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INTRINSIC AND EXTRINSIC MODIFICATION OF NIOBIUM ALUMINIDES AND MOLYBDENUM DISILICIDE COMPOSITES

DISSERTATION

Presented in Partial Fulfillment of the Requirements for
the Degree Doctor of Philosophy in the Graduate
School of The Ohio State University

By

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* * * * *

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ABSTRACT

Molybdenum Disilicide (MoSi$_2$) is considered as a potential structural high temperature material due to the attractive combinations of lower density (6.33 g/cc, 75% of that of conventional superalloys); excellent oxidation resistance due to the formation of a protective oxide film above 900°C; good elevated temperature strength retention at temperatures up to about 1200°C; high thermal conductivity; low coefficient of thermal expansion and thermodynamic compatibility with most of the commonly used reinforcements such as SiC, Mo, W and Nb. However, MoSi$_2$ is brittle at room temperatures. There is, therefore, a need for approaches designed to toughen MoSi$_2$ at lower temperatures. Ductile phase toughening of MoSi$_2$ with Nb fibers and Nb laminae was examined in this study. The toughening levels in the MoSi$_2$ /Nb composites were quantified using micromechanics-based crack-tip shielding models. Fatigue and fracture mechanisms were also be elucidated for the fiber- and laminate-reinforced composites. Transformation toughening was also studied on MoSi$_2$ reinforced with 2 mol.% TZ-2Y. Toughening level due to transformation was also quantified using micromechanical models.

Synergistic toughening was studied in model MoSi$_2$ composites reinforced with 2 mole % yttria partially stabilized zirconia particle, and Nb layers. Synergistic toughening was shown to occur in these composites due to additional transformations that were induced as a result of higher interfacial stresses. However, the overall level of transformation toughening was limited. Nevertheless, a synergistically toughened MoSi$_2$
composite with a toughness of $-20.5 \pm 1.0 \text{ MPa}^\sqrt{\text{m}}$ was produced by hybrid reinforcement with Nb layers and 2 mole % yttria-stabilized zirconia particles.

Following the study of ductile Nb reinforced MoSi$_2$ composites, an effort was made to examine the fatigue and fracture behavior of a new class of damage tolerant niobium aluminide intermetallics. Effects of alloying, microstructure and temperature (25°C and 750°C) on the fatigue and fracture behavior were studied. The role of oxide-induced closure was also elucidated for near-threshold fatigue crack growth at elevated-temperature (750°C). The implications of the results are assessed for potential structural applications of niobium aluminide intermetallics.

Finally, layered Nb-15Al-40Ti/MoSi$_2$ composites were fabricated in an effort to engineer improved oxidation resistance. The MoSi$_2$ layers were used as oxidation resistant layers. The fatigue and fracture behavior of layered MoSi$_2$/Nb-15Al-40Ti composites was studied at room-temperature.
To my parents,

to my wife and to my son
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vi


FIELD OF STUDY

Major Field: Materials Science and Engineering
# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>ABSTRACT</td>
<td>ii</td>
</tr>
<tr>
<td>DEDICATION</td>
<td>iv</td>
</tr>
<tr>
<td>ACKNOWLEDGMENTS</td>
<td>v</td>
</tr>
<tr>
<td>VITA</td>
<td>vi</td>
</tr>
<tr>
<td>LIST OF TABLES</td>
<td>xiii</td>
</tr>
<tr>
<td>LIST OF FIGURES</td>
<td>xiv</td>
</tr>
</tbody>
</table>

## CHAPTERS:

1. INTRODUCTION
   1.1 Background........................................... 1
   1.2 Objectives and Approach.......................... 3
   1.3 Materials Systems Studied....................... 5
   1.4 Organization of the Thesis...................... 6

2. LITERATURE REVIEW
   2.1 Review of Fracture and Fatigue.................. 7
      2.1.1 Fundamentals of Fracture.................... 7
         2.1.1.1 The Griffith Concept.................... 7
         2.1.1.2 Linear Elastic Fracture Mechanics........ 9
      2.1.2 Fundamentals of Fatigue..................... 11
         2.1.2.1 Fatigue of Ductile Solids............... 13
            2.1.2.1.1 Fatigue Crack Initiation............ 13
            2.1.2.1.2 Fatigue Crack Growth................. 13
         2.1.2.2 Fatigue of Brittle Solids............... 18
2.3.5.1 Brittle Reinforcement ........................................................... 59
2.3.5.1.1 Reinforcement with SiC ........................................... 59
2.3.5.1.2 Reinforcement with ZrO₂ ......................................... 60
2.3.5.2 Ductile Reinforcement ....................................................... 60

3. EXPERIMENTAL PROCEDURES ................................................................. 63
3.1 Fracture Toughness Test ....................................................................... 63
3.2 Resistance Curve Behavior (R-Curve) .................................................. 65
3.3 Fatigue Crack Growth........................................................................ 67
3.4 Tensile Test........................................................................................... 68
3.5 Fractography.......................................................................................... 69
3.6 Optical Interference Microscopy (OIM) Techniques......................... 70
3.7 X-ray Diffraction................................................................................... 70
3.8 Laser Raman Spectroscopy (LRS) Techniques..................................... 71

4. FATIGUE AND FRACTURE BEHAVIOR OF MoSi₂ COMPOSITES...... 74
4.1 Effect of Reinforcement Morphology on the Fatigue and Fracture of MoSi₂/Nb Composites................................................................. 74
4.1.1 Introduction......................................................................................... 74
4.1.2 Materials Source and Processing........................................................ 75
4.1.3 Residual Stress Analysis..................................................................... 80
4.1.4 Bending Strength................................................................................ 85
4.1.5 Fracture Toughness............................................................................ 87
   4.1.5.1 Monolithic MoSi₂.................................................................. 87
   4.1.5.2 Fiber-Reinforced MoSi₂ Composite...................................... 88
   4.1.5.3 Laminate-Reinforced MoSi₂ Composite............................... 101
4.1.6 Constraint Effects.............................................................................. 105
4.1.7 Resistance Curve Behavior ................................................................ 109
   4.1.7.1 Experimental Results and Discussion.................................... 109
   4.1.7.2 R-curve Prediction.................................................................. 112
4.1.8 Fatigue Crack Growth ...................................................................... 113
   4.1.8.1 Monolithic MoSi₂................................................................. 113
   4.1.8.2 Fiber-Reinforced MoSi₂ Composite...................................... 115
   4.1.8.3 Laminate-Reinforced MoSi₂ Composite............................... 117
4.1.9 Effects of Annealing.......................................................................... 126
   4.1.9.1 Experimental Procedures..................................................... 126
## 4.1.9.2 Microstructure

