A COMBINATORIAL APPROACH TO THE DEVELOPMENT OF A CREEP RESISTANT BETA TITANIUM ALLOY

DISSERTATION

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ABSTRACT

Timetal 21S has been selected as a baseline for the development of a new high temperature beta titanium alloy. A combinatorial approach employing directed laser deposition of elemental powders has been used to produce a number of test coupons with controlled variations of composition. In addition to the variation of the baseline elements (Ti, Mo, Nb, Al and Si), the alloys contain varying amounts of neutral elements (Zr and Sn), beta-stabilizers (W) and dispersoid formers (B, C and Ge). Subsequently, the creep properties, represented by their minimum creep rates, have been assessed using an Instron Electrothermal Mechanical Tester (ETMT). The microstructures of the test coupons have been characterized using a range of techniques and have been quantified using rigorous stereological techniques to populate databases and subsequently train and test Bayesian Neural Network models for the prediction of creep properties. Additionally, advanced characterization techniques and computation tools have been employed to aid in the identification of the creep rate-limiting microstructural features. For example, SEM and TEM studies show a critical dependence of the size of α-denuded β regions on the creep properties in these β-Ti alloys. The most important microstructural features (volume
fraction $\alpha$, $\alpha$ lath thickness and $\beta$ mean free path) and alloying additions (Sn and Ge) have been identified and are discussed.

The ETMT, used to investigate creep properties in the work, has also been characterized and compared with traditional tensile and creep testing methods. Computational models incorporating heat transfer and electrostatics were used to investigate the temperature profiles that result from the interaction of joule heating, conductive cooling and radiative cooling in subscale Ti-6Al-4V samples at five current densities in the ETMT. The tensile properties, including YS, UTS, E and total elongation, of sub-scale specimens have been evaluated over a range of temperatures and a variation of microstructural features in $\alpha+\beta$ and $\beta$-processed Ti-6Al-4V using the ETMT and traditional methods. The creep properties for Timetal 21S, $\alpha+\beta$ and $\beta$-processed Ti-6242 are compared with legacy data and traditional means. It was found that the applied direct current increases the minimum creep rate.
DEDICATION

To God, my family and to those whose lives I will hopefully influence for the better.

To Vanessa, who means more to me than life itself.
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CHAPTER 1

1 INTRODUCTION AND PROBLEM STATEMENT

There is a need to develop a titanium-based sheet alloy that is both thermally and mechanically stable at elevated temperatures (operating temperatures up to 650°C) for acreage thermal protection systems (acreage TPS) used in hypersonic aerospace vehicles. Titanium is the material of choice due to its advantageous specific strength in comparison with other structural alloys. This application also requires that the material be cold rollable for manufacturing sheet product, have good oxidation and corrosion properties and maintain strength and ductility at reduced and elevated temperatures [1, 2]. Beta titanium alloys are commonly used in aerospace applications where strength, oxidation and corrosion properties are of significant concern; however, their performance at elevated temperature is a limiting factor to their efficacy. Other titanium-based alloys such as α and near-α alloys are often used in these higher temperature regimes, but do not have the formability, oxidation and corrosion properties of typical β titanium alloys. For optimal results, acreage TPS requires an alloy that satisfies all criteria: high specific strength, cold rollable, oxidation and corrosion resistance and creep resistance. Timetal 21S (Ti-15Mo-3Al-2.7Nb-0.2Si wt%), a β-titanium alloy, has been recommended for
creep property improvement to meet these needs due to its excellent corrosion and oxidation resistance and cold rollability (room temperature ductility) compared with other titanium alloys [3].

Generally, creep properties of titanium alloys improve as the $\alpha$-stability (i.e. the volume fraction of alpha) increases. This improvement in creep properties may be illustrated using a Larson-Miller plot (see Fig. 1.1), where creep resistance improves from left to right and from bottom to top. This plot contains data for several titanium alloys, including Timetal 21S, $\alpha+\beta$ and $\beta$-processed Ti-6Al-2Sn-4Zr-2Mo, which are beta and near-alpha titanium alloys, respectively [4]. Timetal 21S exhibits attractive creep properties, including similar, if not improved, creep resistance compared with Ti-6Al-4V, a $\alpha/\beta$ titanium alloy. This is notable given the fact that beta alloys typically exhibit poorer creep performance than $\alpha/\beta$ alloys.

**0.2% Creep Comparison for Multiple Alloys**

![Larson-Miller plot of several titanium alloys](image)

Fig. 1.1: Larson-Miller plot of several titanium alloys [4].
Given that Timetal 21S is nearly an ideal material for acreage TPS, the focus of this research is to slightly improve the creep resistance by increasing its stable operating temperature from approximately 600 to 650°C. This increase in creep resistance can be achieved by modifying the composition or constituents of the microstructure by varying the bulk composition or material processing. Given that Timetal 21S is presently used in an over-aged, stable condition, this research explores whether small changes in composition result in improved creep resistance without significantly degrading other properties of importance in acreage TPS (i.e. the oxidation resistance and cold rollability).

Compositional modifications and additions that are expected to improve creep resistance are added to the base alloy, tested and characterized. To achieve this, certain types of elements are identified and added, based on their potential to favorably influence the creep properties of the alloy. The first set of alloy elements identified may potentially retard diffusion of the atoms and vacancies. These elemental species are relatively large atoms that include variations of Mo and Nb (already included in the alloy) as well as three others: W, Sn and Zr. A secondary effect of these larger atoms is their potential to impede dislocation motion by solid solution strengthening. To further explore whether the α phase stability or solid solution strengthening could improve creep properties, variations in the α-stabilizer, Al, are also studied. The second set of alloying elements includes those that potentially influence creep mechanisms involving dislocation motion and grain boundary sliding. Thus, precipitate forming elements B and C are added to
form coarse precipitates at micrometer length scales, while Si and Ge are added to potentially form fine precipitates at nanometer length scales.

The examination of these elemental additions on the base alloy and their combinations requires an accelerated materials maturation approach. Otherwise, to systematically understand the effect of these additions by traditional experimental means could require significant time and monetary commitments. The use of state-of-the-art equipment, accelerated creep simulators and rules-based models can significantly decrease the time and money required to develop alloys for high temperature applications. The methods used in this work for the rapid development and investigation of these alloy modifications are given below.

- An additive manufacturing process via the LENS™ to make and process the individual alloy compositions.
- A hot isostatic press (HIP) for thermal and pressure treatment of the LENS™ deposits.
- An electrothermal mechanical tester (ETMT) to measure the creep performance of the alloys from sub-scale specimens.
- Stereological procedures to estimate the 3-D size scale of the major microstructural features.
- Artificial experiments via neural network analysis to gain understanding of the effects of each composition and microstructural parameter on a mechanical or microstructural property.
Of these methods, the ETMT has not been previously used to determine significant amounts of mechanical property data, tensile or creep and has not been used to measure the mechanical properties of titanium alloys. Therefore this research includes a special investigation and validation to understand the precision and accuracy of the tensile and creep data produced by the ETMT as compared with conventional test techniques using a common titanium alloy, Ti-6Al-4V.

It is important to keep in mind that the scope of this work is not to characterize or implement a scheme to replace traditional production, testing or characterization techniques for alloy development, but to further develop new techniques to supplement tried and tested traditional methods. Ideally, the present methodology for the improvement of creep properties of Timetal 21S could to be used to quickly identify regions of compositional space that improve and degrade desired properties for other alloy systems.
CHAPTER 2

2 BACKGROUND AND LITERATURE REVIEW

This research incorporates recent characterization and alloy development techniques such as artificial neural network models (Bayesian Statistics), directed laser deposition (LENS™) and subscale thermomechanical tests (ETMT) methods to improve the creep resistance of Timetal 21S. The following chapter first presents and discusses the background and recent work in the literature regarding alloy development by means of neural networks and the LENS™ process. Then a brief introduction of metallurgy of β titanium alloys and Timetal 21S is presented. Creep in β titanium alloys is also discussed along with major creep operating mechanisms and some background behind the potential creep-improving alloy additions used in this work. Finally, small scale mechanical testing will be discussed with a focus on the electrothermal mechanical tester (ETMT) and some of its previous uses.

2.1. Recent Advances in Alloy Development

2.1.1. Use of Neural Networks in Characterizing Titanium Alloys

Due to the complexity of composition-microstructure-property relationships in titanium alloys there has been an increase in the use of rules-based models, such as
artificial neural networks, to relate complex microstructures to the resulting properties [5-14]. As a precursor to neural network modeling of titanium alloys, qualitative estimations of the effect that microstructural features have on mechanical properties were determined by conventional experimentation. Lütjering and Albrecht investigated the effect of cooling rate on various $\alpha/\beta$ titanium alloys and in turn approximated the effect of changing the size of various microstructural features on a range of mechanical properties. For example, it was found that a decrease in alpha lath thickness increases yield stress. It was also discovered that a decrease in the prior beta grain size had no effect on the yield stress but improves the ductility by reducing the slip length along the prior beta grain boundaries [15]. Table 2.1 is a summary of the effects of several microstructural features on mechanical properties as proposed by Lütjering [16]. Qualitative predictions are critical to the understanding of these alloys, but a reliable method or set of tools for quantitative predictions potentially offers more freedom in titanium alloy processing and selection.
Numerical models based upon Bayesian Statistics have been exploited for the prediction of tensile properties in both \( \beta \) and \( \alpha+\beta \)-processed Ti-6Al-4V by Kar et al. [8, 17]. Specifically, their approach was based on neural network models incorporating Bayesian Statistics developed by MacKay [18, 19]. Fig. 2.1 is a simple schematic depicting the layer-type architecture of Bayesian Statistics. The model consists of numerical input data (i.e. measured compositional or microstructural values), equations involving various numbers of nodes, weights and biases in the hidden layer and a computed output value [8, 17, 20]. An explanation of the derivation and details of the hidden layer will not be offered but readers are directed to the previous citations.

Table 2.1: Qualitative descriptions (+/0/-) of the effects of several microstructural features on various mechanical properties [14, 16].

<table>
<thead>
<tr>
<th>( \alpha+\beta ) Titanium Alloys</th>
<th>( \sigma_y )</th>
<th>( \varepsilon_f )</th>
<th>HCF</th>
<th>Microcracks</th>
<th>Macrocracks</th>
<th>Creep Strength</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aging (( \alpha_2 )) Oxygen</td>
<td>+</td>
<td>-</td>
<td>+</td>
<td>-</td>
<td>-</td>
<td>+</td>
</tr>
<tr>
<td>Bi-modal Structure</td>
<td>+</td>
<td>+</td>
<td>-/+</td>
<td>+</td>
<td>-</td>
<td>-/-0</td>
</tr>
<tr>
<td>GB ( \alpha )-Layers</td>
<td>0</td>
<td>-</td>
<td>-</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Small ( \alpha )-Colonies</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>( \alpha )-Lamellae</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 2.1: Qualitative descriptions (+/0/-) of the effects of several microstructural features on various mechanical properties [14, 16].
Neural network models based on Bayesian Statistics typically require larger amounts of data in comparison with other non-linear regression models such as Fuzzy Logic methods, but are unbiased and can result in better predictions. Kar et al. experimentally compiled a dataset of 86 points, each containing microstructural (input) and mechanical property (output) data. Approximately 80% of the data was used to train the model, which involves determining the optimum values for the nodes, weights and biases for the hidden layer equations. The remaining 20% of the data was used to test the model for accuracy. Based on data from the numerical quantification of microstructural features, Kar et al. predicted tensile data to within ±3% error [8]. A plot of experimental versus predicted data can be used as a visual inspector of the model accuracy. Fig. 2.2 shows that that the accuracy is well within ±5% for yield stress prediction. An ideal model that precisely predicted the experimental value would plot a straight line with a slope of one on an experimental versus predictive data plot.
These developed neural network models can be used in one of two ways. The first involves the development of a predictive tool, where the properties of a test dataset are predicted. If the model is accurate, it can be a very powerful tool for industrial applications involving material selection and design. Coupled with additional models that implement the prediction of properties based upon composition and thermomechanical processes, it may be possible for designers to quickly determine ideal composition and processing methods to achieve product specifications. Kar also developed Java-based applets that act as simple user interfaces; giving the ability to artificially vary input parameters such as $\alpha$ lath thickness and volume fraction of $\alpha$ lath colonies to determine an output such as YS, UTS or percent elongation in Ti-64 [17]. Fig. 2.3 is a screen shot of
a Java applet that predicts yield stress. Once ideal parameters are chosen, based on artificially varied parameters, the difficult task can be to realistically achieve the parameters in a real sample.

![Screen shot of a Java-based property predictive tool](image)

**Fig. 2.3:** Screen shot of a Java-based property predictive tool [17].

The second involves the use of the developed model to perform virtual experiments. These are usually controlled experiments where the values of given microstructural features can be set to, or held at, constant values (i.e. their average). In this way, it is possible to obtain information even when actual experiments with such control of individual microstructural features are not possible. One such experiment is the virtual determination of the functional dependencies. The functional dependencies are determined by setting all but one variable at a fixed average value and allowing that
variable to fluctuate while observing the change in the predicted property. The predicted property can then be plotted directly against this single variable, which can provide insight into the functional dependency of the output on the variable. Fig. 2.4 is one such experiment by Kar where it is clearly seen that an increase in \( \alpha \) lath thickness decreases YS [17]. Kar et al. also found that a decrease in colony size and increase in volume fraction total \( \alpha \) increases strength properties. It was also confirmed that fine grain sizes increase strength properties; however, these neural networks also indicated an increase in strength properties for significantly large grain sizes due to the increased formation of basketweave microstructure in larger prior beta grains [8].

![Graph showing the effect of \( \alpha \) lath thickness on YS](image)

Fig. 2.4: Virtual experiment of the effect of \( \alpha \) lath thickness on YS (all other model inputs were held at constant values) [17].

The previously developed models for the prediction of tensile properties have resulted in differences of less than 3% from experimentally measured values for both
yield strength and ultimate tensile strength [8]. While such results have been quite successful in the prediction of tensile properties, the application of neural network models to the prediction of creep properties in β-Ti alloys has never been performed. A portion of this work will be to show the scale of error associated with developed models for the prediction of creep properties.

2.1.2. Use of the LENS™

The Laser Engineered Net-Shape (LENS™) process was developed and produced by Sandia National Labs and Optomec. It is an additive manufacturing technique that employs a Nd:YAG laser with a wavelength of 1.064 μm to melt focused streams of metallic powder and substrate, which then rapidly solidify [21, 22]. Fig. 2.5(a) depicts how the laser, focused powder streams and substrate are at the same focal point as the substrate rasters in the plane perpendicular to the laser; which creates a plane of material with finite thickness. Once a layer is completed, the laser focus raises approximately 0.010” with respect to the substrate and powder streams and continues sequentially to create a three-dimensional object [23]. Fig. 2.5(b-c) depict the process in action and an example of a finished part (turbine blade). An important parameter for LENS™ deposition is the energy density, \( \rho_{\text{energy}} (\text{J/in.}^3) \), which is defined in equation 2.1 by the laser power, \( P_l \) (watts), layer spacing, \( T_{ls} \) (in.), hatch-width, \( T_{hw} \) (see Fig. 2.5a) (in.) and travel speed, \( V_l \) (in./sec) [23]. As an additional resource, a fairly complete literature review of the major aspects of the LENS™ process and the details of the system at The
Ohio State University, which was used for this work, has recently been completed by Collins [23].

Fig. 2.5: Depicting the LENS™ process: (a) schematic, (b) LENS™ in action and (c) completed turbine [23].
Equation 2.1: \[ \rho_{\text{energy}} = \frac{P_l}{(T_s * T_{hw} * V_l)} \] [23].

The LENS\textsuperscript{TM} system at The Ohio State University has dual-powder feeders, which allow for rapid changes in the alloy composition in a controlled, programmed fashion. This offers the capability of using either pre-alloyed powder or blends of elemental powder. Blends of elemental powder can be advantageous due to high costs associated with customized pre-alloyed powders. Schwendner et al. [24] and Collins et al. [25] investigated the use of elemental blends in titanium alloys and found that the enthalpy of mixing between the elemental powders is important. They deposited Ti-10Nb and Ti-10Cr (wt\%) under similar conditions and found that the Cr-containing alloy resulted in a more homogenous deposition because of the lower enthalpy of mixing Cr with Ti than Nb with Ti [24]. Collins et al. performed a very similar experiment with Timetal 21S (Ti-15Mo-3Al-2.7Nb-0.2Si) by depositing pre-alloyed powder, blended elemental powder and blended elemental powder with Cr replacing the Mo (Cr has a lower of enthalpy of mixing with Ti than Mo) for a composition of Ti-9.4Cr-2.7Nb-3Al-0.2Si wt\% [25, 26]. It was again concluded that the enthalpy of mixing appears to have a significant effect on the homogeneity of the deposited alloys from elemental blends. It is suggested that an appropriate increase in energy density (J/in.\textsuperscript{3}) be applied to adapt relatively endothermic combinations of blended elemental powders for LENS\textsuperscript{TM} deposition.

The LENS\textsuperscript{TM} process was recently employed to rapidly investigate the composition-microstructure-property relationships in various titanium alloys by varying
the composition in situ [7, 23, 27-29]. Collins et al. used a dual-powder feeder system to build a graded composition with a LENS™ system by varying the amount of powder from each feeder during a deposition (see Fig. 2.6(a)). This allows for a range of compositions to be examined for microstructural and mechanical property (i.e. hardness) variations (see Fig. 2.6(b)) from a single deposit [29]. Collins et al. also used the LENS™ to rapidly populate a database based on the Ti-xAl-yV system. Composition-mechanical property, microstructure-mechanical property and composition-microstructure relationships were determined via virtual experiments derived from Fuzzy Logic-based statistics. Fig. 2.7(a-b) are virtual experiments that show that increasing Al and V content both increase YS. It was also determined by these methods that increasing Al and V content increase UTS, increasing α lath thickness decreases YS and increasing V content decreases the colony scale factor while increasing Al content increases it [7, 23].
Fig. 2.6: From a Ti-Mo gradient deposit: (a) composition versus distance and (b) hardness as a function of composition [29].
Fig. 2.7: Sample Fuzzy Logic-based virtual experiments of the effect of (a) Al and (b) V on YS (all other inputs held constant) [23].
The LENS™ process has never been directly combined with Bayesian Statistics to develop models exploring composition-microstructure-property relationships. However, based on the success of previous modeling of conventionally processed materials using the LENS™ combined with Fuzzy Logic methods and Bayesian Statistics, the two are expected to be compatible for use in developing a model for increased creep resistance in Timetal 21S.

2.2. Beta Titanium Alloys

2.2.1. Metallurgy

Titanium-based alloys consist of two major phases, $\alpha$ and $\beta$ and the stable quantities at room temperature are used to classify them ($\alpha$, near-$\alpha$, $\alpha/\beta$ and $\beta$). The $\alpha$ phase is the low temperature phase and has a hexagonal close packed (hcp) crystal structure with lattice parameters of 0.295 nm and 0.468 nm for the a and c axis, respectively. The $\beta$ phase, which has a body-centered cubic (bcc) structure with a lattice parameter of 0.332 nm, is the higher temperature phase that is stable above ~882°C in CP Ti [30, 31]. This temperature is classified as the $\beta$-transus. Elemental additions affect this transition temperature as well as the amount of $\alpha$ and $\beta$ phases that are stable in equilibrium at a given temperature. The elements Al, Ga, Ge, La, Ce, O, N and C stabilize the $\alpha$ phase, also driving the $\beta$-transus temperature up. Of the $\alpha$-stabilizing elements, Al is the most widely used in titanium. Hence, an Al equivalency equation (see
Equation 2.2) gives an idea of how much the $\alpha$ phase is stabilized by other $\alpha$-stabilizing elements, using Al as a reference point [32].

Equation 2.2 \[ \text{Al_{equiv.}} = \text{Al} + 1/3\text{Sn} + 1/6\text{Zr} + 10(\text{O+C+2N}) \text{ wt}\% \] [32]

Likewise, a Mo-equivalency equation (see Equation 2.3) generally describes the stability of the $\beta$ phase [26]. As the Mo equivalency increases, the $\beta$–transus temperature drops and more $\beta$ phase is stable at room temperature. Fig. 2.8 is a pseudo-binary phase diagram that describes the effect of $\beta$-stabilizing content on the $\beta$–transus temperature and formation of other phases [33].

Equation 2.3: \[ \text{Mo-equiv.} = \text{Mo} + 0.67\text{V} + 0.44\text{W} + 0.28\text{Nb} + 0.22\text{Ta} + 1.6\text{Cr} + 2.9\text{Fe-Al wt}\% \] [23, 26]

Fig. 2.8: Schematic depicting a pseudo-binary phase diagram as a function of the amount of $\beta$-stabilizers present [33].
Beta titanium alloys (also known as metastable β titanium alloys) are defined to have enough β phase stabilizing elements to completely retain the β phase upon quenching to room temperature. Another characteristic of these alloys is the absence of martensite (α’ or α”) formation, which primarily forms in titanium alloys with low β phase volume fractions with the proper cooling rate. Beta Ti alloys are typically cold rollable and are more ductile than α/β Ti alloys [31].

These alloys are also responsive to aging heat treatments at intermediate temperatures below the β-transus, which nucleate and grow α laths (see Fig. 2.9 as an example SEM micrograph of LENS™ deposited Timetal 21S). Upon cooling from the β phase field, the α phase forms at nucleation sites, which include prior β grain boundaries and other high-energy surfaces [31, 32, 34]. Faster cooling rates and lower aging temperatures increase the density of α laths due to the increased under-cooling, which causes the number of active nucleation sites to increase [32]. Microstructures are typically stabilized at intermediate temperatures to achieve a desired α lath distribution and equilibrium α volume fraction. Li et al. found that lower aging temperatures (600°C) in Ti-25V-15Cr-2Al-0.2C, a burn resistant beta alloy, allowed for evenly distributed α lath formation on and in the grains, creating a more homogeneous microstructure. Higher aging temperatures (700 and 800°C) promoted α growth at the grain boundaries, which decreased the ductility [35]. The α lath thickness, distribution and volume fraction have significant effects on mechanical properties. For a given volume fraction α, as the lath
thickness decreases the strength increases. As the average spacing between the laths decreases, dislocation motion is restricted to smaller volumes [15, 36].

Fig. 2.9: BSE micrograph of a sample microstructure (LENS™ deposited Timetal 21S). The matrix phase is \(\beta\) titanium and the dark, precipitates are \(\alpha\) laths.

2.2.1.1. \(\alpha\) & \(\beta\) Phase Orientation Relationship

The \(\alpha\) phase forms in preferential orientations with respect to the parent \(\beta\) matrix upon cooling according to the Burgers orientation relationship:

Burgers orientation relationship: \(\{110\}_\beta \parallel \{0002\}_\alpha \) and \(<111>_\beta \parallel <\overline{2}110>_\alpha\) [37]

The close packed planes of the hcp \(\alpha\) phase form on the closest packed planes of the bcc \(\beta\) parent phase; the close pack directions of each crystal structure are also aligned (see Fig. 2.10) [38]. There are 12 distinct \(\alpha\) phase variants that form upon cooling. The basal plane in the \(\alpha\) phase is parallel to one of six \(\{110\}\) planes of the \(\beta\) phase and one of the
<11\bar20> directions in the same basal plane is also parallel to one of two <111> directions on the \{110\} plane [39].

