} \right) \frac{1}{2} \left( 2T \right)^{\frac{1}{2}}
\end{equation}

$F$ is the force required to bypass, $r$ is the radius of the particle, $b$ is the Burger’s vector, $f$ is the volume fraction of precipitate, and $T$ is the line tension of the dislocation. Some of the difference strengthening mechanisms are introduced with weak obstacles are coherency and modulus hardening, as well as, chemical and order strengthening [26,27].

Coherency hardening

The particles dispersed will likely have a different lattice parameter than matrix [26,27]. This mismatch between the two different lattices will result in a uniform pressure around a spherical precipitate. As the dislocation approaches this pressure it will experience a force of approximately $F \approx 2G\epsilon r b$, where $G$ is the shear modulus, $\epsilon$ is the misfit parameter, $r$ is the radius of the particle, and $b$ is the Burger’s vector [26]. This force can be used to approximate the strength increase caused by coherency hardening assuming that $T = \frac{1}{2}Gb^2$ [26,27]:

\begin{equation}
\tau_{coh} \approx 2^{\frac{3}{2}} G \epsilon^{\frac{3}{2}} \left( \frac{r \epsilon}{b} \right)^{\frac{3}{2}} \left( \frac{3}{2\pi} \right)^{\frac{1}{2}}
\end{equation}
Modulus hardening
Along with having a different lattice parameter, the precipitate will also have a different shear modulus in most cases [26,27]. When a dislocation encounters the change in the shear modulus the line tension of the dislocation will change \( T \approx \frac{1}{2} G b^2 \). The difference in the line tension will cause an increase in strength of approximately:

\[
\tau_{\text{Mod}} \approx 0.01 \times G \times G_{p}^{\frac{3}{2}} \times \left( \frac{r \times f}{b} \right)^{\frac{1}{2}}
\]

Where \( \varepsilon_{G} \) is defined in equation 12, \( G_{p} \) is the shear modulus of the particle, and \( G_{m} \) is the shear modulus of the matrix:

\[
\varepsilon_{G} = \left| \frac{G_{p} - G_{m}}{G_{m}} \right|
\]

Chemical strengthening
An additional strengthening method comes from the creation of new interfaces as a dislocation passes through a particle [26,27]. A schematic example of this strengthening method occurring when a dislocation passes through the center of a particle can be seen in Figure 3.6 [26]. The strength increase can be approximated by Equation 13 [27].

![Figure 3.6: Schematic of chemical strengthening of a dispersoid particle caused by a dislocation shearing through particle diameter. [26]](image)
In Equation 13, $G$ is the shear modulus of the material, $r$ is the radius of the particle, $f$ is the volume fraction of precipitates, $b$ is the Burger’s vector, and $\gamma_s$ is the surface energy of the matrix-precipitate interface.

**Equation 13**

$$\tau_{\text{Chemical}} \approx 2G \left( \frac{\gamma_s}{Gr} \right)^{\frac{3}{2}} \left( \frac{fr}{b} \right)^{\frac{1}{2}}$$

**Order strengthening**

When a dislocation passes through an ordered precipitate the structure will be disrupted [26,27]. A schematic example of this can be seen in Figure 3.7.

![Figure 3.7](image)

**Figure 3.7:** Schematic of order strengthening of a dispersoid particle caused by a dislocation shearing through particle diameter. [26]

The strength increase from the dislocation can be related to the amount of energy required to form the anti-phase boundary, or anti-phase boundary energy (APBE) [27]. The strength increase gained from the creation of the boundary depends on a factor related to the APBE, shear modulus $G$, and Burger’s vector $b$ seen in Equation 14.

**Equation 14**

$$\varepsilon_{\text{order}} = \left( \frac{\text{APBE}}{Gb} \right)$$
With high values of $\varepsilon_{order}$, Equation 15 can be used to estimate the strength increase where $f$ is the volume fraction of dispersoids and $r$ is the radius of the particle [27]

\[
\tau_{order} \approx 0.7G \left[ \left( \varepsilon_{order} \right)^{\frac{1}{2}} \left( \frac{fr}{b} \right)^{\frac{1}{2}} - 0.7f \varepsilon_{order} \right]
\]

When the value of $\varepsilon_{order}$ is low, Equation 15 can be simplified to Equation 16 to approximate the strength increase.

\[
\tau_{order} \approx 0.7G \left( \varepsilon_{order} \right)^{\frac{3}{2}} \left( \frac{fr}{b} \right)^{\frac{1}{2}}
\]

The summation of the different strengthening methods for weak obstacles will give a total strength from the precipitates as shown in Equation 17.

\[
\tau_{weak} \approx \tau_{order} + \tau_{chemical} + \tau_{Mod} + \tau_{coh}
\]
CHAPTER 4: Ferritic Oxide Dispersion Strengthened Alloys

Mechanical Allying

Oxide dispersion strengthened (ODS) alloys were first created through mechanical alloying in the year 1970 by J.S. Benjamin [59]. The first alloy was a nickel based alloy developed for having high temperature strength and creep resistance. The method for obtaining these properties included having a mix of Ni$_3$Al precipitates along with nanometric oxide precipitates. Mechanical alloying through ball milling followed by consolidation and a series of thermal mechanical treatments were used as shown in Figure 4.1 were used to create this alloy [14]. Master alloy material, elemental material, and oxide phases are combined in a ball mill apparatus in order to form a homogenous, generally supersaturated, alloy for consolidation through hot extrusion [59,14,60].

![Figure 4.1: Mechanical alloying process, ball milling followed by hot deformation for consolidation [14].](image)

Two aluminum containing ferritic oxide dispersion strengthened alloys that were created through ball milling are MA956 produced by Special Metals Corporation and PM2000 produced by Plansee GmbH [61]. The composition of these two alloys can be seen in Table 4.1.
Table 4.1: Composition of Aluminum Containing Ferritic ODS based Alloys PM2000 and MA956 [61]

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Fe</th>
<th>Cr</th>
<th>Al</th>
<th>Ti</th>
<th>C</th>
<th>Y₂O₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>MA956</td>
<td>Bal.</td>
<td>20</td>
<td>4.5</td>
<td>0.5</td>
<td>0.05</td>
<td>0.5</td>
</tr>
<tr>
<td>PM2000</td>
<td>Bal.</td>
<td>19</td>
<td>5.5</td>
<td>0.5</td>
<td>0.05</td>
<td>0.5</td>
</tr>
</tbody>
</table>

Both of the alloys, MA956 and PM2000, utilize a complex Y-Al dispersoid as the strengthening mechanism [61]. The different dispersoids that can be formed are: yttrium aluminum garnet (YAG), Y₃Al₅O₁₂, yttrium aluminum perovskite (YAP), YAlO₃, and yttrium aluminum monoclinic (YAM), Y₄Al₂O₉ [32]. These dispersoids have been shown to coarsen rapidly [32,35]. ODS materials that did not contain aluminum have been shown to form dispersoids of the pyrochlore phase Y₂Ti₂O₇ [51,61]. The pyrochlore phase is highly stable during high temperature holds [54]. The creep properties of MA956 can be seen in Figure 4.2 [61]. The creep stress in the axial direction of the tubing is much higher than that in the transverse direction. The transverse creep strength is roughly 35% of the axial strength in MA956 [61]. The transverse direction is crucial to operation as it corresponds to the hoop stress of these alloys. The strengths of MA956 and PM2000 can be seen in Figure 4.3. Both of the alloys have moderate strength at the temperature of operation for A-USC power plants, 760°C [62,63]. The sample of MA956 is in the recrystallized state while the PM2000 sample had regions that were not recrystallized [62,63].
Figure 4.2: Creep stress of MA956 alloy in tube form, tests performed in transverse (hoop stress) as well as axial directions. Tests done in 100 hour incrementally loaded tests [61].

Figure 4.3: Ultimate tensile strength (UTS) and yield strength (YS) of PM2000 and MA956. UTS is shown in solid line, YS shown as dashed line. PM2000 shown in blue, MA956 shown in red [62,63].

There are a few complications with mechanical alloying that eventually led to stopping the commercial production of these alloys [14]. The first issue with these alloys has to do with the anisotropic properties in the hoop direction that were highlighted by Figure
4.2 [61]. Preferential recrystallization is due to the thermal mechanical heat treatment of these alloys [61].

A second complication with ball milling comes from the long times that is needed in order to get a homogenous mixture [64]. Figure 4.4 illustrates the powder production rate of different scales of ball milling along with the production rate for gas atomized powders used to produce ODS alloys described in the gas atomization reaction synthesis (GARS) section of this chapter [51]. The difficult thermo mechanical heat treatments increase the cost of the ball milled alloys [64]. Along with increased times that increased costs, the contamination gained through ball milling could be detrimental to the properties of the alloys. Some of the impurities that can be taken up during ball milling include oxygen, argon, and other materials that are a part of the balls in the mill or have been milled in the ball mill.

![Figure 4.4](image)

**Figure 4.4:** Different times of production for various powder production methods for ferritic ODS materials[51].
GARS Processing

A new method for producing oxide dispersion strengthened materials has been developed at the Ames Laboratory of Iowa State University [15,16]. Gas atomization reaction synthesis (GARS) utilizes gas atomization in order to produce the precursor alloy powder. This powder bypasses the need for long ball milling cycles in order to solutionize and disperse the mixture as in mechanical alloying [52-56]. Oxygen is added during the atomization process through an oxide shell that can be dissociated and used to react with the powder in order to form the dispersed oxide phase. Droplet cooling models and experimental data have been used in order to predict the amount of oxygen that will be present in the powder particles after atomization with reactive gas [51]. The stability of the dispersed phase has been shown to be dependent upon alloying additions [54]. Powder size used during consolidation has been shown to have an effect on dispersoid distribution, which can be correlated to strength through microhardness measurements [55].

Atomization is the first step in the GARS process path. Close coupled gas atomization has been used to produce ferritic ODS materials [52-56]. In the process of close coupled gas atomization, as shown in Figure 4.5, molten metal is poured through a small orifice where it is met with high velocity gas [15,16]. The gas come from discrete jets around the pour tube and breaks apart the liquid stream in order to form powder particles. The flow of molten metal prior to atomization gas introduction can be seen in the right image of Figure 4.5. In GARS processing for producing ferritic oxide dispersion strengthened materials, oxygen must be introduced to the system some time during the atomization process in order to form an oxide shell on the powders. One way to accomplish this is through the atomization gas containing small levels of oxygen.
Experimental data has been used in order to develop a prediction of the amount of oxygen that powders of varying size ranges will include. Data from oxygen injection by a high pressure gas atomization nozzle (HPGA) can be seen in Figure 4.6, as well as data when using an uber halo in order to inject the reactive gas containing oxygen further downstream [16]. Different levels of oxygen were included in the atomization gas when using the HPGA nozzle. The data indicated that the atomic percent of oxygen that is absorbed correlated linearly with the volume percent of oxygen that was included in the atomization gas.

Figure 4.5: Schematic representation of close coupled gas atomization during GARS processing (left) [16]. Image of melt flow through pour tube during gas atomization, prior to release of gas (right).
In order to find a better model for predicting the oxygen content included in the powders during the high pressure gas atomization process, the cooling behavior of the droplets produced had to be modeled [51]. The method for modeling this was similar to that of Mathur et al. [57]. This method included modeling of the thermal profile experienced by droplets as function of their size and using gas interaction with both particles and the wall in order to understand the time and temperature variation to predict oxidation. The previously calculated thermal profile of the different size ferritic powder particles can be seen in Figure 4.7 [51]. In Figure 4.7, the red arrow at the first inflection point signifies the start of particle solidification, while the green arrow at the second inflection point signifies the completion of solidification. $T_L$ is the liquidus of the ferritic alloy and $T_s$ is the solidus.
Once the thermal profile has been established, as in Figure 4.7, an oxidation model can be applied in order to determine the oxygen uptake and thickness of the oxide shell [51]. A parabolic oxidation model was applied to time intervals of 1µs in order to calculate the uptake of oxygen during the atomization process. The pre-oxidation factor was adjusted from 0.156 seen by Gulbransen et al. to 5.0 in order to fit the experimentally determined oxide thickness of GARS alloys [58]. The parabolic rate constant was also scaled according to the linear relationship with partial pressure of oxygen in the reactive gas, as seen in Figure 4.6 [51]. The mass of oxygen that was absorbed was then converted to an oxide layer thickness as seen in Figure 4.8. The oxidation of each powder size range includes an inflection point highlighted in Figure 4.8 by the red arrow. This inflection point corresponds to solidification of the powder
particle during cooling, which means that the majority of the (near-surface) oxygen uptake occurs prior to solidification of the droplet.