4.1.9.3 Results and Discussion

### 4.2 Transformation Toughening

#### 4.2.1 Introduction

#### 4.2.2 Materials and Microstructure

#### 4.2.3 X-ray Diffraction Analysis

#### 4.2.4 Fracture

#### 4.2.5 Laser Raman Spectroscopy

#### 4.2.6 Analysis of Toughening

### 4.3 Synergistic Toughening

#### 4.3.1 Introduction

#### 4.3.2 Materials and Processing

#### 4.3.3 Fracture Toughness

#### 4.3.4 Resistance Curve Behavior

#### 4.3.5 Fatigue Crack Growth

### 5. FATIGUE AND FRACTURE OF NB-15Al-xTi

#### 5.1 Introduction

#### 5.2 Materials

#### 5.3 Fracture Toughness

##### 5.3.1 Cast Nb-15Al-xTi

##### 5.3.2 Forged Nb-15Al-xTi

#### 5.4 Fatigue Crack Growth

##### 5.4.1 Room Temperature Fatigue Crack Growth Behavior

##### 5.4.1.1 Cast Nb-15Al-xTi

##### 5.4.1.2 Forged Nb-15Al-xTi

##### 5.4.2 High Temperature Fatigue

#### 5.5. Effect of Reinforcement Thickness on the Fatigue and Fracture Behavior of MoSi2/Nb-15Al-40Ti Composites

##### 5.5.1 Introduction

##### 5.5.2 Materials

##### 5.5.3 Results and Discussion

#### 5.5.3.1 Tensile Properties of Nb-15Al-40Ti Foils

#### 5.5.3.2 Fracture Toughness

#### 5.5.3.3 Resistance Curve Behavior
## LIST OF TABLES

<table>
<thead>
<tr>
<th>Table</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1</td>
<td>Room-temperature compression deformation properties of Nb-15Al-xTi alloys</td>
<td>43</td>
</tr>
<tr>
<td>2.2</td>
<td>Slip systems observed in single crystal MoSi₂</td>
<td>53</td>
</tr>
<tr>
<td>2.3</td>
<td>Slip systems observed in polycrystalline crystal MoSi₂</td>
<td>54</td>
</tr>
<tr>
<td>4.1</td>
<td>Constituent properties data</td>
<td>93</td>
</tr>
<tr>
<td>4.2</td>
<td>Crack bridging in MoSi₂/Nb composites</td>
<td>95</td>
</tr>
<tr>
<td>4.3</td>
<td>Crack-tip blunting in MoSi₂/Nb composites</td>
<td>98</td>
</tr>
<tr>
<td>4.4</td>
<td>Overall toughening in MoSi₂/Nb composites</td>
<td>100</td>
</tr>
<tr>
<td>4.5</td>
<td>Modified crack bridging in MoSi₂/Nb composites</td>
<td>108</td>
</tr>
<tr>
<td>4.6</td>
<td>Modified overall toughening in MoSi₂/Nb composites</td>
<td>108</td>
</tr>
<tr>
<td>5.1</td>
<td>Compositions of alloys in atomic percent</td>
<td>169</td>
</tr>
<tr>
<td>5.2</td>
<td>Summary of forging steps for Nb-15Al-40Ti</td>
<td>173</td>
</tr>
<tr>
<td>5.3</td>
<td>Room-temperature tensile properties of forged Nb-15Al-xTi alloys</td>
<td>174</td>
</tr>
<tr>
<td>5.4</td>
<td>Summary of fracture toughness values obtained for cast Nb-15Al-xTi</td>
<td>177</td>
</tr>
<tr>
<td>5.5</td>
<td>Summary of fracture toughness values obtained for forged Nb-15Al-xTi</td>
<td>182</td>
</tr>
<tr>
<td>5.6</td>
<td>Summary of Paris's exponents, m, and constant, C, and fatigue threshold ΔKth for cast Nb-15Al-xTi</td>
<td>187</td>
</tr>
<tr>
<td>5.7</td>
<td>Summary of Paris's exponents, m, and constant, C, and fatigue threshold ΔKth for forged Nb-15Al-xTi</td>
<td>199</td>
</tr>
<tr>
<td>5.8</td>
<td>Summary of rolling steps</td>
<td>216</td>
</tr>
</tbody>
</table>
# LIST OF FIGURES

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.1</td>
<td>Temperature profile of x-33 NASP</td>
<td>3</td>
</tr>
<tr>
<td>2.1</td>
<td>Coordinate system and stresses in the near-tip region of a crack in a plate</td>
<td>9</td>
</tr>
<tr>
<td>2.2</td>
<td>The three basic modes of fracture. (a) Tensile opening (model I); (b) In-plane sliding (mode II); (c) Anti-plane shear (mode III)</td>
<td>11</td>
</tr>
<tr>
<td>2.3</td>
<td>Schematic illustration of the different regimes of stable fatigue crack propagation</td>
<td>14</td>
</tr>
<tr>
<td>2.4</td>
<td>An idealization of plastic blunting and re-sharpening with leads to stage II fatigue crack growth in fully-reversed fatigue. (a) Zero load, (b) small tensile load, (c) peak tensile load, (d) onset of load reversal, (e) peak compressive load, and (f) small tensile load in the subsequent tensile cycle.</td>
<td>15</td>
</tr>
<tr>
<td>2.5</td>
<td>Alternating slip model for stage II crack growth under fully reversed cyclic loads</td>
<td>16</td>
</tr>
<tr>
<td>2.6</td>
<td>Effects of environment on fatigue crack growth by alternating slip.</td>
<td>18</td>
</tr>
<tr>
<td>2.7</td>
<td>Schematic illustration of transformation toughening.</td>
<td>21</td>
</tr>
<tr>
<td>2.8</td>
<td>Schematic illustration of crack bridging.</td>
<td>24</td>
</tr>
<tr>
<td>2.9</td>
<td>Schematic illustration of crack-tip blunting (a) Crack-tip blunting by ductile second phase and change of crack tip stress fields (b) Crack-tip blunting by debonding along two phases boundary.</td>
<td>27</td>
</tr>
<tr>
<td>2.10</td>
<td>Schematic illustration of crack deflection.</td>
<td>30</td>
</tr>
<tr>
<td>2.11</td>
<td>Schematic illustration of synergistic toughening.</td>
<td>33</td>
</tr>
<tr>
<td>2.12</td>
<td>Modified Toughening Ratio for Various Values of Coupling Parameter $p$ (a) $\lambda_b=2$ and (b) $\lambda_b=4$.</td>
<td>35</td>
</tr>
</tbody>
</table>

xiv
2.13 (a) Effect of Temperature on Tensile Properties of Recrystallized Niobium
(b) Strain-rate sensitivity of Niobium .......................................................... 37

2.14 (a) Fatigue Limit of niobium as a function of temperature for various oxygen Contents. (b) Fatigue crack growth rate for different hydrogen concentrations in Nb-H alloys.................................................. 40

2.15 Compressive yield stresses in Nb-15Al-10Ti, Nb-15Al-25Ti and Nb-15Al-40Ti alloys ................................................................. 44

2.16 Three polymorphs of zirconia .................................................................... 46

2.17 Phase diagram of the ZrO₂·Y₂O₃ system near the ZrO₂ Rich end ............. 47

2.18 Phase diagram of Mo-Si system ............................................................. 51

2.19 Schematic of MoSi₂ unit cell..................................................................... 52

2.20 Effect of temperature and strain rate on the yields of MoSi₂ .................... 56

2.21 Elevated temperature fatigue crack growth rate (da/dN) in MoSi₂ and MoSi₂/SiC................................................................. 58

2.22 Summary of particulate reinforced MoSi₂ composites.............................. 62

2.23 Microstructures of particulate MoSi₂/Nb composites............................. 62

3.1 (a) Configuration used for three-point bending
(b) Configuration used for four-point bending.......................................... 65

3.2 Schematic Representation of R-Curve and Applied K Curves
Used to Predict The Conditions For Fracture Instability; (K_c, a_c)............ 66

3.3 Schematic of the DC Potential Drop System ......................................... 69

3.4 Typical Raman Spectra of the Tetragonal and
Monoclinic Phases of ZrO₂ ........................................................................ 72

4.1 Microstructures of MoSi₂ Showing 97% Dense Structure with
equiaxed grains (a) Low Magnification; and (b) High Magnification....... 76

4.2 Microstructures of Fiber-Reinforced MoSi₂/Nb Composites:
(a, b) 250 µm Diameter Fiber; and (c, d) 750 µm Diameter Fiber............. 77

4.3 Microstructures of Laminated MoSi₂/Nb Composites:
(a) Laminate Distribution; and (b) Laminate/Matrix Interface................. 78

4.4 (a) Schematic Diagram of the Axis-symmetric Cell Model
Used in The Analysis (b) Schematic Illustration of Stress
Distribution in the Fiber and Surrounding Matrix...................................... 81

xv
4.38 Volume percentage of monoclinic phase in a typical fatigue specimen of the MoSi₂/TZ-2Y/Nb composite........................................ 164

5.1 Typical Microstructures of Niobium Aluminide Alloys: (a) Nb-15Al-10Ti (As-Cast); (b) Nb-15Al-10Ti (1150°C/2hrs/FC); (c) Nb-15Al-25Ti (As-Cast); (d) Nb-15Al-25Ti (1150°C/2hrs/FC); (e) Nb-15Al-40Ti (As-Cast); (f) Nb-15Al-40Ti (1150°C/2hrs/FC)........................................... 170

5.2 Typical Microstructures of Niobium Aluminide Alloys: (a) Nb-15Al-10Ti (As-Forged); (b) Nb-15Al-25Ti (As-Forged); (c) Nb-15Al-40Ti (As-Forged+DA); (d) Nb-15Al-25Ti (As-Forged+DA); and (e) Nb-15Al-40Ti (S & A)........................................ 172