Fig. 2.10: Burgers orientation relationship between the \(\alpha\) and \(\beta\) phases in titanium alloys.

2.2.1.2. \(\omega\) Formation and \(\beta\)–phase Separation

The formation of the \(\omega\) phase, also found in fig. 2.8, is often found in \(\beta\)–stabilized Ti alloys. It has a hexagonal crystal structure formed either by a diffusionless transformation (athermal \(\omega\)) upon quenching from an elevated temperature or an isothermal transformation by aging at an intermediate temperature (~300°C) [31]. The formation of \(\omega\) can often be undesirable due its embrittling effect on titanium. However, small \(\omega\) precipitates formed first by quenching then followed by aging can act as nucleation sites for the \(\alpha\) phase [40-42]. This can be an effective method for producing a homogenous and finely dispersed \(\alpha\) phase [40]. Selected area diffraction (SAD) patterns
in the transmission electron microscope (TEM) are often used to detect small scale formation of $\omega$ precipitates in the $\beta$ phase (see Fig. 2.11) [31, 34]. As the $\omega$ phase grows from small to larger precipitates the diffuse streaks in the SAD pattern change to definitive extra spots (reflections) [31, 43]. Different shapes of $\omega$ form depending on the misfit of the $\omega$ phase in the matrix [44, 45]. Varying interfacial energies created by lattice misfits in different lattice directions causes various precipitate shapes to form [31, 33]. Ellipsoidal and cuboidal $\omega$ precipitates form in Mo and V $\beta$-stabilized alloys, respectively (see Fig. 2.12 and Fig. 2.13) [31].

Fig. 2.11: Selected area diffraction pattern depicting the presence of $\omega$ [34].
Fig. 2.12: Ellipsoidal $\omega$ stabilized by Mo [31].

Fig. 2.13: Cuboidal $\omega$ stabilized by V [31].
In β–titanium alloys, β₁ forms as a phase separation from the β phase typically during a low temperature age in alloys with high β-stabilizing content (see Fig. 2.8). The β₁ structure is still bcc but with a different concentration and slightly different lattice parameter than β [31, 33]. The β₁ phase is typically small and refined and can be used in subsequent thermal heat treatments at elevated temperatures to nucleate the α phase to form a homogeneous distribution.

2.2.2. Timetal 21S: Ti-alloy with Improved Oxidation and Corrosion Resistance

As mentioned previously, titanium is very susceptible to oxidation at elevated temperatures. It is often used as a ‘getter’ to purify an atmosphere of oxygen. Fig. 2.14 is an Ellingham diagram of several simple metals, including titanium (near the bottom), which shows the free energy of formation of a given oxide (i.e. TiO₂) [46]. Lines lower on the plot oxidize more readily and have stable oxides. The stable oxide of titanium allows it to be used in corrosive environments at room temperature. However, at elevated temperatures, oxygen can diffuse through the surface creating an α-case and a thicker oxide layer, which is often detrimental to mechanical properties. The α-case formation can lead to spalling leaving fresh titanium, which can react violently with oxygen, even causing titanium fires [47, 48]. Ti-V-Cr alloys (β-alloys) have been developed to be burn resistant [49]. After the TiO₂ oxide layer spals, a Cr₂O₃ oxide is still present to prevent the bulk from burning violently.
Fig. 2.14: Ellingham diagram depicting the standard free energy of formation for various oxides as a function of temperature [46, 50, 51].
Timetal 21S (Ti-15Mo-3Al-2.7Nb-0.2Si wt%), also known as β–21S, was designed for improved oxidation and corrosion resistance up to 650°C. Table 2.2 shows the weight gain of Timetal 21S versus two other Ti-based alloys [4]. It has similar creep resistance to Ti-64 and has good thermal stability. After proper heat treatment (500-700°C for 8-16 hours) below the β transus (~815°C), it has a stable microstructure for 1000 hours at temperatures up to 615°C. These favorable attributes combined with its cold rollability also make it ideal for many applications including metal matrix composites [4]. A large portion of the phase stability at temperature is attributed to the moderately large Mo content, due to Mo’s low diffusivity in comparison with Ti and the other elements. Table 2.3 is a list of reported diffusion coefficients and diffusion distances of Mo in Ti at various temperatures. The diffusion coefficients appear to be extremely fast and likely incorrect [52]. Upon back-calculating the diffusion coefficient using the diffusion distance and time, the actual diffusion coefficient should be approximately $2.07 \times 10^{-16}$ m²/sec for 650°C. There is likely an unintended omission of the negative signs in the data table.
### Oxidation Resistance - 650°C exposure

<table>
<thead>
<tr>
<th>Material</th>
<th>Weight Gain (mmg/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>24 hrs</td>
</tr>
<tr>
<td>Timetal 15-3</td>
<td>1.26</td>
</tr>
<tr>
<td>CP Ti</td>
<td>0.18</td>
</tr>
<tr>
<td>Timetal 21S</td>
<td>0.06</td>
</tr>
</tbody>
</table>

Table 2.2: Weight gain of Ti-15-3 (β Ti), CP titanium and Timetal 21S [4].

### Calculated values of the diffusion distance of molybdenum

<table>
<thead>
<tr>
<th>Ageing temperature (°C)</th>
<th>Ageing time (h)</th>
<th>Diffusion coefficient, $D$ (m²s⁻¹)</th>
<th>$(D*t)^{1/2}$ (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>650</td>
<td>2</td>
<td>2.07x10¹⁶</td>
<td>1.22</td>
</tr>
<tr>
<td>600</td>
<td>2</td>
<td>7.20x10¹⁷</td>
<td>0.72</td>
</tr>
<tr>
<td>600</td>
<td>10</td>
<td>7.20x10¹⁷</td>
<td>1.61</td>
</tr>
<tr>
<td>500</td>
<td>2</td>
<td>5.86x10¹⁸</td>
<td>0.21</td>
</tr>
<tr>
<td>500</td>
<td>18</td>
<td>5.86x10¹⁸</td>
<td>0.62</td>
</tr>
<tr>
<td>500</td>
<td>54</td>
<td>5.86x10¹⁸</td>
<td>1.07</td>
</tr>
</tbody>
</table>

Table 2.3: Diffusion distance of Mo in Ti for several temperatures [52].

Compared with other high volume materials (steel and aluminum), titanium has superior corrosion resistant and has found many uses in the petrochemical and aerospace industries. Beta titanium alloys are especially corrosion resistant (see Fig. 2.15) [53]. Hot hydraulic fluid (Skydrol) can be very corrosive to titanium alloys, but Timetal 21S performs very well because of the high Mo content and Nb additions [53, 54].
2.3. Creep and Creep Properties of β Titanium Alloys

Creep is time dependant deformation below the yield stress and at elevated temperature ranges, depending on the material and alloy [55, 56]. Fig. 1.1 is a Larson-Miller plot of various titanium alloys which shows that the creep temperature range of these alloys is approximately 200-650°C (200-450°C for β-Ti alloys) [4]. The Larson-Miller plot is a method to visualize the creep response of a material by combining time and temperature into a single Larson-Miller Parameter, P, which is then plotted versus stress. It is implied from fig. 1.1 that as the α volume fraction increases, the creep resistance improves; from left to right on the L-M plot: β, α/β, near α, α, γ and Ni alloys respectively. One exception is Timetal–21S, which has similar or slightly improved creep properties as compared with Ti-64, an α/β-Ti alloy [4].

Fig. 2.15: Corrosion rate profiles in boiling HCL for several aged alloys [53].
2.3.1. Creep Testing

Creep tests are typically performed near or above half the melting point of the material in a load, stress, or strain controlled test frame in tension or compression. Fig. 2.16 shows an example of a stress controlled tensile creep frame, which varies the applied load to account for changes in cross-sectional area to maintain a constant stress [56]. A stress or load controlled creep test will typically exhibit stage I, II and III creep. The primary (I) stage has increased creep resistance, the secondary (II) stage creeps at an approximately constant rate, while the tertiary (III) stage involves the onset of microcracks and voids which leads to failure (see Fig. 2.17) [56]. Stage II creep can also be defined by a minimum creep rate which occurs before the onset of stage III creep.

Fig. 2.16: Creep machine with variable $l_2$ lever arm to maintain constant stress on the sample. (a) initial position. (b) specimen with increased length [56].
Small variations in test setup and measurement (i.e. temperature, stress, axially and sample dimension measurement) and/or sample composition and microstructure can cause variations in creep data measurement [57]. Creep rupture tests of 316 stainless steel performed in the early 1980’s at 57 different labs in nine countries found that tests to around 10,000 hours had data scatter equivalent to about ±10% deviation in stress [58]. It was found that small differences in chemical composition, heat treatment and test temperature were sources of general creep data variation.

There is limited data in the literature about the variation in minimum creep rate values between tests of identical composition and thermomechanical history. Variation in creep rate values may be expected to be larger in tensile tests where the variation in yield stress may be on the order of one percent. Fig. 2.18 is a plot of steady-state creep rate as a

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**Fig. 2.17:** Creep strain versus time for three separate constant stresses (constant temperature) [56].
function of the volume fraction of primary $\alpha$ for Ti-6242S. It is interesting to note that the size of the error bar on the plot is fairly significant ($\sim 1 \times 10^{-9}$), in comparison with the $y$-axis values. This error can apparently be up to 100% for a given data point, which is significant [3]. Chapter 4 discusses the observed variation in minimum creep rate data for this work.

Fig. 2.18: Effect of primary $\alpha$ on the steady-state creep rate of Ti-6242S [3, 59].

2.3.2. Creep Mechanisms

Various mechanisms based on the temperature, stress and microstructure account for the deformation during creep of metals. Basic factors that affect creep are crystalline structure (1. diamond type, 2. fcc or hcp, 3. bcc), high melting temperature, high elastic
modulus, high valence state and a fine stable grain size [60]. Equation 2.4 describes total creep strain, \( \varepsilon \), as the sum of several different operating creep mechanisms such as dislocation glide, \( \varepsilon_{dg} \), grain boundary sliding, \( \varepsilon_{gb} \), Nabarro-Herring, \( \varepsilon_{nh} \), Coble, \( \varepsilon_c \) and other mechanisms, \( \varepsilon_... \) [61]. These and/or other creep mechanisms may be independent or dependant on each other. A few major creep mechanisms are now briefly discussed, followed by explanations of how the elemental additions may improve creep resistance in Timetal 21S.

Equation 2.4: \[ \varepsilon = \varepsilon_{dg} + \varepsilon_{gb} + \varepsilon_{nh} + \varepsilon_c + \varepsilon_... \]

2.3.2.1 Nabarro-Herring Creep, Coble Creep and Grain Boundary Sliding

Three of the commonly discussed creep mechanisms in the higher temperature/lower stress regime are Nabarro-Herring Creep, Coble Creep and grain boundary sliding. Nabarro and Herring described a mode of diffusion-based creep that occurs by movement of vacancies from the top and bottom to the sides of a grain while loaded in tension vertically (see Fig. 2.19(a)) [62, 63]. Coble described a similar mechanism but instead of the vacancies traveling through the bulk of the grain, the vacancies moved from the top and bottom to the sides of the grain through the grain boundaries (see Fig. 2.19(b)) [64]. At lower temperatures, Coble Creep would dominate since grain boundaries have lower activation energy for diffusion than the bulk of the grain. However, at elevated temperatures the equilibrium vacancy concentration increases, increasing the total number of vacancies in the bulk, which allows Nabarro-Herring Creep to dominate. Grain boundary sliding, which is related to Coble Creep, is
caused by adjacent grains moving with respect to each other by the transfer of vacancies along the grain boundary, as in fig. 2.20. Since the strain rate during creep is inversely proportional to grain size, everything else held constant; these three mechanisms can become significant at relatively high temperatures and small stresses [63].

Fig. 2.19: (a) Nabarro-Herring and (b) Coble Creep mechanisms [56].
2.3.2.2. Dislocation Climb and Glide

For an edge dislocation to change glide planes it must climb. Climb of an edge dislocation is a non-conservative motion that requires the diffusion of vacancies (see Fig. 2.21(a-b)) [60, 65]. Harper and Dorn found that diffusion-assisted dislocation climb accounted for significant amounts of creep in samples with large grain sizes and at low stresses [36, 66]. This type of creep moves dislocations by pure climb with very little dislocation glide along slip planes. Dislocation climb also allows gliding dislocations that would otherwise be pinned, to avoid obstacles and continue gliding on a different glide plane [42, 55, 56]. Obstacles can include other dislocations, sessile dislocations or precipitates. Fig. 2.22(a-b) shows how edge dislocations climb over Cottrell-Lomer Locks, which are sessile dislocations and precipitate-type obstacles [67].
Fig. 2.21: Dislocation climb (a) upwards under compressive stress and (b) downward under tensile stress [56].

Fig. 2.22: Dislocation overcoming (a) Cottrell-Lomer Locks and (b) precipitate obstacles by dislocation glide and climb.
Dislocations are a primary mechanism for creep deformation in metals and may be a significant creep mechanism in the target temperature (650°C) and stress regime for Timetal 21S developed in this research. For the case of dislocation-dominated creep with constant stress and temperature, the density of dislocations increases during stage I. The annihilation of dislocations through recovery increases to form an approximately steady-state dislocation density during stage II (dynamic recovery) [55]. The dislocations can also arrange themselves into subgrain walls of various diameters in stage II. The subgrain size and dislocation density are integral to both Taylor’s (see Equation 2.5) and Orowan’s (see Equation 2.6) relation. Both equations show that stress increases as dislocation spacing decreases, where \( \tau \) is stress, \( \alpha \) is a constant, \( \mu \) is the shear modulus, \( \rho \) is the dislocation density, \( b \) is the Burgers vector and \( \lambda \) is the spacing between obstacles [68, 69].

Equation 2.5: \[ \tau = \alpha \mu \rho \frac{1}{2} \]

Equation 2.6: \[ \tau = \frac{\mu b}{\lambda} \]

2.3.2.3. Effect of Dispersoids

Dispersoids such as small intermetallic phases (i.e. carbides, borides and silicides in titanium alloys), can act as obstacles to the motion of dislocations and/or grain boundaries (see Section 2.3.2.1). Factors such as local stress, diffusion and the size and strength of the dispersoid determine if dislocations bypass by climb, cut through the
dispersoid or are pinned at the particle/matrix interface such as in fig. 2.23. Dislocations are likely to be impeded or even pinned at these interfaces due to the increased energies at particle/matrix interfaces, even if the dispersoids are fully coherent with the matrix. Rosler and Artz proposed that the dislocation climb and glide mechanisms previously discussed enable dislocations to move towards and become pinned at particle/matrix interfaces, then additional thermal energy or stress on the dislocation is required to free them [70].

![Fig. 2.23: Edge dislocation pinned at a particle matrix interface [70.]](image)

2.3.2.4 Creep Modeling and Lifetime Prediction

In general, the success of creep models for service lifetime predictions has been limited for both models based on curve fitting to experimental data and those developed from equation derivation based on mechanisms of deformation. Extensive work has been done to link curve-fit experimental observations with the operating microstructural mechanisms, but definitive models still do not exist, especially for titanium alloys. This is
a challenging task that includes accurately identifying the operating and dominant mechanisms [36, 71].

Equations have been used to describe the creep behavior of a material based on temperature, stress, diffusion and other mechanism-specific parameters and constants [41, 60, 72, 73]. The mechanisms previously described require a certain level of activation energy to become active during creep. The activation energy for creep will typically be close to the activation energy of the rate-limiting mechanism, (i.e. self or vacancy diffusion or dislocation based). Based on equation 2.7, the activation energy for creep, \( Q_{\text{creep}} \), can be determined by plotting \( \log(\dot{\varepsilon}_{ss}) \) versus \( 1/T \) as shown in fig. 2.24, where \( k \) is the Boltzmann’s constant, \( T \) is temperature (K) and \( \dot{\varepsilon}_{ss} \) is the steady-state creep rate [68, 72, 74, 75]. The slope of such a plot is proportional to the activation energy for creep. For example, an activation energy similar to that for self and vacancy diffusion may indicate a primary creep mechanism of Nabarro-Herring creep, Coble creep, pure dislocation climb, or a combination. The stress exponent, \( n \), may also be determined to lend insight into dominant creep mechanism by including the measured stress, \( \sigma \) and modulus, \( E \), from a strain rate controlled test. A stress exponent of one is typically indicative of a vacancy/self diffusion mechanism and \( \sim 5 \) is a dislocation glide/climb mechanism [68].

Equation 2.7: \[ \dot{\varepsilon}_{ss} \propto \left( \frac{\sigma}{E} \right)^n \exp \left( \frac{-Q_{\text{creep}}}{kT} \right) \]
2.3.3. Creep of $\beta$ Titanium

Titanium has been shown to creep below 0.4$T_m$, whereas traditional creep resistant metals begin demonstrating significant creep strains above 0.4$T_m$ [76]. Creep in $\beta$ titanium alloys can be complicated due to the variation of volume fraction $\alpha$ and the morphologies of the constituents [77]. The $\alpha$ phase has shown to perform better in creep than the $\beta$ phase, most likely due to a more densely packed crystal structure, leading to larger activation energies for diffusion and comparatively increased difficulty for dislocation cross-slip [77]. The activation energy for solute atom diffusion in alpha Ti was found to be 85-127 kJ/mol by Paton and Mahoney [78]; for self diffusion in pure alpha Ti and unalloyed Ti it is 242 kJ/mol, according to Doner and Conrad [79] and Ranganath et al. [80]. Greater volume fractions of $\alpha$ and smaller $\alpha$ laths (larger $\alpha$ lath
density) improve creep properties. Beta-CEZ, a near β-alloy, was shown to have the best creep properties when the ratio of α lath surface area to volume was maximized. An ideal creep resistant microstructure would have a large volume fraction α with a high density of small, stable α laths. Grain boundary α also helps prevent grain boundary sliding in β-CEZ and Ti-V-Cr burn resistant β alloys [49, 77]. Beta alloys are typically over-aged at the intended service temperature when destined for use at an elevated temperature in order to stabilize the volume fraction α [71].

The two types of β phase stabilizers, eutectoid (Cr, Mn, Fe, Co, Ni and Cu) and isomorphous (Mo, V, Ta and Nb), play a significant role in determining the creep properties of β alloys [75]. For instance, small amounts of Ni increase creep rates significantly by increasing the self-diffusivity of Ti [36]. Likewise, the heavy elements Mo, W, Ta and Nb decrease diffusion rates, improving creep resistance. Si is often added to Ti alloys such as Timetal 21S and Ti-6242 to act as a solid solution strengthener and to form silicides that pin grain boundaries, α/β interfaces and impede dislocation motion [4]. Pinning α/β interfaces also helps to prevent α laths from coarsening, improving phase stability. The prior β grain size has been shown to have a minimal effect on creep, but sliding of α/β interfaces can have an effect on the strain rate as in equation 2.8, where \( \dot{\varepsilon}_{IS} \) is the strain rate due to interfacial sliding and L is the length of the α lath [36, 77].

Equation 2.8: \( \dot{\varepsilon}_{IS} \propto 1/L \)
2.4. Small Scale Mechanical Testing

As previously discussed, there has been an increase in the use of rules-based models, such as artificial neural networks, to relate complex microstructures to resulting properties in titanium alloys [5-12]. Such models require relatively large databases relating properties to microstructure and the population of such databases is both time consuming and costly. Therefore, recent research has been focused on developing accelerated and (relatively) inexpensive means for rapid database population. For example, some recent work has focused on techniques to quantify titanium microstructures rapidly and accurately by stereological means [81, 82]. However, there is still a significant cost associated with material preparation and testing. Work on ultra-high frequency fatigue testing schemes offer promise for reducing test time, but creep remains an expensive property to measure. One possible method to reduced the time associated with creep and even tensile testing, is to use thermal mechanical testing techniques such as the Gleeble™ [11, 14] and/or the new electrothermal mechanical tester (ETMT) [83-87]. These two techniques are ideal for rapidly creating a range of samples with large variations of thermal histories. Since the ETMT is the subject of a significant portion of this research, its relation with conventional tensile and creep testing and other small scale testing methods will be discussed.

2.4.1. Mechanical Testing at Various Size Scales

A range of sample sizes can be mechanically tested for a variety of information from the bulk to micron scale. For instance, traditional bulk tests produce experimental
data applicable to most structural systems, providing common information such as yield stress, tensile stress and elongation values. Smaller size-scale tests can provide more detailed information about specific deformation mechanisms, which can be used in material computational modeling packages to further understand the deformation behavior of smaller structural systems such as microelectromechanical systems (MEMS).

Traditional tensile and creep mechanical testing techniques for bulk property determination have been standardized by ASTM Standards E8 and E139, respectively [88, 89]. These standards are important since the test machines, procedures and sample geometries are critical in producing comparable data. The lower size limit for bulk property testing is often defined by the grain size or texture of the material. Significant textures or a limited number of grains in the cross-sectional area negatively affect the ability to obtain bulk tensile or creep mechanical property data.

As the ability to create small scale materials has improved, the need for better understanding of small scale materials for individual phase modeling and applications such as MEMS has increased, making size-scale effects increasingly important. Recent advances in characterization and mechanical testing techniques have allowed for the observation of mechanical properties of almost any material in reduced sized samples. Uchic and Dimiduk at the Air Force Research Lab have incorporated the focused ion beam (FIB) and a modified nanoindentation technique to compress single crystal pillars [90]. Fig. 2.25 is a schematic of the compression set-up depicting a flat-tipped, diamond nanoindenter tip compressing a FIB-made pillar. Fig. 2.26(a-b) shows 1 and 2 μm pillars post deformation; fig. 2.26(a) shows intense localized shear on one slip plane and fig.
2.26(b) shows a secondary slip system that was active. Dimiduk et al. found that decreasing the pillar diameter changed the critical resolved shear stress for deformation (see Fig. 2.27). It was found that as the volume decreased, the dislocation sources were altered along with the ability of dislocations to multiply, causing the critical resolved shear stress to increase as the pillar diameter decreased. They also observed bursts of dislocations that occurred to accommodate deformation [90]. These types of micron scale mechanical tests are critical for understanding dislocation behavior in small volumes [91-94].
Fig. 2.25: Schematic of a microcrystal compression test by Dimiduk et al. (a) configuration and (b) diamond nanoindentor tip used for compression [90].
Fig. 2.26: Two post-deformed pillars with diameters (a) 1 μm and (b) 2 μm [90].

Fig. 2.27: Plot showing that the critical resolved shear stress (CRSS) increases as the pillar diameter decreases [90].
In contrast to the compression pillar samples, Hemker and Zupan at Johns Hopkins University have tested microtensile samples (~200 μm wide gage and ~200 μm thickness) to investigate the effect of texture and microstructural features in γ-TiAl and single colony Ti-6242S [95, 96]. Fig. 2.28 is a photograph of the self-aligning grips for the microtensile specimen and fig. 2.29 a micrograph of a microtensile Ti-6242S specimen. Hemker et al. specifically investigated the nature of dislocation behavior on the basal and prism planes in the α phase of Ti-6242S [95]. The work on γ-TiAl also included resistively heating the sample to investigate the effect of temperature on the properties such as thermal expansion, modulus and yield stress [96, 97]. Due to the difficulty of obtaining single crystal or bulk material for macroscopic testing, these microtensile tests offered a unique opportunity to investigate single phase-single crystal γ-TiAl.