**Figure 4.8:** Size dependent oxide thickness predictions of Fe-based GARS produced particle without the inclusion of aluminum, inflection point signifies solidification of droplet [51].

In order to assess the accuracy of this model for predicting the oxide film thickness on high pressure gas atomized precursor powders for the GARS process, the theoretical oxide thicknesses had to be compared to experimentally determined oxide thicknesses. The results of this comparison can be seen in Figure 4.9 [51]. The oxide thickness was predicted accurately for majority of the cases, with a slightly low prediction for CR-118. The alloys with low oxygen content in the atomization gas were CR-160 and CR-156, which had better fitting to the model. The high content of oxygen in the atomization gas led to a lower predicted oxide thickness and may need to be taken into consideration when using this model.
In order for application of this GARS material, the precursor powder that contains an oxide layer must be consolidated into a solid part. One method for achieving this is through hot isostatic pressing (HIP) [16]. In the process of hot isostatic pressing, the powder particles get deformed through high pressures and temperatures. The resulting microstructure is schematically represented by the left image in Figure 4.10. This representation shows the prior particle boundaries with a dark black line. This prior particle boundary is often the oxide film that encases the powder particles [51-56]. The HIP is often at a low enough temperature that the prior particle boundary oxides do not dissociate and require further heat treating [16]. During this heat treatment, the prior particle boundary oxides begin to dissociate and diffuse oxygen towards the center of the particles as shown in the middle image. As time progresses, the oxygen reacts with

Figure 4.9: Theoretically predicted oxide thickness compared to experimental results for Fe-based GARS powders without the inclusion of aluminum [51].
yttrium and other elements in the alloy to form the dispersoid phase. The reaction should continue until the prior particle boundary oxides are depleted, or the yttrium and other reactive elements have been converted to an oxide phase.

![Figure 4.10: GARS exchange reaction: initial consolidation (left), prior particle boundary (PPB) oxide dissociation (middle), partially complete PPB dissociation and dispersoid formation (right)](image)

The addition of the secondary elements that are present in the dispersoids phase can greatly affect the properties of the alloy [51-56]. The pyrochlore phase was commonly found in the GARS produced Fe-based ODS materials. Two different elements were investigated for the thermal stability as seen in Figure 4.11 [54]. Hafnium led to a much smaller radius of the dispersed phase than titanium as shown in the left image of Figure 4.11. The titanium containing alloy also showed a much larger increase in dispersoids size during the coarsening study. The size of the dispersoids can be correlated to the strength of the resulting alloy. The right image of Figure 4.11 shows microhardness data for both the titanium containing and hafnium containing alloy. The titanium containing alloy had a much lower strength that can be attributed to the increased dispersoids size. A large increase in size was seen in the titanium sample when going from 100hr at 1200°C to 1000hr at 1200°C. This large increase in size led to a drop in microhardness of ~25 Vicker’s hardness. The hafnium containing alloy had a much more consistent size during the coarsening study, which correlated to a much more stable microhardness reading.
The size of the particles has a large impact on the dislocation distribution in GARS produced Fe-based ODS materials [55]. Figure 4.12 shows material consolidated from three different powder sizes. The top images of Figure 4.12 show the as consolidated distribution of phases, while the bottom images show the post heat treatment dispersoids distribution. The largest sample (20-53\(\mu\)m powder labeled a)) shows a cellular structure of phases that is much larger in size. The resulting dispersoids distribution contains large dispersoids in a cellular pattern. Samples labeled b) contain powder of size 5-20\(\mu\)m, which had a fairly uniform distribution of a bimodal distribution of dispersoids. The smallest powders, dia.< -5\(\mu\)m labeled c), contained a very fine dispersion of phases. This trend shows that the distribution of the intermetallic phases prior to heat treatment act as a template for the dispersoids phase. The microhardness values for the 20-53 \(\mu\)m, 5-20 \(\mu\)m, and dia.< -5 \(\mu\)m alloys were 137±3 Hv, 158±5 Hv, and 185±8 Hv, respectively. A finer distribution of dispersoids phases had an increase in hardness as explained in Chapter 3. The smaller powder sizes had a finer distribution of phases due to the different solidification rates shown in Figure 4.6 [51].
Figure 4.12: TEM images of GARS produced Fe-based ODS alloys to see dispersed phase distribution. Top images are of As-consolidated at low temperature, and bottom images are of As-Heat Treated microstructure. Images labeled a) from 20-53µm powder, b) from 5-20µm powder, and c) from -5µm powder [55].

GARS processing has been shown to be a viable way to produce ferritic oxide dispersion strengthened alloys [16]. Gas atomization is used in order to produce fine powders with calculated oxygen content [51]. The consolidation of the material leads to dissociation of the prior particle boundary oxides to form dispersed oxide phases. The alloy composition and powder size have a large impact on stability and strength of the resulting alloys [54, 55]. The GARS method removes the need for the long ball milling in order to disperse the oxide phase and homogenize the alloy.
CHAPTER 5: Alloy Design

Aluminum-Containing Fe-Based ODS Alloy Design through Diffusion Studies

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Abstract
In order for the next generation of Advanced-Ultra Supercritical (A-USC) power plants to be operated, new materials need to be made that can withstand the extreme conditions. Previous oxide dispersion strengthened (ODS) alloys, such as MA956 and PM2000, had excellent steam corrosion properties due to the inclusion of aluminum in the ferritic steel alloy as well as high temperature strength from the dispersion strengthening. Due to high cost of making these alloys, they are no longer commercially available, however, new processing through gas atomization reaction synthesis (GARS) has led to materials with similar products to MA956 and PM2000 without the inclusion of aluminum. This study will create a powder alloy through the GARS process with the intent of high temperature strength and corrosion resistance. The created powder alloy was characterized through surface film identification as well as microstructure segregation. The powder was consolidated by hot isostatic pressing (HIP) and characterized by microstructure evaluation with SEM.

Introduction
Increasing the efficiency of coal power plants can be achieved by increasing the pressure or temperature [4,5]. The operation temperature and pressure have steadily been increased throughout time to an operation temperature of 610°C and pressure of
31 MPa as seen (for Japan) in Figure 5.1. The next stage of development for the plants has been deemed advanced ultra-supercritical (A-USC) power plants [4]. The operation conditions include steam conditions of 760°C and 35 MPa. A schematic of a coal fired power plant can be seen in Figure 5.2 with the boiler tubing highlighted by a red oval. The boiler tubing is one material with difficult operation conditions. Thermal stresses are one difficulty as well as different oxidation environments on either side of the tube. Ferritic materials are desired for components due to the increased thermal conductivity and decreased thermal expansion. The lifetime of the structural components is desired to be approximately 60 years or $10^6$ hours.

Figure 5.1: Commercial Coal Power Plant Conditions for Japan [5].
The two different sides of the boiler tubing are exposed to extreme conditions. The inside of the tubing (steamside) is exposed to the 760°C steam at 35 MPa [4]. The steam flows through the tubes and can cause abrasion to the scale. The outside of the tubing (fireside) is exposed to the coal byproducts. The hot corrosion experienced here is due to a combination of various gases, some containing sulfur or carbon. The gas is approximately 800°C which leads to tube temperatures that are approximately 25 degrees C higher than the steam, or 785°C.

The high temperature strength will be achieved through oxide dispersion strengthening (ODS). The traditional aluminum-containing ODS alloys that are looked at are MA956 and PM2000 [29]. These alloys have nominal compositions of Fe-20Cr-9Al-0.45Ti-0.3Y at% and Fe-19.5Cr-11Al-0.55Ti-0.23Y at% respectively. These alloys were produced through mechanical alloying as shown in Figure 5.3. This processing could lead to anisotropic properties with high contamination and cost. Contamination can be introduced in the ball milling process from the atmosphere or the milling media (or vessel walls). There is often a long time requirement for milling to reach the desired state, which can lead to high costs.
Gas atomization reaction synthesis is another processing path that has been able to produce an ODS microstructure [15,16]. During this process an external oxide is formed on the outside of the powders (Figure 5.4) that acts as a reservoir of oxygen for creating the dispersed oxide phase. The process by which the dispersoids are formed is called the GARS exchange reaction shown in Figure 5.5. Processing in this manner has been found to create ODS alloys with strengths comparable to that of MA956 and PM2000 [17]. This processing path has bypassed the need for ball milling and reduces the amount of contamination.
**Experimental Procedure**

**Alloy Design**

The alloy design was completed through a combination of literature review of past alloys, oxidation protection, and processing paths, as well as two diffusion studies. The stability of different dispersoids was tested in the presence of aluminum with the first diffusion study. Two materials, GA-164 and GA-166 (compositions can be found in Table 5.1), were set up in diffusion couples shown in Figure 5.6. The Fe-Cr-Al material had a composition of Fe-28Al-5Cr at% and the GA alloys were from a HIP bar from previous experiments. The alloys were produced through the GARS process and processed according to Rieken, et al [17]. The diffusion couples were heat-treated under vacuum conditions ($10^{-5}$ torr) at 1000°C for 24 hours. After transverse sectioning through the central Fe-Cr-Al part, one side of the diffusion couple was used for creating a diffusion profile through electron probe microanalysis (EPMA) and wavelength dispersive spectroscopy (WDS). The other side of the sample was analyzed through a series of grinding and XRD analysis to determine a depth profile of the phases.
The second diffusion study was an internal oxidation study, following the procedure for Rhine’s pack experiments [30], of three different alloys (Table 5.2) in order to simulate the GARS exchange process. The alloys were placed into a quartz tube containing Cr-Cr2O3, in order to establish a partial pressure of oxygen. The tube was sealed under partial vacuum conditions to prevent expansion and pressurization of the capsule during heating. Heating took place at 1160°C for 10 hours.

Table 5.2: Compositions of internal oxidation alloys (at%)

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Fe</th>
<th>Cr</th>
<th>Al</th>
<th>Y</th>
<th>Ti</th>
<th>Hf</th>
</tr>
</thead>
<tbody>
<tr>
<td>Base</td>
<td>Bal</td>
<td>16</td>
<td>10</td>
<td>0.2</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Ti</td>
<td>Bal</td>
<td>16</td>
<td>10</td>
<td>0.2</td>
<td>0.25</td>
<td>0</td>
</tr>
<tr>
<td>Hf</td>
<td>Bal</td>
<td>16</td>
<td>10</td>
<td>0.2</td>
<td>0</td>
<td>0.25</td>
</tr>
</tbody>
</table>

Gas Atomization

After determining an alloy composition, the GARS powder-based ODS processing began with gas atomization of the alloy. A research scale atomizer (charge size of 4kg) was used to produce the alloy. The charge was superheated to 1700°C in a yttria (Y2O3) washed alumina crucible. After exiting through a yttria-stabilized zirconia pour tube, atomization gas was directed at the stream with a manifold pressure of 5.5MPa. The atomization gas consisted of Ar with 0.19 vol% O2 and exited through a high pressure gas atomization (HPGA) nozzle.
The powders were removed and screen at +106 μm. After this screening, riffling of the powders was used to ensure an accurate representation of the sample for size analysis. Size analysis was performed by using a stack of screens with sizes ranging from 20 μm to 106 μm as well as Microtrac™ analysis. Powder scales were analyzed with AES depth profiling. The thickness of the oxide scale was taken to be the distance from the surface until the intensity of the auger peak for iron was greater than that of oxygen.