5.3 Typical tensile fracture modes in: brittle cleavage in (a) as-forged 10Ti; (b) as-forged 25Ti; ductile dimple fracture in (c) as-forged 40Ti and (d) DA treated 40Ti................................................... 175

5.4 Typical Fracture Modes in SEN Fracture Toughness Specimens: Brittle Fracture in 10 Ti (a) as-cast, (b) as-cast+750°C/25hrs, (c) 1150°C/2hrs and (d) 1150°C/50hrs; Brittle Fracture in 25Ti (e) as-cast, (f) as-cast+750°C/25hrs, (g) 1150°C/2hrs and (h) 1150°C/50hrs; and ductile fracture in 40Ti (I) as-cast, (J) as-cast+750°C/25hrs, (K) 1150°C/2hrs and (L) 1150°C/50hrs; ........................................ 178

5.5 Typical fracture modes in SEN fracture toughness specimens: cleavage in forged 10Ti (a) as-forged, (b) as-forged+750°C/25hrs; cleavage in forged 25Ti (c) as-forged; (d) as-forged+750°C/25hrs; (e) ductile dimple fracture in as-forged 40Ti; (f) ductile dimple fracture and secondary splitting along grain boundaries in as-forged+DA 40Ti; (g, h) intergranular fracture in as-forged+S&A 40Ti; (i) Evidence of plasticity and crack bridging in S & A treated 40Ti.................................................................. 183

5.6 Summary of fatigue crack growth rate data for (a) cast Nb-15Al-10Ti; (b) cast Nb-15Al-25Ti; (c) cast Nb-15Al-40Ti; (d) as-cast Nb-15Al-xTi; (e) as-cast+750°C/25hrs Nb-15Al-xTi; (f) as-cast+1150°C/2hrs Nb-15Al-xTi; (g) as-cast+1150°C/50hrs Nb-15Al-xTi......................................... 188

5.7 Typical fracture modes in fatigue crack growth specimens: transgranular fracture in cast 10Ti (a) as-cast; (b) as-cast+750°C/25hrs; (c) as-cast+1150°C/2hrs; (d) as-cast+1150°C/50hrs; transgranular fracture in cast 25Ti (e) as-cast; (f) as-cast+750°C/25hrs; (g) as-cast+1150°C/2hrs; (h) as-cast+1150°C/50hrs; fatigue striation in cast 40Ti: (i) as-cast; (j) as-cast+750°C/25hrs; (k) as-cast+1150°C/2hrs; (l) as-cast+1150°C/50hrs;......................................................... 195

5.8 Summary of fatigue crack growth rate data for (a) forged 10Ti and 25Ti alloys; (b) forged Nb-15Al-40Ti; (d) as-forged Nb-15Al-xTi alloys; (e) as-forged+750°C/25hrs Nb-15Al-xTi; ..................................................................................... 200
5.9 Typical fatigue fracture modes in as-forged (a) 10Ti; (b) 25Ti; as-forged+750°C/25hrs (c) 10Ti and (d) 25Ti; as-forged 40Ti (e) low & (f) high AK; (e) striation and secondary cracking in DA treated 40Ti and (f) transgranular fracture mode in S & A treated 40Ti ................................................................. 204

5.10 Crack/microstructure interaction in Nb-15Al-40Ti. (a) crack growth profile showing unzipping along slip bands and (b) SEM photomicrograph shows crack grow into slip bands ................................................................. 206

5.11 Fatigue growth rate at elevated temperature for as-forged+DA treated Nb-15Al-40Ti ......................................................................................................................................... 210

5.12 Fatigue crack in 40Ti alloy at 750°C. (a) oxidation debris and striation (b) crack-tip blunting and secondary crack growth along elongated grain boundary ........................................................................................................... 211

5.13 Schematic illustration of oxidation induced closure ................................................................................................................. 212

5.14 Photograph of Nb-15Al-40Ti sheet materials ......................................................................................................................................... 215

5.15 Microstructure of laminate Nb-15Al-40Ti reinforced MoSi_2 composites (a,b) 100 µm, (c) 500 µm and (d) 1000 µm Nb-15Al-40Ti layer ........................................................................................................... 217

5.16 Diffusion profile of MoSi_2/Nb-15Al-40Ti laminated composites. (a) Mo, (b) Si, (c) Nb, (d) Al and (e) Ti ......................................................................................................................................... 218

5.17 Strain vs. stress curves for Nb-15Al-40Ti foils ......................................................................................................................................... 222

5.18 Typical tensile fracture modes observed in Nb-15Al-40Ti foils (a) 100 µm, (b) 500 µm and (c) 1000 µm ......................................................................................................................................... 223

5.19 Summary of fracture toughness of Nb-15Al-40Ti laminate-reinforced MoSi_2 composites ......................................................................................................................................... 225

5.20 Typical fracture modes in Nb-15Al-40Ti laminate reinforced composite. (a) Intergranular fracture of MoSi_2 matrix; (b), (c) and (d) cleavage on the 100, 500 and 1000µm layers ......................................................................................................................................... 226

5.21 R-curve behavior of laminate MoSi_2/Nb-15Al-40Ti composites ......................................................................................................................................... 227

5.22 Fatigue growth rate of laminate MoSi_2/Nb-15Al-40Ti composites ......................................................................................................................................... 229

5.23 Typical fatigue fracture modes in laminate MoSi_2/Nb-15Al-40Ti composites ......................................................................................................................................... 230

xix
CHAPTER 1

INTRODUCTION

1.1 Background

The current interest in the development of transonic and hypersonic aerospace vehicles has stimulated the need for light weight high temperature materials with potential to exceed the capabilities of existing nickel base alloys [Gray and Ginty, 1991; Vasudevan and Petrovic, 1992]. For example, Figure 1.1 shows a temperature profile of a hypersonic vehicle such as the x-33 version on the National Aerospace Plane. The temperature of nose of the plane is as high as 1800°C. This exceeds the limits of currently available aerospace alloys which are generally unsuitable for use at temperatures greater than 1200°C. There is, therefore, a strong interest in the development of alternative materials for hypersonic vehicles. Such materials require a combination of high temperature strength retention, creep resistance, oxidation resistance, damage tolerance and moderate density.

Molybdenum silicide (MoSi$_2$) intermetallics is currently being considered as a high temperature material for structural applications in the next generation of propulsion
aerospace vehicles due to its attractive combinations of high temperature oxidation/corrosion resistance, high melting point (2030°C), good thermal conductivity and moderate density (6.24 g/cm³) [Vasudevan and Petrovic, 1992]. However, the potential use of MoSi₂ in structural applications is currently limited by a catastrophic oxidation (pest) problem at moderate temperatures (500-650°C) [Fitzer and Remmele, 1985; ], and its brittle behavior at room temperature [Meschter, 1992]. Several efforts have been made to improve the room-temperature fracture toughness of MoSi₂ [Carter et al., 1987, 1989; Petrovic et al., 1990].

The two approaches that have been used are generally referred to as intrinsic and extrinsic toughening [Ritchie and Cannon, 1985]. Intrinsic toughening is often accomplished by changing the internal structure of a system via alloying and heat treatment. Extrinsic toughening is generally achieved by introducing external reinforcements, i.e. composite approach. Limited improvements in the toughness of MoSi₂ have been achieved via solid solution alloying (intrinsic toughening) such as with WSi₂ [Vasudevan and Petrovic, 1992]. However, extrinsic toughening which uses ductile phase toughening with thermodynamically compatible (Nb, W or Mo) reinforcements [Deve and Maloney, 1991; Xiao and Abbaschian, 1992; Soboyejo, Rao, Sastry and Ritchie, 1992] and transformation toughening with CaO or Y₂O₃ stabilized ZrO₂ particles [Petrovic et al., 1990; Soboyejo et al., 1995] have been report to significantly improve the toughness and fatigue crack growth resistance of MoSi₂.
1.2 Objectives and Approach

The principal objective of this study was to: (i) Examine the effects of reinforcement morphology on the fatigue and fracture behavior of MoSi$_2$/Nb composites at room-temperature. (ii) Study transformation toughening in MoSi$_2$ reinforced with 2 mole% yttria-stabilized zirconia (TZ-2Y). (iii) Explore the possible levels of synergistic toughening in the MoSi$_2$/Nb composites reinforced with 2 mole% yttria-stabilized zirconia (TZ-2Y). (iv) Explore the potential use of more oxidation resistant ductile phase reinforcement that are based on a new class of Nb$_3$Al-xTi intermetallics.
Ductile phase reinforcement of brittle matrices has been shown to enhance fracture toughness by several mechanisms. These include: crack bridging [Budiansky et al., 1983], crack-tip blunting [Chan, 1992] and crack deflection [Faber and Evans, 1982]. The fatigue and fracture properties of ductile phase reinforced composites are dictated by the mechanical properties of the reinforcement phase, its morphology and volume fraction, and the interfacial properties between the matrix and the reinforcement phase.