Fig. 2.28: Photograph of self-aligning grips for microtensile specimen [98].
2.4.2. *ETMT*

The electrothermal mechanical tester (ETMT 8800), pictured in fig. 2.30(a), was developed by the National Physical Laboratories (NPL, UK) and Instron. It is a modified load frame capable of simultaneously controlling load or position and temperature or current by direct heating of subscale coupons (via joule heating with a DC current) [83, 85, 99]. The direct resistive heating capabilities and small sample sizes (i.e. cross sections in units of mm$^2$) allow for rapid temperature variations that are accurately controlled by a feedback program which measures a controlling thermocouple spot-welded on the sample.
(see Fig. 2.30(b)). The ETMT has a potential cost savings when compared with conventional testing methods. These savings are derived from the ability to test many samples from a small amount of material and decreased time between samples because of a small, high integrity environmental chamber (i.e. argon, air and vacuum atmospheres) and fast temperature ramp rates of up to 200°C per second [83-87]. Fig. 2.31 is a schematic of the ETMT which includes a 480 Amp (max) DC power supply, water chiller and high integrity environmental chamber. Samples used in the ETMT are approximately 40 mm x 2 mm x 1 mm. Approximately 16 of the 40 mm consists of the gage section between the upper and lower grips. The direct resistive heating of the sample by the DC current coupled with the conductive heat loss to the water-cooled grips creates a non-uniform temperature distribution along the vertical length of the sample as diagramed in fig. 2.32. This temperature profile has been experimentally measured by Roebuck et al. for a WC/Cobalt hardmetal and was found to be parabolic in nature with the temperature greatest at the center and lowest closest to the water-cooled grips (see Fig. 2.33) [87]. Although parabolic, the temperature gradient is estimated to have an approximately constant temperature region of about 2 to 5 mm in the center of the sample [87]. It is critical to take this temperature gradient into account for accurate strain measurement and the determination of mechanical properties.
Fig. 2.30: Photographs of (a) the ETMT and (b) a sample at temperature with an attached thermocouple in the ETMT.

Fig. 2.31: ETMT setup with the load frame, power supply, control tower, grip cooling supply, camera for image collection and PC for collection and interpretation.
Fig. 2.32: Diagram showing the spatial relationship between the water-cooled grips, thermocouple and approximate temperature distribution.

Fig. 2.33: Experimental data of the temperature versus ETMT vertical position for four separate maximum temperatures [87].
2.4.2.1. Strain Measurement

For strain measurement, two identically sized Pt13%Rh wires, also termed millivolt wires, are spot-welded onto the sample approximately 2-5 mm apart with the thermocouple centered to measure a voltage drop (see Fig. 2.34). True strain is determined by measuring the change in potential drop (PD), or voltage, due to a change in length between the wires. The theory, history and applications of the PD method have been described thoroughly by Griffiths, et al. [84] and Roebuck, et al. [87] and are only briefly described here.

Fig. 2.34: Photograph of an ETMT sample with the attached thermocouple and millivolt wires.

Equation 2.9 - equation 2.13 describe how true strain, $\varepsilon_t$, is calculated from an initial measured potential, $V_o$ and current, $I_o$ and the instantaneous potential, $V$ and current, $I$. Equation 2.9 calculates true strain based on the instantaneous length, $l$ and
initial length, $l_o$, of a sample between the millivolt wires. Equation 2.10 and equation 2.11 are resistance equations, where $R$ is resistance, $\rho$ is resistivity and $A$ and $A_o$ are the instantaneous and initial cross-sectional areas, respectively. The PD method is only valid for constant volume deformation, before necking (Equation 2.12). Equation 2.13 combines and simplifies the previous four equations to determine true strain in the ETMT. Fig. 2.35(a) is a set of stress versus strain curves for stainless steel welds using the PD strain measurement method [84]. The strain resolution appears to be low for the extraction of precise 0.2% or 0.5% offset yield stress or approximate moduli determination. Chapter 4 will go into more detail concerning PD strain measurement resolution and propose an alternative strain measurement technique for the ETMT applicable from room temperature to about 800°C.

Equation 2.9: $\varepsilon = \ln \left( \frac{l}{l_o} \right)$

Equation 2.10: $R = \frac{\rho l}{A}$, $R_o = \frac{\rho l_o}{A_o}$

Equation 2.11: $R = \frac{V}{I}$, $R_o = \frac{V_o}{I_o}$

Equation 2.12: $\frac{l}{l_o} = \frac{A_o}{A}$ (constant volume)
Equation 2.13: $\varepsilon_i = \ln \sqrt{\frac{R}{R_0}} = \ln \sqrt{\frac{V}{I} \frac{I_0}{V_0}}$

Fig. 2.35: Example of stress versus strain curve using the PD strain measurement method [84].

2.4.2.2. Resistivity Determination

The ETMT can also be used to determine the temperature dependence of resistivity, $\rho$, for a given material [100-103]. Equation 2.14 can be derived by combining equation 2.10 and equation 2.11, where $l$ is the distance between the millivolt wires, $A$ is the cross-sectional area and $V$ and $I$ are again the measured voltage and current. The resistivity is measured as a moderate temperature ramp of ~0.5-5 ($^\circ$C/sec) is applied to a sample. Fig. 2.36 is a plot of such an experiment performed by Tan et al. [103]. In general, an increase in temperature causes an increase in the electrical resistivity.
Equation 2.14: \( \rho = \frac{AV}{Il} \)

Fig. 2.36: Resistivity versus temperature for a stainless steel [103].

2.4.2.3. Present Scope of Use

The decreased time between tests and increased temperature ramp rates makes the ETMT an ideal creep-screening tool for this work on Timetal 21S and, depending on its success, may become more involved in future alloy development processes. Since the ETMT has been yet to be validated for any material in tension or creep, a major portion
of this work is to compare data from the ETMT with data produced by traditional methods. This is the focus of Chapter 4.

Additionally, it is not uncommon for creep tests to last hundreds of hours or even months. The ETMT would be a relatively expensive creep frame if it tested samples for the same duration as a less expensive traditional creep frame. An option for decreased sample test time, in comparison with traditional methods, is to increase the test temperature and/or stress. This may cause the dominant creep mechanism to vary, but under these modified conditions the ETMT could then be used to test larger numbers of samples in shorter amounts of time. Decreased test time may allow for exploration of wider composition ranges and/or processing parameters to identify samples with the most promising properties. Then fewer of the time-consuming traditional creep tests would need to be performed because of preliminary creep testing with the ETMT.
CHAPTER 3

3 EXPERIMENTAL METHODS

This unique work employed several technologies encompassing building geometries from elemental powder with the LENS\textsuperscript{TM}, processing with a HIP, testing with the ETMT, characterizing at multiple length scales and neural network analysis of the data.

3.1. Directed Laser Deposition via the LENS\textsuperscript{TM}

The LENS\textsuperscript{TM} (Laser Engineered Net Shaping) process at The Ohio State University was used to rapidly produce many $\beta$ titanium alloys of varying compositions. A basic description of the system and process has been covered in section 2.1.2. Rather than using costly pre-alloyed powder for each unique composition, this work exploited the use of blended elemental powders, which allowed for rapid customization of overall powder composition and therefore, sample compositions [23].

3.1.1. Elemental Variations

Table 3.1 lists the elements that are included and varied during this work. Varying all elements simultaneously would likely cause the results to be difficult to interpret even by using neural networks to help investigate the effects of both microstructural features
and compositional variations. Therefore, in an effort to limit the total number of interdependencies that might occur, the elemental variations are split into four separate groups based on the type of compositional addition and their potential effect on creep properties. Only two or three elements are varied in each group while all the other baseline elements (Mo, Nb, Al and Si) are held at nominally constant values. They are arranged by $\alpha$ stabilizers (Al, Sn and Zr), $\beta$ stabilizers (Mo, Nb and W), small (Si and Ge) and large (B and C) dispersoid forming elements. Sn and Zr are not $\alpha$ stabilizers (they are approximately neutral), but these larger atoms may have a solid-solution strengthening effect and are combined with Al to form a group named ‘$\alpha$ stabilizers.’

<table>
<thead>
<tr>
<th>Element</th>
<th>Target composition (wt%)</th>
<th>Group</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mo</td>
<td>11-19</td>
<td>$\beta$ stabilizer</td>
</tr>
<tr>
<td>Nb</td>
<td>1-4</td>
<td>$\beta$ stabilizer</td>
</tr>
<tr>
<td>W</td>
<td>1-6</td>
<td>$\beta$ stabilizer</td>
</tr>
<tr>
<td>Al</td>
<td>1-4</td>
<td>$\alpha$ stabilizer</td>
</tr>
<tr>
<td>Zr</td>
<td>1-6</td>
<td>$\alpha$ stabilizer</td>
</tr>
<tr>
<td>Sn</td>
<td>1-5</td>
<td>$\alpha$ stabilizer</td>
</tr>
<tr>
<td>B</td>
<td>0-0.5</td>
<td>Micro-dispersoid</td>
</tr>
<tr>
<td>C</td>
<td>0-0.5</td>
<td>Micro-dispersoid</td>
</tr>
<tr>
<td>Si</td>
<td>0.2-0.8</td>
<td>Nano-dispersoid</td>
</tr>
<tr>
<td>Ge</td>
<td>0.2-1</td>
<td>Nano-dispersoid</td>
</tr>
</tbody>
</table>

Table 3.1: Elements, their target composition range and group for LENS™ deposition.

In addition to limiting the number of elements that are varied at a given time, the elements are randomly varied in an attempt to potentially improve the training of the
neural network model. Instead of varying the compositions in a discrete fashion as shown with Al, Sn and Zr in fig. 3.1(a) (i.e. Al is varied discretely at 2, 3 and 4 wt%), they are randomly varied to provide a more continuous dataset with smaller gaps between data points (see Fig. 3.1(b)). Fig. 3.1(a-b) plots the composition of Al and Sn simultaneously. It appears as if fig. 3.1(b) has three times as many data points as fig. 3.1(a) because Zr is also randomly varied, which cannot be seen due to overlapping points in fig. 3.1(a).

![Discrete and Random Compositional Variation](image)

Fig. 3.1: Schematics showing the possible variation in Al, Sn and Zr compositions: (a) in discrete fashion and (b) in a random fashion that is more continuous. Notice (b) has more compositions than (a) since the Zr content is also allowed to vary but is not plotted on either graph.

3.1.2. Powder Description and Optimization

Table 3.2 contains a list of elemental powders that were used for deposition and includes the thermal and physical properties that are often important during the laser
deposition process. For example, high enthalpies of mixing of an elemental species in liquid titanium, $\Delta H_{\text{mix}}$, low melting points, low reflectivities and low densities will tend to require lower energy densities during deposition (i.e. less laser power) [24]. For example, Mo, W, Sn and Al need special attention to achieve the target composition especially when large weight percents (>10%) are required (i.e. Mo). The elements Mo and W tend to be lean in the final deposits due to low heats of mixing, high melting points and higher densities compared with Ti and Al. For this reason the initial Mo powder composition was increased by a factor of 1.3. In contrast, Sn is highly exothermic, has a low melting point and has a relatively low reflectivity causing many deposits to be Sn rich, so its powder composition was decreased by a factor of 0.38. It has historically been difficult to achieve the target composition of Al because of powder segregation before deposition due to its non-spherical and low-density nature. The non-spherical shape can be seen in fig. 3.2, which is a collection of SEM micrographs of all the powders used. As a remedy, a Ti-50Al (at%) master alloy was used to achieve the target composition of Al to within $\pm0.1$ wt%. Considerable effort was expended to develop experimental techniques that assured each deposit had an experimentally measured composition that was close to the target composition.
<table>
<thead>
<tr>
<th>Alloying Element</th>
<th>$\Delta H$ mixing w/Ti (kJ/mole)</th>
<th>Melting Point (°C)</th>
<th>Reflectivity at 1.064 μm</th>
<th>Density (g/cm$^3$)</th>
<th>Powder Mesh Size</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti</td>
<td>---</td>
<td>1668</td>
<td>63%</td>
<td>4.5</td>
<td>-140 +325</td>
</tr>
<tr>
<td>Mo</td>
<td>-16</td>
<td>2610</td>
<td>57%</td>
<td>10.2</td>
<td>-170</td>
</tr>
<tr>
<td>Nb</td>
<td>10</td>
<td>2468</td>
<td>77%</td>
<td>8.6</td>
<td>-100 +325</td>
</tr>
<tr>
<td>W</td>
<td>-26</td>
<td>3410</td>
<td>58%</td>
<td>19.3</td>
<td>-100</td>
</tr>
<tr>
<td>Al</td>
<td>-137</td>
<td>660</td>
<td>91%</td>
<td>2.7</td>
<td>-100 +325</td>
</tr>
<tr>
<td>TiAl</td>
<td>---</td>
<td>1500</td>
<td>N/A</td>
<td>3.8</td>
<td>-140</td>
</tr>
<tr>
<td>Zr</td>
<td>0</td>
<td>1852</td>
<td>16%</td>
<td>6.5</td>
<td>-100</td>
</tr>
<tr>
<td>Sn</td>
<td>-139</td>
<td>232</td>
<td>46%</td>
<td>5.8</td>
<td>plasma spray grade</td>
</tr>
<tr>
<td>Si</td>
<td>-211</td>
<td>1410</td>
<td>32%</td>
<td>2.3</td>
<td>-100</td>
</tr>
<tr>
<td>Ge</td>
<td>-188</td>
<td>937</td>
<td>40%</td>
<td>5.3</td>
<td>-100</td>
</tr>
<tr>
<td>B</td>
<td>-200</td>
<td>2300</td>
<td>15%</td>
<td>2.3</td>
<td>-325</td>
</tr>
<tr>
<td>C</td>
<td>-200</td>
<td>3527</td>
<td>17%</td>
<td>2.3</td>
<td>-325</td>
</tr>
</tbody>
</table>

Table 3.2: Important parameters of elemental powder additions used during LENS™ deposition [23].
Fig. 3.2: Secondary electron micrographs of the powders used for deposition including: Ti, Mo, Nb, W, Al, TiAl, Zr, Sn, Si, Ge, B and C.
3.1.3. **LENS™ Parameters**

The elemental powders were massed with a Scout II OHAUS® Scale to make a total powder charge of ~450g. This amount of powder was typically sufficient to deposit a single geometry approximately 0.33” wide by 1.70” long by 0.50” tall. Each composition was then mixed in a NALGENE bottle with a WAB Turbula® powder mixer for at least 45 minutes. The various deposition parameters used in equation 2.1 are in table 3.3, which correspond to an energy density range of 6.4-8.0 MJ/in.³. The powder flow rate used was typically about 2.0 rpms for reference with the LENS™ unit at OSU.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hatch width</td>
<td>0.015”</td>
</tr>
<tr>
<td>Layer spacing</td>
<td>0.010”</td>
</tr>
<tr>
<td>Travel speed</td>
<td>20-25 in./minute</td>
</tr>
<tr>
<td>Laser power</td>
<td>400 watts</td>
</tr>
</tbody>
</table>

Table 3.3: LENS™ Deposition Parameters.

3.1.4. **LENS™ Deposit Compositional Homogeneity**

Powder segregation before LENS™ deposition, due to either incomplete mixing of the powder or powder segregation in the hopper, may be an issue in LENS™ deposits, especially if the powder segregation causes the composition to vary throughout a deposit. A sample with an approximate composition of Ti-12Mo-1.4Al-3.4Nb-0.6Si-3.3W had
fiducial marks added with a microhardness indenter with millimeter spacing along the vertical length of the deposit (parallel to the build direction). The composition was then quantified by standardless EDS in an SEM near each of the fiducial marks. Fig. 3.3 is a plot of the results, which shows that there is limited compositional deviation along the vertical axis of the LENS™ deposit.

![Distance vs. Composition in a LENS™ Deposit](image)

Fig. 3.3: Vertical distance versus composition of a LENS™ deposit.

### 3.1.5. Effect of LENS™ Texture

LENS™ depositions may result in a texture due to the unidirectional heat transfer from the build to the substrate during deposition. Fig. 3.4(a-b) show backscattered
electron micrographs from the faces whose plane normal is perpendicular and parallel to the build direction of a single LENS™ deposit (Ti-12.4Mo-2.5Al-2.8Nb-0.5Si-0.1B). The texture in the parent, matrix $\beta$ phase results in a strong, preferential distribution of the resulting $\alpha$ lath precipitates. Fig. 3.4(c) is a set of inverse pole figures from electron backscattered diffraction (EBSD) patterns from an SEM of the face normal to the laser/build direction from a LENS™ deposit. They show that, on average, the beta grains are oriented with the $<001>$ directions parallel to the build direction and have a nominally random texture perpendicular to the $<001>$ directions.
Fig. 3.4: Backscattered electron micrographs showing the effect of texture in a single deposit with an identical composition (a) perpendicular and (b) parallel to the face normal to the laser/build direction in the LENS™ and (c) select inverse pole figures from an electron backscattered diffraction (EBSD) pattern from a scanning electron microscope (SEM) of several grains from the face normal to the LENS™ build direction.
Preliminary simulated creep experiments performed using strain rate controlled compression tests with a strain rate of $\sim 1.0 \times 10^{-5}$ mm/mm/sec of right cylinders 15 mm tall with a 5 mm diameter on a range of Timetal 21S-based alloys tested parallel and perpendicular to the LENS™ build direction indicated a distinguishable difference in mechanical properties resulting from the texture created by the LENS™. Fig. 3.5 is a schematic depicting the geometry built to investigate the texture created by the LENS™ and its effect on creep properties. A series of arc-melted buttons of similar compositions were also prepared with thermal heat treatment identical to the LENS™ deposited alloys and tested using the same slow strain rate compression tests.

![Fig. 3.5: Schematic of LENS™ deposition geometries for texture analysis. Section A is the material tested parallel and Section B was tested perpendicular to the build direction.](image)

Fig. 3.6 is an example stress versus strain plot from one of the displacement controlled compression tests. The steady-state stress is highlighted. Table 3.4 shows representative steady-state stress data from LENS™ deposited material and an arc-melted
sample from material of the same composition (Ti-15Mo-3Al-3Nb-0.5Si-3W). The parallel sample has a steady-state stress ~27 MPa less than the deposit perpendicular to the LENS™ build direction. As a comparison, arc-melted material of a similar composition has data nearest the perpendicular data. Combined with the data that shows that texture is relatively random perpendicular to the build direction, this mechanical property data gives reason to use LENS™ deposited material perpendicular to the build direction for further mechanical testing.

![Stress vs Strain (Ti21S+0.1B+0.4Ge)](image)

Fig. 3.6: Example stress versus strain plot of a displacement controlled compression tests.
### Processing Steady-State Stress (MPa)

<table>
<thead>
<tr>
<th>Processing</th>
<th>Steady-State Stress (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LENS™ deposit tested parallel to the build direction</td>
<td>86</td>
</tr>
<tr>
<td>LENS™ deposit tested perpendicular to the build direction</td>
<td>113</td>
</tr>
<tr>
<td>Arc-melted material</td>
<td>122</td>
</tr>
</tbody>
</table>

Table 3.4: Steady-state stress data from Timetal 21S+W tested in two LENS™ directions and an arc-melted sample.

3.2. Processing with a Hot Isostatic Press (HIP)

Subsequent to deposition, all samples were solution treated above the β-transus (as determined using both ThermoCalc and Pandat for each composition) at 850°C for an hour, stabilized at 700°C for eight hours (50°C above the creep testing temperature) and furnace cooled at 10°C per minute. This thermal processing was conducted using an AIP6-30H hot isostatic press (HIP) made by American Isostatic Press (see Fig. 3.7), while operating at an argon pressure of 30 ksi to remove any residual shrinkage porosity form the LENS™ process. The added hydrostatic force helps to close up any porosity not caused by trapped gases.
The HIP was also used for the heat treatment of the Ti-64 material used for the tensile experiments in section 4.3 due to its excellent temperature control and programmability. A moderate argon pressure of 8 ksi was used during the cycles.

3.3. ETMT Sample Preparation

The ETMT specimens were prepared using wire electrical discharge machining (EDM) to produce a rectilinear piped geometry of dimensions 1 mm by 2 mm by 40 mm for tensile testing and 1.5 mm by 3 mm by 40 mm for creep testing (see Fig. 3.8). Following machining, the EDM recast layer was removed by light sanding with 600 grit silicon carbide paper. It was found that light sanding of all four sides, not including the
two small 2 by 1 mm ends, has superior edge retention and is a simpler process than tested electrochemical methods for EDM recast layer removal. Samples tested at room temperature (22°C) were prepared with a reduced area cross-section, 1 mm by 2 mm, 8 mm long with 1 mm by 3 mm grip sections (i.e. dog-bone geometry, after ASTM E8M) [88]. For tests conducted above room temperature (22°C), a type R (Pt/Pt-13Rh) thermocouple of 0.25 mm diameter wire was attached to the center of the sample using a spot welder (capacitive discharge Miyachi Uniteck 125DP power supply and 80A/EZ weld head) for temperature measurement and control (see Fig. 2.34).

Fig. 3.8: Schematic of how the ETMT samples are taken from the LENS™ deposits.

3.4. Characterization and Stereological Methods

The sample surfaces whose surface normals were perpendicular to the testing direction were characterized. The samples were sectioned with a wire EDM, mounted in inch and a quarter diameter PolyFast SEM mounting material and mechanically polished for light and electron microscopy. The mechanical polishing was typically performed in a
Beuhler Vangaurd 2000 automatic sample polisher with steps of: (1) 125 micron diamond grinding disc, (2) 320 grit silicon carbide paper, (3) 9 mm diamond solution on UltraPol™ cloth, (4) 800 micron silicon carbide paper, (5) 0.02 micron colloidal silica on ChemoMet® cloth and (6) two days on a vibratory polisher with 0.02 micron colloidal silica on MicroCloth®.

Most of the sample images used during this work are backscattered electron (BSE) micrographs operating at 15 kV taken with an FEI scanning electron microscope (SEM) with a Sirion column with a field emission gun (FEG). The micrographs taken for the neural network models were taken in an extra high definition (XHD) format with a total size of 3872 x 2904 pixels, where each pixel was 0.03353 μm. The XHD format allowed for a higher resolution of features taken at a lower magnification for imaging larger areas with adequate resolution. The SEM was also used to measure bulk compositions of the Timetal 21S variants by standardless energy-dispersed spectroscopy (EDS); this data was input into the neural network models.

