DEFORMATION STUDIES ON DIRECTIONALLY SOLIDIFIED EUTECTIC

LaB$_6$-ZrB$_2$

A Thesis in

Materials Science and Engineering

by

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Abstract

Directionally solidified eutectic LaB$_6$-ZrB$_2$ samples were studied for potential use as ultra-high-temperature materials. Novel ultra-high-temperature materials are needed to improve the efficiency of flight vehicles, turbine engines and rocket engines. In evaluation of LaB$_6$-ZrB$_2$’s viability for high-temperature applications, room-temperature indentation and high-temperature creep studies were performed.

A Vickers indenter was used to initiate room-temperature deformation at a 19.6 N load. The area directly under the indent was analyzed by TEM. Fracture and debonding at the interfaces was observed and samples showed numerous dislocations in both phases. Dislocations were observed to initiate and end in the bulk. Dislocations were not observed to initiate or end at the interfaces. Two beam conditions were performed in g$_{200}$ LaB$_6$ and g$_{010}$ LaB$_6$ orientations. Dislocations that were evident in the g$_{200}$ LaB$_6$ were not seen in the g$_{010}$ LaB$_6$ TEM studies. These results are consistent with the $\{100\}/<110>$ slip system being satisfied. Other dislocations appeared in both the g$_{200}$ LaB$_6$ and g$_{010}$ LaB$_6$ orientations. These results indicate that more than one slip system is operable at room-temperature in the LaB$_6$ phase of the directionally solidified eutectic.

An impression creep instrument was modified for controlled-atmospheric testing under high temperatures. Standard samples of SiAlON material were tested for validation of instrument performance. Standard samples yielded comparable results as samples run by a previous researcher. Samples of LaB$_6$-ZrB$_2$ DSE were run for 100hrs at temperatures between 1400-1600°C and stresses of -300, -400, and -420 MPa. Deformation did not occur at these temperatures and stresses. Oxidation occurred during creep testing and additional sample preparations and furnace modifications were performed to try to eliminate oxidation of the LaB$_6$-ZrB$_2$ DSE. Despite extra efforts to prevent oxidation of the surface, oxidation was still observed. This oxidation will limit LaB$_6$-ZrB$_2$ DSEs use as an ultra-high-temperature material in oxygen-containing environments.
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1 Introduction

1.1 Applications and Material requirements

New and advanced ultra-high-temperature materials are needed for turbine and rocket engines, wing leading edges, engine cowl inlets, nose caps, and thermal barriers for hypersonic vehicles, because current temperature limitations reduce optimum performance.¹ Current materials are unable to withstand the high temperatures and therefore, not only limit overall efficiency in turbine and rocket engines but also damage the structural integrity of protective surface materials in flight vehicles.¹ Although this equipment requires materials able to withstand temperatures that range from 1400°C for turbine engines to 3000°C for thermal protection systems, current materials are limited to 1315°C for turbine engines and 1650°C for thermal protection systems.¹,²,³ An improvement in the high-temperature stability of these materials would have far-reaching economic implications. Power produced by turbine engines is utilized to run jets, ships, locomotives, helicopters, tanks, satellites, and small power plants. With a little improvement in the efficiency of turbine engines, a huge improvement in cost can be realized. Even small improvements in thermal efficiency would mean big savings. For example, the Department of Defense is the largest consumer of energy in the United States. The department spent 10 billion dollars on combat fuel alone in 2006.⁴ Cost to refuel vehicles in-flight have been estimated to be about $42/gal.⁴ According to a report by the Defense Science Board Task Force, this estimated value is low, and does not take into account all the cost of transporting the fuel.⁴ Increasing efficiency would in many cases eliminate the need for refueling in-flight and would eliminate the costly refueling expenses. In addition, in 1998, a 1% improvement in the thermal efficiency of gas turbines would have meant a world-wide annual savings in energy costs of around one trillion dollars.⁵ According to a rough calculation based on the consumer price index, in 2009 that would equal an annual savings of around 1.3 trillion dollars.⁶ This introduction serves to provide information and background in order to establish that research on boride based, low-density, high-melting point, directionally solidified eutectics (DSEs) may resolve current temperature limitations. In order to make this
claim, this introduction reviews turbine and rocket engines, surface materials for flight vehicles, current materials and limits, and how new materials would improve efficiency. Second, it provides an overview of new advances in directionally solidified eutectics in order to establish rationale for researching new composite materials as a solution to current temperature limitations in materials. Third, it discusses what researchers currently know about LaB$_6$-ZrB$_2$ DSEs. Fourth, it provides an overview of creep testing which is important for evaluating a materials performance under high temperature and stress. Finally, it introduces the overall project objectives.

1.1.1 Turbine and Rocket Engines

Currently, materials used for turbine engines have high-temperature limitations. Turbine blades, which are composed of nickel-based super alloys, are the majority of blades in use today, but unfortunately, although the combustion gas environment is $\sim$1370°C, Ni-based super alloys have poor strength at 1000°C and low melting points in the range of 1230-1315°C. To enable operation of the combustion engine at 1370°C and to protect the Ni based super alloys from damage due to oxidation, creep, melting, and thermal fatigue, engines are air cooled and low thermal conductivity coatings are applied to the blades. In order to improve the efficiency of gas turbine engines, one must increase the operating temperature.

Rocket engines power space shuttles and missiles and have similar material operational limitations as turbine engines. A niobium alloy with a disilicide coating is currently the material of choice for rocket engines. The combustion chamber has an operational limit of $\sim$ 2900°C which is double the operational limit of the niobium alloy (1450°C) used currently. Presently, cooling of the chamber is performed with the use of fuel-film and regenerative cooling. Fuel-film refers to fuel that does not burn completely. This un-burnt fuel coats the combustion chamber walls acting as a coolant. Improving the combustion chamber material operating temperatures in these applications would minimize or eliminate the need for fuel-film and regenerative cooling. In addition, the un-burnt fuel film is a source of contaminants and adversely affects internal controls of the chamber. Eliminating this would result in a cleaner burning rocket engine that would ultimately result in better fuel efficiency, cost reduction, and farther travel.
1.1.2 Flight Vehicle Surface Materials

In addition to turbine and rocket engines, new ultra-high-temperature materials designed as surface materials for flight vehicles must be able to handle extremely high temperatures and diverse atmospheric conditions. More specifically, these materials need to be operable and reusable in typical air composition as well as monatomic oxygen and nitrogen. For example, upon atmospheric reentry, the space shuttle encounters temperatures of 2000°C and above, as well as monatomic oxygen and nitrogen. The wing leading edges, engine cowl inlets and nose caps of vehicles need materials operable in maximum temperatures between 2000 to 3000°C. To reduce the extreme surface temperatures encountered by the space shuttle and hypersonic vehicles, current designs involve the use of blunt edges. Removing blunt edges and streamlining flight vehicles with leading edges made of ultra-high-temperature materials, would result in improved maneuverability and fuel efficiency, and thus result in the ability to travel further, increase ease of landing on return, and reduce cost.

Some surface materials are reusable thermal protection systems and thus must meet multiple use requirements. Reusable thermal protection systems in hypersonic flight vehicles used today have maximum operation temperatures near 1650°C. Structural materials used presently are predominantly based on SiO₂, SiC, Si₃N₄, and oxide ceramics or composites of these materials. Because SiO₂-and SiC-based materials are excellent oxidation barriers, they are found on various surfaces on the space shuttle. The tile and blanket material, the carbon-carbon leading edges and nose cap material use SiO₂ and SiC-based materials. Monoliths of these materials are not used due to brittle failure during extreme temperature changes. Instead, ceramic-matrix materials are utilized. For example, the HRSI (high-temperature-reusable-surface-insulation) tiles are made up of silica fiber. In hypersonic environments, SiC-based materials have limited thermal cycling lifetimes due to CTE mismatch induced matrix cracking. Deformation of the material decreases the oxidation resistance by allowing a method of direct oxidation of fibers. Therefore, both SiO₂- and -SiC based thermal protective systems are limited in their temperature capability to ~1600°C in an oxidizing atmosphere. Low-pressure and
high-temperature environments are detrimental to the service life of the current silicide-based thermal protection materials used on flight vehicles.\(^1\) Currently, few if any material options meet the future thermal protection systems desired. Even today’s best ultra-high-temperature materials consist of carbon-carbon composites and silicon carbide composites such as C-SiC and SiC-SiC, but these composites are not sufficiently oxidation-resistant.\(^1\) Potential materials that oxidize and form pure scales of SiO\(_2\), Al\(_2\)O\(_3\), Cr\(_2\)O\(_3\), or BeO, cannot be utilized at temperatures of 1800\(^\circ\)C and above in hypersonic flight conditions due to high vapor pressures which arise at the interface of the base material and the scale.\(^1\)

In order to get beyond our present material limitations of ~ 1600\(^\circ\)C and to meet operation needs of 3000\(^\circ\)C we need to evaluate other possible material candidates. Due to processing difficulties borides have historically been overlooked and under-researched, but their refractory nature, high hardness and tensile strengths make these promising materials candidates.\(^{13,14}\) More specifically, refractory borides have melting temperatures above 3000\(^\circ\)C, high thermal conductivity, elastic modulus, good strength at high temperatures, modest thermal expansion, good thermal shock resistance and they have the ability to form refractory oxide scales and can be modified with additives to promote oxidation resistance.\(^{15}\) Until recently, the major limitation to their use has been a lack of an affordable, reproducible manufacturing process because the strong covalent bonding gives them high melting temperatures, but makes them difficult to densify.\(^9\) As a result, ultra-high-temperature ceramics are usually consolidated by hot pressing. However, this process can cause impurities to concentrate in the grain boundaries, which decreases the high-temperature strength.\(^{16}\) Now, however, as discussed in the next section, improved processing methods for directionally solidified eutectics have garnered increased interest in these materials.

### 1.2 Directionally Solidified Eutectics

Eutectics, first named by Guthrie in 1884, are composites with a minimum temperature of melting.\(^{17}\) A directionally solidified eutectic (DSE) is a composite formed by the simultaneous crystallization of two or more phases from one melt with a
well defined solid-liquid interface. These composites have a homogeneous but complex microstructure that can best be described as a reinforcing phase within a higher volume matrix phase. This type of microstructure produces composites with excellent mechanical properties that are very stable up to temperatures close to their melting points. This stability up to the melting point can be attributed to the composites being crystallized from the molten state and therefore being in thermodynamic equilibrium. One benefit of DSE growth is the ability to control morphology and mechanical properties because phase morphology (size, shape, interface, and distribution) of the eutectic directly relates to the mechanical properties of composites. For example, one can utilize the differences in thermal expansion coefficients and Young’s Modulus between phases to engineer a composite that would create compressive stresses in the matrix. Growing a DSE material with a reinforcing fiber phase and matrix of different thermal expansion and moduli creates an environment of residual stress that promotes crack path deviation around the reinforcing phase thus contributing to increased fracture toughness. By controlling growth conditions such as the molten zone height, pull rate, wetting angle and laser power distribution, one can engineer a material with smaller reinforcing fiber phase diameter and spacing, thus improving strength. Much work has been done to understand growth conditions and how they affect the microstructure of the DSE material (processing will be discussed in detail in section 1.3).

Among eutectics, oxide eutectics have received the most attention due to their inherent oxidation resistance. Research on oxide eutectics dates back to 1967 when Galasso et al. grew a directional solidified eutectic $\text{BaFe}_{12}\text{O}_{19}-\text{BaFe}_{2}\text{O}_{4}$ in order to determine how DSE growth would effect its magnetic properties. With improvements in the processing and characterization of oxide DSEs, there is renewed interest in DSEs. In the 1970’s the Bridgman growth process was restricted to thermal gradients below $10^2$ K/cm. Now, higher thermal gradients are achievable of $10^4$ K/cm with the floating zone process which results in improved control over microstructure and understanding of processing parameters. Within the last two decades there has been development of several new DSE ceramic oxides, including $\text{Al}_2\text{O}_3$-$\text{YAG}$, $\text{Al}_2\text{O}_3$-$\text{YSZ}$, and $\text{Al}_2\text{O}_3$-$\text{Er}_3\text{Al}_5\text{O}_{12}$. These $\text{Al}_2\text{O}_3$-based oxides are known for having some of the best
creep resistance in oxide DSEs\textsuperscript{18} (these oxides will be discussed in detail in section 1.5.1).

Even though, boride eutectics have promising material properties that oxide eutectics do not they have been studied to a much lesser degree. Processing difficulties associated with the high melting temperature make it difficult to produce low porosity borides. Although the advantages of oxide DSEs are that they are easily manufactured, have good oxidation resistance, good strength-to-weight ratios, and high hardness, boride eutectics also have good strength-to-weight ratios, and higher hardness and melting temperatures than oxide eutectics. LaB$_6$-ZrB$_2$ DSE stands out above other DSEs with a very high fracture toughness.\textsuperscript{25} Fracture toughness values from 8.7 to 27.8 MPa·m$^{1/2}$ have been reported. The validity of such high fracture toughness values should be questioned. The loading conditions and crack geometry was not given with the higher values.\textsuperscript{25} However, the high fracture toughness as compared to oxide DSEs has been reported by several groups and thus warrants attention. The differences between oxides and non-oxide eutectics are summarized in Table 1.1.\textsuperscript{26}

Table 1.1     Room-temperature mechanical properties of oxide and non-oxide eutectics.