In the current study, the effects of reinforcement morphology were studied in composites reinforced with 20 vol.% of Nb fibers and layers. Toughening mechanisms were elucidated in all of the composites. Toughening in the Nb particulate-reinforced composites was shown to occur largely via crack deflection by tilting and twisting [Soboyejo et al., 1993]. However, toughening in Nb fiber and layer-reinforced composites was shown to occur primarily by crack bridging and crack-tip blunting. The observed crack-tip shielding mechanisms were modeled using fracture mechanics models that are discussed in details in Chapter 2.

Following the initial study of the effects of reinforcement morphology, the possible design of synergy will be explored in MoSi2 composites reinforced with 2 mole % yttria-stabilized zirconia (TZ-2Y) and Nb layers. Synergy will be shown to result in toughening levels that are greater than the sum of the individual toughening components. Synergy will also be shown to occur primarily as a result of the additional transformation that are induced by interfacial tractions and interaction between different toughening mechanisms. Finally, the potential use of oxidation resistant Nb3Al-xTi intermetallics will be explored.
1.3 Materials Systems Studied

Materials systems studied includes: constituents and MoSi$_2$ composites. Constituents includes: (a) MoSi$_2$, (b) Nb, and (c) Nb-15Al-xTi. The composites systems studied are listed below along with their designations.

(i) Effects of Reinforcement morphology:
  (a) MoSi$_2$ + 20 vol.% Nb (44 $\mu$m particle)
  (b) MoSi$_2$ + 20 vol.% Nb (250 $\mu$m fiber)
  (c) MoSi$_2$ + 20 vol.% Nb (750 $\mu$m fiber)
  (d) MoSi$_2$ + 20 vol.% Nb (200 $\mu$m layer)

(ii) Transformation Toughening and Synergistic Toughening:
  (a) MoSi$_2$ + 20 vol.% TZ-2Y
  (b) MoSi$_2$ + 20 vol.% TZ-2Y+20 vol.% Nb (200 $\mu$m layer)

(iii) MoSi$_2$/Nb-15Al-40Ti Composites:
  (a) MoSi$_2$ + 20 vol.% Nb-15Al-40Ti (100 $\mu$m laminate)
  (b) MoSi$_2$ + 20 vol.% Nb-15Al-40Ti (200 $\mu$m laminate)
  (c) MoSi$_2$ + 20 vol.% Nb-15Al-40Ti (500 $\mu$m laminate)
1.4 Organization of the Thesis

The thesis is organized into 6 chapters. Chapter 1 presents the background to this investigation and outlines the objectives and the scope of the project. Chapter 2 reviews some basic fracture mechanic concepts, fundamental of fatigue, toughening mechanisms, and the fatigue and fracture behavior of the constituent materials. Experimental details are described in Chapter 3. The effects of reinforcement morphology are discussed in Chapter 4. Results obtained from detailed studies of transformation and synergistic toughening are also presented in Chapter 4. The fracture and fatigue behavior of ductile Nb-15Al-xTi intermetallics are discussed in Chapter 5 along with the results of a systematic study of the effects of layer thickness on the fatigue and fracture behavior of MoSi2/Nb-15Al-40Ti composites. Finally, some suggestions for possible future work are presented in Chapter 6.
2.1 Review of Fracture and Fatigue

2.1.1 Fundamentals of Fracture

2.1.1.1 The Griffith Concept

Fracture occurs by bond rupture. In order for fracture to occur, two conditions must be satisfied. One is the local stresses must exceed a critical value. The other is that fracture process must be thermodynamically favorable. Griffith [1921] considered an isolated crack in a solid subjected to an applied stress, and formulated a criterion for its extension in terms of the fundamental energy theorems of classical mechanics and thermodynamics. For a static crack system, the total energy, $U_T$, is given by:

$$U_T = (-W_L + U_E) + U_S \quad \ldots (2.1)$$

Where $W_L$ is the work done by the applied load distribution on the system, $U_E$ is the potential energy of loading system and $U_S$ is the free surface energy. Thermodynamic equilibrium can be obtained by balancing the mechanical and surface energy terms required for a virtual crack extension, $da$. Hence, crack growth should occur when $dU_T/da < 0$. At
the critical condition, $dU_T/da = 0$. This leads to the derivation of the Griffith fracture stress, $\sigma_c$, which is given by:

$$\sigma_c = \sqrt{\frac{2\gamma_s E}{\pi a}}$$

...(2.2)

where $\gamma_s$ is the surface energy, $a$ is the crack length, $E' = E$ for plane stress and $E' = E/(1-\nu^2)$ for plane strain, and $E$ is the Young's modulus.

Equation 2.2 was modified by Orowan [1952] to account for plastic work in materials that undergo plastic deformation prior to catastrophic failure. Orowan proposed the following expression for $\sigma_c$:

$$\sigma_c = \sqrt{\frac{2(\gamma_s + \gamma_p) E'}{\pi a}}$$

...(2.3)

where $\gamma_p$ is a plastic energy term that is generally difficult to measure in practice.

Another important parameter is the strain energy release rate, $G$, which was first proposed by Irwin [1964]. This is given by:

$$G = \frac{1}{t} \frac{d(U_L + U_E)}{da}$$

...(2.4)

where $U_L$ is the potential energy of the loading system, $U_E$ is the strain energy of the body and $t$ is the thickness of the body. Fracture would occur if $G$ reached a critical value, $G_c$.

Hence:

$$G_c = 2 (\gamma_s + \gamma_p)$$

...(2.5)
2.1.1.2 Linear Elastic Fracture Mechanics

Linear elastic fracture mechanics (LEFM) applied to the conditions where the size of the plastic zone is much smaller than the length of the crack as well as the dimensions of the component. In general, LEFM is valid when the crack size is at least fifty times greater than the plastic zone size. Furthermore, for a flat surface, elastic, isotropic medium, the stress fields near the crack tip can be described by Equation 2.6:

\[
\begin{bmatrix}
\sigma_{xx} \\
\sigma_{yy} \\
\sigma_{zz}
\end{bmatrix} = \frac{K_1}{\sqrt{2\pi r}} \begin{bmatrix}
\cos \frac{\theta}{2} \\
\sin \frac{\theta}{2} \\
\sin \frac{\theta}{2}
\end{bmatrix} \begin{bmatrix}
1 - \sin \frac{\theta}{2} \sin \frac{3\theta}{2} \\
\sin \frac{\theta}{2} \cos \frac{\theta}{2} \cos \frac{3\theta}{2} \\
\cos \frac{\theta}{2} \sin \frac{\theta}{2} \sin \frac{3\theta}{2}
\end{bmatrix} \begin{bmatrix}
\frac{\theta}{2} \\
\frac{\theta}{2} \\
\frac{\theta}{2}
\end{bmatrix}
\]

\ldots(2.6)
where $\sigma_{xx}$, $\sigma_{yy}$ and $\sigma_{zz}$ are the stress components shown in Figure 2.1, $r$ is the distance of the point $P$ from crack tip, $\theta$ is the angle between the crack plane and the line from the crack-tip to the point $P$, and $K_I$ is the applied stress-intensity factor for mode I (in this case). Except at the point very close to the crack-tip, the $\sigma \propto 1/\sqrt{r}$ stress singularity can be found to be true in many actual cases.