**Consolidation**

Cold isostatic pressing (CIP) was used to consolidate the as-atomized powder in order to obtain cross sections. The as-atomized powder was blended with 70 vol% copper powder (-20 μm) into latex CIP bags. The bags were then CIPped at 400MPa for 60 seconds. The CIP bars were sealed in epoxy and metallographically prepared for scanning electron microscopy (SEM) analysis.

Hot isostatic pressing (HIP) also was used to consolidate the powders. Before being consolidated, the powder samples were placed into a 316L stainless steel HIP can with a diameter of 25mm. The can was evacuated using a diffusion pump to approximately 10⁻⁷ torr. A low temperature HIP was planned in order to consolidate the powders without significant reaction at 850°C with 300MPa for 4 hours. Due to technical difficulties the HIP cycle was held at 850°C with 200MPa for 13 hours prior to being raised to the final conditions for 4 hours.

**Electron Microscopy**

SEM analysis was performed through a combination of two different microscopes. A Hitachi S-2460N SEM with EDS capabilities was used for a large majority of imaging. When higher resolution was needed a, FEI Quanta 250 field emission SEM (FE-SEM) with EDS capabilities was used.

**X-ray diffraction analysis**
X-ray diffraction was conducted using a Philips PANalytical X-Pert Pro Diffraction System. The radiation used was Co-Kα (1.78901 Å). A scanning real time multiple strip (RTMS) detector was used. The diffraction was taken over a range of 20-120° (2θ) and a step size of 0.008°. The dwell time was 300s per step.

**Alloy Design**

**Results**

The two diffusion couples were set up (one for each GA alloy) and metallographically separated and one sample was transversely separated to obtain diffusion profiles. Figure 5.7 shows micrographs of the transverse sections. GA-164 showed a much larger oxide at the interface compared to that of GA-166. Through WDS analysis, Y-(Hf,Ti) oxides were seen near the surface (previously formed during processing). There was no conversion of the previous oxides to complex Y-Al oxides in GA-164; however, a few oxides that were enriched in both Y and Al were seen in GA-166. Through WDS analysis, the compositions of Al immediately past the interface were found to be approximately 18.5 at% for GA-164 and 13.4 at% for GA-166.

![Image](https://via.placeholder.com/150)

**Figure 5.7**: Transverse section of diffusion couples. GA-164 (Hf containing) sample is on the left, GA-166 (Ti containing) sample on the right.

The internal oxidation study was used to simulate the GARS exchange reaction seen in Figure 5.5. The micrographs of the first 75 μm of each sample can be seen in Figures 8-10. All samples formed an external scale of Al₂O₃, indicated with a red arrow. The Base and Ti samples behaved in a similar manner with no internal oxidation being present.
In these two samples there was a region just subsurface, indicated by blue brackets, that spans from 10-20 μm that is depleted in yttrium. In the Ti sample there was enrichment of yttrium on the interface between the surface scale and matrix. The Hf sample, Figure 5.10, had extensive oxide formation throughout the sample [31].

Figure 5.8: Micrograph for Base alloy at surface of sample, yttrium EDS map on right showing yttrium enrichment of bright phase.

Figure 5.9: Micrograph for Ti alloy at surface of sample, yttrium EDS map on right showing yttrium enrichment of bright phase.
Discussion

Oxidation Protection

A balance of aluminum and chromium are necessary in order to achieve oxidation resistance [19,10]. In Figure 5.11 the necessary aluminum content to form a protective oxide can be seen. This graph also includes points from previous oxidation resistant alloys MA956 and PM2000. An additional alloy produced by the University of Kyoto named 16Cr-ODS, has a composition of Fe-16.5Cr-8Al-0.6W-0.17Ti-0.17Y at% [19,10,32]. The necessary amount of aluminum for dry air protection was found to be the point in which a scale did not contain nodules of iron oxide. The point for humid air was taken at 700°C. This point was taken to be where no measureable mass gain was seen after 100, 1h cycles in 10 vol% H$_2$O [19]. This graph will give an appropriate amount of protection on the steamside of the tubing if it is designed around the humid air conditions. The 16Cr-ODS was tested in 600°C supercritical water at 25MPa, and still exhibited some mass gain [32]. The amount of aluminum is slightly below the values necessary according to Pint and Wright and may be the cause of the mass gain [19,32].
The second environment which is detrimental is that exposed to the fireside of the tubing. Tortorelli and DeVan investigated the corrosion properties of Fe₃Al type alloys in these conditions [33]. The addition of chromium to these alloys was detrimental to corrosion properties. This performance problem was remedied by pre-oxidizing or aluminizing the surface being exposed. The corrosion properties of MA956 were investigated in sulfidizing and oxidizing environments. MA956 had excellent corrosion properties, especially when pre-oxidized [34].

**Dispersoid Formation**

The stability of the dispersed phase is important in performance during creep testing. EPMA data from the sample in Figure 5.7 showed that the Hf-containing dispersoids were more stable than that of the Ti containing alloy. This agrees well with literature that showed formation of Y-Al complex oxides without the addition of Hf [32,35]. The
Y-Hf dispersoids also showed better dispersion with a higher number density and smaller size [32,36]. The progression of the oxide throughout the material in Hf sample compared to the Base and Ti show promise for dissociation of the PPB oxide during consolidation. It appears that Hf is effective for inhibiting the diffusion of yttrium to the surface. If yttrium is free to move to the surface, it would result in conversion on the Al₂O₃ to a complex Y-Al oxide instead of creating dispersed oxide phase at previous yttrium enriched areas.

Other Considerations
Thermal aging can lead to detrimental precipitation of chromium rich phases [36]. It has been found that these can be avoided if Cr content is kept below an amount of 16 wt% [32]. Increasing the amount of chromium content is otherwise beneficial to performance of the alloys. Additionally tungsten has been found to be a positive additive [32,36]. Up to 2 wt% W additions have been investigated in reduced activation (upon exposure to neutron irradiation) martensitic steels. This addition has been shown to increase the creep rupture time. The limit for W was set at 2 wt% due to the stabilization of ferrite past that point.

Selection of Alloy for Powder Processing
In order to prevent the formation of chromium rich phases that are detrimental to mechanical properties of ODS alloys, chromium content was chosen to be 16 at% for the Fe-Cr based ODS precursor alloy designed for this study. With this chromium content the necessary aluminum content for oxidation protection was selected to equal 12 at%. The most significant part of the alloy design in this study was related to the selection of Y-Hf complex oxides, most likely Y₂Hf₂O₇ [17,32]. These show the most promise for being able to dissociate the PPB oxide and avoid the formation of the Y-Al-O family of oxides. With a desired amount of 1 vol% dispersed oxide phase, 0.2 at% Y and Hf were chosen. In order also to prevent complex Y-Al oxides from forming, the Hf content was increased slightly, to 0.25 at%. Tungsten was added to increase the creep rupture time as well as act as a solid solution strengthener. Since the alloy is going to be ferritic,
more tungsten can be added than the 2 wt%, where the chosen amount was 0.9 at% or approximately 3 wt %. All the alloying additions are ferrite stabilizers and will allow for ferrite up to the melting temperature, see Fe-Al phase diagram in Figure 5.XX. In the Fe-Al system only 5 at% is required to stabilize the BCC (ferrite) phase. Thus, the desired composition of the alloy is Fe-16Cr-12Al-0.9W-0.25Hf-0.2Y at%.

![Fe-Al phase diagram](image)

**Figure 5.12:** Fe-Al phase diagram showing stabilization of ferritic phase with more than 5 at% Aluminum additions [65].

**Characterization**

**Results**

The alloy chosen in the previous section was created through the process of gas atomization. The powders were screened at 106 μm to remove large byproducts of atomization. In order to verify the composition of the alloy a -45μm sample was sent to NSL analytical for ICP-MS analysis. The compositional results from NSL analytical as well as the nominal composition can be seen in Table 5.3 below.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Fe</th>
<th>Cr</th>
<th>Al</th>
<th>W</th>
<th>Hf</th>
<th>Y</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nominal</td>
<td>Bal</td>
<td>16</td>
<td>12</td>
<td>0.9</td>
<td>0.25</td>
<td>0.2</td>
</tr>
<tr>
<td>Actual</td>
<td>Bal</td>
<td>15</td>
<td>12.3</td>
<td>0.9</td>
<td>0.24</td>
<td>0.19</td>
</tr>
</tbody>
</table>
Two different size analyses were performed on the resulting powder to obtain size distributions. The first was done through sieving and a stack of screens with sizes of 20, 25, 32, 38, 45, 53, 63, 75, and 90 μm. Each powder group was then analyzed by weight and a cumulative size distribution was created. The second size analysis was performed with a MicroTrac™ S3000 through percent volume passing. Both of the size analysis and a SEM image of the powders can be seen below in Figure 5.13.

![Figure 5.13](image)

Figure 5.13: SEM image of gas atomized powder (left); Size analyses performed on powder through MicroTrac™ and sieving (right).

The powders were then CIPed and polished in order to see the segregation microstructure. A line intercept method was used to determine the size of the segregation and can be seen below in Figure 5.14.

![Figure 5.14](image)

Figure 5.14: Example of powder segregation in approximately 20 μm powder (left) and results of microstructural analysis of powder segregation (right).
Auger depth profiling and XPS analyses were used to determine how thick of a film was created on the powders and the composition of the film. Three different size ranges were analyzed; -20 μm, 32-38 μm, and 63-73 μm. The thickness of the film was taken to be where the O intensity was less than that of the Fe. A silicon standard of 10 nm /min was used to find the thickness after a sputtering time was determined.

![Graph showing intensity over time](image1)

**Figure 5.15:** Example of figure used to calculate the thickness of the oxide film during Auger depth profiling (left); Results of oxide thickness taken from an average of 5 particles (right).

<table>
<thead>
<tr>
<th>Size (μm)</th>
<th>Thickness (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>68</td>
<td>32</td>
</tr>
<tr>
<td>35</td>
<td>25</td>
</tr>
<tr>
<td>13</td>
<td>9</td>
</tr>
</tbody>
</table>

![Graphs of surface composition](image2)

**Figure 5.16:** Relative surface composition of Yttrium and Aluminum through XPS analysis.

The oxygen content in the powders was found through analysis at NSL analytical for each of the ranges obtained from sieving. Additionally a -10 μm sample was obtained through air classification. The results of this analysis can be seen in Figure 5.17.
A sample of -20 μm powder was HIPed in a 316L stainless steel can which was outgassed and sealed in vacuum, as described above. The desired cycle was 850°C, 300 MPa for 4 hrs, however, the HIP had some technical issues and was suspended at 850°C, 200MPa for 13 hrs before being raised to the desired conditions for 4 hrs. The can prior to and after consolidation can be seen in Figure 5.18.

The HIPed sample was analyzed through SEM analysis as well as X-ray diffraction. Two different phases appear in the matrix during SEM analysis, one which is W enriched and another that is enriched in Y and Hf. Through diffraction analysis it was
shown that the Hf, Y containing phase was the intermetallic Fe$_{17}$(Hf, Y)$_2$. The W enriched phase was unable to be identified at this time.

![Microstructure of HIP sampled](image1)

**Figure 5.19:** Microstructure of HIP sampled; Overview (left) and high magnification (right).

![X-ray diffraction patterns](image2)

**Figure 5.20:** X-ray diffraction patterns from powder and HIPed sample performed with Co-Kα radiation. Normalized to main α-Fe peak.

**Discussion**

The alloy was created with accurate compositional control as seen in Table 5.3. This run produced mostly spherical powders with some satellites on the larger size ranges. The average size of the powder size distribution was verified through MicroTrac™ and
sieving and was found to be 27 μm. These powders had segregation of Y and Hf in a cellular structure that varied with the size of the powder. There was apparent solute trapping in powders of 7 μm or less. This segregation microstructure has been shown to be a template for the formation of the dispersoid microstructure [17]. A fine substructure is desired for better mechanical properties.