Transmission electron microscopes (TEM) were also used to obtain bright field (BF) and scanning transmission electron microscope (STEM) images, selected area diffraction (SAD) patterns and EDS analysis (FEI CM200 and TF-20). Conventional 3 mm diameter and ~100 μm thick TEM discs were prepared conventionally with a Gatan Dimple Grinder (Model 656), Gatan Duo Ion Mill (Model 600) and a Fischione low angle ion mill (Model 1010). In situ TEM foils were also prepared with a dual beam FIB (focused ion beam – FEI NOVA 600), Omni Probe System and a Fischione Nanomill (Model 1040).
For microstructural feature quantification, SEM micrographs were collected in a random and unbiased fashion and a series of stereological procedures previously developed and described by John Russ [104], Jay Tiley [14] and Tom Searles [81, 82, 105] were applied to the micrographs in Photoshop® with a FoveaPro plug-in made by Reindeer Graphics®. Stereology is the analysis of two-dimensional images to estimate 3-dimensional quantities. The volume fraction $\alpha$, average $\alpha$ lath thickness and the average $\beta$ mean free path were measured. The $\beta$ mean free path is a measure of the average distance between the $\alpha$ laths. Fig. 3.9(a-d) is a series of micrographs depicting the basic premise of how these features are measured using stereological methods. After a threshold image is obtained, the volume fraction $\alpha$ is a simple measure of the number of black pixels divided by the total number of pixels. Sets of parallel lines are randomly oriented several times and the thickness of the $\alpha$ laths are measured by averaging the intersected $\alpha$ lath (dark regions) line distance. The $\beta$ mean free path is measured the same way as the $\alpha$ lath measurement, but with the contrast inverted to measure the distance between the $\alpha$ laths (now dark regions).
Fig. 3.9: Schematic depicting the general stereological steps used: (a) Original BSE micrograph; (b) threshold portion of (a) where the black area is measured for the volume fraction $\alpha$ measurement; (c) sets of parallel lines are randomly oriented several times and the thickness of the $\alpha$ laths are measured by averaging the intersected $\alpha$ lath (dark regions) line distance; (d) the $\beta$ mean free path is measured by performing the $\alpha$ lath thickness measurement on an image with the contrast inverted.
3.5. Artificial Neural Networks

Several neural network models were developed and are shown in detail in Chapter 5. Such models allow for the investigation of the effects of compositional and microstructural properties (inputs) on the measured minimum creep rate (output) from ETMT creep experiments. The effect of composition on microstructure is also investigated. These models are developed and implemented in a similar fashion as discussed in section 2.1.1. The models are first developed as predictive tools for properties, where the quality of a given model is determined by measuring the difference between the experimental and predicted values via a plot (see Fig. 2.2 as an example). The models are then primarily used for virtual experiments. All the inputs for a given model are held at a desired constant value, usually an average value, except for one of the inputs, which is varied between the experimentally determined minimum and maximum values. The output is then predicted via the corresponding developed model and plotted versus the varied input parameter (see Fig. 2.4 as an example). This information gives insight into the functional dependency of the output on the given input via a virtual experiment that is typically impossible to physically perform.

3.6. Oxidation Testing

The oxidation performance for several of the alloy variations were tested by measuring the weight gain of cylindrical disks over a period of 96 hours (4 days) in a Lindberg Model 51442 box furnace at 650°C. Fig. 3.10 is a schematic depicting the shape and dimensions of the disks cut with a Buehler Isomet low speed diamond saw from the
right cylinders used for the compression tests described in section 3.1.4. An ATI CAHN Model CA-26 balance with 0.01 microgram resolution was used to measure the mass of each cylinder every 24 hours and the results are discussed in section 5.8.

Fig. 3.10: Schematic depicting the geometry of the cylindrical disks for oxidation performance testing.
CHAPTER 4

4 VALIDATION OF TENSILE AND CREEP PROPERTY DATA FROM THE ETMT

The ETMT has been used to determine various material properties as discussed in Chapter 2. As previously noted, it has never been used to determine tensile or creep properties of titanium alloys. This chapter discusses some additional characterization of the thermal profile of the samples, an improved strain measurement technique developed for this work and the characterization of tensile and creep data obtained with the ETMT.

4.1. ETMT Thermal Profile Determination of Ti-64 via Heat Transfer and Electrostatic Modeling

It is expected that the gradient in the local temperature in the ETMT will cause a corresponding gradient in mechanical properties of the sample along the gage length. For example, in the case where the yield strength is inversely proportional to temperature, the load required for yielding to occur along the length of the sample varies from a minimum at the center, to a maximum near the water-cooled grips, due to the temperature profile. Characterizing the seemingly complex temperature profile can lend insight into how the samples will mechanically behave for proper mechanical measurement.

While the temperature profile along the length of the sample has been experimentally measured previously, the temperature profile perpendicular to the current
flow has not. This is likely due to the intrinsic difficulties involved with such an experiment, such as the relative number and size of the junctions of the attached thermocouples with respect to the gage width of 2 mm. Similarly, optical pyrometry methods are not reliable due to the spot size of the optics (i.e. 0.45 mm diameter) and are subject to additional challenges such as changes of emissivity resulting from modifications to the surface (i.e. the formation of oxides) [102]. It may be hypothesized that the temperature at the vertical corners of the ETMT samples are cooler than the center due to the locally increased surface area to volume ratio causing increased convectional and radiative heat loss to the surrounding atmosphere. If such a hypothesis is correct and the difference is significant, then the effect that the temperature distribution on the properties should be considered, which may also be significant. Therefore, a brief numerical investigation of the magnitude of the temperature difference is performed to determine whether significant differences in properties may be expected. The temperature distribution along the length and in the plane perpendicular to the electrical current of a commonly used titanium alloy (Ti-6Al-4V) sample was calculated using coupled electro-thermal computational analysis to provide an approximation of the magnitude of the temperature variations in ETMT samples at elevated temperatures.

4.1.1. Theory and Computational Model Setup

Fig. 2.30(b) is a photograph of a sample loaded between the flat-faced steel and brass grips at an elevated temperature in the ETMT. A commercial Computational Fluid Dynamics (CFD) software package, CFD-ACE+™, produced by the ESI Group, was
used to model precisely this experimental setup. CFD-ACE+ is a general-purpose computational tool for modeling coupled fluid-thermal-chemical-electrical-magnetic phenomena for a variety of applications. For this particular application, it predicts local and global distributions of quantities of interest, such as temperature, electric potential and current density by solving the governing conservation equations of energy and electric current. These conservation equations, at steady state, are as follows:

Energy conservation:

Equation 4.1: $\nabla \cdot (k \nabla T) + \frac{1}{\sigma} \frac{\nabla \cdot \mathbf{i}}{\sigma} = 0$

where $k$ is the thermal conductivity of the material, $T$ is the temperature, $\mathbf{i}$ is the current density vector and $\sigma$ is the electrical conductivity of the material. In general, both the electrical conductivity and the thermal conductivity may be functions of temperature, as described below. The first term in equation 4.1 represents heat transfer by conduction and the second term represents heat generation by Joule heating.

Current conservation:

Equation 4.2: $\nabla \cdot \mathbf{i} - \nabla \cdot (\sigma \nabla \phi) = 0$

where $\phi$ is the electric potential. In this approach, any capacitive effect is neglected, thereby allowing solution of the current conservation equation, rather than the charge conservation equation. Equation 4.1 and equation 4.2 are coupled through the temperature and current density. They are first discretized using the finite-volume method [106] and then solved using an iterative procedure.
Fig. 4.1 shows the modeled geometry with dimensions nominally identical to the ETMT grips and sample, as shown in fig. 2.30(b). In order to simplify the model, the eight stainless steel bolts have not been included, the brass portion of the grips has been simplified and the thermocouple (0.25 mm Pt and Pt-13Rh diameter wire) has not been included. The model mimics the ETMT setup with conductive heat loss through the water-chilled grips (25°C) and convection and radiation heat loss from the surfaces to the surrounding atmosphere (heat transfer). The boundary conditions at the top face of the brass upper grip and bottom face of the brass lower grip are set to an isothermal condition of 25°C, mimicking the water-chiller. All other exposed surfaces have boundary conditions that include convection and radiation heat transfer to the ambient. An electrical current is applied through the sample (electrostatics) by setting a current density (Amps/m²) boundary condition at the top face of the brass upper grip and a zero voltage boundary condition at the bottom face of the brass lower grip. All other external surfaces have a zero current flux boundary condition. After a rigorous mesh independence study, an appropriate mesh size was determined, which includes ~130,000 cells. The convective heat transfer coefficient on the external surfaces exposed to the ambient is needed as an input to the model and an approximate heat transfer coefficient from the exposed faces to the surrounding atmosphere was determined by calibrating the predicted results against experimental data for a single case. This was done by adjusting the heat transfer coefficient to match the same maximum temperature in the model with the same applied current through the Ti-6Al-4V sample, resulting in a value of 48 W/m²K. The current required to produce a given maximum temperature at the center of the sample is
experimentally known, 700°C for calibration purposes. Once the heat transfer coefficient was obtained by calibration, it was used for the remaining simulations.

![Schematic of the Ti-64 sample modeled in the ETMT brass and steel grips](image)

Fig. 4.1: Schematic of the Ti-64 sample modeled in the ETMT brass and steel grips (see Fig. 2.30(b)).

4.1.2. Determination of Resistivity

Since the electrical resistivity of Ti-64, like most materials, varies with temperature, the ETMT was used as in Section 2.4.2.2 to determine the electrical resistivity-temperature relationship (\(\rho(T)\)) [3]. A temperature ramp of 1°C per second was performed from 200°C to 1100°C and a polynomial equation was fitted to the resistivity \((\Omega m)\) versus temperature \((K)\) data (see Equation 4.3). Fig. 4.2 shows the measured
resistivity data, which is comparable to the published data for Ti-64. This resistivity data was included in the computational model, which was then executed until it reached a predetermined convergence for five different applied current densities.

\[
\rho(T) = 1 \times 10^{-15} T^3 - 4 \times 10^{-12} T^2 + 4 \times 10^{-9} T + 3 \times 10^{-7}
\]

Fig. 4.2: Resistivity versus temperature of an ETMT Ti64 sample compared with published data for Ti-6Al-4V [3, 107].

4.1.3. Results and Discussion

Fig. 4.3(a) shows a parabolic heat distribution along the length of the sample which agrees with previous reports by Roebuck et al. (see Fig. 2.33) [87]. It has also been reported that the variation of measured temperature within the central 2 mm increases
from ±1K to ±2K from 200°C to 400°C, respectively, again corresponding well with the
data in fig. 4.3(a) where the total temperature variation in the same central 2 mm is
~3.3°C (T_{max} ~ 290°C) [87]. Although there is no previous experimental work detailing
the temperature variation perpendicular to the current flow direction, it is assumed that if
a significant temperature variation were to exist between the vertical corners and middle
of the sample, the variation would be greater for higher temperatures. Fig. 4.3(b) is a
contour plot of the mid-plane, corresponding to the highest temperature for a given set of
conditions, approximately 1104°C at the center, which demonstrates an approximate
temperature drop 10°C from the center to the corners of the sample. Depending on the
experiment performed, a 9.3°C temperature variation may be considered insignificant and
acceptable. For example, a reported variation of the β-transus temperature for Standard
and ELI grade Ti-6Al-4V is ±15°C, which is greater than the temperature variation in the
modeled ETMT sample [3]. The temperature variation was also found to be less for lower
temperatures (see Fig. 4.4(a and b)). Therefore, mechanical testing of Ti-based alloys
may not be affected by the temperature variation. For instance, at ~300°C the temperature
variation is ~1.6°C, which is within the temperature resolution of the ETMT (±2.5°C).
These small temperature variations in the plane perpendicular to the current in
mechanical tests performed from 300-1100°C may be considered insignificant.
Fig. 4.3: Model results: (a) Vertical temperature versus distance plots for five different applied currents, (b) Contour plot of the mid-plane perpendicular to the flow the current for the condition with maximum current (highest temperature of ~1104°C).

Fig. 4.4: (a) Temperature variation at the mid-plane of the sample as a function of maximum temperature. (b) Two thermal profiles of mid plane diagonal.
4.2. Implementation of Digital Image Correlation (DIC)

Traditional contact extensometers cannot be placed on ETMT samples for strain measurement due to the small size of the sample and the fact that the distance between the grips is limited to between 11 and 21 mm (10 mm of total travel), causing the application of contact extensometers, such as knife-edge extensometers, to be rather difficult. The ETMT can measure the displacement of the grips with respect to each other, but this method does not accurately define the effective gage section, as some amount of sample elongation typically occurs within the gripped portions. Additionally, traditional two-point strain measurement techniques and calculations assume uniform deformation between the end points. As noted above, ETMT samples tested at elevated temperature exhibit gradients in temperature and also likely exhibit gradients of mechanical properties between the two end points, further limiting the use of contact extensometers. Indeed, the varying temperature creates non-uniform strain distributions, which cannot be adequately described using a two-point strain measurement technique with an “average” strain defined by the distance between the ETMT grips. Given the limitations of contact extensometers within the ETMT, a different method of strain measurement is required.

Inside a constant temperature zone, two possible options exist for measuring strain. First, a potential drop method using millivolt wires as previously described in section 2.4.2.1 [84, 85], which is not applicable for room temperature testing and was found to produce data that was noisy and difficult for accurate tensile data interpretation and secondly, a video-based extensometer involving digital image correlation (DIC), with
a 2MP Marlin CCD camera from Allied Vision Technologies and VIC-2D® software from Correlated Solutions, Inc [108, 109]. Strain can also be measured via a laser extensometer but this requires reflectors applied to the region of interest on the sample. The DIC method proved to be more practical than the laser extensometer and the location of strain measurement can be easily changed even after a completed test.

For DIC implementation, samples are spray painted with a black speckle pattern on a white background within the region of interest. The camera takes sequential images of the pattern during a tensile or creep test and DIC is used to determine the relative displacement of the contrast created by the speckle pattern between the original and successive images. Fig. 4.5(a-b) shows an example of the small displacements of speckles during a test. The DIC software uses the spatial displacement to determine strain at the surface of the sample and has a lower resolution limit of ~0.01% strain. Surface strains have been found to correlate well with bulk strains in tensile tests [108, 110]. A two-point extensometer region of interest (ROI) is used for strain measurement (see Fig. 4.6). The extensometer is placed in the axial and transverse center corresponding to the region of a nominally constant temperature. Fig. 4.7 is an example of the axial stress/strain curves produced by the ETMT using DIC compared with a conventional stress/strain curve.
Fig. 4.5: Example of the difference between deformed images used in DIC at (a) 0% total strain and (b) 4.6% total strain. The localized strain between image (a) and (b) is approximately 6%.

Fig. 4.6: Example of a digital extensometer placed on the region of interest with the VIC-2D® software by Correlated Solutions, Inc.
Fig. 4.7: Examples of a stress versus strain curve produced by the ETMT for an α+β-processed Ti-64 sample compared with a conventionally tested sample.

The PD method was found to produce satisfactory time versus strain plots for determining minimum creep rates in tests spanning a few hours. However, the time vs. strain plots obtained for constant load tests in excess of 24 hours were difficult to interpret, likely due to the diurnal variations in the ambient room temperature during the tests. A result of these variations is a change in the current required to maintain a constant temperature leading to a variation in the calculated strain. Fig. 4.8 is a plot of a test spanning about two days with the strain being measured by the PD and the DIC method. The strain appears cyclic for the PD method with a period approximately equivalent to one day (24 hours). Conversely, the DIC strain measurement technique produces data that is crisp and lacks the diurnal variation.
Comparing PD and DIC Strain Measurement Methods

Fig. 4.8: Plot of strain versus time of a single α+β-processed Ti-6242 creep test using both the potential drop (PD) and digital image correlation (DIC) methods for strain measurement. The steady-state creep rates for the PD and DIC methods were 3.0E-08 and 1.9E-08 (sec\(^{-1}\)), respectively. Notice that the cyclic period of the PD data is about 24 hours, which correlates well with the small variations of the temperature in the room.

4.3. Tensile Validation

While the ETMT shows promise as a technique both to heat treat and test the properties of a material, it is first necessary to establish a measure of the precision and accuracy of the data acquired using such small scale samples and to compare it with that obtained using larger samples and traditional testing methods. While it is appropriate to test a wide range of metallic materials and compositions to fully understand any limitations associated with this new mechanical testing technique, this section focuses on...
establishing a benchmark for Ti-6Al-4V, an alloy that is widely used and has been the subject of recent attempts to develop microstructure-based modeling schemes in a complex alloy [7, 8, 14, 81]. The material has been processed using traditional means and heat-treated in a hot isostatic press, resulting in a wide range of microstructures and properties.

4.3.1. Material

Various heat-treatments of $\alpha + \beta$ and $\beta$-processed Ti-64 were replicated and tested in tension using the ETMT and by conventional testing methods (ASTM Standards E-8M and E-21) at four temperatures (22, 100, 200 and 300°C) [88, 111]. The heat treatments were chosen based on previous work to establish materials whose properties included low, medium and high yield strength (YS) and ultimate tensile strength (UTS) values. Two tests per condition were performed at a mechanical testing facility (48 tests total) and three tests for each condition were performed in the ETMT (72 tests total). Initial strain rates for all tests were 0.005 mm/mm/min. through the 0.2% offset yield point and then the head rate to failure was 1.27 mm/min.

Conventional tests were prepared with a 5 to 1 gage length to radius ratio (2.54 cm gage and 0.508 cm diameter) and tested at an A2LA, ISO 17025 and NADCAP approved laboratory, Joliet Metallurgical Laboratories, Inc. (Joliet, IL). Elevated temperature tests were performed in the same facility on a load frame with a convection furnace. The 0.2% offset YS, UTS, total elongation data and reduction in area were supplied by the contractor and the modulus values were directly determined from the
elastic region of the stress versus strain curves. The ETMT samples were 1 mm by 2 mm by 40 mm rectangles while the samples tested at room temperature (22°C) were 8 mm long “dog-bones” with reduced area cross-section to ensure that the majority of the deformation and failure occurred in the gage section and not in the ETMT grips.

Specimens were extracted from the middle of the gage and included the fracture surface. These specimens were mounted in a fashion to protect the fracture surface and then polished using conventional metallographic techniques prior to characterization. A FEI scanning electron microscope (SEM) with a Sirion FEG column operating at 15 kV was used to image various samples in the backscattered electron imaging mode.

4.3.2. Results

4.3.2.1. α+β-processed Ti-64

Fig. 4.9 is a representative SEM backscattered electron micrograph of the α+β-processed material depicting the microstructure and the fracture surface. The compositional data for these samples as determined by Timet using ICP are located in table 4.1. Table 4.2 and fig. 4.10(a-d) contain the average tensile properties, including 0.2% offset YS, UTS, modulus, total elongation and reduction in area, determined using both conventional (Joliet) and ETMT techniques for α+β-processed Ti-64 data as a function of temperature. The ETMT and conventional YS and UTS data correlate well; the average YS and UTS data for each condition, as determined using the two techniques, are within ±1% for room temperature and within ±4% for elevated temperatures. The
standard deviations, as shown in parentheses in table 4.2, of YS and UTS for the ETMT data are slightly larger than conventional methods, but both are mostly within 1% of the average values. Of the two measures of ductility, the total elongation determined using the two techniques is nominally identical while the reduction in area deviates significantly at elevated temperatures. For example, at room temperature, the reduction in area in the ETMT is 20% less than the conventionally tested material compared with 38% less for temperatures above 22°C. The average elastic modulus determined using the two techniques is nominally identical at room temperature, but begins to deviate significantly at elevated temperatures. In each case, the modulus of the conventionally tested material is significantly lower than that determined using the ETMT (i.e. by as much as 49% less at 300°C).

Fig. 4.9: Example SEM backscattered electron micrograph of an α+β-processed Ti-64 ETMT fracture surface.
<table>
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<tr>
<th>Element</th>
<th>Average Content (wt%)</th>
</tr>
</thead>
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</tr>
<tr>
<td>V</td>
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</tr>
<tr>
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Table 4.1: Average compositional data for the α+β and β-processed Ti-64 as tested by Timet using ICP.
<table>
<thead>
<tr>
<th>Properties</th>
<th>Method</th>
<th>Temp. (°C)</th>
<th>Avg. YS (MPa)</th>
<th>Avg. UTS (MPa)</th>
<th>Avg. Modulus (GPa)</th>
<th>Avg. Total Elongation (%)</th>
<th>Avg. RA (%)</th>
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Table 4.2: Data table containing the average values of YS, UTS, modulus, total elongation and reduction in area (RA) with the standard deviation of the average in parentheses for the ETMT and conventional α+β-processed Ti-64 tensile properties.
Fig. 4.10: Graphical representation of the medium results for ETMT and conventional methods from table 4.2, depicting average (a) YS, (b) UTS, (c) reduction in area (RA) and (d) modulus, E, as a function of temperature for α+β-processed Ti-64.
4.3.2.2. β-processed Ti-64

In a similar fashion, fig. 4.11 is a representative SEM backscattered electron micrograph of the β-processed material depicting the microstructure and the fracture surface. The compositional data for these samples as tested by Timet using ICP are also located in table 4.1. Table 4.3 and fig. 4.12(a-d) contain the average tensile properties including 0.2% offset YS, UTS, modulus, total elongation and reduction in area (RA), as determined using both conventional (Joliet) and ETMT techniques for β-processed Ti-64 material as a function of temperature. The YS and UTS data obtained using the ETMT are 9% and 13% lower than the conventionally tested material, respectively. The average standard deviations for these values are also larger: 13 and 20 MPa for YS and UTS, respectively, as compared with 7MPa for both in the α+β-processed Ti-64. The average standard deviations, as shown in the parentheses in table 4.3, for the conventionally tested material are also higher for the β-processed material: 5 and 7 MPa for YS and UTS, respectively, as compared with 3 and 4 MPa respectively for the α+β-processed Ti-64. Similar to the α+β-processed material, the total elongation determined using the two testing techniques is nominally identical while the reduction in area deviates at elevated temperatures. The reduction in area of the conventionally tested samples is, on average, 55% greater at elevated temperatures. The average elastic modulus determined using the two techniques is nominally identical at room temperature, but begins to deviate significantly at elevated temperatures. In each case, the modulus of the conventionally tested material is significantly lower than that determined using the ETMT (i.e. 25% less at 300°C).
Fig. 4.11: Example SEM backscattered electron micrograph of a β-processed Ti-64 ETMT fracture surface. Note the apparent differences in major microstructural feature sizes as compared with fig. 4.9.
### β-processed Ti64 Tensile Properties: ETMT vs. Conventional

<table>
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<th>Properties</th>
<th>Method</th>
<th>Temp. (˚C)</th>
<th>Avg. YS (MPa)</th>
<th>Avg. UTS (MPa)</th>
<th>Avg. Modulus (GPa)</th>
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</table>

Table 4.3: Data table containing the average values of YS, UTS, modulus, total elongation and reduction in area (RA) with the standard deviation of the average in parentheses for the ETMT and conventional β-processed Ti-64 tensile properties.
Fig. 4.12: Graphical representation of the medium results for ETMT and conventional methods from table 4.3, depicting average (a) YS, (b) UTS, (c) reduction in area (RA) and (d) modulus, E, as a function of temperature for β-processed Ti-64.
4.3.3. Discussion

4.3.3.1. Effect of Microstructural Feature Size

The results illustrate that the ETMT is able to replicate data more accurately and with less scatter for α+β-processed Ti-64 than the β-processed material. This difference is likely related to differences in the scale of the microstructural features that have been observed to influence the properties (i.e. equiaxed α and colony size for α+β and β-processed Ti-64, respectively). The SEM backscattered electron micrographs of the α+β and β-processed Ti-64 in fig. 4.9 and fig. 4.11 show the relatively large difference in feature sizes. The sizes of the grains and colonies of the β-processed material are clearly on a larger scale (~74 μm average colony scale factor, a measure precisely described by Tiley et al. [82] of the colony size which is a measure of the size of groups of adjacent α-laths of the same variant and lying parallel to one another) than the equiaxed α and the transformed β region in the α+β-processed Ti-64 (~9 μm average particle size of equiaxed α). It is interesting to note that of the β-processed materials, the material with the highest strengths at room temperature has ETMT values that deviate from the conventional values by less than 2%. Although this deviation is more than the α+β-processed material (~1%), it is less than the low and intermediate strength β-processed materials. The notable microstructural difference between the high strength and the low and medium strength materials is the absence of large colonies, which is replaced by a basketweave microstructure (see Fig. 4.13). Therefore, rather than being described by a
colony scale factor, these microstructures may be controlled by the individual $\alpha$ laths, (~0.4 $\mu$m average $\alpha$ lath width). As noted previously, the compositions are nearly identical, with the exception of the $\beta$-processed material, which has, on average, 16 more ppm of hydrogen (~2 ppm hydrogen baseline), which may be considered insignificant. Thus, the large differences observed in strength levels between the two test methods for the $\beta$-processed materials appear not to be attributed to composition and most likely are due to differences in microstructural size scales.