According to Equation 2.6, the stress field of all cracks are identical, except for the scaling factor $K$. Therefore, $K$ can be used to represent the amplitude of the crack-tip fields. More importantly, however, $K$ represents the driving force for crack growth under Linear Elastic Fracture Mechanics (LEFM) conditions. The stress intensity factor, $K$, is generally given by expressions of the form:

$$K = \sqrt{E \Gamma}$$  \hspace{1cm} (2.7a)

or

$$K = f(a/W)\sigma\sqrt{\pi a}$$  \hspace{1cm} (2.7b)

where $\sigma$ is the applied stress, $f(a/W)$ is a function of the crack length, $a$, and $W$ is the width of the specimen/component.

Fracture occurs if $K$ exceeds a critical value, $K_c$. The critical value of the stress intensity factor is referred to as the fracture toughness of the material. The fracture toughness will vary depending on how the specimen is loaded relative to the orientation of the crack. The three modes of crack loading are illustrated in Figure 2.2, where Mode I indicates crack opening, Mode II represents in plane crack sliding and Mode III represents
out-of-plane crack tearing. Each mode of loading has a corresponding fracture toughness value. These are generally referred to as: $K_{IC}$, $K_{IIc}$ and $K_{IIIc}$.

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

Figure 2.2. The three basic modes of fracture. (a) Tensile opening (mode I). (b) In-plane sliding (mode II). (c) Anti-plane shear (mode III).

2.1.2 Fundamentals of Fatigue (Primary reference is from Suresh [1991])

The word 'fatigue' originated from the Latin expression 'fatigare' which means 'to tire'. It was believed that a material 'tires' over time when subjected to repeated loading and finally fails. Fatigue occurs as a result of repeated stresses or strains which lead to crack initiation/propagation prior to catastrophic failure. In most cases, materials fail at stresses well below the static yield or fracture stress. It has been estimated that approximately 80 - 90% of all industrial failures can be attributed to some forms of fatigue, resulting in many cases in severe financial loss or even loss of human lives.

Studies on the fatigue started around 1829 by a German mining engineer, W.A.J. Albert, who performed the first real fatigue test when he studied the behavior of iron mine hoist chains during repeated load proof tests [Albert, 1829]. The first systematic study of
fatigue, however, was conducted by Wohler in 1860 [Wohler, 1860]. He conducted
tensile, bending and torsional loading experiments on railroad axles for the German
Railway Industry. His work led to the development of the famous stress amplitude-life
curve or S-N curves. These are still useful tools used for estimation of characterizing
fatigue life even to this day. Other researchers like Gerber [1874] and Goodman [1899]
also made important contributions to the development of methods for the assessment of
mean stress effects on fatigue life.

Further progress in the study of various stages of fatigue failure was made in the early
1900s. The old crystallization theory of fatigue was laid to rest by the pioneering work of
Ewing and Humfrey in 1903 [Ewing and Humfrey, 1903]. In their studies of crack
initiation and propagation in Swedish iron, they observed the formation of intrusions and
extrusions on the surface of the metal due to slip band formation. Ewing and Humfrey's
work therefore established the basis of our fundamental understanding of fatigue crack
initiation and propagation in metals. Further details on the micromechanisms of fatigue will
be presented later in Section 2.1.2.1 and 2.1.2.2.

Finally, it is important to note that fatigue can occur in many different forms. The first
and probably the most common is simple mechanical fatigue resulting from the application
of cyclic loads to a material. If the material is subjected to temperature fluctuations in
addition to an alternating mechanical loads, the combined effects of mechanical and thermal
fluctuations can give rise to so-called stress thermomechanical fatigue. Alternatively, if
cyclic loading occurs under isothermal conditions at elevated temperature, the material can
undergo a combination of creep and fatigue which is often described as creep-fatigue. The
fourth type of fatigue occurs when the component is exposed to a chemically aggressive
environment. In this case, corrosion-fatigue may be induced. The final type of fatigue is associated with a combination of cyclic fatigue and mechanical wear. This can lead to rolling contact fatigue or fretting fatigue.

2.1.2.1 Fatigue of Ductile Solids

2.1.2.1.1 Initiation of Cracks

The first stage of fatigue is the crack initiation phase. This involves the accumulation of microstructural damage usually in the form of persistent slip bands in regions of the specimen with extremely high dislocation densities. The plastic flow of material in these slip bands can lead to formation of the intrusions and extrusions on the specimen surface. This occurs largely as result of the irreversibility of dislocation movement and chemisorption processes. Studies by Cheng and Laird [1981] have revealed that crack nucleation occurs preferentially at the PSBs with the highest slip offsets and the largest strain localization. The interface between the PSB and matrix is a plane of discontinuity across which there are abrupt gradients in the density and distribution of dislocations and these interfaces serve as preferential sites for fatigue crack nucleation. Furthermore, environment has an important effect on crack initiation. This was demonstrated in early work by Gough and Sopwith [1932], and later work by Thompson, Wadsworth and Louat [1956] who showed that fatigue lives in vacuum and dry, oxygen-free media are much longer than those in moist laboratory air.

2.1.2.1.2 Fatigue crack growth

Fatigue crack growth in ductile solids can be categorized into the three regimes as shown in Figure 2.3. The first region occurs at low $\Delta K$ and is called the near-threshold
regime. This region corresponds to a cleavage-like growth mechanism where the crack follows preferred crystallographic directions. Below the fatigue threshold, \( \Delta K_{th} \), no crack propagation can be detected with existing instruments, and, in practice, the fatigue threshold is often defined as the \( \Delta K \) that corresponds to a crack growth rate of \( 10^{-8} \) mm/cycle (approx. 1 lattice spacing per cycle). The middle regime is a linear region of the plot which follows the Paris equation:

\[
\frac{da}{dN} = C(\Delta K)^m
\]  

...(2.8)

where \( da/dN \) is the fatigue crack growth rate, \( C \) is a unitless constant, \( \Delta K \) is the stress intensity factor range, and \( m \) is the Paris's exponent.

Figure 2.3 Schematic Illustration of The Different Regimes of Stable Fatigue Crack Propagation.
The middle regime is also called the Paris regime [Paris, 1960]. The slope of the line in this region is equal to the Paris exponent, $m$. Crack propagation usually proceeds by a mechanism of alternating slip and crack-tip blunting that results in striation formation in the Paris regime.

![Figure 2.4 An Idealization of Plastic Blunting and Re-Sharpening With Leads to Stage II Fatigue Crack Growth In Fully-Reversed Fatigue. (a) zero load, (b) small tensile load, (c) peak tensile load, (d) onset of load reversal, (e) peak compressive load, and (f) small tensile load in the subsequent tensile cycle. Arrows indicate slip direction. (After Laird, 1967)](image)

An idealization of plastic blunting model was proposed by Laird [1967] to explain the formation of striations and cycle-by-cycle crack growth mechanism for stage II fatigue. A crack tip amenable to duplex slip plastically blunts upon the application of a tensile stress is shown on Figure 2.4. The blunting process also effectively results in the extension of the crack by a distance of the order of the crack tip opening displacement. If the far-field stress is reversed into compression, the crack tip will re-sharpen only to be blunted again during
the next tension sequence. Since the closure of the crack during compression cannot fully negate the blunting and the attendant extension of the crack during the preceding tension load, net crack growth occurs during a fatigue cycle, leading to the formation of striations as depicted schematically in Figure 2.4. Laird's model applies to a wide variety of ductile materials, including polymers [Suresh, 1991], because of its general description of the plastic blunting process.

On the other hand, in ductile metals, where the duplex slip process can occur on, alternating shear on two intersecting slip planes ahead of the crack-tip. These are shown schematically in Figure 2.5 [Neumann, 1969].

Figure 2.5 Alternating slip model for stage II crack growth under fully reversed cyclic loads. The Figure on the top row show tensile loading stages, and those on the bottom pertain to unloading stages. (After Neumann, 1969)
The alternating slip model was first proposed by Neumann [1969]. Two slip planes are operated in this model. The work hardening of the primary slip plane (plane 1) leads to alternating shear on another slip plane (plane 2). Kinematic irreversibility of slip causes net crack growth in a planar fashion along the line of intersection of the two slip planes. This model has been verified experimentally in several face centered cubic (FCC) crystals [Neumann, 1969, 1974].

Environment has also been shown to have important effects on the fatigue crack growth and the formation of striations. It was first shown by Meyn [1968] that striation formation may be completely suppressed in vacuo in aluminum alloys which form well defined striations in moist air. Pelloux [1969] suggested that the alternating shear process is reversible unless an oxide film is formed on the slip steps created at the crack tip. This oxide layer impedes slip upon load reversal. A schematic illustration of the opening and closing of a crack during two fully reversed fatigue cycling in air and in vacuo is shown in Figure 2.6.