<table>
<thead>
<tr>
<th></th>
<th>Te (°C)</th>
<th>Microhardness (GPa)</th>
<th>Fracture Toughness (MPa·m$^{1/2}$)</th>
<th>Strength (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZrC-ZrB$_2$</td>
<td>2660±40$^{47}$</td>
<td>24.0$^{47}$</td>
<td>2.72~5.44$^{7}$</td>
<td></td>
</tr>
<tr>
<td>ZrC-TiB$_2$</td>
<td>2660±40$^{47}$</td>
<td>21.1$^{27}$</td>
<td>2.9$^{27}$</td>
<td></td>
</tr>
<tr>
<td>SiC-TiC</td>
<td>2320±2.0$^{28}$</td>
<td>23.8±1.2$^{28}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SiC-VC</td>
<td>2220±2.0$^{28}$</td>
<td>22.5±1.1$^{28}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>B$_4$C-W$_2$B$_6$</td>
<td>2130±3.0$^{29}$</td>
<td>22.1~24.4$^{29}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>LaB$_6$-HfB$_2$</td>
<td>2750±40$^{40}$</td>
<td>26~28$^{30}$</td>
<td>11~14.4$^{41}$</td>
<td>1150~1250$^{51}$</td>
</tr>
<tr>
<td>LaB$_6$-ZrB$_2$</td>
<td>2470±40$^{25}$</td>
<td>25.50$^{25}$</td>
<td>8.7~27.8$^{25,32}$</td>
<td>1000~1320$^{25}$</td>
</tr>
<tr>
<td>YAG-Al$_2$O$_3$</td>
<td>1827$^{9}$</td>
<td>14.6~18.5$^{53}$</td>
<td>2.1~2.4$^{39}$</td>
<td>600~1900$^{33}$</td>
</tr>
<tr>
<td>Al$_2$O$_3$-ZrO$_2$/Y$_2$O$_3$</td>
<td>1910±2.0$^{35}$</td>
<td>13.5~20.0$^{46}$</td>
<td>4.8~7.8$^{31,21,38}$</td>
<td>750~1580$^{39}$</td>
</tr>
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</table>
1.3 DSE Processing

Several methods exist for processing directionally solidified eutectics. These methods can be separated into two main types, unidirectional growth in a container and growth from a melt which may use dies or be totally container-less. Two main types of container growth methods are the Bridgman method and the Czochralski method. Melting zone methods include: floating zone, edge-defined film-fed growth, and micro pulling down methods. In the float zone method, there are also several different methods of heating the melt, which can affect material properties. Each method has advantages and disadvantages. The DSE material studied in this thesis was processed using a floating zone method, as described below, with induction heating by collaborators at the Institute for Problems of Materials Sciences, Academy of Sciences of Ukraine, Ukraine.

The first step in the floating zone method, as used in this study, is creating a molten zone in a polycrystalline rod. The molten zone can be created with the use of lasers, an electron beam, resistance heaters, or radio frequency induction. Second, a single crystal seed rod of a certain orientation can be used to initiate controlled growth in the orientation desired. Finally, the polycrystalline rod is pulled through the molten zone at a predetermined rate. In Figure 1.1, Sorrell et al. have depicted a layout of a solidification furnace used in the floating zone method.
There are several advantages to choosing the floating zone processing method. First, is the lack of crucible contamination. Second, is the ability to view the growth process “in-situ”. Viewing the growth process can be done by using a laser shadow technique to monitor the diameter of the molten zone\cite{41} or one can use a video camera to monitor the crystal growth. The advantage of viewing the growth process “in-situ” is this information can be used to measure the wetting angle\cite{41}, which is important for insuring uniform crystal growth. When the wetting angle is kept constant then uniform crystal growth is achieved. A third advantage to the floating zone process is the ability to grow the eutectics with high-temperature gradients; this enables higher growth rates that yield smaller interface spacings.\cite{22,42} A final advantage is that many aspects of the growth process, including the molten zone height (length is limited for stable growth to $2\pi R$ for the floating zone method), pull rate (effects fiber diameter and spacing), wetting angle (effects uniformity of rod growth diameter), and laser power distribution (important for thermal gradient) are
The main disadvantage of the floating zone method is size limitations of the produced rod as a result of the relationship between thermal stresses and the large thermal gradients that are necessary to produce the small interface spacing desired. Eutectics grown from a float zone process can have submicron microstructures, few if no grain boundaries, reduced defects, and strong interface bonding, all of which contribute to improved mechanical properties compared to other material compositions and growth processes.

1.3.1 Growth Rate

One important controllable aspect in the float zone process is the growth rate or pull rate. This parameter has been intensively evaluated and its effects are well known. Adjusting the growth parameters ultimately changes the diameter of the reinforcing fiber phase as well as the spacing of the fibers in the eutectic composite. This was observed by Ramirez-Rico et al. (2006) where they grew an Al₂O₃-YAG DSE and observed decreasing interphase spacing with increased growth rate. The Al₂O₃-YAG DSE was grown at 25, 350 and 750 mm/h and they are referenced as AY 25, AY 350 and AY 750 in Table 1.2.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Growth Rate (mm/min)</th>
<th>Interphase Spacing (µm)</th>
<th>Microstructure</th>
</tr>
</thead>
<tbody>
<tr>
<td>AY 25</td>
<td>0.42</td>
<td>2.3 ± 0.2</td>
<td></td>
</tr>
<tr>
<td>AY 350</td>
<td>5.83</td>
<td>0.7 ± 0.1</td>
<td></td>
</tr>
<tr>
<td>AY 750</td>
<td>12.5</td>
<td>0.41 ± 0.08</td>
<td></td>
</tr>
</tbody>
</table>
Paderno et al. also compared growth rates of a DSE LaB₆-ZrB₂ between 0.25 mm/min to 10 mm/min and found that this decreased the reinforcing fiber phase spacing and fiber diameter with increasing growth rate, as shown in Figure 1.2.

![Figure 1.2 LaB₆-ZrB₂ eutectic composite fiber spacing as a function of growth rate (from ref 43)](image)

The general equation $\lambda = kR^{-1/2}$ describes this phenomenon where $\lambda$ is the inter-fibrous spacing, $R$ is the velocity of the solidification interface and, $k$ is a constant determined experimentally. As solidification rate increases, available diffusion time decreases, thereby shortening the diffusion path, reducing fiber diameter and fiber spacing which ultimately improves strength. Haggerty et al. studied ZrO₂ (Y₂O₃)-Al₂O₃ eutectic fibers and saw increased strength with increased growth rate/smaller interphase spacing. Buckling of fibers grown at 1.7 mm/min averaged about 0.5 GPa better than fibers grown at 0.17 mm/min. Still, one has to be careful to not form dendritic or colony growth at faster growth speeds. Dendritic or colony growth reduces homogeneity in the microstructure and therefore can negatively affect material properties as well.
1.3.2 Phase Morphology

In addition to the growth rate, the volume fraction of the constituent phases is another parameter that has been intensively evaluated and the results of which are well known. Whether or not the strengthening/minor phase is fibrous or lamellar depends predominantly on the volume fraction of that phase. In 1964, Cooksey et al.\textsuperscript{46} established a relationship between minimum interfacial energy and the morphology of the minor eutectic phase. According to Cooksey \textit{et al.}\textsuperscript{46}, if the interfacial energy per unit area is equivalent for the fibrous/lamellar phases, then a fibrous minor phase is preferred at less than 0.28 volume fraction, and for greater than 0.28 volume fraction lamellar macrostructures are preferred. In 1966, Jackson and Hunt\textsuperscript{47} expanded on this relationship by taking into account the anisotropy of the surface energy and undercooling. Undercooling occurs during the solidification of two phases. When one phase is rejected by another, the concentration of that phase ahead of the solidification then causes undercooling in the liquid. This undercooling is controlled by eutectic concentration, volume fraction of the minor phase, inter-lamellar and inter-fiber spacing, and growth rate.\textsuperscript{26} According to the Jackson and Hunt model, for isotropic interfacial free energies, a rod (fiber) structure is preferred at volume fractions below 0.32. However if the surface energy is more than 25% anisotropic then lamellar structures are preferred regardless of volume fraction.\textsuperscript{47} In 1981, Stubican and Bradt\textsuperscript{13} evaluated both the Cooksey and Jackson and Hunt models and determined that most eutectics obey the trends however; there are some exceptions. The minor phase volume fraction of ZrB\textsubscript{2} in the LaB\textsubscript{6}-ZrB\textsubscript{2} eutectic is about 20% and a reinforcing ZrB\textsubscript{2} fibrous phase is observed.\textsuperscript{43}

1.4 LaB\textsubscript{6}-ZrB\textsubscript{2} Eutectic

The LaB\textsubscript{6}-ZrB\textsubscript{2} eutectic grown from the float zone process is a candidate for the high-temperature applications discussed in section 1.1. The LaB\textsubscript{6}-ZrB\textsubscript{2} eutectic studied is a directionally solidified material grown with the floating zone method and, as covered in sections 1.2 and 1.3, the growth rate and volume fraction were controlled to give a
material with the desired microstructure. The resulting LaB$_6$-ZrB$_2$ eutectic has a composition of nominally 80 wt% LaB$_6$ and 20 wt% ZrB$_2$. The microstructure is discussed in further detail in section 3.1. The eutectic melting temperature of the LaB$_6$-ZrB$_2$ eutectic is $\sim$2740°C (Figure 1.3). Structurally, LaB$_6$ has a simple primitive cubic crystal structure with space group $Pm\bar{3}m$ (221). La atoms are found at the corners of the unit cell and B$_6$ octahedra form in the body centered position of the unit cell, as shown in Figure 1.4. According to Paderno (1998), the high covalency of the boron enables easy growth of single crystals. ZrB$_2$ has a hexagonal crystal structure with P6/mmm (191), as shown in Figure 1.4. Single crystals of ZrB$_2$ exhibit highly anisotropic physical properties. Pure Zr and pure B atomic planes stack alternatively in layers along the c-axis to give ZrB$_2$ its hexagonal structure. The lattice parameters are LaB$_6$ $a=4.1569\,\text{Å}$ and ZrB$_2$ $a=3.17\,\text{Å}$, $b=3.17\,\text{Å}$, $c=3.533\,\text{Å}$. The densities are LaB$_6$ 4.771 g/cm$^3$ and ZrB$_2$ 6.094 g/cm$^3$. 

![Figure 1.3](image)

LaB$_6$-ZrB$_2$ Phase diagram.
Previous research supports our choice of DSE and helps establish its potential as an ultra-high-temperature material. For example, Paderno \textit{et al.}\textsuperscript{31} processed directionally solidified LaB\textsubscript{6}-ZrB\textsubscript{2} by the RF floating zone process. They chose this particular composite for several reasons. 1) The MeB\textsubscript{6} phase is one of the most thermodynamically stable phases formed that rare earth or f- transition metals make; 2) for the d-transition metals MeB\textsubscript{2} is the most thermodynamically stable phase; 3) the boron sublattices in both structures have similar values of atomic spacing, leading them to believe that their association is possible during the process of combined solidification in the eutectic\textsuperscript{31} The boride phases are not markedly mutually soluble due to differences in the electronic shells of the d- (Zr) and f-(La) transition metals, which results in different chemical bonding and crystal symmetry of the boride phases.\textsuperscript{31} The boron bond lengths in the LaB\textsubscript{6} (intra-octahedral) and ZrB\textsubscript{2} are very close, 0.1765nm, and 0.1829nm respectively; 4) a final factor was the attractive thermo-emissive properties of LaB\textsubscript{6}. In conclusion LaB\textsubscript{6}-ZrB\textsubscript{2} was chosen because it should be thermodynamically and mechanically stable and has attractive thermo-emissive properties.\textsuperscript{43} Paderno observed that during the directional solidification of the composite in the <001> direction, the boron pairs in the (110) LaB\textsubscript{6} and (120) ZrB\textsubscript{2} planes mutually join as shown in Figure 1.5.\textsuperscript{43} Paderno also observed the (1\overline{1}0) LaB\textsubscript{6} was always parallel to (1\overline{1}0) of ZrB\textsubscript{2} regardless of the growth
According to Paderno et al., regardless of the growing direction, the angle between the main crystallographic axes of both phases is the same (15°), as shown in Figure 1.6. Paderno concluded that the mutual orientation of the two phases is independent of the growth direction of the matrix and that the growth direction of the two phases is interdependent. The ZrB₂ growth direction changes with the change in growth direction of the LaB₆ matrix. LaB₆-ZrB₂’s semi-coherent interfaces results in strong interphase bonding and excellent thermal stability. The lattice misorientation in this material is around 3%. The 3% lattice misorientation is considerably lower than Frank & Van Der Merwe’s proposed critical value of 16% for a semi-coherent interphase. Deng’s (2006) work on LaB₆-ZrB₂ interfaces reaffirmed the low energy semi-coherent interfaces and found lattice misorientation between the two phases in ranges of 2° to 5°. It will be shown in later sections that the low energy interfaces are credited for the excellent creep resistance obtained in oxide DSEs and are thus important for us and our expectation that LaB₆-ZrB₂ DSEs will have excellent creep resistance.

Figure 1.5  Structural relation between LaB₆ and ZrB₂ phases during co-crystallization. B-B’ is a common boron pair common to both phases.
1.5 Creep and Impression Creep Background

1.5.1 History of Creep

One main criterion used in this study to evaluate materials and their stability in high-temperature applications over time is creep. Creep is the study of the time-dependent deformation under constant loading and is currently used by engineers to establish whether or not a material is suitable for an application.

The first studies in creep were in metallic systems. The earliest testing of creep in materials seems to be work performed in 1830 by Vicat.\textsuperscript{52} Vicat tested tensile creep of iron wire for a time of 33 months. In 1903, Phillips reported on room temperature tensile creep of glass, rubber and various metal wires (Copper, Platinum, Silver, and Gold).\textsuperscript{53} In 1910, Andrade reported on the creep of lead in tension.\textsuperscript{54} Extensive creep data is available on the creep of metals.

Creep studies in ceramics were slow to evolve as ceramics were thought of as having thermal shock issues and of being brittle.\textsuperscript{55} Most researchers felt ceramics were
not viable options for high-temperature applications. The earliest ceramics were investigated in 1957, when Wachtman et al. studied high-temperature slip systems and creep rates in single crystal sapphire, rutile, quartz, and periclase up to 1100°C by three point bending. Then, in the late seventies to early eighties creep interests in ceramics increased due to the realization that ceramics had some unique and desirable properties. In 1977, Chu et al. were the first to perform impression creep testing. They chose to study polycrystalline succinonitrile (C₂H₄(CN)₂) due to its low melting temperature (57°C) and atmospheric stability. Impression creep has been used to study various materials such as glasses, ceramics, ionic crystals, polymers, metals and alloys that exhibit super plasticity, including Pb-Sn and Zn-Al eutectic alloys, and welds of aluminum, Ti alloys, and various types of steel.

1.5.2 Impression creep method

Impression creep utilizes a small indenter under load to penetrate the surface of a specimen. A flat-ended indenter with a constant load is used so that steady state data is more easily interpreted (Figure 1.7). There are several important parameters that should be controlled when running impression creep tests. First, Chen and Li investigated specimen size effects on impression creep data and determined that the required specimen thickness to reduce size effects on creep is 5x the diameter of the punch. Second, one must ensure that the specimen, ram and punch are aligned evenly to avoid failure of the punch and to ensure that stress remains constant. Finally, one must have the ability to heat the samples high enough to initiate creep but also ensure that temperature fluctuation and variation is minimal.