![Micrograph of the basketweave microstructure found in the $\beta$-processed Ti-64 with high YS and UTS values.](image)

**Fig. 4.13:** Micrograph of the basketweave microstructure found in the $\beta$-processed Ti-64 with high YS and UTS values.

The low and medium strength $\beta$–processed Ti-64 has only a small number of colonies contained within the relatively small cross-sections of the samples, which may
lead to mechanical test results that are not representative of bulk properties. This observation, when considered with the overall lower values and larger standard deviations of YS and UTS, suggest that the local orientation is significantly affecting the mechanical properties. Indeed, it is thought that the samples begin to yield and neck at a location along the gage length within the constant temperature region, where the local grain orientation influences the shear stress resolved onto the various slip systems. Indeed, as YS and UTS are considered “average” properties, the low and medium strength β-processed samples are behaving as if they were strongly textured due to the small size of the sample. However, the high strength β-processed material does not behave as if it were as strongly textured. This is likely due to the increased number of α lath orientations that are contained within the region that yields and necks due to the presence of the basketweave microstructure. Fig. 4.14(a-b) includes enlarged areas of the micrographs in fig. 4.9 and fig. 4.11. The β-processed microstructure (see Fig. 4.14(a)) shows evidence of macroscopic shear bands across the α laths and some void formation near the fracture surface. The shear bands run parallel to the fracture surface and perpendicular to α laths in the colony. It appears that the density of these bands is greatest near the fracture surface. In contrast, the α+β-processed microstructure (see Fig. 4.14(b)) does not have any visible coarse shear bands (i.e. those visible using SEM) but does exhibit a larger density of voids. The voids are not only located near the fracture surface but can also be seen in fig. 4.9 up to ~1 mm below the fracture surface. Typically, they are associated with equiaxed α particles. The shear bands and void locations support the speculation that the YS and UTS are dependent upon the microstructure. The α+β-
processed microstructure is able to accommodate and spread the deformation over a larger volume of material, whereas, for the β-processed microstructure, the deformation is concentrated near the fracture surface. The spreading of the deformation in the α+β-processed microstructures further indicates that the measured properties represent “average” values over many microstructural units.

![Image](image_url)

Fig. 4.14: Enlarged areas of fig. 4.9 and fig. 4.11 depicting the differences in visible deformation between (a) β and (b) α+β-processed Ti-64 microstructure. The β-processed microstructure has evidence of shear bands parallel to the fracture surface and perpendicular to the α laths. The α+β-processed material has void formation at equiaxed α precipitates.

4.3.3.2. Accuracy of Modulus at Temperature

ASTM Standard E-111 (04) specifically notes that modulus determination from resistively heated samples is not accepted [112]. The justifications are probably due to the effects created by the temperature distribution, such as the distribution of mechanical
properties discussed previously. Interestingly, modulus values, determined with the DIC method from the nominally constant temperature region of the sample, are similar to those measured at room temperature and are within 15% of each other for all $\alpha+\beta$ and $\beta$-processed heat treatments. Fig. 4.15(a) shows the difference between the modulus values as a function of temperature for the two testing methods (ETMT and conventional) as compared with Ti-64 legacy data. The difference increases with temperature for all three $\alpha+\beta$ heat-treatments. This is most likely due to the differences in test apparatus and/or extensometers used for displacement measurement. Due to dimensional constraints of the load frame or furnace, displacement measurements are often not made outside the furnace, rather than directly on the sample during conventional tensile tests conducted at elevated temperatures. Hence, the measurement likely includes components of load frame compliance, leading to inaccurate sample moduli. DIC is capable of measuring strain up to the temperature limit of the applied speckle pattern, which is $\sim 815^\circ$C ($1500^\circ$F) for the present high temperature paint. This allows for an improved sample strain measurement at elevated temperatures. Fig. 4.15(a-b) shows the correlation of the $\alpha+\beta$ data with published results. The ETMT data is consistently about 10 GPa higher but the slopes appear to be comparable.
Fig. 4.15: (a) The difference between ETMT and conventional modulus averages and the difference between the ETMT and Ti-64 ASM legacy data as a function of temperature. (b) Modulus versus temperature for $\alpha+\beta$-processed Ti-64 compared with Ti-64 data published by ASM [3, 113].

The ETMT appears to be more accurate than the conventional tests at producing reliable modulus data. However, measurement of the elastic modulus as a function of temperature using tensile testing is difficult and many researchers are turning to alternative techniques, such as resonant frequency techniques for the most accurate measurements. That said, the moduli determined using the ETMT are thought to be sufficient to illustrate relative differences.

4.3.3.3. Comments Regarding Elongation

For each type of test (both conventional and the ETMT), two measures of ductility, namely elongation and reduction in area, were determined. With regard to
elongation, although the data obtained using the ETMT are self-consistent and trend correctly with conventional data, they are, in general, slightly (~1-2%) greater. This is likely due to the inherent difficulty of explicitly setting a uniform initial gage length when using DIC, which tracks two previously chosen points within all tests. Indeed, ASTM Standard E-8M (04) requires that the length of the section be explicitly reported [88]. Therefore, while the ETMT provides data that approximates the true elongation, the reported total values cannot be considered as accurate equivalents to those obtained under proper ASTM Standard E-8M considerations. Appendix B goes into more depth concerning the effect of various lengths of digital extensometers on various mechanical property data. With regard to reduction in area, the data obtained using the ETMT for both the \(\alpha+\beta\) and \(\beta\)-processed Ti-64 are significantly less than their conventional counterparts, on average, 33 and 40% less, respectively. The origin of this difference may be related to the small ETMT sample cross-sectional areas.

4.3.3.4. Accuracy of YS and UTS

Fig. 4.16 graphically depicts the YS and UTS as a function of temperature between ETMT and conventional data for \(\alpha+\beta\) processed Ti-64. The difference in values between those produced by the ETMT and conventional testing is minimal and any small discrepancies may be attributed to differences in sample temperature between the conventional test frames and the ETMT. Since the average uncertainty in values for the \(\alpha+\beta\)-processed Ti-64 is ~1% of the YS and UTS values, the ETMT can be considered self-consistent and can measure differences in YS and UTS values due to differences in
processing. For example, the difference between the conventionally tested low and medium room temperature $\alpha+\beta$ processed YS values is 26 MPa. The difference in the ETMT is 18 MPa for the same data and the standard deviations for these values are less than 6 MPa. From this data and on average, it may be concluded that both methods of testing produce data that is distinguishable (i.e. the differences in thermal processing is detectable from the yield stress values). This is critical for comparison of data from samples that may only have minor differences in composition or processing.

![ETMT vs Conventional Tensile Testing](image)

**Fig. 4.16:** Plot of YS and UTS versus temperature for $\alpha+\beta$-processed Ti-64 ($\alpha+\beta$ low) depicting the minimal differences between the ETMT and conventional data.
4.3.4. Conclusions

The ETMT is a new technique by which material can be tested at a variety of temperatures. The data obtained using subscale specimens, including tensile data (modulus, yield and ultimate tensile strengths and ductility) are of the highest quality (minimal scatter) and fidelity (representative of bulk “average” properties). One important consideration must be made when using the ETMT to obtain tensile data – specifically the size of the largest important microstructural feature. Depending upon its length scale, the results of the test can either be in exceptional agreement with conventional tests (<1% different) or in poor agreement (~13% different). In some cases, the ETMT produced superior data to conventional tests, particularly for modulus values at elevated temperatures. The following salient conclusions can be made:

- For Ti-6Al-4V specimens, the α+β processed material, whose microstructures consisted of equiaxed α, yielded strength values (both YS and UTS) in excellent agreement with conventional tests, while β-processed material that contained coarse colonies were in poorer agreement. The β-processed material that contained basketweave represented an intermediate case (<2% different).
- The yield and ultimate strengths obtained at elevated temperatures were in excellent agreement with results obtained conventionally (<4% different).
- The modulus data obtained using the ETMT is equivalent to conventional tests at room temperature and superior to conventional tests at elevated temperatures (i.e. consistent with legacy data).
- Digital Image Correlation can be used to accurately determine strain during testing.
4.4. Creep Validation

There is limited literature regarding the use of the ETMT as a creep testing tool, hence, considerable efforts are devoted to validate the technique to understand the quality and accuracy of the data produced, similar to the tensile validation already discussed. It is important to determine if the data trends with legacy data and is accurate. It is also important to show the ability of the ETMT to produce data that is statistically different for different materials (composition or processing) with similar creep response. This is critical in Chapter 5 to identify compositional variations of Timetal 21S with increased creep resistance.

4.4.1. Experimental

As previously discussed in Chapter 1, creep properties of titanium alloys improve as the $\alpha$-stability (i.e. the volume fraction of $\alpha$) increases. Fig. 1.1 is a Larson-Miller plot containing data for several titanium alloys, including Timetal 21S (15Mo-3Al-2.7Nb-0.2Si) and $\alpha+\beta$ and $\beta$-processed Ti-6Al-2Sn-4Zr-2Mo, which are $\beta$ and near-$\alpha$ titanium alloys, respectively [4]. These three materials have been tested in constant load and temperature conditions similar to the conditions of each alloy from the Larson-Miller plot. Additionally, identically processed $\alpha+\beta$ Ti-6242 material has been tested conventionally and in the ETMT in order to measure the accuracy of minimum creep strain rate data.

For these tests, rectilinear samples of Timetal 21S and $\alpha+\beta$ and $\beta$ processed Ti-6242, 1 mm by 2 mm by 40 mm, were prepared as described in sections 3.3 and 4.2 with
a thermocouple and black speckles on white background. A total of nine data points representing three sets of conditions for each of the three materials were tested at the temperature and initial stress levels outlined in table 4.4 in an inert, argon atmosphere in the ETMT. A higher temperature and stress of 650°C and 50 MPa (initial stress) was tested for each material to represent data acquired by an accelerated test. All tests were performed long enough to obtain a minimum creep rate, which was identified as the slope of the line at the approximate location of the inflection point of the curve (stage II creep). The creep tests were intentionally stopped prior to stage III creep to record the minimum creep rate. Additionally, $\alpha+\beta-$processed Ti-6242 material was tested at 538°C and 241.3 MPa (initial stress) in both air and argon atmospheres with conventional means and in the ETMT. The two conventional tests (air and argon) were performed according to ASTM Standard E-139 (06) [89] at Metal Technology, Inc. (Northridge, CA) with a gage length and initial radius of 31.8 mm and 6.4 mm, respectively. The ETMT samples were 1 mm by 2 mm by 40 mm.

4.4.2. Results and Discussion

Table 4.4 contains the minimum creep rate results for the samples tested using the ETMT, as well as the calculated Larson-Miller Parameter. As an example of a creep test performed in the ETMT, fig. 4.17 is a plot of true strain versus time of a Timetal 21S sample tested at 650°C with an initial stress of 75 MPa. Fig. 4.18 is a Larson-Miller plot of the data collected with the ETMT combined with the data from the legacy plot in fig. 1.1. All of the ETMT data appears to be shifted to the left of the legacy data (poorer creep
properties). The Timetal 21S and $\alpha+\beta$-processed Ti-6242 data, although not accurate, do trend correctly and have similar slopes as their legacy data counterparts. In contrast, the $\beta$-processed Ti-6242 does not behave as expected. It appears that the higher temperature-lower stress data is coincident with the $\alpha+\beta$-processed Ti-6242 data.

<table>
<thead>
<tr>
<th>Temperature (˚C)</th>
<th>Initial Stress (MPa)</th>
<th>Time to 0.2% strain (hr)</th>
<th>Minimum creep rate (sec⁻¹)</th>
<th>Larson-Miller Parameter to 0.2% Strain</th>
</tr>
</thead>
<tbody>
<tr>
<td>Timetal 21S</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>400</td>
<td>400</td>
<td>30</td>
<td>1.6E-08</td>
<td>14.5</td>
</tr>
<tr>
<td>450</td>
<td>200</td>
<td>8.5</td>
<td>4.9E-08</td>
<td>15.1</td>
</tr>
<tr>
<td>650</td>
<td>50</td>
<td>0.06</td>
<td>1.3E-06</td>
<td>17.3</td>
</tr>
<tr>
<td>Ti-6242 ($\alpha+\beta$-processed)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>400</td>
<td>500</td>
<td>87</td>
<td>4.7E-09</td>
<td>14.8</td>
</tr>
<tr>
<td>540</td>
<td>140</td>
<td>30</td>
<td>6.3E-09</td>
<td>17.5</td>
</tr>
<tr>
<td>650</td>
<td>50</td>
<td>0.7</td>
<td>5.9E-08</td>
<td>18.3</td>
</tr>
<tr>
<td>Ti-6242 ($\beta$-processed)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>500</td>
<td>400</td>
<td>5</td>
<td>3.3E-08</td>
<td>16.0</td>
</tr>
<tr>
<td>575</td>
<td>140</td>
<td>3</td>
<td>1.7E-08</td>
<td>17.4</td>
</tr>
<tr>
<td>650</td>
<td>50</td>
<td>0.6</td>
<td>2.7E-08</td>
<td>18.3</td>
</tr>
</tbody>
</table>

Table 4.4: Test conditions and data from the Timetal 21S, $\alpha+\beta$ and $\beta$-processed Ti-6242 samples tested in the ETMT.

![Strain vs Time](image)

Fig. 4.17: Sample creep experiment: Timetal 21S at 650°C, initial stress of 75MPa.
Fig. 4.18: Larson-Miller plot of data from the ETMT combined with data from fig. 1.1.

The legacy data shows that the β-processed material should have improved creep resistance over the α+β-processed material [3, 4, 114]. While this discrepancy in data is not fully understood, the prior beta grain size appears to be large (mm) compared with the cross-sectional area of the sample (see Fig. 4.19a) as previously seen in section 4.3.3.1 for tensile tests of β-processed Ti-64. On average, the sample cross-section contains a small number of grains (~1-5) in the β-processed materials, while the refined α+β-processed microstructure contains many equiaxed α grains whose size are on the order of about 20 μm (Fig. 4.19b). Fewer grains in the cross-section may cause samples to not exhibit bulk creep properties. The Timetal 21S material has a grain size on the order of
about 10 μm (Fig. 4.19c), which is comparable with the α+β-processed microstructure.

These two microstructures have grain sizes much smaller than the cross-sectional area and correspondingly obtain creep results that are comparable (trend and slope) with legacy data. This coincides with ASTM Standard E-139 (06) [89], which notes that creep results typically do not depend on sample size as long as the size of the sample is representative with enough grains and limited texture in the cross-section of the samples.
Fig. 4.19: Representative microstructures of (a) β, (b) α+β-processed Ti-6242 and (c) Timetal 21S acquired from an SEM at 15kV in backscattered (BSE) mode.
Although accelerated creep tests (higher temperature and/or stress) may lead to different dominant creep mechanisms, there is an incentive to use the ETMT as a creep property screening tool to decrease the time required for alloy development. Several alloys with variations of processing parameters, microstructures and/or composition can be tested in accelerated creep conditions (higher temperature or stress) to determine rapidly which samples will most likely exhibit attractive properties when tested conventionally. The curves for each alloy on the Larson-Miller plot in Fig. 1.1 do not intersect, possibly meaning that for the legacy data for Timetal 21S and α+β-processed Ti-6242 the times to 0.2% strain are significantly different (enough that if there is a change in mechanism when testing at higher temperatures, the data should still be distinguishable). Likewise for the ETMT, the data was found to be easily distinguishable between Timetal 21S and α+β-processed Ti-6242 (see Fig. 4.18).

Accelerated creep tests (increased temperature or stress) requires one major assumption: that the dominant creep mechanisms that result in an increased creep rate at higher temperature and stress will still cause creep rates (creep properties) to trend in the same direction as those that operate in the temperature and stress regime of the intended use. As long as rate-limiting creep mechanisms do not significantly change as a function of material processing and composition parameters, the ETMT can be very effective as a rapid creep property-screening tool.
4.4.2.1. Effect of Current Density

Table 4.5 and fig. 4.20 contain the minimum creep results of the α+β-processed Ti-6242 material tested conventionally and in the ETMT. The ETMT minimum creep rate is about half an order of magnitude greater than the conventionally tested samples in argon and air atmospheres. This data appears to be distinctly different and the difference leads to a conclusion that something unexpected is occurring, possibly related to:

- Variations in temperature
- Microstructural feature size or texture
- Small processing variations between samples
- Effect of the applied current through the ETMT

Temperature differences between the ETMT and conventional tests are likely to be small, since both tests have thermocouples attached to the samples. Both the conventional and ETMT tests are sampling bulk properties due to the reduced microstructural feature size. For example, the equiaxed α particle size, ~20 μm, (see Fig. 4.21) is considerably smaller than the cross-sectional area. Fig. 4.22(a-b) also show that there is limited texture in the sample from the inverse pole figure (IPF) map and pole figure (PF) from orientation microscopy. Small variations in processing can lead to noticeable differences in the creep rate [3, 89], but samples for both test methods have the same thermal and processing history, which means that the composition and microstructures are virtually identical. The effect of a DC current through the ETMT samples may be a contributing factor for increasing the creep rate.
<table>
<thead>
<tr>
<th>Method</th>
<th>Temperature (°C)</th>
<th>Stress (MPa)</th>
<th>Environment</th>
<th>Minimum Creep Rate (sec⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conventional</td>
<td>538</td>
<td>241.3</td>
<td>Argon</td>
<td>6.0E-09</td>
</tr>
<tr>
<td>ETMT</td>
<td>538</td>
<td>241.3</td>
<td>Argon</td>
<td>1.7E-08</td>
</tr>
<tr>
<td>Conventional</td>
<td>538</td>
<td>241.3</td>
<td>Air</td>
<td>4.0E-09</td>
</tr>
<tr>
<td>ETMT</td>
<td>538</td>
<td>241.3</td>
<td>Air</td>
<td>2.4E-08</td>
</tr>
</tbody>
</table>

Table 4.5: ETMT and conventional results from the α+β-processed Ti-6242 material from the same bulk material.

Fig. 4.20: Strain versus time plot of α+β-processed Ti-64 tested conventionally and in the ETMT in an argon atmosphere.
Fig. 4.21: Representative micrograph of $\alpha+\beta$-processed Ti-6242.
Fig. 4.22. Orientation microscopy of Ti-6242 depicting (a) an inverse poll figure (IPF) map and (b) a poll figure (PF) showing limited texture.

The first three factors mentioned are likely to have an insignificant effect on the minimum creep rate. If they did have an effect, it would likely not cause an approximately five-fold increase in the minimum creep rate. It is likely that the final reason, the current density through the sample, has the most significant effect due to the
difference in heating methods. Convective and radiative heating (conventional) simply changes the temperature of the material, but joule heating (ETMT), may also have an electroplastic (ep) effect, in addition to changing the temperature of the material. It has been reported from pulsed current experiments by Conrad et al. that an applied current can reduce the flow stress of materials. Conrad also gives a more in-depth history of the various experiments performed to deduce the effect of an applied current and/or field on material deformation [115-117]. Electromigration, or mass transfer due to an applied current, has been significantly characterized in integrated circuit applications where current densities can exist in the range of $\sim 10^4$ to $10^7$ A/cm$^2$ [118-121]. As the integrated circuit designs have decreased in size, current densities through metallic interconnects (i.e. aluminum-based) have increased, leading to reliability issues due to the formation of voids and hillocks. These current densities are greater than those created by the ETMT ($\sim 1070$ A/cm$^2$ for Ti-6242 at 538°C), but coupled with a significant applied stress, even these low current densities may have a significant influence on the deformation behavior of materials.

Characterizing the effect of current in the presence of load and temperature on ETMT specimen is important for the present research and may also be complementary to previous research on electroplasticity. Many of the experiments performed on metals to date involve the pulsing of AC or DC current through a sample and measuring the decrease in flow stress or increase in stress relaxation rate or creep rate. It is believed that previous researchers pulsed the current to eliminate the effect of joule heating (apply current without raising the constant temperature), which also decreases flow stress and
increases creep rates. It is also interesting to note that previous tests were performed at or below room temperature, likely for the increased ability to maintain a constant temperature [115-117]. To investigate the effect of current density on samples in the ETMT a secondary convective/radiative heat source was added to the ETMT.

Fig. 4.23(a-b) show the experimental setup of a Nichrome (60Ni-40Cr) wire surrounding the ETMT sample in series with two variacs to control the AC current through the wire. The wire has four turns around the sample spaced for a uniform temperature profile generated by the heater. The heater also has enough space between the turns to allow for the thermocouple to be attached and the black on white speckle pattern to be visible to the recording camera for DIC. This dual heater setup allows for the temperature and current through the sample to be varied independently. For a range of approximately 100-600°C, the current through the Nichrome heater is adjusted to supplement the heat generated by joule heating from the ETMT. The ETMT controls the temperature of sample, which allows the current density through the sample to be varied, by controlling the current through the Nichrome heater with the variacs. Applying zero current through the Nichrome heater achieves the highest DC current density through the sample. Likewise, the lowest current density through the sample is maintained by inputting enough current through the additional heater to achieve near zero amps output by the ETMT power supply. It is experimentally difficult to achieve zero amps through the ETMT power supply, since the ETMT requires some amperes of current to maintain a constant temperature in the sample.
Fig. 4.23: (a) Photo of the Nichrome wire heater setup. (b) Close-up of the heater during a test.
The Ti-6242 sample was tested at varying current densities with the Nichrome heater setup. The temperature and load were again held constant (538°C and 241.3 MPa – initial stress) as the current through the Nichrome heater was adjusted incrementally once a day and left to develop a steady-state creep rate. The heater current was also ramped down, up and back down to find if there were any significant effects from an unknown source such as oxidation or accumulated strain. Table 4.6 and fig. 4.24 contain the measured current densities and corresponding minimum creep rates. There is approximately a 10-fold increase in creep rate due to the applied current density through the sample, which supports the results from the literature. The low current density values of ~200 A/cm² gave an average creep rate of $5.2 \times 10^{-9}$ (sec⁻¹), which corresponds very well with the conventional data in table 4.5 of $4.0 \times 10^{-9}$ and $6.0 \times 10^{-9}$ (sec⁻¹) for the tests in air and argon, respectively.