The powders contained a surface oxide film that varied in thickness and composition based on powder size. The larger powders had a thicker surface film that contained more Y, while finer powders had a thin oxide film that contained less Y and more Fe, Cr, and Al. The cooling of the powders is a large factor when determining the size of the film due to the diffusion of oxygen. The slower cooling of the larger powders also allowed for more diffusion of Y to the surface. Even though the small powders had a thinner oxide film, the surface area to volume ratio is much higher and resulted in drastically more oxygen in the very fine powders. The ideal oxygen content for this composition would be approximately 0.7 at% oxygen that would occur with powders approximately less than -7 μm if the trend is accurate.

A -20 μm powder sample was consolidated through HIP. The HIP cycle malfunctioned and was heated for longer than desired. Due to this error an additional heat treatment study will need to be performed in order to determine the proper conditions for full transformation to the desired ODS microstructure. SEM imaging showed that two different micron sized phases could be seen. The same Fe\textsubscript{17}(Hf, Y)\textsubscript{2} phase that was present in the powders was seen as well as an unknown W enriched phase. Also from the X-ray diffraction work the Y\textsubscript{2}Hf\textsubscript{2}O\textsubscript{7} phase was seen. This is the desired dispersoid phase that has been seen in previous ODS alloys produced through GARS processing [17]. The reduction in the Fe\textsubscript{17}(Hf, Y)\textsubscript{2} phase and appearance of the dispersoid phase is expected and shows that GARS exchange reaction was at least partially successful. Ideally the Fe\textsubscript{17}(Hf, Y)\textsubscript{2} phase would disappear but the powder is oxygen deficient and finer (less than about 7 μm) powder (with more total oxygen content, due to increased
surface area) would need to be consolidated to completely react the intermetallic phase, according to our experimental results.

**Conclusion**

In this study an alloy, Fe-16Cr-12Al-0.9W-0.25Hf-0.2Y at%, was designed for the steamside oxidation resistance for next generation A-USC power plants. Spherical powders with low satellites were created of this alloy through gas atomization. These powders were characterized through microstructure segregation and surface film thickness and compositional analyses. The segregation was found to approach solute trapping at 7 μm. The composition and thickness of the oxide film was found to be size dependent. Finer powders contained less surface Y and had thinner oxide films due to the higher cooling rates. Oxygen content of the powder was also highly size sensitive. Below 20 μm the surface area to volume effects dominate and oxygen content rapidly increases. A -20 μm sample was consolidated through HIP. The malfunction in the HIP cycle will require further investigation in order to identify proper heat treatment conditions. The consolidated sample was analyzed through microstructural characterization and X-ray diffraction. An unidentified W phase was seen with a fine dispersion. Residual Fe\textsubscript{17}(Hf, Y)\textsubscript{2} phase was found after converting some to the desired Y\textsubscript{2}Hf\textsubscript{2}O\textsubscript{7} phase. The residual intermetallic phase was a result of low oxygen content in the powders that were HIPed. The data indicates that a smaller powder size range would need to be consolidated for full reaction completion to the desired ODS microstructure. The GARS process was shown to be viable for Fe-based ODS alloys that contained Al through the inclusion of Hf as a dispersoid former.
CHAPTER 6: Alloy Preparation

Abstract

In order to determine the ideal heat treatment parameters an internal oxidation Rhine’s pack study along with a heat treatment matrix of experiments was conducted. The Rhine’s pack experiments utilized Fe-Cr-Al type material in order to calculated the diffusion coefficient of oxygen in these alloys as well as simulate the reaction front progression. The diffusion coefficient of oxygen was found to be similar to that of Fe-Cr type material. In order to provide a conservative estimation of the heat treatment times for the Fe-based ODS materials containing aluminum, the diffusion coefficient of oxygen in pure Fe was used. Consolidated material of -8µm powder from Chapter 5 was used in order to evaluate the different heat treatment options. The microstructure was evaluated using a combination of X-ray diffraction (XRD), scanning electron microscopy (SEM), and micro hardness measurements. From this data a heat treatment time and temperature of 5 hours at 1200°C was found.

Purpose of Study

The goal of this study is to better understand and decide on processing parameters for heat treating this material. In order to predict the heat treatment times, an understanding of the rate of the reaction front is necessary. Internal oxidation Rhine’s packs of cast alloys will give a basis for understanding the diffusion coefficient of oxygen in these alloys with comparison to previously created gas atomization reaction synthesis (GARS) alloys. With a diffusion coefficient being determined, other alloy properties can be used to estimate the time necessary for reaction (Equation 63).

The temperature effect on heat treatment was investigated using 4 different temperatures; 950°C, 1000°C, 1100°C, and 1200°C. After determining the temperature at which the heat treat would be conducted the effect of differing ramp rates and hold times was investigated. An annealing step was used in order to determine if solutionization of the elements would prevent intermetallic compound formation that
could degrade rolling properties. This analysis was used in order to determine the heat treatment parameters for Chapter 7.

**Experimental Procedure**

*Diffusion Coefficient Determination*

In order to determine the heat treatment times for this alloy, the kinetics of the reaction front must be understood. A good system for determining the kinetics is an internal oxidation study [30, 46]. The system is designed so that a constant partial pressure of oxygen is available at the surface and can diffuse into the material to react and form internal oxides. The speed of the reaction will be determined by the diffusion of the oxygen into the sample as well as the diffusion of the metal towards the surface [46]. Other factors that will affect the reaction rate include the amount of oxygen in the formed oxide, the amount of material that needs to be converted and the concentration of oxygen at the surface. Equation 59 shows how the distance reacted, $\xi$, is related to the diffusion rate of oxygen, $D_O$, a relative kinetics parameter, $\gamma$, and the time, $t$.

**Equation 59**

$$\xi = \sqrt{4D_O\gamma^2 t}$$

Equation 60 shows the relationship for evaluating the relative kinetics parameter, $\gamma$:

**Equation 60**

$$\frac{N_O^\delta}{N_B^0} = \frac{\exp(\gamma^2) \text{erf}(\gamma)}{\frac{1}{\vartheta^2} \exp(\gamma^2 \vartheta) \text{erfc}\left(\gamma \vartheta^2\right)}$$

In equation 60 $N_O^\delta$ is the surface concentration of oxygen, $N_B^0$ is the mole fraction of the metal in the alloy, and $\vartheta$ is the ratio of the diffusion coefficients $D_O/D_B$. In a special case that can be seen in equation 61 is true, then this model can be greatly simplified.

**Equation 61**

$$\frac{D_B}{D_O} \ll \frac{N_O^\delta}{N_B^0} \ll 1$$
This case is true since the diffusion of Y in α-Fe is very low (considered diffusion-less) [181].

Need to get calculations for NOS from Computer at Ames Lab To show that the rest of this case is true.

Equation 70

\[ N_O^s = (?)^{1/2} \]

Since equation 61 is true, the value of \( \gamma \) can be simplified and represented by equation 62 [46].

Equation 62

\[ \gamma = \left( \frac{N_O^s}{2vN_B^0} \right)^{1/2} \]

In equation 62, \( v \) is the stoichiometric ratio of oxygen to metal in the internally created oxide. This value of \( \gamma \) being substituted in to equation 59 leads to a reaction front distance of:

Equation 63

\[ \xi = \sqrt{\frac{2D_0 N_O^s t}{v N_B^0}} \]

Rhine’s pack samples were created as shown in Figure 6.1. The sample started from a cast rod ~10mm in diameter. From this rod, ~6mm cubes were EDM from the center as shown in part A-B of Figure 6.1. The composition of the rods that were investigated can be seen in Table 6.1. The cubes were then placed into a quartz tube sealed with Cr/Cr₂O₃ powders in order to establish a partial pressure of oxygen to diffuse into the sample. The samples were then heated at 1160°C for various lengths of time for 2.5, 10 and 100hrs. The diffusion constant at 1160°C was compared to previous GARS
produced alloys without aluminum as well as the diffusion coefficient of oxygen in pure iron.

**Figure 6.1:** Rhine’s pack production from as-cast bars (A), to machined ~6mm cubes (B), then packed in Cr/Cr$_2$O$_3$ sealed quartz tubes (C).

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Fe</th>
<th>Cr</th>
<th>Al</th>
<th>Hf</th>
<th>Y</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nominal</td>
<td>Bal</td>
<td>16</td>
<td>12</td>
<td>0.25</td>
<td>0.2</td>
</tr>
</tbody>
</table>

SEM analysis was used in order to determine the distance which the reaction front reached for determination of diffusion coefficient. X-ray diffraction analysis can be found in “Promotion of Alumina Scale Protected Iron-Base Oxide Dispersion Strengthened Alloys” by Spicher et al [31].

**Heat Treatment Determination**

The alloy used for determination of the heat treatment parameters was created from the same powder distribution from chapter 5. Hot isostatic pressing (HIP) also was used to consolidate the powders. Before being consolidated, the powder samples were placed into a 316L stainless steel HIP can with a diameter of 25mm. The can was evacuated using a diffusion pump to approximately $10^{-7}$ torr. A low temperature HIP was planned in order to consolidate the powders without significant reaction at 850°C with 300MPa for 4 hours.
The minimum amount of time for heat treatments at different temperature can be calculated using equation 64. \( \xi \) is the radius of the particle, \( v \) is the stoichiometric ratio of oxygen in the dispersoid formed, \( N_B^o \) is the mol fraction of yttrium in the alloy, \( D_0 \) is the temperature dependent diffusion coefficient of oxygen in the alloy, and \( N_O^s \) is the partial pressure of oxygen at the metal/oxide interface of the powder. The temperatures used in this study were 950°C, 1000°C, 1100°C, and 1200°C.

\[
\text{Equation 64}
\]

\[
t = \frac{\xi^2 v N_B^o}{2 D_0 N_O^s}
\]

The heat treated microstructures were evaluated using scanning electron microscopy, X-ray diffraction, and micro hardness indentations. The scanning electron microscopy was used in order to identify large intermetallic compounds or oxides that form within the microstructure which could be points of initiation for cracks during rolling operations. X-ray diffraction was used to classify the types of dispersoids formed in the microstructure and to identify secondary phases that may be present. Micro hardness indentation was used as a tool to look at initial strength of the alloy, as this is a precursor for the strength of the rolled alloy, see Chapter 4.

**Electron Microscopy**

SEM analysis was performed through a combination of two different microscopes. A Hitachi S-2460N SEM with EDS capabilities was used for a large majority of imaging. When higher resolution was needed a, FEI Quanta 250 field emission SEM (FE-SEM) with EDS capabilities was used.

**X-ray diffraction analysis**

X-ray diffraction was conducted using a Philips PANalytical X-Pert Pro Diffraction System. The radiation used was Co-K\(\alpha \) (1.78901 Å). A scanning real time multiple strip (RTMS) detector was used. The diffraction was taken over a range of 20-120° (2\(\Theta \)) and a step size of 0.008°. The dwell time was 300s per step.
**Micro hardness analysis**

Micro hardness measurements were done with a Vicker’s pyramid indenter with 500gmf. Averages of 5 hardness readings were used per sample.

**Results**

The Rhine’s pack cubes were made and cross sectioned as exampled in figure 6.2 below. This figure shows 4 unique zones with distinct phases present [31]. The yellow zone (Zone 4) shows the intermetallic compounds that were present in the As-cast samples. The blue zone (Zone 3) contains primarily Y₂Hf₂O₇ oxides. The interface between Zones 3 and 4 signifies the end of the diffusion distance or $\xi$. The red and green zones (Zones 1 and 2 respectfully) contain additional oxides of HfO₂ and Al₂O₃.