Impression creep has several distinct advantages as compared to conventional compression creep testing. First, the sample is simple to prepare. The main parameters controlled prior to testing are ensuring that samples are flat and parallel, and have a uniform polished surface finish. The sample should be surface ground square and then polished to at least 1µm to reduce any surface effects. Secondly, a small area can be investigated, which is advantageous for studying material where sample size is limited. This also enables multiple creep tests on a single specimen for applications where the
sample number is limited. A third benefit is localized testing of specific areas of the sample. Finally due to the constant applied stress of the flat indenter, the data is easy to analyze.

LaB₆-ZrB₂ DSEs have potentially very good high-temperature properties based on what is known of the room-temperature properties. LaB₆-ZrB₂ DSEs yield excellent fracture toughness values, melting temperatures above 3000 ºC, high thermal conductivity, high strength at high temperatures, modest thermal expansion, and good thermal shock resistance. Obtaining impression creep data would provide high-temperature deformation data that is lacking in refractory borides. Transmission Electron Microscope (TEM) evaluation under the impression can yield information on dislocation densities, interface structure and defects, and dominant slip systems as a function of load and orientation.

1.5.3 Stages of Creep

Most materials have three distinct stages of creep (Figure 1.8). In primary creep, the material goes through strain hardening which increases the material’s resistance to creep. This primary stage is depicted by a decreasing creep rate. At some point there is a mixture of strain hardening and recovery which is depicted as a steady-state region in the curve. This secondary creep stage is typically the longest stage and the one of most
interest. The creep rate at this stage is often considered when an engineer decides whether or not a material is suitable for an application. The third stage is characterized by a sudden increase in creep rate and often happens just before final fracture of the material. However, not all materials exhibit tertiary creep. The secondary steady-state stage of creep is used in this study to evaluate a LaB₆-ZrB₂ DSE material for uses in high-temperature applications.

The steady-state creep rate is usually characterized by the Norton equation⁶⁰:

\[ \dot{\varepsilon} = A\sigma^n \exp(-Q/RT) \]  

In the Norton equation where \( \dot{\varepsilon} \) is the steady state creep (strain) rate, A is an empirical constant (dependent on temperature), \( \sigma \) is the applied creep stress, \( n \) is a dimensionless stress exponent, \( Q \) is the activation energy for creep, \( R \) is the gas constant, and \( T \) is absolute temperature. From a plot of strain versus time for various temperatures and pressures one can determine the stress exponent \( n \), the activation energy \( Q \), creep constant \( k \), as well as determine strain rates.⁶¹

When characterizing deformation mechanisms and creep in materials most engineers refer to the activation energy and the stress exponent to characterize the material. Stress exponents of 1 are indicative of Nabarro-Herring or Coble creep.⁶² Nabarro- Herring and Coble creep refer to pure diffusion-type deformation. Polycrystalline materials typically have stress exponent around 1 due to diffusion along grain boundaries. Stress exponents from about 2-3 are indicative of a mixed mode type deformation that includes contributions from diffusion and dislocation creep.⁶² The best creep rates for oxide DSEs that have been reported are based on sapphire. \( \text{Al}_2\text{O}_3\)-YAG DSE \ has been reported to have stress exponents in the mixed mode range.²²,⁶³ Sapphire-based oxide DSEs will be discussed further in the next section. Stress exponents above 3 are indicative of pure dislocation type creep mechanisms.⁶² A stress exponent above three is typical for single crystals.⁶⁴
1.5.4 Known Oxide DSE Creep Data

As mentioned previously, most DSE creep data available is for oxide DSEs. Drivers of interest for oxide DSEs are good oxidation resistance, ease of manufacturing, high strength/weight ratios and high hardness.

The best creep rates for oxide DSEs that have been reported are based on sapphire. Binary and tertiary sapphire systems have been investigated and have very high creep resistance, similar to single-crystal sapphire. This section, will review these results in order to establish a correlation between creep in these oxide DSEs and the expected creep in LaB$_6$-ZrB$_2$ DSEs. In Figure 1.9 Martinez-Fernandez et al. compared the creep of several single crystal oxide eutectics. The Al$_2$O$_3$-YAG (yttrium-aluminum-garnet), Al$_2$O$_3$-YSZ (yttrium-stabilized-zirconia), and Al$_2$O$_3$-Er$_3$Al$_5$O$_{12}$ systems appear to have the best creep resistance. The Al$_2$O$_3$-Er$_3$Al$_5$O$_{12}$ system is one of the best, with a creep rate of $\sim 10^{-8}$ s$^{-1}$ at 1600°C and a stress of 100MPa.
Because of the submicron interphase spacings and therefore high interface density that DSEs possess, one might expect DSEs to deform via Coble creep like polycrystalline materials do and have lowered creep resistance. However, it has been shown that in oxide DSEs this is not the case. In fact, it has been observed that a decrease of interphase spacing shows increased creep resistance. Matson et al. (2005) studied $\text{Al}_2\text{O}_3$-YAG DSEs with growth rates of 0.254, 1.27 and 2.54 cm/min and observed the best creep resistance at 1600°C in the 1 in/min growth rate sample (Figure 1.10). Unlike some sintered composites, in oxide DSEs interfacial sliding does not occur due to lack of glassy phases at the interfaces. This requires deformation to occur by plastic deformation in the bulk. A review of the deformation mechanisms in $\text{Al}_2\text{O}_3$ based oxides was performed and summarized in Table 1.3. In all of the DSEs reviewed, none were found to have stress exponents indicative of Coble creep, instead, they showed a mix of bulk diffusion and dislocation motion. Waku et al. (1998) studied compressive creep rates in argon for Bridgman-processed $\text{Al}_2\text{O}_3$-YAG. The creep rate of an $\text{Al}_2\text{O}_3$-YAG DSE was shown to have a 13 times lower rate than a sintered composite of $\text{Al}_2\text{O}_3$-YAG.
Activation energies of 670-905 kJ/mol and stress exponents around 5-6 were ascertained. Waku et al. did not go into detail about deformation mechanisms and referred to an earlier work by Parthasarathy,67 who in 1993 studied the deformation of a Bridgman-processed Al₂O₃-YAG material versus single crystal sapphire and YAG. Parthasarthy discussed in some detail the possible deformation mechanisms and determined based on the high stress exponents and activation energies that dislocation creep was the main mechanism for deformation in the composite eutectic. Again, in another example of improved creep resistance in Al₂O₃-based composite DSEs, Martinez et al. showed that an Al₂O₃/Er₃Al₂O₁₂ DSE had better creep resistance than c-axis sapphire up to 1550°C and 3 to 4 orders of magnitude better creep resistance as compared to 15° off-axis sapphire (Figure 1.9). 66 Another example of the improved mechanical properties of two phase composite oxide DSEs vs single phase DSEs can be credited to clean and strong low energy interfaces. Single crystal sapphire shows a reduction in strength at high temperatures (above 600°C) where as Al₂O₃-YAG DSE systems retain their high-temperature strength up to 1700°C. 18 Improved creep resistance in composite oxide DSEs was also shown by Sayir and Farmer (2002) in a creep study performed on Al₂O₃/ZrO₂(Y₂O₃) DSEs. They compared Al₂O₃/ZrO₂(Y₂O₃) DSEs to an off-axis sapphire and found the DSE composite to have superior creep resistance 68. This improved creep resistance in oxide DSE composites was credited to the low energy and strong interface bonding in these materials. 27,69,70

Deng26 (2006) characterized the interfaces in three LaB₆-ZrB₂ DSEs grown at different growth rates by the float zone method by utilizing the TEM in conjunction with some geometric modeling analysis. This study concluded that the interfaces in these LaB₆-ZrB₂ DSEs were relaxed and in low energy semi-coherent configurations. The excellent creep resistance in oxide DSE composites has been attributed to low energy semi-coherent interfaces so it is hypothesized that since the LaB₆-ZrB₂ DSEs have semi-coherent interfaces that they will have excellent creep resistance, comparable to the properties of the single crystal constituents.
Figure 1.10 Longitudinal cross-sections and creep data for a) 0.1 in/min Alumina/YAG eutectic (AYE) grown by USE, Inc. b) 0.5 in/min AYE-USE and c) 1 in/min AYE grown by Saphikon, Inc. The best creep resistance at 1600°C is observed in the faster 1 in/min growth rate. Note the fiber rim is a different morphology than the fiber core.
Table 1.3 Oxide DSE Creep Properties. Data from references - Ramirez-Rico 2006\textsuperscript{22}, Matson 2005\textsuperscript{63}, Waku 1998\textsuperscript{5}, Harada 2004\textsuperscript{71}, Yi 2006\textsuperscript{14}, Martinez 2001\textsuperscript{72}, Martinez 2003\textsuperscript{66}. LFZ (Laser Floating Zone), EFG (Edge-defined, Film-fed Growth)

<table>
<thead>
<tr>
<th>Oxide DSEs</th>
<th>Growth process</th>
<th>Microstructure</th>
<th>Microstructure</th>
<th>Activation energy (kJ/mol)</th>
<th>Creep Exp. (n)</th>
<th>Load Type</th>
<th>Stress (MPa)</th>
<th>Creep rate (s(^{-1}))</th>
<th>Deformation Mechanism</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{Al}_2\text{O}_3)-YAG\textsuperscript{22}</td>
<td>LFZ</td>
<td>Interlocked (2.54 mm/min)</td>
<td>Interlocked</td>
<td>720 ± 20 (5.82 mm/min)</td>
<td>1.3-3</td>
<td>Compression</td>
<td>100</td>
<td>10(^{7.2}) to 10(^{8.9})</td>
<td>Bulk diffusion in YAG, dislocation motion</td>
</tr>
<tr>
<td>(\text{Al}_2\text{O}_3)-YAG\textsuperscript{63}</td>
<td>EFG</td>
<td>Interlocked</td>
<td>Interlocked</td>
<td>841-1275</td>
<td>5.8</td>
<td>Tensile</td>
<td>200,300,400</td>
<td>10(^{5.2}) to 10(^7.8)</td>
<td>Bulk diffusion in YAG, dislocation motion</td>
</tr>
<tr>
<td>(\text{Al}_2\text{O}_3)-YAG\textsuperscript{2}</td>
<td>Bridgman</td>
<td>Interlocked</td>
<td>Interlocked</td>
<td>670-905</td>
<td>2.8</td>
<td>Compression</td>
<td>200,250,300,350</td>
<td>10(^{7.9}) to 10(^{9.5})</td>
<td>Bulk diffusion in YAG, dislocation motion</td>
</tr>
<tr>
<td>(\text{Al}_2\text{O}_3)-YAG\textsuperscript{71}</td>
<td>Bridgman</td>
<td>Interlocked</td>
<td>Interlocked</td>
<td>800-1000 (200-350 MPa)</td>
<td>2.1</td>
<td>Tension</td>
<td>143</td>
<td>10(^{10}) to 10(^{12})</td>
<td>Bulk diffusion in YAG, dislocation motion</td>
</tr>
<tr>
<td>(\text{Al}_2\text{O}_3)-(\text{ZrO}_2)\textsuperscript{14}(Y\text{2O}_3)\textsuperscript{12} (hypoeutectic)</td>
<td>LFZ</td>
<td>colony/fibrous/lam</td>
<td>Interlocked</td>
<td>5-6</td>
<td>5-10</td>
<td>Temperature</td>
<td>10.0</td>
<td>10(^{7.5}-10.6)</td>
<td>10(^{-8})</td>
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<tr>
<td>(\text{Al}_2\text{O}_3)-(\text{Er}_3\text{Al}<em>5\text{O}</em>{12})\textsuperscript{14}(eutectic) (10.75 mol % (\text{Er}_2\text{O}_3))</td>
<td>LFZ</td>
<td>Transverse/Longitud.</td>
<td>Interlocked</td>
<td>10(^{7.5}-10.6)</td>
<td>10(^{-9})</td>
<td>10(^{-9}), 10(^{-8})</td>
<td>10(^{-9})</td>
<td>10(^{8.2})</td>
<td>10(^{-7.5})</td>
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<tr>
<td>(\text{Al}_2\text{O}_3)-(\text{Er}_3\text{Al}<em>5\text{O}</em>{12})\textsuperscript{66} (hypoeutectic) (19.5 mol % (\text{Er}_2\text{O}_3))</td>
<td>LFZ</td>
<td>Interlocked</td>
<td>Interlocked</td>
<td>338 ± 68</td>
<td>1.3</td>
<td>Tension</td>
<td>100</td>
<td>10(^{-7.1}) to 10(^{-8.9})</td>
<td>Bulk diffusion in YAG, dislocation motion</td>
</tr>
</tbody>
</table>

Notes:
- \text{Al}_2\text{O}_3\)-YAG: Aluminum Oxide-Yttrium Aluminum Garnet
- LFZ: Laser Floating Zone
- EFG: Edge-defined, Film-fed Growth
- Bridgman: Bridgman growth process
- Microstructure: Interlocked, colony/fibrous/lamella
- Activation energy: 720 ± 20 kJ/mol
- Creep Exponent: 5-6
- Temperature: 10.0 ± 1723 k
- Stress: 10\(^{7.9}\) to 10\(^{9.5}\)
- Creep rate: 10\(^{10}\) to 10\(^{12}\)
- Deformation Mechanism: Bulk diffusion, dislocation motion, both phases

* Two vendors produced fibers. Highly aligned fibers grown at 25.4 mm/min had the best creep rates.
* The high stress exponent and high activation energy suggest dislocation creep mechanisms. Dislocations observed in both phases with higher dislocation observed in sapphire.
* Controlled by dislocation motion in each phase. Induced by lattice diffusion. Dislocations observed in both phases with higher dislocation observed in sapphire.
* Bulk diffusion in YAG, dislocation motion. Directed by lattice diffusion. Dislocations observed in both phases with higher dislocation observed in sapphire.
* Dislocation activity controlled (strong interface bonding, large aspect ratio, high stress exponent) * TEM performed * TEM-limited sapphire dislocations, no garnet dislocations. Dislocation controlled sliding at interface does not accommodate t- system deform non-steady leads to overestimation of stress exponent. Other diameter spacing.
1.5.5 Creep in Single-Crystal ZrB$_2$ and LaB$_6$

Creep in boride eutectics has not been examined as intensively due to the difficulties with processing low porosity materials. The creep behavior of LaB$_6$-ZrB$_2$ DSEs has not been published. In fact, very limited data exist on the creep of single crystal ZrB$_2$ and single crystal LaB$_6$. No literature concerning compression creep, impression creep or tensile creep of single crystal LaB$_6$ was found. However, it is still important for this study to understand what is known about deformation in the constituent phases of the eutectic. One such study by Chen et al. in 2003 correlating the temperature and loading time dependence of micro hardness to creep of single crystal LaB$_6$ prepared by the floating zone method was found. In this study, Vickers hardness was performed from 25ºC to 1000ºC. At 700ºC an inflection point was observed. Below 700ºC cracking was observed which lead to a decrease in the accuracy of the hardness measurements. Above 700ºC no cracking was observed and Chen et al. reported decreased hardness with an increase of loading time. According to Chen et al., this loading time dependence of hardness indicates the occurrence of creep above 700ºC (Figure 1.11).\textsuperscript{73} As stated previously, changes observed in the hardness data below 700ºC are not attributed to creep and are discounted due to the unreliability of the hardness numbers because of cracking of the indentations. The activation energy for creep was calculated to be about 343 kJ/mol from the following equation:

$$H^m = Ae^{-Q/RT}t$$

(5)

Where $H$ is hardness, $Q$ is the activation energy, $R$ is the gas constant, $T$ is temperature, $t$ is the loading time, and $m$ and $A$ are constants. This is the only study found on creep in LaB$_6$ single crystal and due to the cracking observed the occurrence of creep at these temperatures is questionable.
Creep studies have been performed on ZrB$_2$ single crystal and will be discussed in this section. In 1971, Haggerty et al. reported on the plastic deformation of single crystal ZrB$_2$ grown by rf floating zone method. Plastic deformation was initiated by compression creep at temperatures of 1490°, 2000°, and 2125° C. At temperatures of 1490°C and 2000°C failure occurred by brittle fracture. Slip on the basal plane was achieved at 2125° C.