<table>
<thead>
<tr>
<th>Day</th>
<th>Avg. ETMT Current (Amps)</th>
<th>Avg. ETMT Current Density (Amps/cm²)</th>
<th>Minimum Creep Rate (sec⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>3.4</td>
<td>1.7E+02</td>
<td>4.92E-09</td>
</tr>
<tr>
<td>3</td>
<td>10.7</td>
<td>5.5E+02</td>
<td>9.01E-09</td>
</tr>
<tr>
<td>3</td>
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<td>7.9E+02</td>
<td>1.66E-08</td>
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<td>2.8E+02</td>
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</tr>
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<td>10</td>
<td>20.3</td>
<td>1.0E+03</td>
<td>4.61E-08</td>
</tr>
</tbody>
</table>

Table 4.6: Measured current density and minimum creep values for each day of the Nichrome heater experiment.
Additional experiments were performed to determine the effect of current density on the activation energy for creep, $Q_{\text{creep}}$. As before, the Nichrome heater was adjusted incrementally to vary the current density through a Timetal 21S specimen. Fig. 4.25 depicts how the creep activation energy, $Q_t$, is measured as a function of current density, $J_i$, based on equation 2.7. The stress was held constant at 175 MPa, the temperature was varied between 500, 550 and 600°C and the current through the sample was varied between 10, 15 and 20 Amps, which corresponds to current densities of about 530, 800 and 1070 Amps/cm². Table 4.7 contains the measured creep rate data used to determine the creep activation energies from the creep rate versus inverse temperature plot in fig.
4.26. Fig. 4.27 demonstrates that the creep activation energy decreases with increasing current density, which may be expected based on the increase in creep rate found in Fig. 4.24. The measured creep activation energies (301-410 kJ/mol) are greater than other titanium alloys with a primary dominant creep mechanism of self diffusion-based creep mechanisms (242 kJ/mol) [79, 80]. The dominant creep mechanism for this alloy may be based on a dislocation glide/climb combination that has a greater creep activation energy than self diffusion or the activation energy for self diffusion is inherently greater in Timetal 21S, which has not been measured previously.

\[
\ln(\dot{\varepsilon}) = \frac{Q_i}{RT} + \text{constant}
\]

Fig. 4.25: Plot depicting the measurement of the creep activation energy, \(Q_i\), as a function of current density, \(J_i\), through the ETMT specimen based on equation 2.7.
<table>
<thead>
<tr>
<th>Avg. Temp. (°C)</th>
<th>Avg. Current (Amps)</th>
<th>Current Density (A/cm²)</th>
<th>Minimum Creep Rate Rate (sec⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>500</td>
<td>10.6</td>
<td>561</td>
<td>3.5E-09</td>
</tr>
<tr>
<td>550</td>
<td>10.1</td>
<td>536</td>
<td>1.3E-07</td>
</tr>
<tr>
<td>600</td>
<td>10.1</td>
<td>536</td>
<td>5.5E-06</td>
</tr>
<tr>
<td>500</td>
<td>14.7</td>
<td>783</td>
<td>9.1E-09</td>
</tr>
<tr>
<td>550</td>
<td>15.3</td>
<td>815</td>
<td>3.6E-07</td>
</tr>
<tr>
<td>600</td>
<td>15.0</td>
<td>797</td>
<td>8.6E-06</td>
</tr>
<tr>
<td>500</td>
<td>20.6</td>
<td>1095</td>
<td>8.4E-08</td>
</tr>
<tr>
<td>550</td>
<td>20.0</td>
<td>1062</td>
<td>1.2E-06</td>
</tr>
<tr>
<td>601</td>
<td>19.9</td>
<td>1059</td>
<td>1.9E-05</td>
</tr>
</tbody>
</table>

Table 4.7: Creep rate and current density data used to determine the creep activation energies.

![Creep Activation Energy Determination](image)

**Creep Activation Energy Determination**

- 544 (A/cm²)
- 798 (A/cm²)
- 1072 (A/cm²)

$Q_1 = 301$ kJ/mol
$Q_2 = 383$ kJ/mol
$Q_3 = 410$ kJ/mol

Fig. 4.26: Plot of creep rate versus temperature used to determine the creep activation energy for three approximately constant current densities.
4.4.2.2. Effect of Oxidation on ETMT Samples

A few ETMT samples were characterized to investigate the extent of sample oxidation during testing in argon and air at elevated temperatures compared with non-tested baseline samples. Vickers hardness profiles were effected and SEM backscattered images were recorded along the 1 mm width of several ETMT samples. Significant oxidation should cause the hardness and visible volume fraction $\alpha$ to increase. Fig. 4.28 is a compilation of several hardness profiles, including, Ti-64, Ti-21S and Ti-6242. Each data point is an average of three hardness measurements. For all three alloys, the hardness measurements neither show a significant deviation from the baseline after testing nor an increase in hardness near the surface of the sample. Fig. 4.29 is a set of micrographs of the materials used for hardness testing in fig. 4.28, which shows that there is not an
apparent increase in volume fraction $\alpha$. Oxidation of ETMT samples does not appear to be a significant factor in determining mechanical properties.

Fig. 4.28: Hardness versus distance from the edge for Ti-64, Ti-21S and Ti-6242 tested at the noted temperature and atmosphere and compared with the baseline.
Fig. 4.29: BSE SEM micrographs of Ti-64, Ti-21S and Ti-6242 taken from the grip (baseline) and near the thermocouple for each.
4.4.2.3. Variation in Creep Rate Measurement

Several creep tests were performed to characterize the variation in creep rate measurement between identically processed samples. The average and scatter (standard deviation) of the creep rate for five separate tests performed at 650°C and 50 MPa with DIC were determined for Timetal 21S (conventional plate and LENS™ processed) and α+β-processed Ti-64 (see Table 4.8). The standard deviation is greatest for the LENS™ processed Timetal 21S, likely due to possible processing defects such as voids and unmelted powder typically associated with the LENS™ process. The average creep data shows that the three materials have very similar creep resistance, which is supported by similar stress versus L-M parameter trends in fig. 1.1. The ETMT and Larson-Miller legacy data both show that conventionally processed Timetal 21S plate has slightly improved creep resistance when compared with the Ti-64 material. It is also important to point out that even though the average steady-state creep rate data is similar; it is distinct and distinguishable between the three materials. This data helps demonstrate that the ETMT can resolve mechanical property differences due to small variations in material and processing, which is critical for subtle variations in mechanical properties due to compositional variation used for the neural network analysis in this research.
<table>
<thead>
<tr>
<th>Material</th>
<th>Avg. Creep Rate (sec⁻¹)</th>
<th>Standard Deviation (sec⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Timetal 21S Plate</td>
<td>1.5E-06</td>
<td>2.0E-07</td>
</tr>
<tr>
<td>Timetal 21S LENS</td>
<td>4.0E-06</td>
<td>1.0E-06</td>
</tr>
<tr>
<td>Ti-64 (α+β-processed)</td>
<td>2.0E-06</td>
<td>8.5E-07</td>
</tr>
</tbody>
</table>

Table 4.8: Average minimum creep rate and standard deviation for Timetal 21S conventionally processed plate, LENS™ deposited Timetal 21S and α+β-processed Ti-64.

4.4.3. Conclusions

The ETMT can be used to reliably produce minimum creep rate data that trends correctly with existing data as long as the rate-limiting microstructural feature(s) are small enough to exhibit bulk properties in the ETMT sample cross-section. The ETMT be used to rapidly survey and further investigate the creep properties of new materials. For example, instead of full scale testing on few alloy variations, many alloy variations surveying a large composition space can be done in a relatively short period of time with limited amounts of material. Then conventional and full scale testing can be performed on the most promising alloy compositions. It is not fully understood whether the current density is changing the creep-limiting mechanism or if it is affecting the energy required for dislocation motion. It is only known that for the case of Ti-6242 the current increases the minimum creep rate.
5.1. Compositional, Microstructural and Property Data for the Models

Table 5.1 lists all the elements used in the compositional variation of Timetal 21S, their target composition and their expected method for improving creep resistance. As previously described in Section 3.1.1, the elemental variations were divided into four groups to limit the total number of interdependencies that existed between elements. The four groups include β-stabilizing elements (Mo, Nb and W), micron-scale precipitates (B and C), nano-scale and solid solution strengtheners (Si and Ge) and a combination of neutral solid solution strengtheners (Sn and Zr) and an α-stabilizer (Al), for convenience termed the α-stabilizer group. Table 5.1 also contains the actual measured compositional ranges as determined by standardless EDS. The composition of the low atomic numbered elements, B and C, were not measured. The oxygen content of several deposits were measured using inert gas fusion by Stavely Services Materials Testing to be less than 0.23 wt%, which is less than the oxygen content of Grade II CP Ti (0.25 wt%) [122]. All
of the target compositional ranges were more or less achieved except for Zr, which had about twice as much content (12.4 wt%) than the maximum target value (6 wt%).

<table>
<thead>
<tr>
<th>Element</th>
<th>Target composition (wt%)</th>
<th>Actual composition (wt%)</th>
<th>Group</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mo</td>
<td>11-19</td>
<td>11.8−21.5</td>
<td>β stabilizer</td>
</tr>
<tr>
<td>Nb</td>
<td>1-4</td>
<td>1.3−5.7</td>
<td>β stabilizer</td>
</tr>
<tr>
<td>W</td>
<td>1-6</td>
<td>2.3−9</td>
<td>β stabilizer</td>
</tr>
<tr>
<td>Al</td>
<td>1-4</td>
<td>1.4−4.1</td>
<td>α stabilizer</td>
</tr>
<tr>
<td>Zr</td>
<td>1-6</td>
<td>1.2−12.4</td>
<td>α stabilizer</td>
</tr>
<tr>
<td>Sn</td>
<td>1-5</td>
<td>0.3−6.7</td>
<td>α stabilizer</td>
</tr>
<tr>
<td>B</td>
<td>0-0.5</td>
<td>Not measured</td>
<td>Micro-dispersoid</td>
</tr>
<tr>
<td>C</td>
<td>0-0.5</td>
<td>Not measured</td>
<td>Micro-dispersoid</td>
</tr>
<tr>
<td>Si</td>
<td>0.2-0.8</td>
<td>0.4-1.3</td>
<td>Nano-dispersoid</td>
</tr>
<tr>
<td>Ge</td>
<td>0.2-1</td>
<td>0-2.1</td>
<td>Nano-dispersoid</td>
</tr>
</tbody>
</table>

Table 5.1: Elements, target compositions, actual compositions and group used for this investigation.

Samples (at least three for each composition) were tested in the ETMT at 650°C and 75 MPa (initial stress) until the slope of the strain versus time curve (strain rate) began to noticeably increase (see Fig. 4.17 as an example of one of the tests). The potential drop method was used for strain measurement since it predated the implementation of the digital image correlation. All tests were completed within a few hours so the small variations in ambient temperature as discussed in section 4.2 did not have a significant effect on the measured data. The minimum creep rates were measured and introduced into the models. Each tested sample was cross-sectioned, polished and imaged in the SEM (see Section 3.4). Three BSE micrographs were taken from the first
sample in each composition and a single micrograph was taken from the rest of the sample tested from an individual composition, for a minimum of five micrographs from three samples of a single composition. The stereological procedures, also discussed in Section 3.4, were applied to quantify the microstructural parameters used in the models. Fig. 5.1(a-f) is a series of micrographs that show a range of microstructures achieved during this work.
Fig. 5.1: A series of SEM BSE micrographs of select compositions. (a) Baseline Timetal 21S, (b-c) from the $\alpha$ stabilizer dataset and (d-f) from the $\beta$ stabilizer dataset with increasing $\beta$ stabilizer content leading to an observable decrease in volume fraction $\alpha$. 
5.2. Model Development

As described in Section 2.1.1, an experimental versus predicted data plot provides a visual method to estimate the degree to which a developed model can predict minimum creep rate. Fig. 5.2(a) offers such an analysis for the $\alpha$ stabilized dataset, where 60 data points were used to train and 28 data points were used to test the model. Similarly, the $\beta$ stabilized dataset used 50 data points to train and 25 data points to test the model (see Fig. 5.2(b)). Ideally, a perfect model (i.e. one that captures all of the interdependencies and predicts each data point without any deviation from what is experimentally determined) will result in a straight line with a slope of unity. Clearly, these models, shown in fig. 5.2(a-b), have not captured all of the possible variables or interdependencies, or are results of insufficient databases. A subsequent model, which includes some of these possible inputs, is discussed in detail in section 5.5. It serves as an example of how to properly interpret a model that leads to data that is unexpected or contrary to previous work.
Fig. 5.2: Plot of the experimental versus predicted minimum creep rate for the (a) \( \alpha \) stabilizer and (b) \( \beta \) stabilizer dataset.

5.3. Virtual Experiments

5.3.1. Effects of Composition and Microstructure on Minimum Creep Rate

In comparison with previous tensile property models, these creep models have significantly larger scatter, which may be explained by the complex nature of creep and the need to continue to identify and include missing model inputs. It is still possible to explore the effect of each measured microstructural input on the minimum creep rate since the inputs that most significantly influence the minimum creep rate may result in reasonable functional dependencies. Fig. 5.3(a-c) are a summary of the \( \alpha \) and \( \beta \) stabilizer dataset models which show the effect of volume fraction \( \alpha \), \( \alpha \) lath thickness and \( \beta \) mean free path on the minimum creep rate. Volume fraction \( \alpha \) results in an increase in the
creep resistance (decrease in the minimum creep rate), while an increase in the $\alpha$ lath thickness and $\beta$ mean free path both result in a decrease in the creep resistance (increase in the minimum creep rate).
Fig. 5.3: Virtual experiments of various microstructural features on the minimum creep rate: (a) volume fraction $\alpha$ ($\alpha$ stabilizer dataset), (b) $\alpha$ lath thickness ($\beta$ stabilizer dataset) and (c) $\beta$ mean free path ($\beta$ stabilizer dataset).
The first functional dependency, shown in fig. 5.3(a), indicates that the creep resistance increases with the volume fraction $\alpha$. This is not surprising, considering that the $\alpha$-Ti alloys intrinsically have better creep performance. This has been attributed to both the decreased diffusivity in the close-packed $\alpha$ phase and the fact that the $\alpha$-Ti has fewer active slip systems for dislocation glide [77]. The functional dependencies in fig. 5.3(b-c) are likely related to slip length and $\alpha/\beta$ interfacial area arguments. Kar observed that the tensile properties decrease as $\alpha$ laths coarsen [17]. This conclusion was made for room temperature testing, but may possibly be extended to dislocation glide-controlled creep for elevated temperature testing. Fig. 5.4(a-b) are TEM bright field micrographs of LENS\textsuperscript{TM} deposited Timetal 21S tested in tension to \(~1\%\) strain at room temperature and at 650°C and 75 MPa to steady-state creep. The visible dislocation densities are much greater for the room temperature sample; subgrain boundaries were also present. The presence of dislocations in the crept sample indicates that dislocation glide/climb is a significant deformation process at the elevated temperature and stress.
Fig. 5.4: TEM bright field micrographs of LENS™ deposited Timetal 21S tested in (a) tension at room temperature to ~1% strain and (b) creep at 650°C and 75 MPa to steady-state creep.
To further understand the dislocation deformation mechanisms across a broad temperature range, the Burgers vector, line direction and possible slip planes were determined for several dislocations and compiled in table 5.2. The dislocation types are predominantly the same (i.e. same type of Burgers vectors and similar type of dislocations); further supporting the conclusion that the creep mechanism is dislocation-based and that the dislocation slip length may indeed affect the creep response. Ponsonnet et al. investigated the creep response of a beta titanium alloy (β-CEZ) and found the α/β interface to be an effective barrier to dislocation motion. They also noticed an increase in dislocation densities at and near the α/β interfaces and found that increasing the α lath surface area to volume ratio through thermal treatment decreased the dislocation creep deformation [76]. For a constant volume fraction α, a decrease of the α lath thickness should and does improve the dislocation-based creep response.

<table>
<thead>
<tr>
<th>Dislocation #</th>
<th>Sample</th>
<th>Temperature (°C)</th>
<th>Strain</th>
<th>Burgers vector</th>
<th>line direction</th>
<th>slip plane</th>
<th>Dislocation Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Ti-18Mo-2.5Nb-2.7Al-0.5Si</td>
<td>650</td>
<td>Creep</td>
<td>[111]</td>
<td>[110]</td>
<td>(112)</td>
<td>edge</td>
</tr>
<tr>
<td>2</td>
<td>Ti-18Mo-2.5Nb-2.7Al-0.5Si</td>
<td>650</td>
<td>Creep</td>
<td>[111]</td>
<td>[111]</td>
<td>(011)</td>
<td>mostly edge</td>
</tr>
<tr>
<td>3</td>
<td>Ti-16Mo-3.2Nb-2.7Al-0.5Si</td>
<td>Rm Temp</td>
<td>1%</td>
<td>[111]</td>
<td>[101]</td>
<td>(121)</td>
<td>edge</td>
</tr>
<tr>
<td>4</td>
<td>Ti-16Mo-3.2Nb-2.7Al-0.5Si</td>
<td>Rm Temp</td>
<td>1%</td>
<td>[111]</td>
<td>[101]</td>
<td>(121)</td>
<td>edge</td>
</tr>
<tr>
<td>5</td>
<td>Ti-16Mo-3.2Nb-2.7Al-0.5Si</td>
<td>650</td>
<td>Creep</td>
<td>[111]</td>
<td>[121]</td>
<td>---</td>
<td>mostly screw</td>
</tr>
<tr>
<td>6</td>
<td>Ti-13Mo-5.0Nb-2.7Al-0.8Si-3W</td>
<td>650</td>
<td>Creep</td>
<td>[111]</td>
<td>[101]</td>
<td>---</td>
<td>screw</td>
</tr>
<tr>
<td>7</td>
<td>Ti-13Mo-5.0Nb-2.7Al-0.8Si-3W</td>
<td>650</td>
<td>Creep</td>
<td>[111]</td>
<td>[001]</td>
<td>(110)</td>
<td>mixed</td>
</tr>
<tr>
<td>8</td>
<td>Ti-13Mo-5.0Nb-2.7Al-0.8Si-3W</td>
<td>650</td>
<td>Creep</td>
<td>[111]</td>
<td>[012]</td>
<td>(121)</td>
<td>mixed</td>
</tr>
</tbody>
</table>

Table 5.2: Burgers vector, line direction and possible slip planes for several dislocations in deformed room and elevated temperature samples.

It is anticipated that the β mean free path (see fig. 5.3(c)) is also related to a slip-length argument and an average spacing between pinning sites. Fig. 5.5(a-b) show the difference in visible dislocation densities and configurations between regions with and
without \( \alpha \) laths. The visible dislocations in the region denuded of \( \alpha \) laths appear to be straight and the density is lower than the region with \( \alpha \) laths, indicating a possible lack of pinning sites along the line length of the dislocations. The creep resistance improves as the distance between the \( \alpha \) laths decreases (\( \beta \) mean free path).

![TEM bright field micrographs depicting the difference in visible dislocation densities and configurations between regions (a) with \( \alpha \)-laths and (b) denuded of \( \alpha \)-laths.](image)

**Fig. 5.5:** TEM bright field micrographs depicting the difference in visible dislocation densities and configurations between regions (a) with \( \alpha \)-laths and (b) denuded of \( \alpha \)-laths.

To further confirm that these alloys deform predominantly by dislocation creep, several platinum lines were deposited with a focused ion beam across grain boundaries before deformation. If grain boundary sliding is a significant source of deformation, the platinum lines may separate at the grain boundaries. Fig. 5.6 is a micrograph of the
LENSTM deposited ETMT sample (post deformation), which showed no evidence of platinum line separation. This sample was taken to several percent strain (~10%) and none of the lines were found to be separated, supporting the conclusion that grain boundary sliding is not a significant deformation mechanism.

Fig. 5.6: BSE SEM micrograph of a deformed sample with deposited platinum lines, which do not show any evidence of grain boundary sliding during creep.

In addition to microstructural variables, composition also influences the minimum creep rate. Fig. 5.7(a-b) show that Al, Sn, Zr, Mo, W and Nb all improve creep resistance.
Given that three main microstructural features are artificially held constant, including volume fraction $\alpha$, the improved creep resistance by composition can possibly be attributed to solid solution strengthening effects retarding dislocation glide.

Fig. 5.7: Virtual experiments depicting the effect of elemental variations, including (a) $\alpha$ stabilizers and (b) $\beta$ stabilizers on the minimum creep rate.

5.4. Effects of Composition on Microstructure

The neural networks can also be used to explore the effect of composition on microstructural features. Fig. 5.8 is an experimental versus predicted plot from a model that predicts the $\beta$ mean free path based on compositional inputs. Models based on predicting microstructural features appeared to be more precise than the models predicting minimum creep rate (compare Fig. 5.2 with Fig. 5.8), which may be related to a strong relationship between composition and microstructure.
It is important to consider which of the microstructural variables are intrinsic variables (i.e. predominately related to thermodynamics) and which are extrinsic variables (i.e. related to processing). For example, fig. 5.9(a) shows the intrinsic effect of two stabilizers (Al and Mo) on the volume fraction of $\alpha$ after stabilization at 700°C for 8 hours, while fig. 5.9(b) shows the extrinsic effect of Zr and Mo on the $\beta$ mean free path. While the trends in fig. 5.9(a) would be expected for any sample of the same composition subjected to the same stabilization treatment, fig. 5.9(b) will be affected by any previous processing/working operations. However, while the magnitude of the trends will change in fig. 5.9(b), the general form of the curves (i.e. positive or negative) may remain unless
there is an effect of processing on precipitation sequences or preferential nucleation sites (i.e. formation of ultrafine dispersions of other phases). With respect to fig. 5.9(a), in order to maximize the volume fraction $\alpha$, Al should be maximized and Mo should be minimized. This compositional effect is in keeping with general titanium knowledge. Nb and W have a smaller decreasing effect and Sn and Zr were found, as expected, to be neutral elements (see Fig. 5.10). Mo and Zr have the greatest effect on the $\beta$ mean free path, likely due to a retarding in the phase transformation kinetics for the former and an unknown mechanism for the latter.