![Figure 6.2: Example of interface diffusion distance used in order to calculate the diffusion coefficient of oxygen in Fe-15.6Cr-10Al-0.24Hf-0.12Y at%. Four different zones are present; Zone 1 in red contains Al₂O₃, HfO₂, and Y₂Hf₂O₇, Zone 2 in green contains HfO₂, and Y₂Hf₂O₇, Zone 3 in blue contains Y₂Hf₂O₇, and Zone 4 in yellow is the un-oxidized Fe₁₇(Y,Hf)₂ intermetallic [31].](image-url)

To calculate the diffusion coefficient equations 63 and 59 as well as the measured diffusion interface distance. The average diffusion constant for the aluminum
containing alloys was. This value can be seen compared to internal oxidation experiments from Fe-based alloys as well as different diffusion coefficients in pure iron in Figure 6.3.

![Figure 6.3: Comparison of aluminum diffusion study to experimental data produced from other GARS produced Fe-Cr-Al alloys and published diffusion coefficients [51].](image)

With the increased diffusion coefficient in the Rhine’s pack alloys possibly being caused by increased diffusion pathways in the cast structure, the coefficient used to calculate the heat treatments was the diffusion of O in Fe from the literature. These values come from taking \( D = A \exp(-Q/RT) \) with values for \( A \) of , and \( Q \) of [48]. The average size of particle size distribution was taken so that 90% of the powder by volume was \( -8\mu m \). In order to completely react the particle, the reaction front would have to travel the length of the radius of the powder particles with the GARS process (See chapter 4). A safety factor of 2 was used in order to ensure that the samples had adequate time to complete the reaction. The values for minimum time for reaction as well as heat treatment times used in this experiment can be found in Table 5.2.
Table 6.2: Reaction Interface and Heat Treatment Calculations

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Diffusion Coefficient (m²/s)</th>
<th>Radius of Particle (µm)</th>
<th>Time until reaction completion</th>
<th>Heat Treatment Time</th>
</tr>
</thead>
<tbody>
<tr>
<td>950</td>
<td>2.42 x 10⁻¹⁰</td>
<td>4</td>
<td>5.73 hours</td>
<td>11.5 hours</td>
</tr>
<tr>
<td>1000</td>
<td>3.52 x 10⁻¹⁰</td>
<td>4</td>
<td>1.97 hours</td>
<td>4 hours</td>
</tr>
<tr>
<td>1100</td>
<td>6.90 x 10⁻¹⁰</td>
<td>4</td>
<td>14.5 minutes</td>
<td>30 minutes</td>
</tr>
<tr>
<td>1200</td>
<td>1.23 x 10⁻⁹</td>
<td>4</td>
<td>2.6 minutes</td>
<td>10 minutes</td>
</tr>
</tbody>
</table>

Figure 6.4: HIP can prior to consolidation (top) and after consolidation (bottom).

Figure 6.4 shows 90% by volume powder -8µm powder, as created in Chapter 5, loaded into a 316L stainless steel can and consolidated by hot isostatic pressing. The top figure was prior to consolidation, while the bottom image is of the post 850°C at 300 MPa HIP cycle for 4 hours.
Figure 6.5: SEM images of temperature effects of heat treatment procedures; A (light blue) 1200°C 10 min, B (dark blue) 1100°C 30 min, C (red) 1000°C 4 hr, D(green) 950°C 11.5 hr, and E (purple) As-HIPed.
SEM images were taken of each of the different temperatures as shown in Figure 6.5. Figure 6.5 E shows the as HIPed microstructure with prior particle boundaries enriched in intermetallic as well as some cellular intermetallic compounds. Images C and D show formations of larger intermetallic clusters as well as small intermetallic particles along the prior particle boundaries. Images A and B show small intermetallic particles along the prior particle boundaries. Phase characterization was done through X-ray diffraction analysis shown in Figure 6.6.

**Figure 6.6:** XRD scans of temperature effects of different heat treatment procedures. Data normalized to main α-Fe Peak (Same coloring as Figure 6.5)

All X-ray diffraction in Figure 6.6 was normalized to the main α-Fe peak. The intermetallic phases were identified as different forms of the FeHf$_2$ intermetallic system. The room temperature phase was found in all of the materials, while the high temperature phase was found heavily in the 950°C and 1000°C samples with some XRD data showing some inclusion in the 1100°C sample. EDS work showed that all of the
intermetallic compounds were enriched in Hf. The Fe$_{17}$(Y,Hf)$_2$ intermetallic peak was also seen throughout all of the samples and was included in the intermetallic compounds along the prior particle boundary phases.

![Graph showing microhardness vs. temperature](image)

**Figure 6.7:** Microhardness of temperature effects of different heat treatments.

Microhardness measurements were completed using the average value from 5 Vickers hardness indentions. The hardness reading at 850°C represents the as consolidated microstructure.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Sample Description</th>
<th>Heat Treatment Time</th>
<th>Ramp Type</th>
<th>Quench Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>1200</td>
<td>10 min</td>
<td>10 min</td>
<td>Placed into furnace</td>
<td>Water Quench</td>
</tr>
<tr>
<td>1200</td>
<td>10 min Slow Ramp</td>
<td>10 min</td>
<td>1200°C/hr</td>
<td>Furnace Cooled</td>
</tr>
<tr>
<td>1200</td>
<td>5 hours</td>
<td>5 hours</td>
<td>1200°C/hr</td>
<td>Furnace Cooled</td>
</tr>
<tr>
<td>1200 + 1000</td>
<td>5 hours + Anneal 1000°C 2hr</td>
<td>5 hours</td>
<td>1200°C/hr + placed into furnace</td>
<td>Furnace Cooled + Air Cooled</td>
</tr>
</tbody>
</table>

Addition heat treatments were made in order to investigate the effects of ramp rates of furnaces as well as hold times. The sample “10 min” was placed directly into a 1200°C furnace for 10 minutes and then quenched in water. The “10 min Slow Ramp” and “5 hours” samples were heated in a furnace under Ar, with a ramp rate of 1200°C for both
heating and cooling. The “5 hours + Anneal 1000°C 2hr” sample was created by placing the “5 hour” sample in a furnace at 1000°C for 2hrs in air with air cooling.

![Figure 6.8: SEM images of time effects of heat treatment procedures; F (Brown) 1200°C 5hr + 1000°C 2hr, G (gray) 1200°C 5hr, H (Gold) 1200°C 10 min/slow ramp, and I (light blue) 1200°C 10 min.](image)

SEM images were taken of the different ramp rate and hold times. Samples F-I have intermetallic compounds along the particle boundaries.
X-ray diffraction was used to characterize the phases present in the heat treatment samples in Table 6.4. All X-ray diffraction in Figure 6.6 was normalized to the main $\alpha$-Fe peak. The “10 min” sample was the only sample with an asymmetric dispersoid peak. A combination of FeHf$_2$ rt and Fe$_{17}$(Y,Hf)$_2$ intermetallic compounds were present in all heat treatments. The presence of the FeHf$_2$ ht was not found when the samples were initially heat treated at 1200°C.

**Discussion**

The Rhine’s packs that were created gave a good understanding for the reaction progression in Fe-based ODS alloys that contain aluminum. The diffusion coefficient seen in Figure 6.3 shows how close the Fe-Cr-Al alloys behave compared to the Fe-Cr alloys. Even though there was a small layer of alumina on the surface of the alloy, for this calculation the partial pressure of oxygen used was that of Cr-CrO$_2$. If the Al-Al$_2$O$_3$
partial pressure was used the diffusion coefficient would have been orders of magnitude higher which was unreasonable to assume.

The progression of the oxide phases in the cast alloy shows the stability of oxides in this system. The closer the oxide formed is to the reaction front, the more stable the oxide is. The most stable oxide in this system was \( \text{Y}_2\text{Hf}_2\text{O}_7 \) found in the blue zone 3 of Figure 6.2. Zone 2 (green zone) of Figure 6.2 contains \( \text{HfO}_2 \) as well as \( \text{Y}_2\text{Hf}_2\text{O}_7 \), while Zone 1 (red zone) contains \( \text{Al}_2\text{O}_3 \) as well as the previously mentioned oxides. This leads to an oxide stability progression of:

\[ \text{Y}_2\text{Hf}_2\text{O}_7 > \text{HfO}_2 > \text{Al}_2\text{O}_3 \]

This stability progression means that \( \text{Y}_2\text{Hf}_2\text{O}_7 \) will be the most likely phase to form and should be used as the stoichiometric ratio when calculating the progression of the reaction front.

Table 6.2 shows the original heat treatment design of experiments. Four different temperatures were chosen; 950°C, 1000°C, 1100°C, and 1200°C. All of these samples were sealed in quartz under argon and placed directly into a furnace at the desired temperature. Once the heat treatment time was reached, the samples were water quenched. The SEM micrographs of these can be seen in Figure 6.5. The As-HIP structure shows intermetallic compounds around the prior particle boundaries. Upon heating the prior particle boundary compounds spheroidize in all cases. For images C and D of Figure 6.5 (950°C and 1000°C) a large intermetallic phase, \( \text{FeHf}_2\text{ht} \) structure, precipitates in clusters. These clusters could be points for crack initiation during rolling operations to increase the strength of these materials through establishing a dislocation structure. The XRD data in Figure 6.6 shows that the \( \text{FeHf}_2\text{ht} \) phase may be present in the 1100°C sample as well in smaller quantities. The unknown phase is not a complex \( \text{Y-Al} \) oxide.

The dispersoid phase noted with a star on Figure 6.6 shifts through temperature increase. In the As-HIP condition, the dispersoid phase corresponds to \( \text{Y}_2\text{Hf}_2\text{O}_7 \) in very
fine quantities. Upon increasing the temperature during heat treatment, the dispersoid peak shifts to smaller values of $2\theta$. This shift corresponds to decreasing the oxygen content in the dispersoid phase away from stoichiometric ratio of 1:3.5, as seen in [51]. The cause of this shift is the lower than ideal oxygen content in the powder. With ideal oxygen content, 3.5x at% of yttrium, would result in formation of stable $Y_2Hf_2O_7$. It is important to note that the unknown phase in Figure 6.6 is not any complex Y-Al oxide, which have been known to coarsen rapidly leading to decreased performance [61,32]. A comparison of the microhardness of the different temperature heat treatments can be seen in Figure 6.7. With increase of temperature the hardness decreases. The conversion of the dispersoid phase does not appear to be complete in any of the heat treatment samples, represented by the asymmetrical peak shape of the dispersoid phase. The strength decrease from increasing the heat treatment temperature can be accounted for by an increase in dispersoid size. Scherrer peak broadening was used to calculate the crystallite size of the dispersoids and can be seen below in Figure 6.10. By increasing the dispersoid size you are increasing the mean free path of dislocation movement leading to a decrease in strength [26].

![Figure 6.10: Dispersoid crystallite size and microhardness values for various temperatures of heat treatments.](image_url)
In order to investigate complete reaction of the dispersoid phase, second set of heat treatments were completed as shown in Table 6.3. The ramp rate was slowed instead of immersing the sample into a hot furnace; the furnace was heated at 1200°C per hour. The length of the dwell time at temperature was also increased to 5 hours in order to ensure that all the dispersoid phase was converted and to attempt to solutionize the sample in order to prevent formation of the FeHf₂ht phase during a two hour hold at 1000°C, representing the amount of time that the sample would be at temperature during a rolling operation (as seen in Chapter 7). The slight asymmetry of the peak seen with the “10 min” sample was rectified in the “10min slow ramp” sample. With the increase of the hold time of the “5 hour” sample, the FeHf₂ht phase was not seen with a 2 hour anneal at 1000°C.