In 2002, Melendez-Martinez et al. reported on the compression creep behavior of a pressed polycrystalline ZrB$_2$ (86.5% dense). Below 1400°C no deformation could be measured. At 1400°C, a strain rate of $\sim$6x10^{-8}s^{-1} was measured under a stress of 298MPa. At 1500°C, strain rates close to 10^{-7}s^{-1} were obtained under stresses between 298 and 408MPa; finally, at 1600°C, a strain rate close to 2x10^{-7}s^{-1} was obtained under $\sigma$=220MPa. $n$=1.7 at 1500°C, $n$=0.6 at 1600°C. As stated previously stress exponents around one are indicative of Nabarro-Herring or Coble creep diffusion-type deformation.

In summary, creep data are not available on LaB$_6$-ZrB$_2$ DSEs and limited data are available on the single crystal monophases. Compression creep has been performed on single crystal and polycrystalline ZrB$_2$. With the polycrystalline ZrB$_2$ sample, a strain rate close to 2x10^{-7}s^{-1} was obtained at 1600°C under $\sigma$=220MPa and a stress exponent of
n=0.6 was determined. In the single crystal ZrB$_2$ sample deformation without fracture could not be produced by compression creep until a temperature of 2125$^\circ$C. These results along with the creep data from oxide DSE studies again, give an indication that LaB$_6$-ZrB$_2$ DSEs should exhibit very good creep resistance up to high temperatures.

### 1.6 Deformation Mechanisms

In addition to creep, examining deformation areas using TEM can give valuable information with regards to dislocation types, and slip systems. Although deformation and slip system studies have not been studied in LaB$_6$-ZrB$_2$ DSEs, indentation studies have been performed on some similar diborides including single crystal ZrB$_2$ as well as single crystal LaB$_6$.\textsuperscript{76,74,77,78,79,80,81,82} This thesis uses Vickers indentations to induce deformation along with TEM for analysis. Some of the suggested slip systems found in literature for these materials were not based on this type of deformation study, but rather used anisotropy of hardness to determine the slip systems. In order to determine the slip system in the material for this study and how it might deform, it is essential to review these previous studies.

Vahldiek \textit{et al.} (1977) reported on slip systems in the diborides, TiB$_2$ and HfB$_2$, that were initiated by Knoop and Vickers indentations.\textsuperscript{76} These are relevant to ZrB$_2$ slip systems because Ti, Hf and Zr are all IVB metals and TiB$_2$, HfB$_2$ and ZrB$_2$ all have AlB$_2$-crystal type lattices. Vahldiek \textit{et al.} used transmission electron microscopy (TEM) to evaluate dislocations under TiB$_2$ indents. Dislocation pile-ups, stacking fault ribbons, and wavy slip were observed (Figure 1.12, Figure 1.13). Wavy slip is defined as slip that is curved, branched, broad and diffuse.\textsuperscript{83} Based on these results, it is probable that dislocation pile-ups, stacking fault ribbons, and wavy slip will be observed in the LaB$_6$-ZrB$_2$ DSE.
Figure 1.12  TEM of TiB$_2$ showing slip (s) and dislocation pile-ups (d) on the (0001) plane of TiB$_2$ single crystal.$^{76}$

Figure 1.13  Wavy slip (s) and stacking fault ribbons (f) for TiB$_2$.$^{76}$
Several groups have researched ZrB\(_2\) single crystal deformation. Haggerty \textit{et al.} \cite{haggerty1971} reported on slip planes and Burgers vectors in a rf-heated float zone prepared sample. Dislocations were observed in float zone processed samples, with dislocations parallel to \textlangle1120\textrangle. Room-temperature Knoop microhardness at 600-g loads was used to initiate deformation and evaluate possible slip systems. Slip was found in the prismatic \{10\overline{1}0\} plane.

In order to determine slip systems in single crystal materials, one can use the anisotropy in hardness values. Brookes \textit{et al.} \citeyear{brookes1971} aimed at establishing a clear relationship between shear stress, hardness anisotropy, and slip systems for many crystals.\cite{brookes1971} According to Brookes \textit{et al.}, the anisotropy of hardness for a crystal structure can be directly related to its slip systems. Brookes \textit{et al.} evaluated the equation for effective resolved shear stress (\(\tau_e\)) proposed by Daniels and Dunn\cite{daniels1971}:

\[
\tau_e = \left(\frac{F}{A}\right) \cos \lambda \cos \phi \cos \psi.
\]  

where, \(F\) is the applied force, \(A\) is the cross-sectional area of specimen, \(\lambda\) is the angle between the stress axis and slip direction, \(\phi\) is the angle between the stress axis and the normal to the slip plane, \(\psi\) is the angle between the face of an adjacent facet and the axis of rotation for a given slip. They determined that in order for the effective resolved shear stress to be more accurate, one had to account for the rotational constraint of the rod under an indent\cite{brookes1971}:

\[
\tau'_e = \frac{1}{2} \left(\frac{F}{A}\right) \cos \lambda \cos \phi (\cos \psi + \sin \gamma)
\]  

where, the bracketed () area accounts for rotational constraint. The modified equation was verified with a magnesium oxide sample. Brookes \textit{et al.} summarized in table form the relationship between anisotropy of hardness and slip systems in single crystal hexagonal crystal structures. Hexagonal crystals evaluated were Ti, Zr, SiC, Mg, Zn, Co,
Mo$_2$C, and Al$_2$O$_3$. In the hexagonal crystals studied, the prismatic plane had the highest degree of anisotropy. Two common sets of slip planes were identified in the hexagonal crystals, \{0001\} $< 1\bar{1}20 >$ and \{10\bar{1}0\} $< 1\bar{2}10 >$. For Zr, the primary slip system \{10\bar{1}0\} $< 1\bar{2}10 >$ was suggested (Table 1.4).

Table 1.4  
Slip systems thought to control the hardness anisotropy in hexagonal structures.$^{77}$

<table>
<thead>
<tr>
<th>Crystal structure</th>
<th>Knoop hardness number</th>
<th>Slip system*</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(0001)</td>
<td>(01\bar{1}0)</td>
<td>(1\bar{2}10)</td>
</tr>
<tr>
<td>Ti h.c.p.</td>
<td>$&lt; 10\bar{1}0 &gt;$</td>
<td>117</td>
<td>56</td>
</tr>
<tr>
<td>Ti h.c.p.</td>
<td>$&lt; 1\bar{1}20 &gt;$</td>
<td>90</td>
<td>38</td>
</tr>
<tr>
<td>Ti h.c.p.</td>
<td>115</td>
<td>115</td>
<td>55</td>
</tr>
<tr>
<td>Zr h.c.p.</td>
<td>271</td>
<td>264</td>
<td>115</td>
</tr>
<tr>
<td>SiC hex.</td>
<td>2917</td>
<td>2954</td>
<td>2027</td>
</tr>
<tr>
<td>Mg h.c.p.</td>
<td>28</td>
<td>24</td>
<td>36</td>
</tr>
<tr>
<td>Mg h.c.p.</td>
<td>28</td>
<td>23</td>
<td>32</td>
</tr>
<tr>
<td>Zn h.c.p.</td>
<td>18</td>
<td>15</td>
<td>44</td>
</tr>
<tr>
<td>Co h.c.p.</td>
<td>1580</td>
<td>1540</td>
<td>250</td>
</tr>
<tr>
<td>Mo$_2$C hex.</td>
<td>1300</td>
<td>1400</td>
<td>1800</td>
</tr>
<tr>
<td>Al$_2$O$_3$ hex.</td>
<td>1300</td>
<td>1400</td>
<td>1800</td>
</tr>
</tbody>
</table>

In 1972, Nakano et al., evaluated the hardness anisotropy in the single crystal IVa-diborides at room temperature.$^{78}$ They compared the hardness anisotropy of TiB$_2$, ZrB$_2$, and HfB$_2$ and found that the anisotropy in TiB$_2$, ZrB$_2$, and HfB$_2$ were different. The prismatic planes in TiB$_2$ had the highest hardness and anisotropy. In ZrB$_2$, the basal
plane had the highest hardness and anisotropy. However, the anisotropy between the 
basal and prismatic planes was not big and was not as pronounced as it was for TiB$_2$. 
Also, the hardness anisotropy observed due to indenter direction was the opposite of 
TiB$_2$. HfB$_2$ was the least anisotropic of the borides studied and the prismatic planes 
were slightly higher in hardness than the basal. Nakano et al. used the modified Brookes et al. 
effective shear stress equation to determine an anisotropy hardness number for each slip 
system possible. Based on the calculated anisotropy factor, \{10\10\} < 1\2\10 > was 
determined to be the major slip system for ZrB$_2$. This suggested slip system is consistent 
with the previously cited research.

In 1976, Nakano et al. calculated the major slip system operative in single crystal 
ZrB$_2$. The calculations were based on Knoop hardness anisotropy values between 
temperatures of 20° to 1100° C. The major slip system based on these calculations was 
believed to be \{10\10\} < 1\2\10 >. In 2002, Xuan et al. examined the high-temperature 
hardness of a single crystal ZrB$_2$ prepared by the floating zone method. Based on 
inflection points of 400°C (0.19T$_m$) and 700°C (0.28T$_m$) Xuan et al. believe a single slip 
system for ZrB$_2$ as suggested by Nakano does not accurately reflect the inflection points 
(sudden change in hardness) observed.

In 1986, Aida et al. reported on slip systems and dislocation densities in single crystal 
LaB$_6$. Aida et al. grew different diameter rods (2.5, 3, 5mm) using a float zone process 
heated by a xenon arc furnace. Due to the good emittance properties of the (100) plane, 
rods were grown with no rotation, at a rate of 0.17mm/min in the <100> direction. 
Samples were mechanically cleaved perpendicular to the <100> growth direction, and 
dislocation type and densities were studied by first etching the rods with a 1:1 HNO$_3$:HCl 
solution for 30 sec. Aida et al. observed that the larger the crystal diameter, the higher 
the dislocation density. Another trend observed by Aida et al. was that dislocations were 
highest in the core and decreased at the edge of the rods. A 5mm rod had dislocation 
densities a magnitude higher in the core vs. the periphery. According to Aida et al. 
higher dislocations in the core vs. the periphery could be explained by a much steeper 
temperature gradient in the core vs. the periphery of the rod. Dislocation densities 
between $10^6$ and $10^{5.4}$ cm$^{-2}$ were observed in the 5 mm rod. An electrolytic technique was 
used to analyze the dislocation directions. Based on the dislocation directions, it was
determined that the main slip system in LaB₆ is \{100\} / \langle 110 \rangle . Furthermore, because the slip system was of a simple cubic lattice, they concluded that the boron network dictates deformation mechanisms in single crystal LaB₆. The float zone processed LaB₆-ZrB₂ DSE composite studied is ~4.4mm in diameter. Therefore, one might expect to see dislocations close to \( 10^5 \) cm\(^{-2} \) in the LaB₆ phase.

In 1991, Li et al. reported on slip systems in single crystal LaB₆ grown in a [110] orientation. Utilizing the relationship between hardness anisotropy and slip systems reported by Brookes et al. (discussed earlier) they explained the hardness of LaB₆ single crystals in relation to slip systems. Li et al. calculated resolved shear stress diagrams and compared them to Knoop microhardness data and concluded that the inverse relationship between microhardness anisotropy and resolved shear stress is valid. From this relationship they were able to conclude that the main slip systems in the (100), (110), and (111) planes. The suggested main slip system in the (100) plane is \{100\} \langle 01\overline{1} \rangle , for the (110) plane two possible slips systems \{111\} \langle 1\overline{1}0 \rangle \text{ and } \{110\} \langle \overline{1}1\overline{1} \rangle \text{ were suggested, and for (111) two possible slip systems } \{100\} \langle 01\overline{1} \rangle \text{ and } \{110\} \langle \overline{1}1\overline{0} \rangle \text{ were also suggested.}

In summary, no data exist for deformation of LaB₆-ZrB₂. However, data exits on the monophases of this system as well as similar lattice structures. Based on this data it is hypothesized that dislocation pile ups, stacking fault ribbons, and wavy slip may be observed in the LaB₆-ZrB₂ system. Beyond dislocation types some information on the slip systems in the LaB₆ and ZrB₂ monophases was reviewed. Slip systems have been proposed in both single crystal ZrB₂ and LaB₆ based on hardness data (Table 1.5). Due to lack of data, suggested slip systems were obtained by deformation studies as well as anisotropy of hardness studies discussed in detail previously. Both of these methods had similar results and suggested slip systems of \{100\} \langle 110 \rangle \text{ for LaB₆ and } \{10\overline{1}0\} \langle \overline{1}210 \rangle \text{ for ZrB₂. In this thesis study a LaB₆-ZrB₂ DSE will be evaluated under a Vickers indentation of 19.6 N via TEM in order to determine dislocation types and slip systems in the composite material.}
Table 1.5  Single crystal ZrB$_2$ and LaB$_6$ suggested slip systems