Fig. 5.9: Virtual experiments of select compositions on (a) volume fraction $\alpha$ and (b) $\beta$ mean free path.
It was discovered that high contents of Zr, in the presence of Sn and Ti, forms a phase that has a deleterious effect on the creep properties of the alloy. This phase, observed as a bright white phase in the BSE micrograph in fig. 5.11, not only decorates the grain boundaries, but is also present within the grains at a refined scale. A standardless EDS line scan in STEM (see Fig. 5.12(a-b)) has identified not only the enrichment in Zr in this phase (>70 wt%), but also indicates that the maximum solubility in the $\alpha$ and $\beta$ phases may be ~6 wt% Zr (see Table 5.3). Therefore, any alloys that are further developed should contain no more than 6 wt% Zr to avoid the formation of this phase. Since Zr increases the $\beta$ mean free path significantly (see Fig. 5.9(b)), which is not beneficial, (see Fig. 5.3(c)), it may be best to eliminate Zr altogether. A virtual experiment in fig. 5.7(a) showed that Zr decreased the minimum creep rate, but it is
important to remember that that model was developed with the \( \beta \) mean free path held at an average and constant value. Zr may have a beneficial solid solution strengthening effect but it is also detrimental because it increases the \( \beta \) mean free path. It may be prudent to maintain only a small weight fraction of Zr for solid solution strengthening effects.

Fig. 5.11: SEM BSE micrograph showing the \( \beta \) (matrix), \( \alpha \) (dark) and Zr-rich (white) precipitates. (17Mo-4Nb-3.2Al-10Zr-5Sn).
Fig. 5.12: (a) STEM micrograph with the location of the EDS line scan highlighted and (b) the corresponding standardless EDS elemental quantification.

<table>
<thead>
<tr>
<th></th>
<th>Dark</th>
<th>Light</th>
<th>Matrix</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al(K)</td>
<td>3.4</td>
<td>0.6</td>
<td>2.2</td>
</tr>
<tr>
<td>Si(K)</td>
<td>0.4</td>
<td>0.1</td>
<td>0.0</td>
</tr>
<tr>
<td>Ti(K)</td>
<td>85.5</td>
<td>15.4</td>
<td>62.1</td>
</tr>
<tr>
<td>Zr(K)</td>
<td>6.0</td>
<td>71.5</td>
<td>6.3</td>
</tr>
<tr>
<td>Nb(K)</td>
<td>0.8</td>
<td>0.0</td>
<td>1.7</td>
</tr>
<tr>
<td>Mo(K)</td>
<td>1.1</td>
<td>0.0</td>
<td>25.7</td>
</tr>
<tr>
<td>Sn(L)</td>
<td>3.0</td>
<td>12.4</td>
<td>2.0</td>
</tr>
</tbody>
</table>

Table 5.3: Spot quantification data from three locations along the EDS line scan of the three different phases in fig. 5.12(a-b).

5.5. Identification of Missing Input Variables

A subsequent model based on the α stabilizer dataset was developed with an increased number of inputs, which still included the bulk composition of Al, Sn, Zr and
volume fraction $\alpha$. Additional inputs included the composition of Mo, Nb and Zr in the $\beta$ phase based on the complete bulk composition, as determined with Thermo-Calc, a commercially available thermodynamic software package. The $\beta$ mean free path was also modified to further describe the microstructure. Fig. 5.13 is a microstructure with large $\beta$ regions denuded of $\alpha$ that are common to several of the compositions. The volume fraction and size of these $\alpha$-denuded $\beta$ regions and the $\beta$ mean free path within the $\alpha$ lath clusters (see Regions 1 and 2 in Fig. 5.13) were included as additional inputs for the developed model. It is anticipated that if the $\alpha$-denuded regions are truly free of $\alpha$, including sub-scale $\alpha$ laths that may only be visible in a TEM, the operable dislocations may experience a large region of unobstructed $\beta$ over which to glide.

Fig. 5.13: An example SEM BSE micrograph showing the types of $\alpha$-denuded $\beta$ regions (Region 1) and $\alpha$ lath clusters (Region 2) that can form.
The experimental versus predicted plot (see Fig. 5.14) for the additional model shows a decrease in scatter when compared with fig. 5.2(a-b). Fig. 5.15(a-d) are the virtual experiments performed using this model, which show that the size and volume fraction of α-denuded β regions, total volume fraction α and β mean free path within the α lath clusters all increase the minimum creep rate. These results are expected based on the arguments already presented, except for the volume fraction α, which was previously predicted to decrease the minimum creep rate (see Fig. 5.3(a)). It is important to realize that this model did not contain α lath thickness as an input for this model. Typically, as volume fraction α increases, α lath thickness also increases, which is supported by fig. 5.16, a plot of the raw data used for model training for these two microstructural features. Indeed, α lath thickness does generally increase with volume fraction α and as shown by the previous virtual experiment, has a significant effect on the minimum creep rate (see Fig. 5.3(b)). This effect is sufficiently dramatic that it manifests itself by dominating the effect of volume fraction α causing the virtual experiment to perform unexpectedly. A similar model was performed again but with the volume fraction α input exchanged with the α lath thickness. Fig. 5.17 shows that α lath thickness increases the minimum creep rate. This shows that it is important to interpret the trends determined from virtual experiments carefully, including identifying inputs that are not in the model but may have a significant effect on the measured property.
Experimental vs Predicted Creep Rate

Fig. 5.14: Experimental versus predicted plot for a subsequent model predicting the minimum creep rate from the composition of Al, Sn and Zr, β phase composition of Mo, Nb and Zr, volume fraction α, size and volume fraction of α-denuded β regions and the β mean free path within the α lath clusters.
Fig. 5.15: Virtual experiments based on the model developed in fig. 5.14 predicting the minimum creep rate: (a) average size and (b) volume fraction of α-free β regions, (c) β mean free path within the α lath clusters, (d) total volume fraction α, (e) Al, Sn and Zr bulk composition and (f) Mo, Nb and Zr composition in the β phase.
Fig. 5.16: A plot of α lath thickness versus volume fraction α (raw data).

Fig. 5.17: Virtual experiment of α lath thickness versus minimum creep rate from a model with the α lath thickness substituted for the volume fraction α.
Fig. 5.15(e-f) also shows that the Sn and Zr bulk composition and the composition of Mo in the β phase increase the minimum creep rate, which is in contrast to what was previously predicted (see Fig. 5.7(a-b)). The bulk Al and the compositions of Nb and Zr in the β phase decrease the minimum creep rate as previously suggested in fig. 5.7(a-b). Again it is important to carefully interpret the developed models. For the case where the composition of Mo in the β phase is predicted to increase the creep rate, again this may be attributed to the fact that the volume fraction α was not included in the model. Considering that Mo is the strongest of the β stabilizers, it may be directly affecting the volume fraction α and α lath thickness. For the case of Zr and Sn, the trend may be giving a better interpretation of the actual performance. For small weight fractions (<1wt% Sn and <6wt% Zr) the benefit is neutral, but for greater compositions the creep resistance significantly degrades.

5.6. Effects of Ge and Si, and B and C

5.6.1. LENS™ Deposited Timetal 21S+Ge Gradient

The small (Ge and Si) and large (B and C) dispersoid compositional datasets produced experimental versus predicted plots, not shown in this work, that had poor correlation and large scatter. However, various virtual experiments are shown only for a qualitative insight. The most promising is the effect of Ge on the minimum creep rate and the volume fraction α, shown by the virtual experiments in fig. 5.18(a-b). This may be related to its effect on the nucleation and/or growth of the α phase. For further
investigation, a sample with a compositional gradient of Timetal 21S with 0wt% Ge at one end and 0.5wt% on the other was deposited with the LENS™ (see Fig. 5.19). Collins, et al. has also previously built compositional gradients for rapid investigations of the feasibility of compositional gradient deposition, Vickers Microhardness of Ti-xV and Ti-xMo alloys (where x is varied) and precipitation in Ti-8Al-xV alloys [23, 27].

The Timetal 21S+Ge deposit was hot isostatic pressed at 30 ksi, solution treated for an hour at 850°C, over aged for eight hours at 700°C and furnace cooled. Fig. 5.20 shows a progression of the microstructure as a function of Ge composition. The volume fraction $\alpha$ increases in a similar fashion as the trend in fig. 5.18(b) and the $\alpha$ lath morphology changes to a bimodal distribution in the 0.4 wt% Ge micrograph. The exact mechanism is not well understood but it is likely that the Ge is aiding in the nucleation and/or growth of the $\alpha$ phase, possibly due to the formation of a nano-scale Ge-containing intermetallic phase. Fig. 5.21 is a bright field TEM micrograph with highlighted bowing dislocations that appear to be impeded in multiple locations along its line length, which suggests the possible presence of such nano-scaled precipitates.
Fig. 5.18: Virtual experiments depicting (a) Ge versus minimum creep rate and (b) Ge versus volume fraction $\alpha$.

Fig. 5.19: Schematic depicting the LENS™ deposited Timetal 21S+Ge gradient.
Fig. 5.20: A series of SEM BSE micrographs depicting the composition and microstructural variations in a LENS™ deposited Timetal 21S+Ge gradient.

Fig. 5.21: Bright field TEM micrograph of Timetal 21S+0.8wt% Ge alloy with a highlighted dislocation bowing in several locations along its line length.
5.6.1.1. STEM Analysis

Fig. 5.22 is the Ti-Ge binary phase diagram, which shows that various intermetallic phases can form, including a Ti$_5$Ge$_3$ phase that is similar in stoichiometry to titanium silicide, Ti$_5$Si$_3$. An arc-melted button of Timetal 21S+5wt% Ge was made to further investigate this composition space by intentionally precipitating out larger Ge-rich phase(s). TEM foils were prepared and imaged in a STEM. An EDS line scan that intersected the $\alpha$, $\beta$, and Ti-Ge phases is shown in fig. 5.23. Fig. 5.24 is a plot of the compositional results of the EDS line profile and table 5.4 is summary of the compositions along three points of the linescan. The $\alpha$ and $\beta$ phases are readily identifiable where the $\alpha$ phase is Al-rich and the $\beta$ phase is Mo and Nb-rich. The Ge-rich phase is likely a Ti$_5$Ge$_3$ phase as shown by the atomic percent, which supports the Ti-Ge binary phase diagram.
Fig. 5.22: Ti-Ge binary phase diagram.
Fig. 5.23: STEM micrograph with the location of the standardless EDS line scan and the three points that are used for compositional comparison (#1 = $\beta$, #2 = $\alpha$ and #3 = Ti-Ge phases).

Fig. 5.24: Composition versus distance for the EDS line profile depicted in fig. 5.23.
<table>
<thead>
<tr>
<th>Element</th>
<th>Point #1: $\beta$</th>
<th>Point #2: $\alpha$</th>
<th>Point #3: Ti-Ge</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Weight %</td>
<td>Atomic %</td>
<td>Weight %</td>
</tr>
<tr>
<td>Ti(K)</td>
<td>75.3</td>
<td>83.8</td>
<td>95.6</td>
</tr>
<tr>
<td>Mo(K)</td>
<td>22.6</td>
<td>12.6</td>
<td>0.0</td>
</tr>
<tr>
<td>Al(K)</td>
<td>1.7</td>
<td>3.3</td>
<td>3.4</td>
</tr>
<tr>
<td>Nb(K)</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>Si(K)</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>Ge(K)</td>
<td>0.4</td>
<td>0.3</td>
<td>1.0</td>
</tr>
</tbody>
</table>

Table 5.4: Table containing the composition for each of the three points in fig. 5.23.

5.6.1.2. Atom Probe

An atom probe sample was prepared from a sample with a composition of Timetal 21S+0.8Ge and examined in an Imago LEAP–3D atom probe. The LEAP instrument is described in detail by Imago Scientific Instruments [123]. The technique uses an applied electric field to extract ions from a nano-scaled tip (~100 nm radius). Time-of-flight mass spectrometry is used to measure the original position and type of atom and then the data is reconstructed for analysis. Fig. 5.25(a-c) is a series of compositional iso-contours reconstructed from the data that show where the $\alpha$ (Al-rich) and $\beta$ (Nb and Mo-rich) phases are located. Fig. 5.26 is an alternate view depicting an ion map of the Al and Ge atoms which shows that there is Ge segregation to a particle and the $\alpha$ phase, indicating that Ge is also a slight $\alpha$ phase stabilizer. Fig. 5.27(a-b) shows how the atomic composition is extracted along the length of a cylindrical sampling of data from the volume and is plotted as a function of distance. The plot shows that the small precipitate containing an enrichment of Ge in fig. 5.26 is indeed Ge-rich and also Mo and Si-rich.
Fig. 5.25: Compositional iso-contours from the atom probe data collected for a Timetal 21S+0.8Ge sample. (a) Al (>10 at%), (b) Nb (>3 at%) and (c) Al (>10 at%) and Mo (>6 at%).

Fig. 5.26: A 3-D ion map of Ge ions (yellow) and Al ions (blue).
Fig. 5.27: (a) Cylindrical volume of atoms is examined by (b) plotting the atomic composition of elements versus the length of the cylinder.

5.6.2. *B and C Deposits*

Implementing elemental B and C (graphite) into the LENS™ deposits proved to be difficult. The microstructures appeared randomly agglomerated with regions of high density of $\alpha$-Ti, TiC and TiB phases (see Fig. 5.28). These agglomerations combined with the high $\beta$ stabilizer content created very inhomogeneous microstructures and the neural network results were also inconclusive (not shown).
Fig. 5.28: SEM BSE micrograph of a sample with carbon and boron additions. The nominal composition is approximately (Ti-19Mo-4Nb-2.7Al-0.3B-0.4C).

5.7. Summary and Recommendations

Only a portion of the most significant data from the neural network models and virtual experiments has been shown thus far. In an attempt to summarize the data from the virtual experiments a series of tables is provided which include the difference between the minimum and maximum (range) and the approximate linear slope of the data. For example, the virtual experiment examining the effect of Mo content on the minimum creep rate in fig. 5.7(b) has a range of $\sim 7 \times 10^{-6} \text{sec}^{-1}$ and slope of $\sim 0.7 \times 10^{-6} \text{sec}^{-1}/\text{wt}\% \text{ Mo}$. The effect of an input parameter (compositional or microstructural) on a measured property is rarely linear, experimentally or in a virtual experiment, but the general slope of the virtual experiment can be used as a qualitative comparison between
the inputs. Table 5.5 contains the range and slope for the compositional inputs and their effects on microstructure (volume fraction $\alpha$, $\alpha$ lath thickness and $\beta$ mean free path) and the minimum creep rate. Table 5.6 is a summary of the microstructural effects on the minimum creep rate. Also included in this table is a rank of importance based on the total range that the microstructural feature affects the minimum creep rate. The range appears to be a better measure for comparison than the average slope due the difference of units. For example, the $\beta$ mean free path in the $\beta$ stabilizer dataset affects the minimum creep rate the most as shown by the magnitude of the range as compared with the other features.
<table>
<thead>
<tr>
<th>Group</th>
<th>Element</th>
<th>Vol. fraction α avg. slope</th>
<th>Δ of min &amp; max</th>
<th>α Lath Thickness (μm) avg. slope</th>
<th>Δ of min &amp; max</th>
<th>β Mean Free Path (μm) avg. slope</th>
<th>Δ of min &amp; max</th>
<th>Minimum Creep Rate (10^-6/sec) avg. slope</th>
<th>Δ of min &amp; max</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alpha Stabilizers</td>
<td>Al</td>
<td>3.049</td>
<td>7.699</td>
<td>-0.004</td>
<td>0.024</td>
<td>-0.6</td>
<td>1.2</td>
<td>-1.1</td>
<td>3.1</td>
</tr>
<tr>
<td></td>
<td>Sn</td>
<td>-0.005</td>
<td>0.029</td>
<td>-0.013</td>
<td>0.076</td>
<td>0.1</td>
<td>0.4</td>
<td>-1.4</td>
<td>8.6</td>
</tr>
<tr>
<td></td>
<td>Zr</td>
<td>-0.002</td>
<td>0.017</td>
<td>-0.003</td>
<td>0.029</td>
<td>0.4</td>
<td>4.2</td>
<td>-0.5</td>
<td>6.0</td>
</tr>
<tr>
<td>Beta Stabilizers</td>
<td>Mo</td>
<td>-4.136</td>
<td>34.031</td>
<td>-0.006</td>
<td>0.052</td>
<td>0.5</td>
<td>5.3</td>
<td>-0.7</td>
<td>7.1</td>
</tr>
<tr>
<td></td>
<td>Nb</td>
<td>-1.016</td>
<td>4.312</td>
<td>0.004</td>
<td>0.017</td>
<td>0.1</td>
<td>0.4</td>
<td>-2.0</td>
<td>8.8</td>
</tr>
<tr>
<td></td>
<td>W</td>
<td>-0.373</td>
<td>2.447</td>
<td>-0.001</td>
<td>0.004</td>
<td>0.1</td>
<td>0.4</td>
<td>-0.9</td>
<td>5.8</td>
</tr>
<tr>
<td>Small Dispersoids</td>
<td>Si</td>
<td>10.015</td>
<td>9.211</td>
<td>-0.021</td>
<td>0.023</td>
<td>-0.2</td>
<td>0.2</td>
<td>-0.1</td>
<td>0.1</td>
</tr>
<tr>
<td></td>
<td>Ge</td>
<td>4.494</td>
<td>9.211</td>
<td>-0.009</td>
<td>0.023</td>
<td>-0.1</td>
<td>0.2</td>
<td>-0.1</td>
<td>0.2</td>
</tr>
<tr>
<td>Large Dispersoids</td>
<td>B</td>
<td>-14.004</td>
<td>4.959</td>
<td>0.056</td>
<td>0.023</td>
<td>-0.7</td>
<td>0.3</td>
<td>-9.2</td>
<td>3.2</td>
</tr>
<tr>
<td></td>
<td>C</td>
<td>-4.077</td>
<td>2.753</td>
<td>0.126</td>
<td>0.069</td>
<td>1.9</td>
<td>1.3</td>
<td>1.4</td>
<td>1.1</td>
</tr>
</tbody>
</table>

Table 5.5: Summary of the bulk compositional effects on microstructure and minimum creep rate with a rank of importance based on the total range the feature affects the creep rate.
Table 5.6: Summary of the microstructural effects on the minimum creep rate.

<table>
<thead>
<tr>
<th>Group</th>
<th>Microstructure</th>
<th>Minimum Creep Rate (10^{-6}sec^{-1})</th>
<th>Rank of Importance</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Avg. Slope</td>
<td>Δ of min &amp; max</td>
</tr>
<tr>
<td>Alpha Stabilizers</td>
<td>Vol. fraction α</td>
<td>-0.3</td>
<td>7.6</td>
</tr>
<tr>
<td></td>
<td>α Lath Thickness</td>
<td>76.7</td>
<td>8.6</td>
</tr>
<tr>
<td></td>
<td>β Mean Free Path</td>
<td>0.4</td>
<td>3.7</td>
</tr>
<tr>
<td>Beta Stabilizers</td>
<td>Vol. fraction α</td>
<td>-0.1</td>
<td>5.3</td>
</tr>
<tr>
<td></td>
<td>α Lath Thickness</td>
<td>96.9</td>
<td>13.0</td>
</tr>
<tr>
<td></td>
<td>β Mean Free Path</td>
<td>2.4</td>
<td>19.0</td>
</tr>
</tbody>
</table>

Table 5.7 ranks the importance of each of the three main microstructural features solely based on adding the range values from the α and β stabilizer datasets. A rank of one denotes the highest values and a rank of three denotes the lowest value. The elements that affect each of the features are listed. Table 5.8 lists the recommended composition space for future alloys with improved creep resistance along with the possible industrial implications. Mo and W are elements that typically perform well at elevated temperatures due to slow diffusion rates, but for the same reason, they can be difficult and/or expensive to process. Ge is also a naturally prohibitive element due to raw material costs. Sn appears to be an element that may be cheaply added, yet provide an improvement in creep resistance.
<table>
<thead>
<tr>
<th>Rank</th>
<th>Priority</th>
<th>Increase</th>
<th>Decrease</th>
<th>Neutral</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Decrease</td>
<td>β Mean Free Path</td>
<td>Al, Si, Ge, B</td>
<td>Zr, Mo</td>
</tr>
<tr>
<td>2</td>
<td>Maintain/Increase</td>
<td>α Vol Fraction</td>
<td>Al, Si, Ge</td>
<td>Mo</td>
</tr>
<tr>
<td>3</td>
<td>Decrease</td>
<td>α Lath Size</td>
<td>Al, Sn, Zr, Si, Ge, Mo</td>
<td>Nb, W, B, C</td>
</tr>
</tbody>
</table>

Table 5.7: Ranking of select microstructural features along with which elements affect each feature.

<table>
<thead>
<tr>
<th>Group</th>
<th>Element</th>
<th>Recommendations</th>
<th>Industrial Implications</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alpha Stabilizers</td>
<td>Al</td>
<td>Max content ~ 4wt%</td>
<td>α₂, processing</td>
</tr>
<tr>
<td></td>
<td>Sn</td>
<td>2-4wt%</td>
<td>none known</td>
</tr>
<tr>
<td></td>
<td>Zr</td>
<td>Eliminate</td>
<td></td>
</tr>
<tr>
<td>Beta Stabilizers</td>
<td>Mo</td>
<td>12-15wt%</td>
<td>processing</td>
</tr>
<tr>
<td></td>
<td>Nb</td>
<td>3 wt% (present for corrosion props)</td>
<td>no change</td>
</tr>
<tr>
<td></td>
<td>W</td>
<td>2-3wt%-added in substitute of Mo</td>
<td>processing, revert problems</td>
</tr>
<tr>
<td>Small Dispersoids</td>
<td>Si</td>
<td>0.2-0.4wt%</td>
<td>silicide formation issues</td>
</tr>
<tr>
<td></td>
<td>Ge</td>
<td>0.4-0.8wt%</td>
<td>increased cost</td>
</tr>
<tr>
<td>Large Dispersoids</td>
<td>B</td>
<td>0.2wt%</td>
<td>processing, revert problems</td>
</tr>
<tr>
<td></td>
<td>C</td>
<td>Minimize</td>
<td></td>
</tr>
</tbody>
</table>

Table 5.8: Compositional recommendations for future alloys and development along with their possible industrial implications.

It is also important to remember that these virtual experiments were performed with the other inputs held at constant, average values. As long the constant values are within the range of the data used for model training, they can be varied in subsequent models to further explore the compositional space.
5.8. Oxidation Testing

Fig. 5.29 is a plot of some of the data from the oxidation testing, which appears to show that oxidation properties do not significantly degrade with compositional variations, when compared with the values of other materials in table 2.2.

![Time vs. Weight Gain due to Oxidation](image)

Fig. 5.29: Select results from oxidation testing.
6.1. Summary and Conclusions

This work has focused on optimizing creep properties for alloys based on Timetal 21S by way of the LENS™ process, rapid creep screening (ETMT), microstructural characterization and Bayesian Neural Networks. The primary foci were the validation of the ETMT as a valid tensile and creep tester at room and elevated temperatures and the use of the ETMT to help develop alloys with improved creep resistance.