The third regime is called the high ΔK regime. An increase in crack growth rate is usually observed in this regime and the material is generally close to fracture in this regime. Accelerated crack growth occurs by a combination of fatigue and static fracture processes in this regime. Finally, fast fracture occurs when $K_{\text{max}}$ is approximately equal to the fracture toughness, $K_{\text{fc}}$, of the material.
2.1.2.2 Fatigue of Brittle Solids

2.1.2.2.1 Initiation of Cracks

For highly brittle solids with strong covalent or ionic bonding, and very little mobility of point defects and dislocations, defects such as pores, inclusions or gas bubble entrapments serve as potential sites for the nucleation of a dominant crack [Suresh, 1991]. In most brittle solids, residual stress generated at grain boundary facets and interfaces give rise to microcracking during cooling from the processing temperature. This occurs as result of thermal contraction mismatch between adjacent grains or phases. These microcracks may nucleate as major cracks under extreme conditions. However, in general a range of microcrack sizes will be nucleated, and the larger cracks will tend to dominate the behavior of the solid.
For semi-brittle solid like MgO [Majumdar et al, 1987], microcracks may also form as a result of dislocation/microstructure interactions. In such solids, slip may initiate when the resolved shear stress exceeds a certain critical value on favorably oriented low index planes. Dislocation sources (of the Frank-Read type) are activated, and subsequent the glide of the dislocation loops, moving outwardly from the sources, is impeded by obstacles such as grain boundaries and/or inclusions. This results ultimately in dislocation pile ups and subsequent microcrack nucleation when critical conditions are reached [Cottrell, 1958].

2.1.2.2 Fatigue Crack Growth

For most brittle solids, fatigue crack growth is very difficult to monitor, especially under tensile loading at room temperature. Paris’s exponent, m, for brittle materials are generally very high, i.e., approx. 20~200 [Dauskart et al, 1990]. However, stable crack growth, attributable solely to cyclic variations in applied loads, can occur at room temperature (even in the absence of an embrittling environment) in single phase ceramics, transformation-toughened ceramics, and ceramic composites. This was demonstrated for cyclic compression loading of notched plates by Ewart and Suresh [1987]. Unlike ductile solids, where, macroscopic fatigue can arise from cyclic slip, the driving forces for the crack growth at room temperature may involve microcracking, martensitic transformations, and interfacial sliding [Suresh, 1991]. However, at high temperature, some semi-brittle solids can exhibit characteristics of fatigue damage that are apparently similar to those found in ductile metals at elevated temperature [Argon and Godrich, 1969].
2.2 Review of Toughening Mechanisms

2.2.1 Transformation Toughening

Considerable effort has been expended in the development of a theoretical framework for the prediction of the toughening levels that can be achieved as a result of crack-tip stress-induced transformations [Evans et al., 1980, 1986; Marshall et al., 1983, 1990; Budiansky et al., 1983, 1993; Lange, 1982]. These transformations induce zone shielding effects that are associated with the volume increase (approx. 3-5% in many systems) that occurs due to stress-induced phase changes. For simplicity, most of the micromechanics analyses have assumed spherical transforming particle shapes, and critical transformation conditions that are controlled purely by mean stresses, i.e., they have generally neglected the effects of shear stresses that may be important, especially when the transformations involve deformation-induced twinning phenomena [Evans et al., 1986]. Nevertheless, the existing toughening models have been shown to provide reasonably good estimates of the level of transformation toughening, even when the stress-induced transformations are assumed to occur only as a result of mean stresses [Marshall et al., 1983]. Transformation toughening will, therefore, be assumed to be induced only by mean stresses in this study, although the possible effects of shear stresses are recognized [Evans et al., 1986; Claussen et al., 1982].

In general, the level of crack-tip shielding due to stress-induced transformations is related to the transformation zone size and the volume fraction of particles that transform in the regions of high stress triaxiality at the crack-tip. A transformation zone, akin to the plastic zone in ductile materials, is thus developed as a crack propagates through a composite reinforced with transforming particles. This is illustrated schematically in Figure 2.7.
The size of the transformation zone associated with a Mode I crack under small scale transformation condition has been studied [McMeeking et al., 1982]. Based on the assumption that the transformation occurs when the mean stress level at the crack tip exceeds a critical stress value \( \sigma_c^T \). McMeeking and Evans [1982] estimated the zone size for an idealized case in which all the particles within the transformation zone are transformed. Following a similar procedure, Budiansky et al. [1983] give the following equation for the estimation of the height of the transformation zone (Figure 2.7):

\[
21
\]
where $h$ is the half-height of the transformation wake (Figure 2.7), $K$ is the far field stress intensity factor and $\nu$ is the Poisson's ratio. The toughening due to the transformation can also be expressed as [Budiansky et al., 1983]:

$$\Delta K_t = \frac{0.22E_c f e_C^T \sqrt{h}}{1 - \nu} \quad \ldots (2.10)$$

where $E_c$ is the elastic modulus of the composite, $f$ is the volume fraction of transformed particles, $e_C^T$ is the transformation volume strain. The above model assumes that the volume fraction of the transformed material to be constant with increasing distance, $x$, from the crack face. However, in reality, the actual volume fraction of transformed phase varies with increasing distance from the crack face. Equation 2.10 must therefore be expressed in an integral form to account for the variation in the degree of transformation with increasing distance from the crack face. This yields the following expression for the toughening due to stress-induced transformations:

$$\Delta K_t = \frac{0.22E_c e_C^T}{1 - \nu} \int_0^h \frac{f(x)}{2\sqrt{x}} \, dx \quad \ldots (2.11)$$

where $f(x)$ is a mathematical function that represents the fraction of transformed zirconia as a function of distance, $x$, from the crack. The critical transformation stress necessary to
achieve the transformation can be expressed as a function of the total Gibb's free energy associated with the transformation from tetragonal-to-monoclinic phase. This may be estimated from [Becher, 1986]:

\[ \sigma_C^T = \frac{\Delta G}{\epsilon_C^T} \] ...(2.12)

where \( \sigma_C^T \) is the critical stress and \( \Delta G \) is the Gibb's free energy of the transformation.

The above expression does not account for the effect of the enthalpy terms in the equivalent Kirchoff circuits for the transformation. Also, the potential residual stresses induced as a result of the thermal expansion mismatch between MoSi\(_2\) and PSZ particles have not been considered in the above analyses. Depending on the thermal expansion coefficients, the zirconia particles may be subjected to either mean tension or compression. In general, however, if the mean stress is compressive, the far-field applied stress necessary for transformation will increase. On the contrary, the existence of tensile mean stress will trigger the transformation at a lower level of applied stress. As a result of this, the mean stress, \( \sigma_m \), that is needed to induce the transformation of ZrO\(_2\) particles is modified by the radial residual stress, \( \sigma_r \). The modified critical condition for transformation is thus given by [Becher, 1986]:

\[ \sigma_m = (\sigma_c - \sigma_0) \] ...(2.13)
2.2.2 Crack Bridging

Crack bridging is illustrated schematically in Figure 2.8. The bridging sphere restricts the opening of the crack, and thus promotes shielding of the crack-tip. The effective stress intensity factor at the crack-tip is therefore lower than the remote/applied stress intensity factor. Alternatively, an energy approach may be used to explain the toughening due to ductile phase reinforcement. Within this framework, ductile phase toughening by crack bridging may be attributed to the plastic work required for the plastic stretching of the constrained ductile spherical particles. The increase in strain energy, $\Delta G_{ss}$, due to the plastic work required for the stretching of the ductile phase is thus given by [Ashby et al., 1989]:

$$\Delta G_{ss} = V_f \sigma_y \xi$$  \hspace{1cm} \ldots(2.14)
where $V_f$ is the volume fraction of ductile phase that fails in a ductile manner (note that the actual reinforcement volume fraction is $f$), $C$ is a constraint parameter which is typically between 1 and 6, $\sigma_y$ is the uniaxial yield stress and $\zeta$ a plastic stretch parameter. The extent of ductile phase toughening may also be expressed in terms of the stress intensity factor. This gives the applied stress intensity factor in the composite, $K_c$, as the sum of the matrix stress intensity factor, $K_m$, and the toughening component due to crack bridging, $\Delta K_b$. The fracture toughness of the ductile-reinforced composites may thus be estimated from [Budiansky et al., 1988]:

$$K_c = K_m + \Delta K_b = K_m + \sqrt{\frac{2}{\pi}} L \alpha V_f \int_{0}^{\sqrt{x}} \frac{\sigma_y}{\sqrt{x}} dx$$