<table>
<thead>
<tr>
<th>Author</th>
<th>Method</th>
<th>ZrB$_2$</th>
<th>LaB$_6$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nakano et al. 79</td>
<td>Knoop</td>
<td>${10\bar{1}0} &lt; 1\bar{2}10 &gt;$</td>
<td></td>
</tr>
<tr>
<td>Xuan et al. 80</td>
<td>Vickers</td>
<td>Multiple slip system suggested based on hardness inflection points at 400° C and 700° C</td>
<td></td>
</tr>
<tr>
<td>Haggerty et al. 74</td>
<td>Knoop</td>
<td>${10\bar{1}0}$</td>
<td></td>
</tr>
<tr>
<td>Brookes et al. 77</td>
<td>Knoop</td>
<td>Zr HCP</td>
<td>${10\bar{1}0} &lt; 1\bar{2}10 &gt;$</td>
</tr>
<tr>
<td>Aida et al. 81</td>
<td>HNO$_3$ etch</td>
<td></td>
<td>${100} / &lt; 110 &gt;$</td>
</tr>
<tr>
<td></td>
<td>(dislocation analysis)</td>
<td></td>
<td>${110} &lt; 01\bar{1} &gt;$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>${111} &lt; 1\bar{1}0 &gt; &amp; {110} &lt; 1\bar{1}0 &gt;$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>${111} = {100} &lt; 01\bar{1} &gt; &amp; {110} &lt; 1\bar{1}0 &gt;$</td>
</tr>
</tbody>
</table>

1.7 Conclusion

In this Introduction, the importance of new materials for ultra high-temperature applications was established. Directionally solidified eutectics were discussed and suggested as good candidates for these ultra high-temperature applications. In particular LaB$_6$-ZrB$_2$ DSE was emphasized as a good candidate due to its extremely high fracture toughness as compared to other DSEs. There is, however, a lack of understanding of the high-temperature creep properties of LaB$_6$-ZrB$_2$ DSEs, which needs to be known to evaluate the material’s applicability in high-temperature environments. Creep in oxide DSEs was reviewed and the improved creep resistance of the DSE materials over sintered polycrystalline and single-crystal monophase material was discussed. The superior creep resistance has been attributed to the low-energy semicoherent interfaces that DSEs possess. Similar results in the LaB$_6$-ZrB$_2$ DSEs are expected, based on the fact that LaB$_6$-ZrB$_2$ DSEs low energy semicoherent interfaces were established by Deng 26 (2006).
More specifically, the best DSE oxide has a creep rate around $10^{-8}$ s$^{-1}$ at 1600°C and under a 100MPa stress.$^{72}$ Based on the higher melting temperature and therefore stronger bonding in the LaB$_6$-ZrB$_2$ DSEs (2467°C) vs. the oxide DSEs (1900°C) (Table 1.1), the creep rate is expected to be greater than $10^{-8}$ s$^{-1}$ at 1600°C and a 100MPa stress. In research performed by Matson $et$ $al.$$^{63}$ in 2005, the best creep rate obtained was from an oxide eutectic with an aligned microstructure similar to LaB$_6$-ZrB$_2$ DSE. According to Matson $et$ $al.$, an aligned microstructure yields a larger diffusion path that makes diffusion movement more difficult.$^{63}$ Similar high activation energies, as were seen in the oxide DSEs, indicative of dislocation mechanisms, are expected. For the stress exponent, a stress exponent between 2 and 3 is expected.
2 Hypothesis and Objectives

Known room-temperature mechanical properties as well as high-temperature melting-points, identify LaB$_6$-ZrB$_2$ directionally solidified eutectics as promising candidates for ultra-high-temperature applications. Directionally solidified eutectic single-crystal LaB$_6$-ZrB$_2$ eutectics are unique in that fracture toughness (>8.7 MPa·m$^{1/2}$)\textsuperscript{25}, melting temperature (2470 ± 40 °C)\textsuperscript{25} and micro-hardness (25.5 GPa)\textsuperscript{25} are extremely high. Because of the excellent room-temperature properties of LaB$_6$-ZrB$_2$ eutectics, along with strong covalent bonding and previous studies on oxide DSEs, it is expected that LaB$_6$-ZrB$_2$ possesses excellent creep resistance. It is the objective of this thesis to measure the creep behavior of LaB$_6$-ZrB$_2$ DSEs up to 1600°C. It is hypothesized that the semi-coherent interfaces\textsuperscript{26} between the two phases will lead to a very creep resistant material, better than its polycrystalline counterparts. In addition, the deformation mechanisms at both room-temperature and high-temperature will be studied.

Room-temperature deformation will be initiated using Vickers indentation. Deformation under the indent will be evaluated using FIB/SEM/TEM (Focused Ion Beam/ Scanning Electron Microscope/Transmission Electron Microscope) techniques in order to analyze dislocations and primary slip systems in the individual LaB$_6$ and ZrB$_2$ phases. Dislocation interaction between interphases will be evaluated by TEM. Specifically, assessment will be done to determine whether or not dislocations originate or end in the bulk matrix, and or originate at the interface of the fiber and matrix. High-temperature creep will be performed using impression creep testing. Close monitoring of deformation over time will be performed in order to determine creep rates at high-temperature. Deformation mechanisms, dislocations, and slip systems will be evaluated using FIB/SEM/TEM techniques. The results of this study should provide information on the deformation mechanisms in composite directionally solidified boride eutectics and help determine its applicability for ultra-high-temperature applications.
3 Room-Temperature Deformation Study

3.1 LaB$_6$-ZrB$_2$ Microstructure

A LaB$_6$-ZrB$_2$ DSE rod grown via a floating zone method was received from collaborators at the Institute for Problems of Materials Sciences, Academy of Sciences of Ukraine, Ukraine$^{31}$. The LaB$_6$-ZrB$_2$ DSE rod “as received” was 152.4mm long and had a diameter of 4.9mm. The outside of the rod had periodic striations and another periodic defect referred to as “ripples” (Figure 3.1)$^{41}$ It is believed that the ripples are damaged areas resulting from overheating during growth$^{41}$. This is of some concern because fracture has been linked back to these damaged areas$^{41}$. The second type of surface periodicity referred to as “striations” are about 508 µm’s apart. Sayir et al. 1998 discussed the possible mechanisms and concluded that more research into the mechanisms of the striations needed to be done$^{41}$. However, they proposed that the striations could be a result of molten zone mechanical oscillations induced by processing related disruptions$^{41}$.

![Figure 3.1](image) “As Received” LaB$_6$-ZrB$_2$ rod showing banding and ripples.
The microstructure can be characterized as having uniform areas of distributed ZrB₂ fibers along with areas of significant banding (Figure 3.2).

Banding is a typical phenomenon observed in DSEs. Some other examples of where banding has been observed, is in directionally solidified alumina-zirconia and alumina-YAG. The banding observed in the LaB₆-ZrB₂ DSE has areas where the LaB₆ matrix phase occurs with little if any of the ZrB₂ fibrous phase, as shown in Figure 3.2a. The ZrB₂ phase observed in this banding is of various diameters, widths and lengths. The reason for this banding is not well understood. However, it does seem to be a general consensus that the banding is related to temperature fluctuations during growth of the rod. Deng et al. proposed that the source of LaB₆-ZrB₂ banding could be thermal instabilities due to variation in the position of the induction coil.

The size and volume fraction of ZrB₂ fibers in the homogenous region was analyzed utilizing Image J software. In the homogeneous areas (Figure 3.2 c) the average inter-fiber distance is 1.1 ±0.4 µm, and the average fiber diameter is 0.7 ± 0.1 µm. The volume fraction of the minor phase (ZrB₂) in the homogenous region is ~18% which is consistent with the suggested LaB₆-ZrB₂ phase diagram and a 17vol% for ZrB₂ (Figure 1.3). The fiber diameter, volume fraction, and inter-fiber distance are all typical for a LaB₆-ZrB₂ DSE.
In summary, the LaB$_6$-ZrB$_2$ DSE reviewed has a typical microstructure that has been observed in previous LaB$_6$-ZrB$_2$ DSE samples.\textsuperscript{26,31} To further characterize the sample prior to deformation studies, the as-processed sample defects, the orientation at the LaB$_6$-ZrB$_2$ interface, and hardness are analyzed below.

### 3.2 Method

The LaB$_6$-ZrB$_2$ DSE samples were cut from the “as-received” rod with a low-speed Buehler, Isomet diamond wafering saw parallel to the growth direction. Samples 7.6 mm in length were cut from the rod using a low speed diamond saw. Two types of samples were then prepared using a Grizzly Surface Grinder (Model 60567). In order to analyze samples parallel and perpendicular to the growth direction samples were surface ground parallel and perpendicular to the growth direction using a 150 grit diamond embedded grinding wheel to ensure the sample ends were flat and parallel. Prior to analysis, the surface ground LaB$_6$-ZrB$_2$ DSE samples were polished using a tripod holder and diamond abrasive film. Samples were glued to the tripod holder using crystal bond adhesive. The tripod holder consisted of three leveling feet which were used to level the sample prior to polishing. Samples were successively polished with 30\(\mu\)m, 15\(\mu\)m, 9\(\mu\)m, 6\(\mu\)m, 3\(\mu\)m, and 1\(\mu\)m diamond embedded film purchased from Buehler. Between each step of polish, samples were checked by optical microscopy for uniformity and also in the final step for a smooth finish without scratches.

Samples were locally extracted from homogeneous areas of as-processed rods using a FEI Quanta 200 3D, which combines a scanning electron microscope (SEM) with a focused ion beam (FIB). In the first step prior to extracting a sample from the as-processed rod, a protective tungsten deposit was applied in order to prevent damage to the specimen from the beam. A 20\(\mu\)m x 2\(\mu\)m x10\(\mu\)m area of tungsten was deposited at a beam current of 30keV and an ion current of 0.3 nA (Figure 3.3a).

After application of the protective layer, milling of a sample wedge was performed. A wedge was used in order to protect the sides of the sample and also as an aid in dislodging the sample. Once the wedge was cut free from the bulk of the sample by the FIB, a tungsten probe with a tip radius of 0.5\(\mu\)m and a 13° taper angle was deposited to
the sample and the sample was pulled out (Figure 3.3b). The sample was then deposited to an Omniprobe copper lift-out grid specifically designed for in-situ lift out of TEM specimens (Figure 3.3c). Once deposited on the copper grid, the sample was thinned to electron transparency by the ion beam (Figure 3.3d). The TEM sample was initially thinned at 30keV and an ion beam current at 50pA followed by a final thinning at 5keV and an ion beam current at 29 pA was performed (Figure 3.3e).

Figure 3.3  TEM specimen preparation sequence.  a) 20µm x 2µm x 10µm W deposit on 19.6 N indent (b) Plucking a sample (c) Attaching the sample to the Omniprobe grid (d) Thinning sample (e) Final thinned electron transparent sample

The final thinning at 5keV was performed in order to try to remove high-energy milling damage. Giannuzzi et al. reduced the surface damage that occurs due to milling from ~
22 nm to less than 2 nm by using a 2keV Ga+ FIB beam as opposed to 30keV. During thinning of the samples the protective tungsten top layer can sometimes be thinned before the sample is electron transparent. In the cases where that occurred, additional thinning was performed in a Fischione Ion Mill with settings of 4.5kV, 4mA, 12° tilt, and 360° rotation. A Philips EM420T TEM operated at 120kV was used to evaluate thinned samples.

Vickers hardness testing was performed in a representative homogenous area of the LaB$_6$-ZrB$_2$ DSE sample where the volume fraction of the ZrB$_2$ phase was ~18% (Figure 3.4).

![Figure 3.4](image)

Deformation was initiated using a Leco V1-100-C1 indentation instrument. The ASTM C 1327-99 Vickers indentation hardness procedure was followed. This included making sure the sample was level and secure by bonding the bottom of the sample to a glass microscope slide with crystal bond and then securing the glass slide with tape to the Leco indentation equipment stage. A load of 19.6 N was applied for 15 seconds. Deformation was initiated on the growth axis of the rods (001) plane at random in-plane orientations, making sure to keep a distance of at least 4 indentation diagonal lengths apart. In order to get an idea of the scale of the indent in comparison to the size of the microstructure, the measurements of the widest part of the indent are around 45 µm as compared to an
average of about 0.7 µm diameter for a ZrB₂ fiber. Therefore, it was concluded that a representative area of the eutectic microstructure was indented.

3.3 Results

3.3.1 As-Grown Orientation and Deformation

Bright-field TEM images from the processed samples discussed above and shown in Figures 3.4 and 3.5 were obtained by TEM.

Figure 3.5  TEM sample from an as-grown LaB₆-ZrB₂ DSE parallel to growth axis thinned to transparency.
Samples parallel and perpendicular to the growth orientation were tilted over a wide angular range to find dislocations; however, none were observed (Figure 3.7). This is surprising because directionally solidified samples prepared by the floating zone process typically have some as-processed dislocations. One such example of as-processed float zone grown LaB$_6$-ZrB$_2$ DSE rods with dislocations can be seen in observations made by Deng in unpublished data where dislocations were observed in an as received LaB$_6$-ZrB$_2$ DSE rod (Figure 3.8). Dislocations are observed in the ZrB$_2$ fibers as well as the LaB$_6$ matrix. Reasons for this difference can be attributed to possible differences in growth conditions, growth rate, and temperature gradient and therefore related to the flatness of the solid/liquid interface.
Figure 3.7  TEM micrographs of an as-grown LaB$_6$-ZrB$_2$ DSE with no dislocations observed, contrast is due to bend contours. a) Parallel to growth axis.  b) Perpendicular to growth axis
Dislocations are observed in the LaB$_6$ matrix as well as the ZrB$_2$ fibers. These same samples were also analyzed for orientation relationship between the LaB$_6$ and the ZrB$_2$ phases. A different orientation relationship was observed between the LaB$_6$-ZrB$_2$ phases than reported in previous literature. The orientation relationship observed was:

Growth direction: $[001]_{LaB_6} // [00.1]_{ZrB_2}$

Interfacial Plane: $(0\bar{1}0)_{LaB_6} // (0\bar{1}0)_{ZrB_2}$
In 1995 Paderno et al. reported on a LaB$_6$-ZrB$_2$ grown by induction zone melting. In 1998 Chen et al. grew a LaB$_6$-ZrB$_2$ eutectic using an electron beam zone heating technique. In 2004 Deng et al. investigated a LaB$_6$-ZrB$_2$ grown by the Paderno group using induction zone melting. The orientation relationship observed in all cases was

Growth direction: $[001]_{LaB_6} // [00.1]_{ZrB_2}$

Interfacial Plane: $(110)_{LaB_6} // (110)_{ZrB_2}$

In both cases, the growth axis is the same, but the in-plane orientation varies by 15 degrees. The orientation relationship difference observed between this DSE LaB$_6$-ZrB$_2$ and previous DSE LaB$_6$-ZrB$_2$ samples discussed in literature could, in principle, result in different deformation mechanisms between the ZrB$_2$ fibers and the LaB$_6$ matrix as compared to the samples discussed in the literature due to slip systems being aligned differently. This is not discussed in detail in this thesis.
### 3.3.2 Hardness

The average Vickers hardness values obtained for 8 randomly applied loads of 19.6 N for 15s was 20.2 GPa in the longitudinal section (perpendicular to growth axis Figure 3.11) and 18.0 GPa in the transverse section (Figure 3.11). This is lower than values obtained from literature (Table 3.1).