Conclusions

The heat treatment of Fe-based ODS alloys containing aluminum produced through the GARS process was investigated. An internal oxidation study on cast alloys was used in order to determine the rate at which oxygen could be diffused through the samples. The addition of aluminum did not have a significant effect on the oxygen diffusion coefficient. The diffusion coefficient of oxygen in pure iron was used in order to provide a conservative estimate of the times necessary to complete the GARS process at four different temperatures. A phase with the FeHf₂ht structure was observed when the heat treatment temperature was 950°C or 1000°C. X-ray diffraction showed that the FeHf₂ht structure was present in the 1100°C sample as well. This phase could be a point of crack initiation during rolling operations, and for this reason, the heat treatment temperature was chosen to be 1200°C. The dispersoid phase was converted from Y₂Hf₂O₇ to an oxygen lean dispersoid phase. The conversion coarsened the oxide and lowered the strength of the material. This strength decrease would not be expected with an ideal oxygen content. The conversion was not complete with a 10 min heat treatment time with water quenching. By slowing the ramp rate of the sample to 1200°C per hour, the conversion of the dispersoid phase was completed without the
formation of the FeHf$_2$ ht structure. The heat treatment dwell time was increased to 5 hours to ensure that the most stable oxide phase was formed as well as solutionize the sample in order to prevent the formation of the FeHf$_2$ ht phase with an annealing treatment at 1000°C for 2 hours to simulate hot rolling. The sample with the 5 hour dwell time and anneal did not form FeHf$_2$ ht phase. The chosen heat treatment was a 5 hour hold at 1200°C with a ramp rate of 1200°C per hour.
CHAPTER 7: Alloy Properties

Abstract

The demanding operating conditions of the next generation Advanced Ultra-Supercritical (A-USC) coal fired power plants requires new materials to be made. Previously available commercial alloys, such as PM2000 and MA956, would have been good candidates for this application but are no longer being produced due to cost concerns. A new processing method, gas atomization reaction synthesis (GARS), has been shown to create oxide dispersion strengthened (ODS) materials without the inclusion of aluminum. This study is comparing the physical properties of two different GARS produced ODS alloys; with the only difference being an addition of aluminum to one alloy. Both alloys were consolidated through hot isostatic pressing (HIP) and used x-ray diffraction and scanning electron microscopy to evaluate the microstructure. The properties evaluated include alloy microhardness values, high temperature tensile testing, and corrosion in dry air and humid environments.

Introduction

In an effort to increase the efficiency of coal fired power plants the next generation of advanced ultra-supercritical (A-USC) plants will have increased operating pressures and temperature [4,5]. The new proposed steam operation conditions are 760°C and 35 MPa of pressure [4]. A crucial material that will need to be developed for these applications are boiler tubing that transports the steam; as shown in Figure 7.1 [8]. This material has two extreme conditions on either side of the tubing. One side is exposed to the super critical steam, while the other has highly corrosive coal byproducts [4]. Ferritic materials are good candidates for these applications due to the decreased thermal expansion and increased thermal conductivity. The planned lifetime of these materials is roughly 60 years or $10^6$ hours.
In order to achieve the high temperature strength needed for these conditions, oxide dispersion strengthening (ODS) should be utilized [25,26]. Previously available commercial ferritic ODS alloys that had inclusion of aluminum that would give corrosion resistance were MA956 and PM2000 [29]. These alloys have nominal compositions of Fe-20Cr-9Al-0.45Ti-0.3Y at% and Fe-19.5Cr-11Al-0.55Ti-0.23Y at% respectively. The processing method for these alloys was mechanical alloying shown in Figure 7.2 [14]. This production method can lead to highly anisotropy properties, contamination, and long production times that increased the cost of production to the point that these alloys are no longer commercially available [60,61].
Gas atomization reaction synthesis (GARS) is a new process under development that shows potential to reduce the cost of producing ODS alloys by bypassing the balling step of mechanical alloying [15,16]. In the beginning of the process, the molten metal is atomized with high pressure gas that has some inclusion of oxygen. When the powders are created a thin oxide shell is formed that acts as a reservoir of oxygen for creating the dispersed phase in these alloys, as shown in Figure 7.3. During heat treatments this oxide shell can dissociate and react with intermetallic particles to form the dispersed oxide phase, see Figure 7.4. This method has been shown to produce ODS alloys that do not contain aluminum with strengths comparable to MA956 and PM2000 [17].
Figure 7.4: GARS exchange reaction: initial consolidation (left), prior particle boundary (PPB) oxide dissociation (middle), partially complete PPB dissociation and dispersoid formation (right) [16].

The inclusion of aluminum in the GARS processing model was shown to be viable for creation of ODS alloys (see Chapter 5). In order to see the effects that the aluminum addition had on physical properties, an alloy identical to the alloy created in Chapter 5 was created without the inclusion of aluminum (see Table 7.1 and Table 7.2)

**Experimental Procedure**

**Gas Atomization**

A research scale atomizer (charge size of 4kg) was used to produce the alloy. The charge was superheated to 1700°C in a yttria (Y2O3) washed alumina crucible. After exiting through a yttria-stabilized zirconia pour tube, atomization gas was directed at the stream with a manifold pressure of 5.5MPa. The atomization gas consisted of Ar with 0.19 vol% O2 and exited through a high pressure gas atomization (HPGA) nozzle.

The powders were removed and screened at +106 μm. After this screening, riffling of the powders was used to ensure an accurate representation of the sample for size analysis. Size analysis was performed by using a stack of screens with sizes ranging from 20 μm to 106 μm as well as Microtrac™ analysis. Powder scales were analyzed with AES depth profiling. The thickness of the oxide scale was taken to be the distance from the surface until the intensity of the auger peak for iron was greater than that of oxygen.
Consolidation

Hot isostatic pressing (HIP) also was used to consolidate the powders. Before being consolidated, the powder samples were placed into a 316L stainless steel HIP can with a diameter of 25mm. The can was evacuated using a diffusion pump to approximately 10-7 torr. A low temperature HIP was planned in order to consolidate the powders without significant reaction at 850°C with 300MPa for 4 hours. Due to technical difficulties the HIP cycle was held at 850°C with 200MPa for 13 hours prior to being raised to the final conditions for 4 hours.

Electron Microscopy

SEM analysis was performed through a combination of two different microscopes. A Hitachi S-2460N SEM with EDS capabilities was used for a large majority of imaging. When higher resolution was needed a, FEI Quanta 250 field emission SEM (FE-SEM) with EDS capabilities was used.

X-ray diffraction analysis

X-ray diffraction was conducted using a Philips PANalytical X-Pert Pro Diffraction System. The radiation used was Co-Kα (1.78901 Å). A scanning real time multiple strip (RTMS) detector was used. The diffraction was taken over a range of 20-120° (2Θ) and a step size of 0.008°. The dwell time was 300s per step.

Micro hardness analysis

Micro hardness measurements were done with a Vicker’s pyramid indenter with 500gmf. Averages of 5 hardness readings were used per sample.

Hot Rolling

Hot rolling specimens were prepared as shown in Figure 7.5. The samples were cut using an EDM and were then ground and polished through 1 µm diamond compounds. The edges of the samples were rounded in order to prevent crack initiation during the rolling procedure. The samples were then soaked in a furnace exposed to atmosphere at 1050°C for 1 hour prior to rolling. The samples went through a series of passes with
set reduction in thickness, the first pass being 5%, passes two through 6 being 10%, and
the final pass taking 5% for a total of 70% reduction in thickness. Between each of the
passes the samples were held at 1050°C for 10 minutes to reestablish the correct
temperature.

Figure 7.5: Surface finish and geometry of specimens used for hot rolling

Tensile Testing
Tensile test specimens were prepared from rolled bars of ODS materials. The
specimens were prepared according the SS3 type tensile bars. Hot testing was
performed at temperatures of 400°C, 600°C, and 800°C.

Corrosion Testing
Corrosion testing was performed in two different atmospheres. The first atmosphere
was air at 1200°C. Samples in this atmosphere were cycled in one hour cycles up to
with mass gains being recorded every 50 cycles. The second atmosphere was Ar with
10 vol% H₂O. The samples in this testing atmosphere were cycled in 100 hour cycles up
to 1000 hours total.
Results

-8µm Powder

Table 7.1 shows the nominal compositions of alloy GA-1-198 (The alloy created in Chapter 5) and alloy GA-1-204 created for this study.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Fe</th>
<th>Cr</th>
<th>Al</th>
<th>W</th>
<th>Hf</th>
<th>Y</th>
</tr>
</thead>
<tbody>
<tr>
<td>GA-1-198</td>
<td>Bal</td>
<td>16</td>
<td>12</td>
<td>0.9</td>
<td>0.25</td>
<td>0.2</td>
</tr>
<tr>
<td>GA-1-204</td>
<td>Bal</td>
<td>16</td>
<td>0</td>
<td>0.9</td>
<td>0.25</td>
<td>0.2</td>
</tr>
</tbody>
</table>

Alloy GA-1-204 was gas atomized and the size distribution of this run along with comparison of the powder morphology can be seen in Figure 7.6 and Figure 7.7. Table 7.2 shows the actual composition of the different powder alloys created.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Fe</th>
<th>Cr</th>
<th>Al</th>
<th>W</th>
<th>Hf</th>
<th>Y</th>
</tr>
</thead>
<tbody>
<tr>
<td>GA-1-198</td>
<td>Bal</td>
<td>15</td>
<td>12.3</td>
<td>0.9</td>
<td>0.24</td>
<td>0.19</td>
</tr>
<tr>
<td>GA-1-204</td>
<td>Bal</td>
<td>16</td>
<td>0</td>
<td>0.9</td>
<td>0.25</td>
<td>0.24</td>
</tr>
</tbody>
</table>

Figure 7.6: SEM image of gas atomized powder for alloy GA-1-198 with blue border (left); SEM image of gas atomized powder for alloy GA-1-204 with red border (right).
Figure 7.7: Powder size distribution of gas atomized powder for alloy GA-1-198 (left); Powder size distribution of gas atomized powder for alloy GA-1-204 (right).

The oxygen content and oxide thickness of the resulting powder was compared between the different alloys. Figure 7.8 shows the size dependent oxygen concentration for both alloys. Auger depth profiling was used to calculate the oxide thickness of three different powder sizes. The oxide thickness was determined to end where the intensity of oxygen falls below that of iron as depicted in Figure 7.9. A silicon standard of 10nm per minute was used to convert the sputtering time into an oxide thickness. Table 7.3 shows the comparison of oxide thickness for alloys GA-1-198 and GA-1-204.

Figure 7.8: Size dependent oxygen content of two gas atomized ferritic ODS alloys.
Figure 7.9: Example of figure used to calculate the thickness of the oxide film during Auger depth profiling (data shown in Table 7.3).

Table 7.3: Oxide thickness of gas atomized alloys

<table>
<thead>
<tr>
<th>Alloy</th>
<th>~13µm Powder</th>
<th>~35µm Powder</th>
<th>~68µm Powder</th>
</tr>
</thead>
<tbody>
<tr>
<td>GA-1-198</td>
<td>9 nm</td>
<td>25 nm</td>
<td>32 nm</td>
</tr>
<tr>
<td>GA-1-204</td>
<td>11 nm</td>
<td>26 nm</td>
<td>34 nm</td>
</tr>
</tbody>
</table>

The GA-1-204 -8µm powder was sealed into a 316L stainless steel can after being outgassed at 600°C. The sample was then consolidated through hot isostatic pressing (HIP) under conditions of 800°C for 4 hours with 300 MPa of pressure. The HIP can at various stages can be seen in Figure 7.10.
Figure 7.10: HIP can of GA-1-204 -8µm powder prior to consolidation (Top); HIP can after consolidation (Bottom).

After consolidation the HIPed sample was analyzed through SEM analysis. The HIPed sample was then heat treated (HT) under vacuum at 1200°C for 5 hours with a ramp rate of 1200°C per hour. The SEM images for GA-1-204 as well as samples from GA-1-198 -8µm in the As-HIPed and As-HTed condition can be seen in Figure 7.11. The two different alloys, GA-1-198 and GA-1-204 both have prior particle boundary precipitates with some internal intermetallic phases in the larger particles. The As-HT GA-1-198 alloy in the bottom left of Figure 7.11 contains spherodized intermetallic compounds around the prior particle boundaries. The As-HT GA-1-204 alloy in the bottom right of Figure 7.11 has spherodized throughout the sample.
Figure 7.11: SEM micrographs of GARS alloys seen in Table 7.2. Top left image with blue border is GA-1-198 in the As-HIP condition, top right image with red border is GA-1-204 in the As-HIP condition, bottom left image with blue border is GA-1-198 in the As-HT condition, and bottom right image is GA-1-204 in the As-HT condition.