...(2.15)

where $K_m$ is the matrix fracture toughness, $x$ is the distance behind the crack-tip, and $L$ is the bridge length (Figure 2.8). The toughening ratio due to crack bridging under monotonic loading may thus be expressed as:

$$\lambda_b = \frac{K_c}{K_m} = 1 + \frac{1}{K_m} \sqrt{\frac{2}{\pi}} L \alpha V_f \int_{0}^{\sqrt{x}} \frac{\sigma_y}{\sqrt{x}} dx$$

...(2.16)

Equation 2.16 can be used for the estimation of the toughening due to bridging under monotonic loading conditions. However, a modification is needed to account for the effects of load reversal on the toughening due to crack bridging under cyclic loading conditions. The approach proposed by McMeeking and Evans [1990] was used in this study. This yields:
\[ \Delta K_{\text{tip}} = 2K_{\text{tip}}(\Delta \sigma/2) \]  \hspace{1cm} \text{...(2.17)}

where \( K_{\text{tip}}(\Delta \sigma/2) \) is the near-tip stress intensity factor at the cyclic mean stress, \( \Delta \sigma/2 \), for a bridged crack subjected to a maximum stress of \( \Delta \sigma \) at a stress ratio, \( R = K_{\text{min}}/K_{\text{max}} \), of zero.

### 2.2.3 Crack-tip Blunting

Crack-tip can be blunted when they move from a brittle phase into a ductile phase (Figure 2.9a). Crack-tip blunting may also occur by debonding along the interface of a composite (Figure 2.9b). Crack growth in ductile phase can be considered in terms of a critical strain criterion, which assumes that fracture occurs when the strain at a characteristic distance from the crack tip exceeds a critical value. When crack-tip is blunted by a ductile phase, the critical strain value is increased by the presence of a ductile phase (Figure 2.9a). Shielding due to crack-tip blunting effects can be estimated using a micromechanics model developed recently by Chan [1992]. In his model, he postulated that the near-tip effective strain distribution in the matrix/composite in a ductile phase reinforced brittle matrix composite could both be described by Hutchinson Rice-Rosengren (HRR) field expressions given below:

\[ \bar{e}_m = \alpha_m \varepsilon_m^y \left[ \frac{J_m}{\alpha_m \varepsilon_m^y \sigma_m I_{n_m}} \right] \frac{n_m/n_{m+1}}{\bar{e}(\theta, n_m)} \]  \hspace{1cm} \text{...(2.18)}
Figure 2.9 Schematic Illustration of Crack-tip Blunting
(a) Crack-tip blunting by ductile second phase and change of crack tip stress fields
(b) Crack-tip blunting by debonding along two phases boundary.
and

$$
\bar{\varepsilon}_c = \alpha_c \varepsilon^y_c \left[ \frac{J_c}{\alpha_c} \varepsilon^y_c \sigma_c \varepsilon^y_c I_{c}^{1/n_c} \right]^{n_c/n_c+1} \bar{\varepsilon}(\theta, n_c) \quad \ldots (2.19)
$$

where subscripts m and c represent matrix and composite respectively, superscript y represents yield stress, $J_m$ and $J_c$ are path independent parameters (J integrals) that vary with the applied load, crack length, and the geometry of the specimen, $I_{m}$ and $I_{c}$ are numerical constants the values of which depend on the stress relation of the material, $\bar{\varepsilon}(\theta, n_m)$ and $\bar{\varepsilon}(\theta, n_c)$ are also numerical constants related to the angle away from the crack plane at a particular n value, $\alpha_m$, $\alpha_c$, $n_m$ and $n_c$ are constants in the Ramberg-Osgood stress strain relation which is given by:

$$
\frac{\varepsilon}{\varepsilon_y} = \frac{\sigma}{\sigma_y} + \alpha \left[ \frac{\sigma}{\sigma_y} \right]^n \quad \ldots (2.20)
$$

where $\sigma_y$ and $\varepsilon_y$ are yield stress and strain respectively, $n$ is the strain hardening exponent, and $\alpha$ is a dimensionless material constant. The second term on the right side of Equation describes the plastic or nonlinear behavior. By assuming that stress strain behavior is the same in both the matrix and composite, i.e., $\alpha_m = \alpha_c = \alpha$ and $n_m = n_c = n$, the following expression is obtained by dividing Equation 2.20 by Equation 2.19:
\[
\frac{\varepsilon_c}{\varepsilon_m} = \frac{\varepsilon_c^y}{\varepsilon_m^y} \left[ \frac{J_c}{J_m} \right]^{\eta/n+1} \left[ \frac{\sigma_c^y}{\sigma_m^y} \right]^{\eta/n+1} ...
\] (2.21)

By invoking \( \varepsilon_c^y = \sigma_c^y / E_c \), \( \varepsilon_m^y = \sigma_m^y / E_m \), \( J_c = (1 - \nu_c^2)K_c^2 / E_c \), and

\[
J_m = (1 - \nu_m^2)K_m^2 / E_m \]

and rearranging both sides of the resulting equation, Equation 2.21 reduces to:

\[
\frac{K_c}{K_m} = \left[ \frac{\sigma_c^y}{\sigma_m^y} \right]^{n+1/2n} \left[ \frac{\varepsilon_c}{\varepsilon_m} \right]^{n+1/2n} \left[ \frac{E_c}{E_m} \right]^{n+1/2n} ...
\] (2.22)

The toughening ratio, which is defined as the ratio of the applied stress intensity factor to the stress intensity factor in the matrix, is thus given by:

\[
\lambda_{bl} = \frac{K_c}{K_m} = \left[ 1 + V_f(\Sigma - 1) \right]^{\eta+1}/2n \left[ 1 + V_f(\Gamma - 1) \right]^{\eta+1}/2n \left[ \frac{E_c}{E_m} \right]^{\eta+1}/2n ...
\] (2.23)

or

\[
\Delta K_{bl} = (\lambda_{bl} - 1)K_m ...
\] (2.24)

with

\[
\Sigma = \frac{\sigma_c^d}{\sigma_m^d} ...
\] (2.25)
and

\[ \Gamma = \frac{\varepsilon_f}{\varepsilon_y^n} \] \hspace{1cm} \text{(2.26)}

where \( K_\infty \) is the applied stress intensity factor, \( K_m \) is the matrix stress intensity factor, \( \sigma_y \) is the yield stress, \( \varepsilon_f \) is the fracture strain, \( n \) is the inverse of the strain hardening exponent, \( E_m \) is the matrix modulus, and subscripts \( m \) and \( d \) denote matrix and ductile phases, respectively.

2.2.4 Crack Deflection

Second phase particles located in the near-tip field of a propagating crack will perturb the crack path as shown on Figure 2.10, causing a reduction in the stress intensity. The degree of toughening the particulate reinforced composites can therefore be estimated from
the analysis by Faber and Evans [1982] in which the combined effects of deflection by tilting and twisting are considered. For all the possible combinations of tilt and twist angles, the critical strain energy density of the composite is given by:

\[ G_e = G_m(1 + 0.87V_t) \]  \hspace{1cm} \text{(2.27)}

Assuming linear elastic behavior of the composite. This yields:

\[ K_e = \sqrt{E_eG_e} \]  \hspace{1cm} \text{(2.28)}

where \( K_e \) is the fracture toughness of the composite and \( E_e \) is Young's modulus of the composite.

Crack-tip shielding due to deflection can be estimated from the mode I and mode II stress intensity factors, \( K_I \) and \( K_{II} \), induced at the crack tip as a result of crack deflection through an angle [Suresh, 1988, 1990]. For a crack with equal undeflected and deflected segments, this results in \( K_I \) and \( K_{II} \) values that are given by:

\[ K_I = \cos^2(\phi/2)K_\infty \]  \hspace{1cm} \text{(2.29)}

and

\[ K_{II} = \sin(\phi/2)\cos^2(\phi/2)K_\infty \]  \hspace{1cm} \text{(2.30)}
where $K_{\infty}$ is the applied stress intensity factor, $\phi$ is deflection angle.