![Figure 3.11](image) Illustration of c axis and longitudinal orientations of the LaB$_6$-ZrB$_2$ DSE sample used for hardness evaluation.

<table>
<thead>
<tr>
<th>Hardness (GPa)</th>
<th>Sample ID</th>
<th>Transverse section</th>
<th>Longitudinal section</th>
<th>Load</th>
<th>Microstructure</th>
</tr>
</thead>
<tbody>
<tr>
<td>This Work</td>
<td>LaB$_6$-ZrB$_2$ DSE</td>
<td>$18.0 \pm 0.75$</td>
<td>$20.2 \pm 1.8$</td>
<td>19.6 N</td>
<td>FD=0.7µm ± 0.1  $V_m$= 0.18</td>
</tr>
<tr>
<td>Deng$^{108}$</td>
<td>LaB$_6$-ZrB$_2$ DSE</td>
<td>$22.6 \pm 0.7$</td>
<td>$21.7 \pm 0.6$</td>
<td>9.8 N</td>
<td>FD=0.6µm $V_m$= 0.18</td>
</tr>
<tr>
<td>Chen et al.$^{20}$</td>
<td>LaB$_6$-ZrB$_2$ DSE</td>
<td>31.4</td>
<td>28.8</td>
<td>19.6 N</td>
<td>FD=0.2 to 1.2µm $V_m$= 0.2</td>
</tr>
<tr>
<td>Paderno et al.$^{25}$</td>
<td>LaB$_6$-ZrB$_2$ DSE</td>
<td>25.5 (orientation unknown)</td>
<td>Unknown</td>
<td>9.8 N</td>
<td>$V_m$= 0.2</td>
</tr>
<tr>
<td>Monteverde et al.$^{99}$</td>
<td>ZrB$_2$ (poly)</td>
<td>8.7±0.4</td>
<td></td>
<td>9.8 N</td>
<td>NA</td>
</tr>
<tr>
<td>Melendez et al.$^{75}$</td>
<td>LaB$_6$ Single Crystal</td>
<td>26±0.6</td>
<td>NA</td>
<td>unknown</td>
<td>unknown</td>
</tr>
</tbody>
</table>

Table 3.1 Vickers hardness values for LaB$_6$-ZrB$_2$ DSE. $V_m$ equals volume fraction of the LaB$_6$ matrix phase and FD equals the ZrB$_2$ fiber diameter.
There are a variety of reasons for why the hardness values obtained could be lower than previous literature reports. One reason could be differences in microstructure (Table 3.1). Optically, the microstructure appears to be similar to other LaB₆-ZrB₂ DSEs discussed in literature and the volume fraction of the matrix phase in all reports was about the same. However, the fiber diameter is not discussed in most of the previous literature reports. Another reason for a difference in values could be differences in testing method and load. The indentation load used in this study is higher than two of the studies referred to in Table 3.1. However, there is one previous study which used the same load for indentation hardness testing (Chen et al.⁹⁰) and they still obtained a typical hardness value which is higher than the hardness value obtained in this study. This can be explained by the smaller diameter fiber spacing (Table 3.1) and it was not clear which indentation method was used in the Chen et al. study. Another notable difference that could be a factor in the lower hardness value is the different orientation relationship in this sample versus other LaB₆-ZrB₂ samples reported on previously. Therefore, this may play a role in the lower hardness values obtained.

3.3.3 Deformation

3.3.3.1 Stress distribution

Another important baseline factor to consider prior to analyzing the indentation-induced deformation is the stress distribution under the indent. According to Fisher-Cripps⁹⁰, the mean contact pressure of the indenter is about 7% less than the Vickers hardness number. Therefore, based on a hardness of ~ 18 GPa, the mean contact pressure should be around 17 GPa. The total penetration depth can be calculated based on the length of the diagonal of the indentation. The length of the diagonal is 7 times the total penetration depth, so in these experiments the total penetration depth was ~6.4 µm. From the value of mean contact pressure, the stress under the indent was estimated. Estimates were based on stress graphs located in reference 94. Stress graphs from Fisher Cripps were based on a material with a Poisson’s ratio of v=0.26, and α = 68°. Alpha (α) is the
semi-angle between the opposite faces of the indenter. The LaB$_6$-ZrB$_2$ DSE material composite Poisson’s ratio was calculated to be $v=0.27$ when the load is in the same direction as the growth direction.$^{20}$ Therefore, the stress graphs should be applicable to this material. To estimate stress at a particular position under the indent, the mean contact pressure ($P_m$) is multiplied by the numbers for that position in the graphs (Figure 3.12).

![Stress graphs based on $v=0.26$, $\alpha = 68^\circ$.](image)

Figure 3.12 Stress graphs based on $v=0.26$, $\alpha = 68^\circ$.100

### 3.3.3.2 TEM Analysis

In the TEM sample perpendicular to the growth axis, plastic deformation from the room-temperature Vickers indentation can be seen in both the LaB$_6$ and ZrB$_2$ phases of the indented specimen (Figure 3.13). The fracture path of the cracking that is observed is also of significance. Fracture and debonding of the specimen takes a path around the ZrB$_2$ fibers. This fracture path is well known for the ZrB$_2$-LaB$_6$ DSE eutectic. Deng
discusses this fracture path in detail in her 2006 PhD thesis. The tortuous path of fracture is a major reason the fracture toughness of this material is very good.

Numerous dislocation arrays were also observed. The dislocations seem to originate/end in the matrix and don’t appear to originate or end at the fibers (Figure 3.14). Two beam conditions $g_{200}$ LaB$_6$ and $g_{010}$ LaB$_6$ were performed in order to evaluate slip systems in the eutectic. It is well known that when $\overline{g} \cdot \overline{b} = 0$, pure edge-component dislocations can not be seen, where $\overline{g}$ is the diffraction vector and $\overline{b}$ is the Burgers vector. This is referred to as the invisibility criterion. Some of the dislocations appear to satisfy the invisibility criterion for slip plane and direction $\{100\}/<110>$ (Figure 3.14).

Dislocation arrays are observed in the $g_{200}$ LaB$_6$ two beam condition and are indicated in Figure 3.14 by striped lines. These same dislocations are not observed in the $g_{010}$ LaB$_6$ two beam condition. Dislocations that did not satisfy the invisibility criterion for the slip system $\{100\}<110>$, were also observed and are indicated by oval markers.
Figure 3.14  TEM perpendicular to the growth axis. One can see numerous dislocation arrays. The dislocation arrays appear to initiate or end in the matrix and do not appear to initiate or end at the fibers. Two beam conditions $g_{200}$ LaB$_6$ and $g_{010}$ LaB$_6$. Stripes satisfy slip plane and direction $\{100\}/\{110\}$. Circled areas are dislocations that did not satisfy the invisibility criterion. [100] and [110] Cleavage planes are indicated.

In the TEM sample parallel to the growth axis, plastic deformation from the room-temperature Vickers indentation can again be seen in both the LaB$_6$ and ZrB$_2$ phases of the indented specimen (Figure 3.15). A fracture path around the fibers is also observed. The cleavage planes appear to occur primarily in the [110] and [100] directions (Figure 3.14).
Figure 3.15 TEM micrographs of LaB$_6$-ZrB$_2$ DSE from under a 19.6 N Vickers indent (parallel to the growth axis.  a) High magnification showing numerous dislocations in the ZrB$_2$ fiber and a crack starting on the outside. Some dislocation arrays are evident in the LaB$_6$ matrix as well. b) Low magnification of same sample with crack path more obvious.

3.4 Conclusions

Vickers indentation at room-temperature was used to initiate deformation in LaB$_6$-ZrB$_2$ DSE. Crack progression, dislocation types, and slip systems were evaluated. Fracture and debonding at the interfaces was observed. Crack propagation navigated around ZrB$_2$ fibers. Unlike observations made in previous studies of single crystal LaB$_6$, ZrB$_2$, and LaB$_6$-ZrB$_2$ DSE, dislocations were not observed in as received DSE rods. As discussed previously, dislocation density is believed to be a function of the melt solid interface. The flatter the melt solid interface the fewer the dislocations. Other factors that could affect dislocation density are growth and rotation rates. After Vickers indentation under a 19.6 N load, dislocations were observed in both phases. Dislocations appear to initiate and end in the matrix and do not appear to initiate nor end near the fiber
interfaces. Some dislocations in the $\text{LaB}_6$ phase of $\text{ZrB}_2$-$\text{LaB}_6$ DSE appear to satisfy the slip system $\{100\} <110>$. Other dislocations observed do not appear to satisfy the invisibility criterion for this slip system. Further evaluation of 2 beam TEM conditions should be performed. Dislocations in $\text{ZrB}_2$ need to be evaluated in the TEM by two beam conditions in order to verify the same slip systems observed in previous single crystal studies.
4 High-Temperature Impression Creep

4.1 Method

4.1.1 Instrument Modification

High-temperature deformation of the LaB$_6$-ZrB$_2$ DSE was examined by high-temperature impression creep. Due to the complexity of the testing equipment, a standard operating procedure (SOP) was written and followed for each sample (see appendix I). A diagram of the impression creep instrument is shown in Figure 4.1. The sample and punch were held between two alpha SiC tabs inside a high-temperature furnace with an open area of 14x14x16.5cm. An internal layer of 1” KVS 1704 insulation and an external 1” BR Fractilin board insulation lined the inside walls. Cooled water was run through pipes around the exterior of the furnace and specifically around the transducers to keep the furnace cooled and reduce fluctuations in the transducers. The cooled water was maintained at a constant temperature of 16°C with the use of a chiller. The temperature was monitored with type B thermocouples (Platinum-30% Rhodium, Platinium-6% Rhodium) encapsulated in an alumina protection tube.
Prior to creep testing, the creep instrument was modified for controlled atmosphere. This entailed enclosing and making airtight the furnace and all tubing running in and out of the furnace. The bellows that was installed had some slight air leaks that could not be fixed. Attempts were made to patch the holes, however due to the very small size and difficulty in getting in between the grooves of the bellows these attempts were unsuccessful. In order to ensure that the external oxygen atmosphere could not enter the furnace during testing, the exhaust tubing was bubbled into a 6 foot tube filled with dibutyl phthalate to ensure backpressure while testing. UHP argon was used and the atmosphere in the furnace was monitored with a DS-400 probe from Australian Oxytrol Systems.

The most critical parameter for a successful creep test is aligning the indenter properly. An aluminum jig was designed and utilized to ensure proper alignment between the SiC rams, SiC plates, indenter (punch) and sample (Figure 4.2).
4.1.2 Instrument Calibration

The first step prior to running creep tests on the LaB$_6$-ZrB$_2$ DSE was to run calibration samples possessing known creep rates. The initial calibration of the instrument was performed by Fox who measured creep of Si$_3$N$_4$ NT154 samples for comparison with published data. The results obtained were within the expected published creep data range for Si$_3$N$_4$ NT154. A 2nd calibration was performed just prior to LaB$_6$-ZrB$_2$ DSE testing to verify the instrument was still in alignment. SiAlON samples used for calibration were tested on the instrument previously by Fox and run again under the same conditions to verify instrument calibration. Test sample sizes were 13.5 x 13.5 x 8mm samples of SiAlON. The LaB$_6$-ZrB$_2$ DSE rod tested was 4.9mm in diameter. Due to the size variance in the tested samples and to eliminate concerns regarding a possibility of changing creep rates with sample size and alignment, 4.9mm rods were bored from standard samples of 13.5 x 13.5 SiAlON. The 13.5mm SiAlON and the 4.9mm SiAlON rods were tested for comparison. Sample test conditions were -300MPa, 1400°C, and 100hrs. As shown in Table 4.1 all samples had strain rates of $\sim 10^{-7}$ verifying that the smaller diameter specimens did not affect the indentation creep results.
Table 4.1  Calibration results for Creep Test Instrument and small diameter specimens. Highlighted columns are calibration runs performed in this study. Non-highlighted are previous runs performed on the same instrument. ab581 = 35.4%Si, 6.9%Al, 5.8% O, 51% N, 0.7%Yb₁₀²

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Size</th>
<th>Temp.</th>
<th>Stress</th>
<th>Strain Rate (s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Run 41 ab581</td>
<td>13.5x13.5.8mm</td>
<td>1400°C</td>
<td>-300MPa</td>
<td>4.02E⁻⁷ (s⁻¹) ± 6.04E⁻⁹</td>
</tr>
<tr>
<td>Run 57 ab581</td>
<td>13.5x13.5.8mm</td>
<td>1400°C</td>
<td>-300MPa</td>
<td>6.88E⁻⁷ (s⁻¹) ± 1.03E⁻⁸</td>
</tr>
<tr>
<td>Run 58 ab581</td>
<td>13.5x13.5.8mm</td>
<td>1400°C</td>
<td>-300MPa</td>
<td>8.38E⁻⁷ (s⁻¹) ± 1.27E⁻⁸</td>
</tr>
<tr>
<td>Run *39 ab581</td>
<td>13.5x13.5.8mm</td>
<td>1400°C</td>
<td>-300MPa</td>
<td>4.65E⁻⁷ (s⁻¹) ± 6.89E⁻⁹</td>
</tr>
<tr>
<td>Run 2 ab581</td>
<td>4.9x7.4mm</td>
<td>1400°C</td>
<td>-300MPa</td>
<td>6.22E⁻⁷ (s⁻¹) ± 9.34E⁻⁹</td>
</tr>
</tbody>
</table>

4.1.3 Sample Preparation

Samples prior to deformation testing were surface ground on a Grizzly Surface Grinder (model 60567) using a 150 grit diamond embedded wheel to ensure the samples were flat and parallel. Squared samples were then polished using a tripod holder and diamond abrasive film. Samples were successively polished with 30µm, 15µm, 9µm, 6µm, 3µm, and 1µm film. After final polishing, the surface finish of the samples was evaluated using an optical microscope. Samples were evaluated to make sure no cracks were visible and that there was a homogenously smooth surface. A carbon sputter coating was then applied to both ends of the sample to act as a protective getter.
4.2 Results

4.2.1 1st Creep Run

Several creep runs were attempted before optimization of the furnace and creep method was obtained. The first LaB$_6$-ZrB$_2$ DSE creep test was performed at 1400°C in UHP argon for 22 hrs and under a stress of -300MPa. The sample was under load for 22 hrs before the transducer reading was unattainable. Upon examination of the sample, severe deformation of the sample was observed. The sacrificial tab that the sample rested on was cracked and had a white reaction product covering the surface (Figure 4.3b).