In order to prepare the samples for hot rolling, the As-HT samples from both alloys were prepped as shown in Figure 7.5. These samples were then rolled by a combination of two 5% reduction in original thickness and six 10% reduction in original thickness passes to a total reduction of 70% thickness. This corresponds to approximately 50% reduction in area. The as-rolled samples can be seen in Figure 7.12.
Figure 7.12: As-rolled GA-1-198 shown in top image; As-rolled GA-1-204 shown in bottom image.

The as-rolled samples were ran through the rolling operation in alternating directions in order to minimize the curvature formed from going through the rolls. At the end of rolling a slight curvature was still present as shown in Figure 7.12. The samples were then pressed to remove the curvature and surface ground flat, as seen in Figure 7.13.

Figure 7.13: As-rolled GA-1-198 shown in top image; As-rolled GA-1-204 shown in bottom image. Rolling direction is noted with a red arrow.
In order to determine the effects of orientation on strength of the material, a clear understanding of the orientation on the rolled bar is necessary. Figure 7.14 shows a rolled bar with the three orthogonal directions colored. The green direction labeled perpendicular was used in order to determine the reduction in area.

**Figure 7.14:** Image of GA-1-198 rolled bar highlighting three orthogonal directions. Blue direction called as “normal,” red direction called “parallel,” and green direction called “perpendicular.”

SEM micrographs of each of the orthogonal directions were taken for both GA-1-198 and GA-1-204, as seen in Figure 7.14. The GA-1-198 alloys are outlined with a blue border while the GA-1-204 alloys are outlined with a red border. The rolling directions on the samples are denoted with a red arrow. The FeHf$_2$ rt phase is present around the prior particle boundary for all images, some FeHf$_2$ ht phases are present (larger phases marked with yellow arrow). The top images in Figure 7.15 are of the normal surface. These images are at a lower magnification than the rest in order to highlight the “pancake” prior particle boundary pattern caused by rolling, which was down vertically throughout the image. The middle images are of the parallel direction with rolling occurring in the horizontal direction of the image. The bottom images of Figure 7.15 are of the perpendicular direction, with the rolling direction going in/out of the page. X-ray diffraction data for GA-1-198 can be found in Figure 7.16, while data for GA-1-204 can be seen in Figure 7.17. Data was normalized to the main $\alpha$-Fe peak for all alloys (seen at approximately 52 degrees 2θ).
Figure 7.15: Images of GA-1-198 alloys on left side (blue), GA-1-204 on right (red). Arrow denotes rolling direction. Top images of “normal” surface, middle images of “parallel” surface, bottom images of “perpendicular” surface.
Figure 7.16: X-ray diffraction data for alloy GA-1-198 throughout the processing parameters (As-HIPed, As-HTed, and As-Rolled). All data normalized to main Fe Peak at 52 degrees 2θ.

Figure 7.17: X-ray diffraction data for alloy GA-1-204 throughout the processing parameters (As-HIPed, As-HTed, and As-Rolled). All data normalized to main Fe Peak at 52 degrees 2θ.
Figure 7.18 shows microhardness measurements were taken for both alloys, GA-1-198 (blue) and GA-1-204 (red) in the As-HIP, As-HT, and each of the three rolling directions. Data was collected using a Vicker’s pyramidal indenter with 500gf.

![Graph showing microhardness measurements](image)

**Figure 7.18:** Microhardness measurements of both alloys GA-1-198 (Blue) and GA-1-204 (Red). Measurements were taken throughout processing path and in every rolling direction. Data taken as an average of five measurements.

Type SS3 tensile specimens were machined from the as rolled bars in two different directions. Samples were taken along the rolling or longitudinal direction, as well as samples being taken perpendicular to the rolling direction or transverse direction. These samples were tested at temperatures of room temperature (20°C), 400°C, 600°C, and 800°C. Tensile data for GA-1-198 alloy can be seen in Figure 7.19, while tensile data for GA-1-204 can be seen in Figure 7.20.
Figure 7.19: Tensile testing data for alloy GA-1-198. SS3 type samples were tested with crosshead speeds of 0.01800 in./min.

Figure 7.20: Tensile testing data for alloy GA-1-204. SS3 type samples were tested with crosshead speeds of 0.01800 in./min.
Corrosion testing was performed in two different atmospheres. The first was in 1200°C air with cycle times of 1 hour. The second was with 1100°C air with 10 vol% H₂O with cycle times of 100 hours. The resulting mass gain for the 1200°C air can be seen in Figure 7.21. Additional samples tested at Oak Ridge Nation Lab (ORNL) can be seen as a comparison. Mass gains for the 1100°C air with water vapor can be seen in Figure 7.22, along with other samples tested at ORNL.

Figure 7.21: Mass Gains for samples in 1200°C air with cycle times of 1 hour. Additional alloys tested at ORNL used for comparison purposes.
Figure 7.2: Mass Gains for samples in 1100°C air with 10 vol% water, cycle times of 100 hours. Additional alloys tested at ORNL used for comparison purposes.

15-25 µm Powder

In an effort to determine the effects of oxygen content on the corrosion resistance of ODS alloys, the 15-25 µm powder from the GA-1-198 was taken in the as-atomized state as well short term ball milled (~5hrs). The powders used can be seen in Figure 7.23.

Figure 7.23: 15-25 µm GA-1-198 powder in image on left; 15-25 µm GA-1-198 powder after Ball Milling in image on right
The 15-25 µm powder in both the as-atomized and ball milled states were consolidated in the same manner described in Chapter 5 (Conditions of 300 MPa, 850°C, for 4 hours). The consolidated samples were heat treated at 1200°C for 5 hours with a ramp rate of 1200°C / hour. The as-HIPed and as-HT microstructures of both as-atomized and ball milled samples can be seen in Figure 7.24.

**Figure 7.24:** 15-25 µm GA-1-198 As-HIPed sample shown in image on the top left; 15-25 µm GA-1-198 As-HIPed Ball Milled Powder shown in image on the top right; 15-25 µm GA-1-198 As-HTed sample shown in image on the top left; 15-25 µm GA-1-198 As-HTed Ball Milled Powder shown in image on the top right;
X-ray diffraction was performed on the powders, as-consolidated samples, and as-heat treated samples. The X-ray diffraction results for the 15-25µm as atomized powders can be seen in Figure 7.25, while the results for the ball milled specimens can be seen in Figure 7.26.

Figure 7.25: X-ray diffraction data for alloy GA-1-198 15-25µm powder throughout the processing parameters (As-atomized, As-HIPed, and As-HT). All data normalized to main Fe Peak at 52 degrees 2θ.

Figure 7.26: X-ray diffraction data for alloy GA-1-198 15-25µm ball milled powder throughout the processing parameters (As-atomized, As-HIPed, and As-HT). All data normalized to main Fe Peak at 52 degrees 2θ.
Discussion

Alloy GA-1-204 was designed to be nearly identical to the previously created GA-1-198 (see Chapter 5), with compositions shown in Table 7.1. The only difference between the two alloys in design was 12 atomic percent of aluminum included in GA-1-198 alloy. The actual compositions of the created alloys can be seen in Table 7.2. The alloys were created close to nominal with slightly higher yttrium concentration in the GA1-1-204 alloy. Aluminum additions have been shown to have the potential to be detrimental to the properties of traditional ODS alloys that use titanium as a dispersoid former [32,35]. The majority of this strength was regained through adding additions of hafnium or zirconium during ball milling [32].

Alloy GA-1-204 was gas atomized with parameters identical to the GA-1-198 alloy produced in Chapter 5. The powder morphology, oxygen content, and oxide thickness were compared between the two alloys. Both powder alloy samples have a spherical morphology, as seen in Figure 7.6. There are few satellites in both powder samples. Both alloys, GA-1-198 and GA-1-204 have a similar size distribution as shown in Figure 7.7.

The size dependent oxygen content of the two alloys can be seen in Figure 7.8. The same trend of greatly increased oxygen at lower powder sizes can be seen (due to the increased surface area to volume). Alloy GA-1-204 shows slightly elevated oxygen levels at all powder sizes compared to GA-1-198. The increased oxygen content could come from a slightly higher pour temperature during atomization. The thickness of the oxide scales for three different powder sizes were analyzed through Auger depth profiling (as shown in Figure 7.9). A silicon standard was used in order to estimate the thickness (taken to be the point in which the intensity of iron was greater that oxygen). The results of this analysis can be found in Table 7.3. Alloy GA-1-204 had oxide layers that were 1-2 nm thicker for all size ranges. This corresponds well with the increased
oxygen levels that were seen during bulk analysis through combustion and infrared detection.

Alloy GA-1-204 was sealed in the same manner as GA-1-198 in Chapter 5. The HIP can before and after consolidation can be seen in Figure 7.10. After consolidation the 316L stainless can was machined off of the sample and the majority of the sample was heat treated. The heat treatment used was 1200°C for 5 hours with a ramp rate of 1200°C per hour. This heat treatment was chosen based upon a heat treatment study conducted on the GA-1-198 alloy in Chapter 6. The time and temperature were used in order to fully react the alloy, limit precipitation of the FeHf₂ ht phase, and homogenize the material for hot rolling. The microstructure of the two different alloys in both the as-hot isostatic press (As-HIP) and as-heat treated (As-HT) states can be seen in Figure 7.11. Prior particle boundary phases as well as internal intermetallic compounds can be seen in the As-HIPed samples for both alloys. During HT the prior particle boundary phases were spherodized with larger intermetallic compounds being seen in the GA-1-204 alloy.

After heat treatment, rectangular bars were prepped for hot rolling from both GA-1-198 and GA-1-204. The bars were EDM machined and polished to a 1 μm finish. The resulting bars from hot rolling at 1000°C can be seen in Figure 7.12. The bars were rotated each pass in order to minimize curl, however as can be seen in Figure 7.12 slight deformation was present. After rolling the bars were annealed at 1000°C for 1 hour. A press was used in order to remove a large portion of the curl and then the bars were annealed at 1000°C for 1 hour. After annealing the bars were ground flat using a surface grinder, as seen in Figure 7.13. The surface texture seen in Figure 7.13 comes from surface grinding and is not related to the rolling direction of the material, as noted with a red arrow.

Figure 7.14 was used in order to label the different orientations used for SEM and microhardness analysis. The “normal” surfaces of the bars are the same surfaces that were ground flat with the surface grinder. The microstructure of the both alloys in all
three directions can be seen in Figure 7.15. Elongation of the prior particle boundary phases can be seen in both alloys in the “normal” orientation (Top left image for GA-1-198 and Top right image for GA-1-204). These “pancake” shaped prior particle boundaries are elongated in the rolling direction. In the “transverse” and “longitudinal” orientations the prior particle boundary phases can be seen along with larger FeHf$_2$ht phases denoted with a yellow arrow.

Figures 7.16 and 7.17 show XRD data for both alloys in the powder, As-HIP, As-HT, and As-rolled states. The As-rolled surface is the normal surface from both alloys as this allowed for the necessary surface area to get XRD measurements. Both alloys had a precursor intermetallic that was consumed upon consolidation to form the dispersoid phase of type Y$_2$Hf$_2$O$_7$. During consolidation an additional unknown phase was precipitated. This phase is not the complex Y-Al oxides that coarsen rapidly, from the location of the peak [36]. Additionally, since the phase is present in both alloys and GA-1-204 does not contain aluminum, the phase cannot be an Al containing oxide. The dispersoid phase was converted to a lower oxygen concentration in the GA-1-198 alloy during heat treatment, which can be seen through a peak shift to lower angle 2θ, as seen by Rieken et. al [51]. This shift was seen after rolling in the GA-1-204 alloy.