6.1.1. ETMT

It was found that the ETMT can measure tensile properties (YS and UTS properties) within ±1% of conventionally tested material for α+β-processed Ti-64 at room temperature and within ±4% at elevated temperatures. Testing of β-processed Ti-64 with prior beta grain and colony sizes that were on same scale as the cross-sectional area of the samples provided data that was lower, but within 10% of the conventionally tested material. This showed that the size scale of the property-limiting feature should be significantly smaller than the size of the sample for bulk property measurement.
Creep testing with the ETMT revealed that the use of resistance heating by passing a current through the samples affected the creep rate. A Nichrome wire heater was used to determine that, for a constant temperature and stress, the current through the sample increased the creep rate about an order of magnitude. By using the Nichrome wire heater, the ETMT achieved a very similar minimum creep rate as the conventionally tested Ti-6242 material at the same temperature and load conditions. Multiple tests of LENS™ deposited Timetal 21S, Timetal 21S plate and Ti-64 showed that the statistical variation between tests is limited and the creep rates between these three alloys are distinguishable. The ETMT can and should be used to rapidly investigate creep in multiple alloys as a screening tool to improve alloy selection for longer-term, traditional creep tests.

6.1.2. *Alloy Development of Timetal 21S*

Implementing Bayesian Neural Networks for the predicting of creep properties in β-Ti alloys proved to be effective, but with noticeable error that can likely be attributed to inherent difficulties associated with modeling creep, missing inputs or an insufficient database. This work suggests that the volume fraction and morphology of the α phase influence markedly the creep performance. This includes the β mean free path and the size and volume fraction of the α-denuded regions in the microstructures. Elements that appear to dictate the β mean free path include Mo and Zr. Small additions of W (>3 wt%) in place of Mo and small additions of Sn (2-4 wt%) appear to be beneficial for creep properties.
6.2. Future Work

6.2.1. ETMT Validation and Comparison

All of the tensile and creep validation was performed on a single titanium alloy (Ti-64). Performing smaller scale testing on various Ni, steel and Al structural alloys systems may provide information in regards to other benefits and/or limitations associated with tensile tests in the ETMT. This also includes expanding the test matrix to investigate the effect of current density on other alloys such as Ni, Al and steel during creep experiments.

6.2.2. Alloy Development for Creep Properties

Future work should focus on continuing to identify possible missing inputs to improve the neural network models. A few more compositions deposited with the LENS™ based on the range in table 5.8 should be tested in the ETMT to enhance the potentially ideal composition space. Recommendations should then be made to Timet Corp. for select heats (about 5) to be made, heat-treated and tested conventionally to compare with the baseline alloy.


properties of shielded metal arc welds, with varying compositions of carbon, manganese, and nickel were explained in terms of the relative amounts of different microstructural constituents. Welding Journal, 2006. 85(10): p. 218S-224S.

11. Lee, E., Microstructure evolution and microstructure/mechanical properties relationships in α+β titanium alloys. 2004, The Ohio State University


17. Kar, S., Modeling of Mechanical Properties in Alpha/Beta-Titanium Alloys, in Graduate School. 2005, The Ohio State University: Columbus, OH.


33. Fraser, H.L., *from MSE 663 class notes*. Fall 2005: The Ohio State University.


105. Searles, T., Microstructural Characterization of the alpha/beta Titanium Alloy Ti-6Al-4V, in Materials Science and Engineering. 2005, The Ohio State University: Columbus, OH.


APPENDIX A:

ABBREVIATED ETMT GUIDE AND INSTRUCTIONS
A.1. Introduction

The Electrothermal Mechanical Test (ETMT) was developed by Instron and NPL and is located in FL 338 at The Ohio State University. These instructions are to complement the Instron user manual and detailed training of the machine. It may be best to read through these notes before official training by the proper Fraser Group member and refer back to it, the Instron user manual and Instron service when needed. The ETMT is a fairly simple machine to use, but like all mechanical testing, there needs to be a good understanding of what is going on at all times because it will always do what it is told to do. Since it may not always do what it is wanted, it is favorable to work slowly and systematically to limit the number of wasted samples.

In the case that something fails and it is evident that a step has not been forgotten or omitted, Instron has been very helpful in resolving issues in the past. When contacting Instron for support, keep in mind that there are not many ETMT machines in the world, so very few people at Instron even know what it is. For reference, the ETMT model name is officially the ETMT 8800 and, presently, the person that is most knowledgeable in their service department is Dave Elliot. He is great to work with and has helped resolve nearly everything over the phone and within a few days. Also, if needed, please feel free to contact the author for recommendations and system history.
A.2. Sample Preparation

Standard samples are 40x2x1 mm, but can vary. The width must fit in between the sample mounting bolts, which have about a 6 mm separation. The distance between the upper and lower grips is 16 mm and the upper grip has ±5 mm of travel. This allows for the distance between the grips to be increased or decreased to fit a smaller or larger geometry. Just remember to allow enough travel to complete a given test.

There are two other main sample size limitations. First, there is a 5kN load cell, but the motor can only sustain 3kN continuously. This means it can measure above 3kN, but the cross-sectional area must be small enough to achieve the UTS before reaching 3kN (tensile test). It is has also been found that if the test goes above 2kN samples have often slipped in the straight sided grips. Longer samples or adding a texture to the sacrificial stainless steel or brass plates helps to reduce slipping. The second limitation is related to the desired maximum temperature. Higher temperatures are achieved with samples that have larger electrical resistance. Smaller cross-sections, larger distances between the grips and higher material resistivities all increase the sample resistance. Larger samples are not always better, so keep these two points in mind.

For temperature control, type R thermocouples are made from 0.25 mm diameter Pt and Pt-13Rh wire that are melted together with an acetylene torch. A Miyachi Unitek spot welder with an 80A/EZ weld head at settings of 2.0 and 3.5% output (for Ti-based alloys) for the first and second pulses, respectively, is used to attach the thermocouple to
the center of the sample. Same size diameter and material wires can also be attached for strain measurement via the potential drop method (see Fig. 2.34 and Section 2.4.2.1).

The speckle pattern for digital image correlation (DIC) is applied to the central 16 mm of the sample with Plasti-Kote® high temperature spray paint, which is rated for elevated temperatures up to ~815°C and is only sold at CARQUEST. Two coats of white background are typically sufficient and then the black speckles are applied with a fine mist. This takes some practice, but hold the can a foot or two above the sample and let the fine black mist fall onto the sample. Fig. 4.6 is an example of a good spray paint job.

A.3. Standby Condition

The standby condition should include: sample not loaded, grips at the zero displacement position, argon tank valve open but the valve on the ETMT should be closed, actuator turned off (0 button on the pendent should be illuminated), current power supply turned off, chiller turned off, vacuum valve closed and vacuum pump turned off. Rarely should the 8800 control tower or computer be turned off. The 8800 control tower can be turned on or off by the switch that is in the upper left of the back of the unit. It takes a few minutes to boot-up and go through its various system checks. The system is ready when the activity light is flashing (8800 control tower) and the FT Console actuator display has a grayed circle. Remember to turn on and let the power supply, chiller supply and vacuum pump warm up before calibrating the system.
A.4. Logging in and FT Console

Log into the computer and start the FT Console software, which should bring up a log file (which can be minimized if desired) and a series of buttons at the top of the screen (see Fig. A.1). Become familiar with this software before doing anything. Every little icon and color means something. There are menus for the actuator drive (right-hand set of menus) and the temperature drive (left-hand set of menus). The actuator side has menus for the strain gage, linear position encoder, load, motor encoder, set point and specimen protect. The temperature side has menus for volts, temperature, current, set point and specimen protect. The motor encoder, linear encoder, load, current and temperature can be made the controlling channel (highlighted green) by right-click->mode transfer on a given icon.

Displays can be added by right-clicking on the Actuator controller menu and selecting live displays. Each individual display can be changed to the desired read out. Pre-saved displays can also be loaded by right-clicking on the display and opening a previous display.

Fig. A.1: FT Console Header and a row of displays.
A.5. Calibration

Full calibration and/or balance of all the channels (temperature, current, voltage, motor encoder, linear encoder, strain gage and load) typically needs to take place if the 8800 control tower is turned off for any reason. Otherwise, frequent balancing of the load is the most common action.

A.5.1. Temperature Calibration

Right click the Temperature controller in the FT Console software and run the Calibration Wizard. Select restore calibration from file. The temperature and voltage calibration are the only two calibrations that are previously done and restored from a file. Do not overwrite any of these files and keep back-ups of them. For the temperature calibration, use the file: axis2_channel2_temperature_9Feb06_linearized.cal. Select okay and finish. Next, right-click the main temperature menu and select Analog I/O. For the X and Y tabs configure the settings as shown in Fig. A.2 and Fig. A.3. For the current calibration perform the same steps but load the axis2_channel1_current.cal file and select okay and finish. There are no additional changes needed for the Analog I/O.
Fig. A.2: Analog I/O X tab configuration
A.5.2. Position Calibration (motor encoder and linear position encoder)

Set the gage length to 16 mm by using the supplied black aluminum block and raising or lowering the upper grip with the handset controls. Caution: never move the actuator with block between the grips; this will prevent smashing the aluminum block in the grips. Once the gage length is set, run the calibration and balance for the motor and linear position encoders in a similar fashion as the load calibration. These two calibrations may not need to be done if the grips are returned to the zero position before turning off the 8800 control tower. The actuator does not move while it is off, but it does forget where it was when it is turned off and then on.
It is also prudent and safe to apply limits on the motor displacement to protect the ETMT. Right-click>limits on the motor encoder icon and set the primary limits to 4.2 and -2.0 mm and the physical limits to 4.5 and -3.0 mm. These limits can be set to accommodate a desired test. For example, they should be lower for a simple thermal treatment. This gives two sets of digital limits before the mechanical limits are reached.

A.5.3. Strain Gage Insertion and Calibration

The strain gage has a pin that is inserted like a grenade to set the zero displacement position. With the pin in place and using the homemade dental tool (copper tube with an Allen key in one end), carefully place the springs on the white poles to the right of the grips. With motor and linear position encoders at zero, pull the pin and then calibrate the strain gage (Strain 2) in a similar fashion as the motor and linear encoders. All three positions should read a very similar position at this point.

A.5.4. Load Calibration

Make sure the actuator is in position control (icon is highlighted green), turn on the actuator with the handset control (pendent) and right-click the load menu and select calibration wizard. Select the auto and manual calibration and click next until the menu with the start button comes up. Click start and let it calibrate itself. Do not save the calibration data and click finish. This calibration should not need to be performed often.

The load must be set to zero periodically (typically at least once a day). Remember that the environmental chamber and all of the connected hoses are resting on
the load cell. Small variations in room temperature cause the zero point to fluctuate. With
the door on, sample free from the top grip, argon flowing and the position at zero, zero
the load by right-click>Balance on the load.

A.6. Loading the Sample

With the sample secured to a machined aluminum loading block (which centers
the sample horizontally and vertically), insert the sample between the grips and the
stainless steel (or brass) sacrificial plates. It is necessary to remove at least one of the grip
bolts, if not more, to be able to fit the sample into the grips. It will also be necessary to
raise the upper grip to make room for the loading block (remember to set the position and
load to zero before tightening the upper grip). Make sure the ETMT is in position control
(motor encoder is highlighted green) the appropriate limits are set. Tighten the lower grip
screws completely and then gently tighten the upper grip screws, being mindful of the
measured load. Do not exceed the yield stress of the material. Mode transfer immediately
to load control by right-clicking on the load control menu. Click on the set point menu
and set the load to zero. If the position creeps along, this means that the sample is loose.
If the sample is not secure, loosen the upper screws, set the position to zero and try again.
Now tighten the screws completely while in load control. Use the torque wrench to
tighten the bolts equally each time. The sample is now loaded correctly!

A.6.1. Thermocouple/Volt Wire Connection, Pressure Vessel Door Installation,
Current Power Supply Initiation

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Solder the grey (Pt) and yellow (Pt-13Rh – stiffer of the two) wires to the thermocouple wires and the red (lower) and white (upper) wire to the voltage wires. If the temperature reading decreases instead of increasing with an applied current, the thermocouple wires are reversed. It is also very important that the thermocouple wires come directly off the sample without touching anything else including the edge of the sample, another wire and either of the grips. As a quick check it may be good to turn on the power supply and apply a few amps to make sure the thermocouple wires are soldered correctly. The pressure vessel door can be attached to the chamber.

With the pressure vessel secure, open the vacuum valve. Wait for the chamber to pump down to a sufficient vacuum level (60-100 millitorr) and backfill with argon. Typically three purge cycles are performed. The pressure vessel is designed to have a continuous purge at about a third of a psi positive chamber pressure. With the argon outlet hose in soapy water, it should bubble about once per second.

Once the sample environment is achieved the power supply can be enabled. The current command must be a negative value before enabling the power supply by pushing the green button. If this value reads positive amps, either hit the stop button in the upper right hand corner of the monitor or use the set point to change the current to a value of -5 amps.

A.7. Testing

There are several software packages available for testing. MAX (Instron) is the most commonly used program for thermal treatment and tensile tests. The FT Console
interface has some built in ramp and waveform generators. Combined with the data logging capabilities of DAX (Instron), manual tests can be performed with FT Console. These two have been used together when displacement control is desired, but load control is needed during temperature ramp to account for thermal expansion. Another package, ETMT (NPL), is available for dynamically cycling the temperature with a varying mean combined with load or displacement control. RSScope is a tool used for real-time system monitoring and logging. RSSave is a utility package to save customized settings. For simplified startup, it is recommended to copy another user’s test setup files to perform a similar experiment and modify them as needed.

A.7.1. Example Tensile Test Using the MAX Software

This section briefly discusses how a typical tensile test is performed with the ETMT using the MAX software package. This test specifically has a strain rate increase that takes place after the yield stress is achieved. Mechanical testing laboratories will often apply a strain rate increase when 2% total strain is achieve to decrease the time to complete a tensile test. Since the ETMT does not have a method to directly measure the strain in the sample as discussed in Section 4.2, only displacement-controlled tests can be performed in the ETMT. Hence, the strain rate increase is set to a take place at a position that should at least be after the yield stress is achieved.

MAX is able to perform simple linear ramps or cycles by controlling load or displacement and current or temperature and can also perform tests using a randomly generated file. In this case, the file is not necessarily random but contains multiple linear
ramps. Microsoft® Excel is used to make a three column text file as shown in Table A.1. The first column is the absolute time (seconds). The greatest difference between sequential rows should be no more than 1800 seconds (0.5 hour). The MAX software will not accept files that have more than 2147 seconds between the rows. The second and third columns are normalized values between -1 and 1, where -1 is the maximum negative amplitude and 1 is the maximum positive amplitude of the values set in the MAX software. The second column represents the actuator axis, which is the load, motor encoder, linear encoder, or strain gage control and the third column represents the temperature axis, which is current or temperature control as determined by the user. The amplitudes are set in the waveform menu of the MAX software as shown in Fig. A.4. For a tensile test at 300°C, as performed in Chapter 4 of this work, the amplitude for the actuator axis was set to 5 mm with the motor encoder controlling (see Fig. A.4) and the temperature axis amplitude was set to 300°C with a mean of 0°C. This implies that the displacement is 5 mm and the temperature is 300°C when a value of one is in the second and third columns of the .csv file, respectively. The .csv file in Fig. A.4 has a three second temperature ramp, a 27 second temperature hold and then the first displacement rate lasts for 150 seconds and the second displacement rate lasts for 345 seconds. The two displacement rates corresponded to approximately 0.005 and 0.05 min⁻¹, respectively.
Table A.1: Example .csv file created with Microsoft® Excel for a tensile test with a strain rate increase which is to be imported into MAX. The table has no headers when imported. The first column is time (seconds). The second column represents axis one (actuator). The third column represents axis two (temperature).

<table>
<thead>
<tr>
<th>Time (seconds)</th>
<th>Actuator Axis</th>
<th>Temperature Axis</th>
</tr>
</thead>
<tbody>
<tr>
<td>Start Test</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Temperature Ramp</td>
<td>3</td>
<td>0</td>
</tr>
<tr>
<td>1st Displacement Rate Begin</td>
<td>30</td>
<td>0</td>
</tr>
<tr>
<td>Transition to 2nd Displacement Rate</td>
<td>180</td>
<td>0.08</td>
</tr>
<tr>
<td>Test End</td>
<td>525</td>
<td>1</td>
</tr>
</tbody>
</table>

Fig. A.4: Screen shot of the waveform menu in the MAX software.
The prepared three column .csv file is then imported into MAX and converted to a .rdf file (File>Import CSV). The .rdf file is saved with linear ramps selected (see Fig. A.5) and then the newly saved .rdf file is selected within the waveform. Finally, the logging menu is used to define what, where and how often the data is to be saved. The test is now ready to be started. When complete, the data can then be analyzed for properties such as modulus, yield stress, UTS and elongation. Data analysis is performed manually in Microsoft® Excel, but macros have been and can be written to simplify the data analysis.

Fig. A.5: Screen shot of the Import CSV menu in the MAX software.
APPENDIX B:

ETMT STRAIN MEASUREMENT VIA DIGITAL IMAGE CORRELATION
Digital image correlation (DIC) was implemented in Chapter 3 for improved strain measurement in the ETMT and used in Chapter 4 for ETMT tensile property validation. The Application Notes and Vic-2D® software instructions are simple, helpful and should be read to gain a basic understanding of digital image correlation. Please refer to the manuals supplied by Correlated Solutions for specific setup, testing and data analysis. This appendix is a supplement and extended explanation to help use the DIC hardware and software unique to OSU.

B.1. ETMT Hardware Additions and Software Modifications

The hardware additions and software modifications are designed to collect sequential images and link them correctly with the load, displacement, temperature and current values output from the ETMT. For this data collection, a National Instruments BNC 2110 board (see Fig. B.1) collects the voltage signal output by the 8800 control tower for each channel via BNC connectors. The 8800 control tower has BNC analog data output capabilities that are defined in the Analog I/O menus in the FT Console for each of the actuator and temperature axis. The Vic-Snap® software on the support PC collects the output voltage, converts the units and saves it as a .csv file. Each row in the file is numbered to correspond with an image taken by the camera.
The camera uses a firewire cable to send the images to the support PC. The PC firewire port uses a special driver for enhanced image transfer performance that makes the port incompatible with anything but the camera. See the supplied application notes for instructions on how to switch between the standard and special firewire driver. The camera has a camera length of about 50 cm and can be focused by turning the lens. A halogen light source has been mounted to the Instron frame and has light guides for specimen illumination (see Fig. B.2). Increased light allows for the frame rate to be
reduced, which reduces blurring due to a moving specimen. The Vic-Snap® software can crop the image to reduce the single file image size by selecting the region of interest>right-click>clip and has a timed capture mode where the interval and total acquisition time can be set.

Fig. B.2: Photo of the Halogen light source and guides.
A small fan was added to the inside of the high integrity chamber for increased air circulation (see Fig. B.3(a-b)). It was found that during a slow temperature ramp rate (2.5°/sec) at zero load of a Ti-64 specimen the strain began to increasingly oscillate with increased temperature. Fig. B.4 is a plot of strain versus distance along the vertical axis of the Ti-64 specimen without using a fan. Each curve represents the strain at a different maximum temperature. Notice the amplitude of the oscillations increase with the temperature. Fig. B.5 is the same plot of strain in Fig. B.4 but from a second test using the fan. The reduction of the oscillations shows that the fan effectively circulated the heated air in front of the specimen, changing the indexes of refraction, improving the strain measurement.

Fig. B.3: Photograph of the (a) fan inside the high integrity chamber and (b) its switch and control knob.
Fig. B.4: Plot of strain versus distance for various maximum temperatures without the ETMT fan on.
B.2. Effect of Various Two-Point Extensometer Lengths on Mechanical Properties

Section 4.2 briefly discusses how a digital two-point extensometer is placed on a sample within the Vic-2D® software for strain measurement. Section 4.3.3.3 also discusses that a possible reason why the tensile elongation data from the ETMT varies with respect to conventional data is due to the non-uniformity of extensometer lengths between tests. An extensometer length in a conventional test is often one inch as specified by the ASTM Standards, versus a possible wide variation in the ETMT due to elevated temperature and reduced cross-section gage lengths. This appendix section shows and discusses the effect of various digital extensometer lengths on measured
mechanical properties of a single room (22°C) and elevated temperature (300°C) tensile test.

Fig. B.6 shows the initial image of the room temperature (dog bone shape) and elevated temperature (straight sided) samples and the approximate lengths of the three digitally applied two-point extensometers. Vic-2D® was then used to determine the strain and Table B.1 contains the mechanical property data from each of the short, medium and large extensometers.

![Fig. B.6: Schematic depicting the approximate locations of short, medium and long digitally applied extensometers in Vic-2D® on a room and elevated temperature sample.](image)

<table>
<thead>
<tr>
<th>Extensometer Type</th>
<th>Room Temperature (22°C)</th>
<th>Elevated Temperature (300°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Short</td>
<td><img src="image" alt="short_extensometer" /></td>
<td><img src="image" alt="short_extensometer" /></td>
</tr>
<tr>
<td>Medium</td>
<td><img src="image" alt="medium_extensometer" /></td>
<td><img src="image" alt="medium_extensometer" /></td>
</tr>
<tr>
<td>Long</td>
<td><img src="image" alt="long_extensometer" /></td>
<td><img src="image" alt="long_extensometer" /></td>
</tr>
<tr>
<td>Extensometer Size</td>
<td>Temp. (°C)</td>
<td>Modulus (MPa)</td>
</tr>
<tr>
<td>------------------</td>
<td>-----------</td>
<td>---------------</td>
</tr>
<tr>
<td>Short</td>
<td>22</td>
<td>140</td>
</tr>
<tr>
<td>Medium</td>
<td>22</td>
<td>134</td>
</tr>
<tr>
<td>Long</td>
<td>22</td>
<td>130</td>
</tr>
<tr>
<td>Short</td>
<td>300</td>
<td>108</td>
</tr>
<tr>
<td>Medium</td>
<td>300</td>
<td>110</td>
</tr>
<tr>
<td>Long</td>
<td>300</td>
<td>108</td>
</tr>
</tbody>
</table>

Table B.1: Mechanical property data from each of the extensometers represented in Fig. B.2.

The modulus data does not vary dramatically and the UTS is independent of the strain in the sample. There is a large deviation in the total elongation between the two different samples. For the room temperature test, the elongation increases with extensometer length. Upon review of the test, the room temperature sample failed outside of the short extensometer. The short extensometer did not capture the large strain localization that occurred in the necked region at the location of failure. The long extensometer was able to capture the most amount of strain since it contained the necked region. The lower elongation values (shorter digital extensometer) caused a slight increase in the yield stress values.

The elevated temperature extensometers created opposite trends as compared with the room temperature sample. The shorter extensometer had greater elongations and lower yield strength values, which may be caused by failure in the middle of the sample. The vertical parabolic distribution in temperature ensures that the weakest location in the sample is in the middle (highest temperature). The yield stress is least in this region and the sample should neck and fail in the middle causing the central region to observe the greatest elongation. All three extensometers captured the necked region and contained the
important displacements. It is not surprising that the shorter extensometer has the largest elongation values since strain is a change in length divided by the initial gage length. For failure within all three extensometers, larger initial gage lengths should lead to lower elongation values. ASTM has standardized the gage length and requires that the gage length be explicitly reported for consistent data interpretation [88].