![Figure 4.3](image)
a) Optical micrograph of the side of the LaB$_6$-ZrB$_2$ sample after creep test #1 showing severe deformation, b) sacrificial SiC Tab from creep test #1 showing severe reaction product.

To check for any reaction products, the sample and tablet were analyzed by SEM. Analysis via SEM/EDS found Zr and La on the surface of the sample and did not reveal any elements out of the ordinary. Analysis of the SiC tablet found Zr and La from the sample and Si from the SiC tablet and therefore no elements out of the ordinary were detected (Figure 4.4, Figure 4.5) It was concluded based on these results along with the visual deformation of the sample that severe oxidation caused the sample to deform at a rapid rate thus preventing us from obtaining creep data.
Figure 4.4  SEM/EDS results on outer surface of LaB₆/ZrB₂ sample after creep test #1. Zr and La were the only elements detected. These elements are expected therefore nothing unusual was detected by SEM/EDS.

Figure 4.5  SEM/EDS Analysis from creep test #1 tablet Residue. Zr, La and Si were detected. La and Zr are from the sample and Si would be expected from the SiC tablet.
4.2.2 2nd Creep Run

A second sample was run under the same conditions as the first, but with more attention being paid to making sure as much oxygen as possible was purged from the furnace. As mentioned previously, as part of the SOP, the sample was exposed for two hours to an atmosphere of UHP argon at 1400°C, this is performed to stabilize the temperature. Once stabilization was completed the load was placed on the sample. However, the alpha silicon carbide indenter broke on application of the load. Post testing optical inspection revealed a glassy residue on the surface of the sample and sacrificial alpha silicon carbide tab (Figure 4.6a). SEM/EDS analysis detected La, Si, C, O, and Zr on the sample (Figure 4.6b).

![Figure 4.6](image)

Figure 4.6  a) Top outer surface of Creep Test # 2 sample and tablet. A glassy residue was observed after two hours @ 1400°C with no load.  b) SEM/EDS taken from the surface of the LaB₆-ZrB₂ DSE sample (circled) detected La, Si, C, O, Zr.
The sample was also analyzed by XRD to confirm suspicions of oxidation, LaBO$_3$ and La$_3$BO$_6$ lanthanum borate were observed on the sample (Figure 4.7). A second XRD was performed on the tab area where the sample was sitting. This was done in order to try to determine if contamination was a factor in the reaction observed. However, again only a lanthanum borate pattern was observed (Figure 4.8). A third XRD was performed on the glassy looking residue seen on the tablet (Figure 4.9). A broad amorphous peak was observed. An amorphous peak is a typical XRD pattern for an amorphous specimen like glass. The glassy phase can be explained by the La$_2$O$_3$-B$_2$O$_3$ phase diagram which shows liquid immiscibility at 1136°C and extends from pure B$_2$O$_3$ to 21.5 mol% La$_2$O$_3$. Therefore, at 1400°C the formation of liquid B$_2$O$_3$ and La$_2$O$_3$ is expected.

![XRD 2nd outer surface of creep sample confirming oxidation of the sample in the form of lanthanum borate](image)

**Figure 4.7**  XRD 2nd outer surface of creep sample confirming oxidation of the sample in the form of lanthanum borate
Figure 4.8  XRD 2nd creep sample area of tab on which sample was sitting tested to ensure no contamination was responsible for reaction. Again, lanthanum borate was detected.
Figure 4.9  XRD of 2\textsuperscript{nd} creep sample reaction product found on the SiC tablet. XRD is comparing glassy residue to white center ring where LaB\textsubscript{6}-ZrB\textsubscript{2} sample was sitting.

Figure 4.10  Phase diagram for the system La\textsubscript{2}O\textsubscript{3}-B\textsubscript{2}O\textsubscript{3}.104
High-temperature oxidation of a LaB$_6$-ZrB$_2$ eutectic has been previously studied by Chen et al.$^{105}$ Oxidation studies were performed at various temperatures and oxidation partial pressures. The surface morphology of the LaB$_6$-ZrB$_2$ eutectic was found to progressively oxidize at higher temperatures, as shown in Figure 4.11. Chen et al. studied temperatures from 912°C to 1223°C and they observed severe oxidation under atmospheric conditions of 39 kPa P$_{O_2}$. The study that Chen et al. performed was at a lower temperature than the 1400°C used in this test. The results of Chen et al., show that above 1053°C the LaB$_6$-ZrB$_2$ eutectic reaction to increasing oxidative atmosphere becomes near linear (paralinear) (Figure 4.12). In this second creep run the oxygen partial pressure is not known. However, based on the appearance of the sample, the XRD results, and the previous studies on a LaB$_6$-ZrB$_2$ eutectic, the atmospheric conditions during this run were conducive to oxidation of the sample.

Figure 4.11  SEM photographs of the surface morphology of oxidized LaB$_6$-ZrB$_2$ at oxygen partial pressure of 39 kPa (a)-912°C; (b)1016°C; (c)1094°C; (d) 1223°C.$^{105}$
Figure 4.12  Parabolic plot of specific weight change of the LaB$_6$-ZrB$_2$ composites vs. time at various oxidation temperatures in an oxygen partial pressure of 39 kPa.$^{105}$
4.2.3 3rd Creep Run

Several changes were made to the creep instrument prior to a third creep run in order to prevent the oxidation issues that occurred in the first two attempted creep runs. First, an oxygen sensor was attached to the furnace in an attempt to monitor the oxygen partial pressure in the furnace. Second, the bellows was found to have a significant leak and therefore was changed. However despite these changes made on the 3rd creep attempt, the sample oxidation was even more severe and the sample was only under load for 1 hr (Figure 4.13).

![Creep test # 3 sample as is- after one hour under a stress of -300MPa @ 1400°C- the LaB₆-ZrB₂ DSE sample is melted.](image)

The sample severely melted and changed shape. The sample tablet was analyzed by SEM/EDS for contamination and only La and Si were detected (Figure 4.14).
A gray scale was observed on the cross-section of the 3rd creep sample. In this area, an unidentifiable pattern was observed by XRD analysis. Peaks observed in this unidentifiable pattern were analyzed by EDS and included O, Zr, Al, B and La (Figure 4.15). Aluminum is an element that is contained in the insulation found in the furnace. The insulation used in the furnace is an alumino-silicate refractory ceramic fiber referred to as Fiberfrax. Therefore, the aluminum was assumed to come from the insulation.
Figure 4.15  XRD 3rd creep sample post test cross-sectioned in half longitudinally. Three areas were analyzed. In the outer area lanthanum borate and ZrO₂ were detected. The Center area was not oxidized and pure LaB₆-ZrB₂ was detected. The scale around the sample didn’t yield an identifiable pattern but O, Zr, Al, B, La were detected by EDS. Al was assumed to be from the insulation in the furnace.

SEM micrographs of the 3rd creep sample showed significant porosity in the outer LaBO₃ and ZrO₂ layer (Figure 4.16). This phenomenon was explained by Chen et al. in their high-temperature oxidation studies on a LaB₆-ZrB₂ eutectic. According to Chen et al., the porosity is due to evaporation of B₂O₃. They performed electron microprobe (EMP) analysis on their sample and the boron x-ray image obtained confirmed boron evaporation at the surface of the sample (Figure 4.17).
Based on the results from the first three creep runs, three more changes were made to the creep test furnace and method. First, to improve the detection of oxygen the oxygen probe was changed to a DS-400 oxygen probe from Australian Oxytrol systems. The probe has the capability to measure from pure oxygen down to $10^{-17}$ Pa at temperatures from 700°C to 1700°C. Installation of the probe required a vertical orientation at temperatures above 1100°C. However, due to the design of the furnace this was impossible. Therefore, the oxygen probe was installed in a separate tube furnace run at a temperature of 800°C. The atmosphere was monitored via a tube that was attached between the tube furnace and the outlet gas line of the creep furnace. Another change was the addition of graphite oxygen getters. Seven getters were installed in the furnace prior to a run. One getter was wrapped around the exterior of the sample, two getters were installed next to the transducers, and then one getter was installed in each corner of the furnace (Figure 4.18).
A final change was a switch to a different atmospheric gas. The gas was changed from UHP argon to Forming gas (4% H₂ in Nitrogen). The theory behind using forming gas is that the hydrogen in the forming gas getters O₂ and the nitrogen creates a reducing atmosphere to prevent oxidation.

After making these changes a fourth creep run was attempted and completed. The sample ran for 100hrs at 1400°C and under a stress of -300MPa. The results were much improved over the previous test attempts. The sample still had some oxidation but was still intact (Figure 4.19).
Figure 4.19  LaB$_6$-ZrB$_2$ DSE creep #4 sample after 100 hrs at 1400°C -300 MPa in forming gas. The load was applied normal to the impression region shown.

However, there was a reaction that occurred in the furnace between the H$_2$ in the forming gas and the Fiberfrax insulation (Figure 4.20). It was realized after the fact, that in reducing atmospheres silica is attacked, dissociates and volatizes resulting in premature failure of the Fiberfrax. The molybdenum disilicide elements are reduced as well, which ends up being an expensive option if you have to replace elements every run.

Figure 4.20  Inside of furnace after creep test 4, depicting white Si coating due to reaction of fiberfrax fibrous insulation with the forming gas.

The creep data was very jumpy which was attributed to the reactive conditions in the furnace and the coating that was found all over the interior. The impression depth jumped around from ~ 1515 µm to ~1518 µm, indicating that very little if any creep occurred
(Figure 4.21). From this creep data a creep rate of $-3.3 \times 10^{-11} \text{ s}^{-1} \pm -5.8 \times 10^{-11}$ was calculated. The steady state creep rate was calculated using a linear regression fit of the strain versus time data. The fitting error is the standard error calculated from the regression fit.

![Graph showing creep rate](image)

**Figure 4.21** LaB$_6$-ZrB$_2$ DSE creep #4 deformation over time for 100 hrs at 1400$^\circ$C, -300MPa in forming gas.

SEM analysis of the sample showed numerous cracks under the indent (Figure 4.22). Crack locations appeared to be randomly distributed under the indent with some observed on the edges, in the middle and in areas in-between. Cracks were observed travelling normal from the indent. The longest crack length observed was 944 µm in length with the average length being 220 µm with a standard deviation of 250 µm. It is not surprising to find cracks under the indent at 1400$^\circ$C. As discussed previously in the introduction, during compression testing at temperatures below 2000$^\circ$C failure in a single crystal ZrB$_2$ occurred by brittle fracture.\textsuperscript{74}
High magnification evaluation by SEM showed a microstructure that was essentially unchanged. The average fiber diameter was 0.65 ± 0.09 µm as compared to as-processed fiber diameter in the sample which was 0.7 ± 0.1 µm. The average inter-fiber distance in the crept sample was determined to be 0.7 ± 0.2 µm compared to 1.1 ± 0.4 µm in the as-processed sample (Figure 4.23). Stability of the microstructure of DSEs has been referenced in previous literature and was discussed previously in the introduction. This stability is attributed to the composites being crystallized from the molten state and therefore being in equilibrium.19
Using the method described previously in section 3.2, TEM samples were prepared of the area under the indenter in order to confirm the lack of deformation. TEM analysis revealed no deformation or dislocation activity (Figure 4.24) consistent with the essentially zero creep rate.

Figure 4.23  High magnification SEM cross-section of 4th creep sample under the indent showing an unchanged microstructure compared to the as-processed sample. Fiber diameter and spacing are 0.65 ± 0.09 µm and 0.7 ± 0.2 µm respectively.

Figure 4.24  Typical TEM of creep # 4 sample @1400°C, -300MPa, 100 hrs crept ZrB₂-LaB₆ DSE sample. No dislocations were observed in any orientation. The contrast between the fibers is associated with bend contours and not crystalline defects.
For the 5th run three additional changes were made to the test method. The first change was prompted by the fact that oxidation was still observed on the test specimen in the previous run. A double getter system was utilized to combat this remaining oxidation. This double getter system consisted of a bored-out graphite rod with a diameter slightly bigger than the sample. In the remaining space, powdered graphite was inserted between the sample and the graphite rod to minimize the initial direct exposure of the sample to atmosphere. Secondly, due to the reaction of the Fiberfrax with forming gas, it was decided to go back to UHP argon. In the first two creep runs UHP argon was used without a graphite getter system. UHP argon, in combination with the graphite getters should provide a lower oxygen ppm in the furnace and will not attack the molybdenum disilicide elements like the forming gas will. Another change was made in order to run creep tests at 1600°C. The previous runs used Fiberfrax insulation which has an operational upper temperature limit around 1423°C. Therefore, the third change was to remove the old insulation and replace it with a material rated for higher temperature use. A double insulation system was utilized. The outer walls were installed with 1” KVS 174 ceramic fiber board which has an operational maximum temperature of 1700°C. The second inside layer was installed with a 1” BR Fractalin board. The BR Fractalin board has a maximum suggested operational temperature use of ~1760°C and, unlike fibrous boards, is a solid (99.9% Al2O3) board that should be an easier surface to remove trapped oxygen from.

The 5th creep test ran for 100 hrs under a stress of -400MPa at 1500°C in UHP argon. A creep rate of $9.8 \times 10^{-09} \text{ s}^{-1} \pm 1.88E-10$ was calculated for this 5th creep sample. As discussed in the previous section on the 4th creep sample, the steady state creep rate was calculated using a linear regression fit of the strain versus time data. The fitting error is the standard error calculated from the regression fit. However, the $R^2$ for the graph is 0.69 and the total impression change was about 2µm in 74 hrs (Figure 4.25). Therefore, based on this data it was concluded that very little if any creep of the material occurred.
This was confirmed by SEM and TEM analysis where no deformation was observed.

![Graph showing deformation](image)

Figure 4.25  LaB$_6$-ZrB$_2$ DSE sample #5 deformation over time 74 hrs, 1500°C, -400MPa in UHP argon.