Microhardness measurements were performed on both alloys in the As-HIP, As-HT, and each of the rolled directions, see Figure 7.14 for orientations. The average of 5 microhardness measurements can be seen in Figure 7.18. A large microhardness drop can be seen after heat treatment in the GA-1-198 alloy. This corresponds to well with the conversion to an oxygen lean dispersoid seen in Figure 7.16 XRD. The conversion of the sample lead to an increase in the dispersoid size that is responsible for the decrease in strength. After this initial decrease, the strength of the GA-1-198 alloy remains fairly constant. The GA-1-204 alloy did not lose as much strength during heat treatment, but showed a drop in strength after rolling. This also corresponds to the coarsening of the dispersed phase. The GA-1-198 alloy had slightly higher strength than GA-1-204 and did not suffer due to the inclusion of aluminum as seen by Kimura et al [32]. The
strength in all of the different rolling directions was comparable, unlike previously available mechanically alloyed ODS materials that showed a 35% decrease in strength in the transverse direction [61].

Tensile specimens were created in the form of SS3 small type specimens. These specimens were created from both GA-1-198 and GA-1-204 in the transverse and longitudinal directions. The tensile bars were tested at temperatures of 20°C, 400°C, 600°C, and 800°C. The results of these tests can be seen in Figure 7.19 for GA-1-198 and in Figure 7.20 for GA-1-204 (due to sample material available the 600°C test was not able to be performed on GA-1-204). With increasing temperature the strength of the materials decreases, while the total elongation increases. The values for yield strength can be seen in Figure 7.27 and total elongation can be found Figure 7.28. In these figures, the values for MA956 and PM200 can be seen [62,63]. The strength of alloy GA-1-198 is intermediate between the alloys until 800°C where the strength falls below MA956. The operation temperature and planned $10^5$ rupture strength can be seen in Figure 7.27. It appears that the yield strength of the GA-1-198 alloy would be slightly below the desired rupture strength. By having an ideal oxygen content the dispersoids would have a finer distribution that would increase the strength of the alloys, likely to a point that it would be above the $10^5$ rupture strength. There is a peak in ductility that can be seen in MA956 and PM200 that occurs around 600°C. This ductility peak has also been observed in GARS produced alloys that do not contain Al [51]. This peak is not present in the GA-1-198 and GA-1-204 alloys, as shown by the high elongation in the 800°C test. This peak is present due to a transition from transverse to intergranular failure.
Figure 7.27: Tensile yield strength of GARS alloys compared to MA956 and PM2000 [62,63].

Figure 7.28: Total Elongation of GARS alloys compared to MA956 and PM2000 [62,63].

The corrosion rate of GA-1-98 and GA-1-204 in air can be seen in Figure 7.21 along with other samples tested at Oak Ridge National Laboratory. GA-1-204 sample had failure within 100 cycles due to the extreme operation temperature and protective nature of
chromia. GA-1-198 had a higher corrosion rate than PM2000, this is due to the low oxygen content of the alloy. Internal oxidation occurred similar to that of the FeCrAlY + Hf sample. Spallation occurred after an extended period of time, the corrosion behavior of GA-1-198 would be expected to improve with a more ideal oxygen content. Corrosion rates for the GARS alloys, as well as PM2000 and a FeCrAlY + Hf, can be seen in Figure 7.22. The increased corrosion rate in GA-1-198 is due to the low oxygen levels. A protective scale was formed and did not spall after 1000 hours in this atmosphere. Alloy GA-1-204 showed continuous decrease in weight after the initial mass gain. This is due to the volatilization of the chromia layer in the presence of water above 600°C. It would be expected that the corrosion rate of GA-1-198 would be closer to that of PM2000 with a more ideal oxygen content.

In order to investigate the effects of oxygen on corrosion resistance, the 15-25µm powder was consolidated in the as-atomized and ball milled for ~5 hour state. Ball milling will increase the oxygen content of the powders [64]. The as-atomized and ball milled powders can be seen in Figure 7.23. After ball milling the powders grow in size due to agglomeration and lose the spherical morphology. These powders were consolidated at 850°C for 4 hours at 300MPa. The same heat treatment, 1200°C for 5 hours, as the -8µm powders were used on these samples. The as-HIP and as-HT microstructures can be seen in Figure 7.24. The ball milled sample shows significant solute trapping and solutionization compared to the as-atomized powders. There are large Fe_{17}(Y,Hf)_{2} intermetallic phases present in the as-atomized sample at prior particle boundary junctions. Smaller intermetallic precipitates can be seen in the ball milled sample.

XRD data for the as-atomized sample in the powder, as-HIP, and as-HT states can be seen in Figure 7.25. The same data can be seen for the ball milled sample in Figure 7.26. It can be seen in both alloys that a precursor intermetallic compound is consumed during heat treatment in order to for the dispersoid phase. By balling a much finer dispersoid was able to be created with a crystallite size of 11nm in the ball milled state.
compared to 22nm in the as-atomized state. These sizes were found by looking at peak broadening and applying the Scherrer equation.

**Conclusion**

A non-aluminum containing comparison alloy, GA-1-204 was created with a similar composition to GA-1-198 from Chapter 5. The compositions of these alloys were extremely close in nature, with slightly elevated levels of yttrium and oxygen in alloy GA-1-204. The alloys were then consolidated through hot isostatic pressing and heat treated at 1200°C for 5 hours. This heat treatment was decided in Chapter 6 of this study, and was chosen in order to prevent the formation of FeHf$_2$ ht phase that could lead to crack initiation during rolling. The as heat treated bars were then prepped for rolling at 1000°C. Both alloys were successfully rolled to 70% reduction in thickness in 10% passes. This corresponds to ~50% reduction in area. The microstructures of both alloys were found to be similar. After rolling there was elongation of the prior particle boundary phases that could be seen in the normal direction. Both alloys progressed from precursor alloys to dispersoid phase to oxygen lean dispersoid phase during processing. Alloy GA-1-204 did not convert to an oxygen lean dispersoid until rolling, while GA-1-198 was converted during heat treatment. Microhardness was performed in as-HIP, as-HT, and all three rolling directions. Anisotropy seen in mechanically alloyed ODS materials was not evident in the as-rolled sample.

Type SS3 tensile bars were machined from both alloys and tested at room temperature and several elevated temperatures. Increasing the temperature of testing decreased the strength of the alloy while increasing elongation. The strength of GA-1-198 was between MA956 and PM2000 prior to 800°C. This strength at 800°C was below the desired specification for the next generation A-USC coal fired power plants. This strength may be possible with a more ideal oxygen content. The ductility peak typically observed ODS alloys around the 600°C temperature as failure transitions from transverse to intergranular failure was not present in alloys GA-1-198 or GA-1-204. Alloy GA-1-204 had much lower strength at lower temperatures, but had slightly higher tensile strength at 800°C. Corrosion testing was
performed on both alloys in air and in 10 vol% water atmospheres. Alloy GA-1-204 was not protective in either atmosphere. GA-1-198 showed elevated levels of mass gain caused by internal oxidation from low oxygen content. By increasing the oxygen content of the alloy, corrosion rates should improve. GA-1-198 formed a protective oxide layer that did not spall in the water containing atmosphere. However, spallation did occur in the 1200°C atmosphere. This spallation may be prevented by having an ideal oxygen content.

A short term ball milling was shown to lead to a better distribution of intermetallic compounds that are the precursor for the dispersoid phase. The balling milling can also be used to increase the oxygen content as a process refinement method. These characteristics can lead to more utilization of an atomization run by making larger particles more desirable.
CHAPTER 8: Conclusions

In an effort to meet the conditions of the next generation advanced ultra-supercritical (A-USC) coal-fired power plants, an investigation into ferritic oxide dispersion strengthened (ODS) alloys containing aluminum was performed. Two different production methods, mechanical alloying (MA) and gas atomization reaction synthesis (GARS), were analyzed. GARS was chosen to produce an aluminum containing ODS alloy. In order to meet the corrosion resistance in steam atmospheres, a balance of aluminum and chromium were chosen. Aluminum has been shown to decrease the strength of ODS alloys, due to formation of complex Y-Al oxides. Hafnium has been shown to have the potential to retain the strength with aluminum. The final alloy composition was chosen to be Fe-16Cr-12Al-0.9W-0.25Hf-0.2Y at%.

The aforementioned alloy was created through the GARS process and named GA-1-198. Powder that was -20µm was consolidated through hot isostatic pressing (HIP). Y₂Hf₂O₇ dispersoids were created during the HIP cycle, showing that the GARS process was viable for aluminum containing ODS materials created with aluminum. A further investigation into the heat treatment process was necessary due to reaction of the powders during the HIP cycle. A -8µm sample was consolidated in order to investigate the heat treatment parameters. Temperature effects on heat treatments were investigated. It was found that all heat treatment temperatures below 1200°C had precipitation of the FeHf₂ ht phase. This phase was present in clusters and could be points of crack initiation during rolling operations during processing. For this reason 1200°C was chosen as the heat treatment temperature. The time effects on heat treatment were also considered in order to try to homogenize the alloy to prevent precipitation of the FeHf₂ ht phase during rolling at 1000°C. The rolling operation was simulated by a 2 hour anneal at 1000°C, which was found to not lead to precipitation after a heat treatment at 1200°C for 5 hours. For this reason, the heat treatment time was chosen to be 5 hours.
A comparison alloy GA-1-204 was created through the GARS process with the same composition as GA-1-198 without aluminum. This alloy was consolidated through a HIP cycle at 850°C for 4 hours with 300MPa hold time. Both alloys were rolled to 70% reduction in thickness in 10% passes at 1000°C. The microhardness of the As-HIP, As-HT, and all three rolled directions for each sample was taken. It was found that there was a decrease in hardness after heat treating in GA-1-198 that corresponded to conversion of the dispersoid to an oxygen lean composition. There was no strength decrease in the transverse direction that is typical in mechanically alloyed ODS alloys. Tensile specimens were also created from the rolled bars. The strength of the alloy GA-1-198 was between MA956 and PM2000 until it fell just below the MA956 strength at 800°C. GA-1-204 had lower strength at low temperatures than GA-1-198, but upon testing at 800°C, the strength was very comparable, probably due to dispersoid strengthening being the primary mechanism. The total elongation of the GA-1-198 alloy did not exhibit a ductility peak around 600°C that is typical in ODS alloys, instead the ductility continued to rise nearing 100% elongation at 800°C. A similar trend was seen in alloy GA-1-204. Corrosion testing was performed in air at 1200°C and in air with 10 vol% water at 1100°C. GA-1-204 failed in the air atmosphere and exhibited mass loss in the water containing atmosphere. GA-1-198 had increased mass gains compared to MA956 and PM2000 due to low oxygen content in the alloy. Spallation occurred in the air containing atmosphere for GA-1-198, however a protective oxide film was found in the water containing atmosphere up to 1000 hours.

In the current condition, the materials created should be able to operate in the conditions desired, but not at the goal requirements. The tensile strength of the alloys is slightly below that of the goal for the 10^5 hr creep testing. The oxidation in air showed some spallation which may be detrimental to performance, but in a H_2O containing atmosphere the scale seemed to be protective, indicated by a stable parabolic growth. The oxidation testing was performed at a much higher temperature than the operation conditions and will be greatly accelerated. Improvements to both the strength and
corrosion resistance should come through a balanced ratio of O to dispersoid forming elements. Through refinement of alloy selection to include a better balance, the strength required for the A-USC conditions may be attainable. Powder yield from atomization runs can be improved through short term ball milling. During the ball milling, oxygen can also be introduced to obtain a more optimal alloy composition. The target powder size was initially set for -5µm and caused issues with low oxygen numbers since a larger powder size had to be used for an adequate sample. A target size range of -10µm may be a better estimation in order to obtain enough material for testing of the material properties.
References


[18] Joel’s Thesis


[51] Ask Joel what paper to cite for his oxidation results, not listed in his thesis what paper.