The changes made to the test procedure resulted in less oxidation of the sample (Figure 4.26).

![SEM micrograph](image)

Figure 4.26  Low magnification SEM micrograph of top view and longitudinal cross-section LaB$_6$-ZrB$_2$ sample after 5$^{th}$ creep run.
High magnification SEM micrographs reveal oxidation still on the surface of the sample and cracking (Figure 4.27). Like the previous run cracking was observed under the impression area. Two main areas of chipping were observed under the impression area (Figure 4.26). Chipped out areas dimensions were 72µm deep by 160 µm wide and 90 µm deep by 180 µm wide. A third area of cracking with a crack of a depth of 19µm connected to another crack coming diagonally down from the surface 13 µm long was observed (Figure 4.27). The scale of microstructure was measured and the average fiber diameter and interfiber distance in the homogenous region was 0.71 ± 0.1 µm and 0.90 ± 0.09 µm respectively (Figure 4.27). This is consistent with observations in the previous creep run and previous research on DSEs.

![Figure 4.27](image)

**Figure 4.27** SEM micrograph of LaB$_6$-ZrB$_2$ cross-section after the 5th creep run showing fracture on the cross-section area under the impression and oxidation on the surface of the sample impression area.

### 4.2.6 6th Creep Run

A sixth and final creep run was performed for 25 hrs at 1600°C under a stress of -420MPa in UHP argon. A creep rate of $1.7 \times 10^{-7} \text{ s}^{-1} \pm 2.8 \times 10^{-9}$ was calculated for this 6th creep sample (Figure 4.28). As discussed in the previous sections on the 4th and 5th
creep samples, the steady state creep rate was calculated using a linear regression fit of the strain versus time data. The fitting error is the standard error calculated from the regression fit.

![Image](image.png)

Figure 4.28 LaB$_6$-ZrB$_2$ DSE creep sample #6 deformation over time for 100 hrs at 1600°C, -420MPa in UHP argon.

Based on the creep curve it appeared that creep in the material occurred with an overall impression depth change of around 30 µm. However careful SEM analysis showed no deformation under the indent other than fracture in the material. A little more oxidation was observed on the surface of the sample vs. the 1500°C test but this is expected for an increase in temperature of 100°C (Figure 4.29).

![Image](image.png)

Figure 4.29 Top view of LaB$_6$-ZrB$_2$ DSE sample #6 after 25 hrs, 1600°C, -420MPa in UHP argon. The load was applied normal to the indenter area shown. Oxidation is observed on the surface of the sample.
The increased oxidation was observed outside the indentation area and corresponded to a decrease in surface depth of around 40 µm (Figure 4.30).

Figure 4.30     High magnification SEM of LaB₆-ZrB₂ DSE after 1600°C - 420MPa creep test. Surface oxidation outside of the indent area is observed with ~40um surface depth reduction.

Crack locations appeared to be randomly distributed under the indent with some observed on the edges, in the middle and in areas in-between. The longest cracks were observed in high stress areas near the edges of the indent (Figure 4.31). Compressive stresses are concentrated at the contact edge of the punch therefore; it is not unexpected to see larger cracks in this area (Figure 4.34). This will be discussed further in section 4.3. The cracks observed traveled normal to the impression surface and were about 1.2 mm in length. The average depths of the rest of the cracks were 170 µm in length. Also observed was a raised area under the indent. SiC was the main reaction product. Analysis by XRD found SiC
and LaB$_2$C$_2$ (lanthanum boron carbide). Therefore, it appears that the reaction product observed is from the indenter and also includes a reaction product between LaB$_6$ and the graphite powder used as an oxygen getter.

Figure 4.31  Cross-section of 6$^{th}$ creep run of DSE LaB$_6$-ZrB$_2$. Cracks were observed under the indent area and a raised area (reaction product) determined to be SiC and LaB$_2$C$_2$ by XRD.

TEM analysis showed very little dislocation activity. A dislocation array between two ZrB$_2$ fibers was observed and some dislocations around the edge of the fiber but little else was observed (Figure 4.32). A typical fracture path for a LaB$_6$-ZrB$_2$ DSE was observed travelling around the fibers. The orientation at the interface is the same as was observed in the as-processed specimen (Figure 4.33).
Figure 4.32 TEM micrograph of 6\textsuperscript{th} LaB\textsubscript{6}-ZrB\textsubscript{2} creep sample.

Figure 4.33 TEM micrograph and interface diffraction pattern for the 6\textsuperscript{th} creep run of LaB\textsubscript{6}-ZrB\textsubscript{2} DSE.
Therefore, based on the above SEM and TEM results it was concluded that creep in the DSE did not occur. It is possible that the creep rate observed is due to creep of the $\alpha$-SiC punch and tabs. However, Lane et al. reported a creep rate of $1.14 \times 10^{-8}$ s$^{-1}$ at 1600°C under a compressive stress of -414 MPa for $\alpha$-SiC. This is an order of magnitude slower than the creep results obtained. Therefore, creep in the punch material and tabs may not be the only contributor to the observed creep data. It is possible the reaction product observed had some contribution.

### 4.3 Summary and Discussion

Impression creep testing was performed under conditions of 1400, 1500, and 1600°C at stresses of -300, -400 and -420MPa respectively. Creep rates obtained for the three runs are summarized in Table 4.2.

<table>
<thead>
<tr>
<th>Test Temperature</th>
<th>Atmosphere</th>
<th>Stress</th>
<th>Test Time</th>
<th>Steady-state creep rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>1400°C</td>
<td>Forming gas</td>
<td>-300 MPa</td>
<td>100 hrs.</td>
<td>$-3.3 \times 10^{-11} \pm 4.8 \times 10^{-13}$ s$^{-1}$</td>
</tr>
<tr>
<td>1500°C</td>
<td>UHP Ar</td>
<td>-400 MPa</td>
<td>74 hrs.</td>
<td>$-9.8 \times 10^{-9} \pm 1.5 \times 10^{-11}$ s$^{-1}$</td>
</tr>
<tr>
<td>1600°C</td>
<td>UHP Ar</td>
<td>-420 MPa</td>
<td>25 hrs.</td>
<td>$-1.7 \times 10^{-7} \pm 2.5 \times 10^{-9}$ s$^{-1}$</td>
</tr>
</tbody>
</table>

Despite obtaining what appears to be creep under these conditions. It was concluded based on the lack of deformation seen under the indentation region in high magnification SEM, EDS and TEM analysis that the creep values obtained were probably not due to creep in the sample but due to creep in the alpha silicon carbide tabs and punch. More specifically the values obtained maybe due to reactions between the SiC punch, tabs, and sample with the furnace environment. Another possible contributor to creep values is reaction of the graphite getter material with the sample.

Samples were evaluated under the impression punch by SEM, FIB, and TEM. Cracking was observed under the impression creep area in all three successful creep runs. Cracks were randomly oriented throughout the impression area and tended to run normal
to the impression load. The longest cracks were observed in the sample under the highest stress (-420 MPa). These large cracks were ~1.2 mm in length normal to the indentation load and close to the edge of the indenter. The longer length cracks near the edge of the indenter punch can be explained using stress graphs for a cylindrical flat punch. Equations by Barquins and Mauquis were used by Fishcher-Cripps in a finite element model to graph the stress state underneath the cylindrical flat punch (Figure 4.34). There is an area around the edge of contact between the punch and sample where compressive stress concentrates. The magnitude of the stress acting normal to the sample was plotted by Fox and aptly demonstrates this singularity at the edge of contact between the punch and sample.

Figure 4.34  Stress graphs for a cylindrical flat punch. A polar coordinate system is used to describe the stress beneath a cylindrical flat punch. The stress graph distances $r$ and $z$ are normalized to the contact radius $a$ and stresses are expressed in terms of the mean contact pressure $P_m$. 

Various atmospheric conditions were attempted until an acceptable creep run was obtained. Ultra high purity argon with a graphite gettering system yielded the best results for oxidation prevention. However, oxidation was never completely eliminated. In conclusion, LaB$_6$-ZrB$_2$ appears to have excellent creep resistance between 1400 -1600°C, however severe oxidation occurs even under a controlled Ultra High Purity Argon environment.
5 Conclusions

New materials are needed for ultra-high-temperature applications. Directionally solidified eutectics possess some desirable mechanical properties for ultra-high-temperature applications. The majority of directionally solidified eutectic knowledge is on oxide eutectics, while knowledge of boride eutectics is minimal. However, they possess desirable mechanical properties that oxide eutectics do not. Directionally solidified eutectics can be processed by a variety of methods. The float zone method produces microstructures in the sub micron range. The known room-temperature mechanical properties of the LaB₆-ZrB₂ eutectic identify it as a promising ultra-high-temperature material. Deformation of a floating zone processed directionally solidified LaB₆-ZrB₂ eutectic was analyzed at room-temperature as well as high-temperature. After Vickers indentation dislocations were observed in both phases. Dislocations appeared to initiate and end in the matrix and do not appear to initiate nor end near the fiber interfaces. Some dislocations in the LaB₆ phase appear to satisfy the slip system \( \{100\} <110> \). Other dislocations observed did not appear to satisfy the invisibility criterion for this slip system. Impression creep testing at 1400, 1500 and 1600°C under stresses of -300,-400 and -420MPa did not deform the LaB₆-ZrB₂ DSE sample. Oxidation was an issue in all high-temperature testing conditions. The LaB₆-ZrB₂ appears to have excellent creep properties. However, LaB₆-ZrB₂ does not appear to be a viable candidate for ultra-high-temperature applications in air because of the poor resistance to oxidation.
6 Future Work

LaB$_6$-ZrB$_2$ DSE is not a viable candidate for ultra-high-temperature applications in air because of its poor oxidation resistance. However, because LaB$_6$-ZrB$_2$ does have excellent creep resistance, knowledge of deformation mechanisms has the potential to help with the identification and fabrication of other materials that are viable candidates. Current creep testing at temperatures up to 1600ºC did not reveal deformation by SEM and TEM analysis of the material. Performing higher temperature and higher load creep tests are necessary to induce deformation in the DSE. This would also give deformation data at temperatures closer to application conditions. Based on the known creep data for ZrB$_2$ presented earlier, in conjunction with the known mechanical improvements realized for DSE composites, a significant increase in testing temperature may be necessary. Modification of the furnace with refractory metal elements and heat shields in order to achieve a higher temperature and prevent oxidation should be performed. Another way of guarantying deformation of the substrate at high-temperature would be to use a different type of indentation mechanism for higher loads. Using a controlled atmospheric Vickers indentation at high-temperature is a possible way of getting high-temperature deformation results. Creep testing so far on the LaB$_6$-ZrB$_2$ DSE was only performed normal to the [001] growth direction, turning the sample 90° and performing creep testing should be done to evaluate creep in a different fiber orientation and would give us information on how the ZrB$_2$ fiber reinforcing phase influences creep. Finally for complete creep analysis of the LaB$_6$-ZrB$_2$ DSE system and its components, impression creep testing on the LaB$_6$ and ZrB$_2$ DSE single crystal monophases should be performed. As stated previously no known creep testing has been performed on single crystal LaB$_6$ and very limited compression creep testing has been performed on single crystal ZrB$_2$.

To complete the slip system studies at room-temperature, more two-beam TEM conditions should be performed on the Vickers indented LaB$_6$ and ZrB$_2$ phases. Two beam conditions were performed in the $g_{200}$ LaB$_6$ and $g_{010}$ LaB$_6$ orientations. Because other dislocations did not meet the invisibility criterion for the $\{100\} <110>$ slip system other two beam conditions should be performed. Two beam conditions for the suggested slip systems ($\{0001\} <11\bar{2}0>$, and $\{1010\} <1\bar{2}10>$) of ZrB$_2$ should be investigated in the
DSE. Finally, looking at slip systems in terms of Brooks et al. and the hardness anisotropy in the LaB$_6$ZrB$_2$ DSE would give a more complete study of the slip system. Unfortunately this study confirms that this LaB$_6$-ZrB$_2$ DSE sample is not capable of meeting the requirements necessary for use in an ultra-high-temperature environment. In conclusion, none of the current available composite materials has all the properties needed for high-temperature use. DSEs with better oxidation resistance should be investigated further. New and unique ultra-high-temperature materials need to be researched. The use of complex materials consisting of more than a binary composite should be investigated further.
Appendix

Creep Test SOP  Modified: 4-29-08

1. Polish sample to 1um and take pictures of end at 50x for record.
2. record length and diameter of sample and punch
3. give sample to John Cantolina for Carbon sputter layer on both sides
4. make sure sample, punch and tabs are clean of debris.
5. Turn on water and cooling tower
6. plug in fan on side of the controller to cool back of furnace
7. Turn on tube furnace and heat to 800°C on labview thermocouple/900 on controller
8. make sure safety block is inserted under weights
9. load tabs, sample and punch into aluminium jig and place in the furnace
10. Start labview and record file
11. Test punch integrity and alignment by temporarily adding the full weight on punch, if punch does not fail reduce weight to 25lbs.
12. Insert transducers and align in proper positions.
13. Ensure that impression depth is at least 500um. If not adjust front transducer with hex wrench
14. add graphite getter system around sample and in furnace
15. add powdered graphite to hole on top of sample
16. Close side door and tighten all hex screws
17. Insert KVS 1704 insulation and then BR. Fractulin board into the front door
18. Close door and add two brackets to areas of missing knobs and tighten brackets in knobs in a uniform fashion.
19. turn on Argon and run until you get a reading of $10^5$ (usually overnight)
20. Start profile. Hit (PAR) until you get [PRUN]
21. use the (↑) to [PR-1]
22. hit (PAR) to start
23. Wait until furnace heats up to desired temp. *when heating to ~1400 deg. C the controller does not shut off so make sure you are there when it is close to the desired temp and once it is at that temp drop the temp controller set value down to 1400 until temp starts going back down then raise it back up to desired temp and it should stabilize.
24. check water flow and temp of cooling rings on tube furnace
25. Then let temp. stabilize for two hours
26. recheck temp of cooling rings and furnace walls
27. Profile is set to turn off after 999 min so once your desired temp is reached you need to put the profile into pause mode by holding the (↑) for 3 seconds
28. Check on creep test at least twice a day.
29. After 100hrs cool furnace by pushing (↓)to 0º
30. Turn tube furnace off by pushing (↑)to 0º
31. Turn furnace profile off by pushing (↑)(↓) buttons simultaneously for 3 seconds
32. turn Furnace master switch to off once temp is down
33. turn water and cooling jacket off.
34. turn flow controller off
35. open furnace to check on sample
36. copy excel data to another computer and turn labview program off.
References