Assuming that crack growth is driven purely by $K_I$, Equation 2.29 can be rearranged to obtain the following expression for $\lambda_d$, the toughening ratio due to crack deflection:

$$\lambda_d = \frac{K_{\infty}}{K_m} = \frac{1}{\cos^2(\phi/2)} \quad \text{...(2.31)}$$

2.2.5 Superposition Concept

In case where multiple toughening mechanisms operate, the total toughen ratio can be estimated using the linear superposition concept. This neglects possible interactions between the individual toughening mechanisms. Hence for toughening by transformation toughening, crack bridging, crack-tip blunting and crack deflection, the overall toughening is given by:

$$\lambda_{\text{total}} = \lambda_T + (\lambda_b-1) + (\lambda_{bl}-1) + (\lambda_{dl}-1) \quad \text{...(2.32)}$$

or $$\Delta K_{\text{tot}} = \Delta K_T + \Delta K_b + \Delta K_{bl} + \Delta K_{dl} \quad \text{...(2.33)}$$

2.2.6 Synergistic toughening concept

The synergistic toughening concept was first proposed by Amazigo and Budiansky [Amazigo et al., 1988]. In their original paper, they studied the combined toughening due to crack-bridging by ductile particles and transforming toughening by particles that undergo purely dilational stress-induced phase transformations in a brittle matrix. It is possible to induce more transformation by enhancing the interfacial stresses as shown schematically in Figure 2.11. In any case, the theoretical studies by Amazigo and Budiansky [1988]...
showed that the interactions between transformation toughening and crack bridging mechanisms may promote synergy in certain parametric ranges of constituents (Figure 2.12). Under such conditions, they predicted that the overall toughening is greater than the sum of the individual toughening components.

![Diagram of synergistic toughening](image)

- Prior Crack-Tip Stress-Induced Transformation
- Additional Transformation Induced by Bridging Trawctions

Figure 2.11 Schematic Illustration of Synergistic Toughening

The theoretical analysis of the interaction of bridging and transformation toughening was given in terms of $\lambda_b$ (toughening ratio due to bridging), $\lambda_T$ (toughening ratio due to transformation).
transformation) and a coupling parameter $\rho$ given by:

$$\rho = \frac{(1 + \nu)vS}{\sigma_m^c} \quad \ldots(2.34)$$

where $\nu$ is Poisson's ratio, $v$ is the volume fraction of ductile reinforce phase, $S$ is the strength of reinforcement and $\sigma_m^c$ is the mean stress in the transformation region. The equation governs the interaction between particulate and transformation toughening when they occur simultaneously during steady crack growth. Numerical results are shown in Figure 2.12 for $\lambda$ versus $\lambda_T$, for $\lambda_b = 2, 4$, respectively. The individual curves in each figure are selected values of the coupling parameter in the range of $[0, \infty]$. The limiting results for $r = \infty$, and 0 are of special interest. Their value are given by:

$$\lambda = \lambda_b \cdot \lambda_T \quad \text{for } \rho \to \infty$$

and

$$\lambda = (\lambda_b^2 + \lambda_T^2 - 1)^{1/2} \quad \text{for } \rho \to 0 \quad \ldots(2.35)$$

For sufficiently large values of $\rho$, transforming and bridging interact synergistically, producing a larger increase in toughness than the sum of the individual toughening contributions, $\lambda_T$ and $\lambda_b$. On the other hand, as $\rho$ approaches zero, the combined increase can be substantially less than the sum of $\lambda_T$ and $\lambda_b$. 

34
Figure 2.12 Modified Toughening Ratio for Various Values of Coupling Parameter $\rho$
(a) $\lambda_b=2$ and (b) $\lambda_b=4$
2.3. Review of Constituent Materials

2.3.1. Niobium

2.3.1.1 Introduction

Niobium (bcc, a=3.2941Å) is widely used as alloying element in nickel- and cobalt-base superalloys. Nb is also used as an alloying element in some grades of stainless and low-alloy steels. Niobium itself has excellent ductility and it can be cold worked over 90 percent before annealing become necessary. Niobium also has a high melting point of 2468°C, relatively high elevated-temperature strength and relatively low density 8.57gm/cc compared to other high temperature material like molybdenum (10.2gm/cc) and tantalum (16.6 gm/cc). Such attractive combinations of properties have led to a range of structural applications of Nb and its alloys over the past 30-35 years. Pure niobium is employed in a wide variety of end uses, such as beams and girders in buildings and offshore drilling towers, special industrial machinery, oil and gas pipelines. The niobium contained superalloys are used for jet and turbine engines and as a carbide in machining cutting tools [Technical Report, Teledyne Wah Chang Albany, 1996]. However, the range of applications has been restricted by the poor oxidation resistance of Nb and Nb alloys at elevated temperature [Austin et al., 1992].

2.3.1.2 Tensile Properties

The properties of electron-beam melted and arc-melted niobium are shown as a function of temperature in Figure 2.13 (a), which is taken from Mincher and Sheely [1961]. The maxima in strength at about 300°C for arc-melted material, and 500°C for the electron-beam melted material. The corresponding minima in ductility are indicative of dynamic strain...
Figure 2.13. (a) Effect of Temperature on Tensile Properties of Recrystallized Niobium (b) Strain-rate sensitivity of Niobium [Micher and Sheely, 1961].
aging. Hydrogen is responsible for strain aging at about 120-260°C; Oxygen is responsible at about 260-300°C; and nitrogen is responsible at about 400-600°C [Dyson et al., 1958; Mincher and Sheely, 1961]. Niobium is also found to be sensitive to the strain rate [Mincher and Sheely, 1961], and an increase in the proportional limit with increasing strain rate, as shown in Figure 2.13 (b).

2.3.1.3 Fatigue Behavior

The fatigue behavior of niobium was first studied by Enrietto, Sinclair and Wert [Enrietto et al., 1961]. Their results are shown in Figure 2.14 (a). Oxygen content was found to have an important effect on the fatigue properties. At temperatures below 500 °C, the fatigue limit increased with oxygen content. The peak at 400 °C was attributed to oxygen strain aging. In addition, hydrogen was found to have a strong effect on the fatigue crack growth threshold [Polvanich and Salama, 1987; Fariabi et al., 1983]. In general, the fatigue crack growth threshold decreases sharply with increasing hydrogen concentration, as shown in Figure 2.14 (b). The fatigue threshold also increases when hydrides are formed during exposure to hydrogen [Fariabi et al., 1983].

2.3.1.4 Oxidation Behavior

Niobium oxidizes rapidly at temperatures above 400°C. The principal reaction product is Nb₂O₅ at temperatures below 800°C. In most cases, β-Nb₂O₅ is normally detected below 800°C. However, above 800°C, the oxide scale consists primarily of α-Nb₂O₅ [Stringer, 1969]. At 400-500°C, oxidation produces irregular attack, with severe pitting and some root-like penetrations of pentoxide into the bulk of the metal. The penetration is
not apparently related to grain-boundaries or to specific crystallographic planes at this temperature. However, in the temperature range between 500-600°C, the penetration is generally associated with grain-boundaries or specific crystallographic planes [Kolski, 1962]. Below 600°C, rapid oxidation is observed on {100} planes and NbO₂ platelets are formed on {100} planes. This results in the pentoxide. These pores acts as potential sites for crack nucleation. However, between 600°C and 625°C, the NbO₂ platelets vanish, and the anisotropy in the oxidation phenomena also disappears [Stringer, 1969].

2.3.1.5. Hydrogen Embrittlement

Hydrogen embrittlement has been studied extensively in Nb in the 1970s. Two mechanisms have been considered to the basic causes of hydrogen embrittlement. The first mechanism, namely hydrogen decohesion, was first proposed by Troiano [Troiano, 1960] for the embrittlement of high-strength steels. The mechanisms deals with the presence of hydrogen as a point defect which has been shown to be favored by the application of macroscopic stress [Oriani and Josephic, 1972]. Hydrogen diffuses along a stress-induced activity gradient to regions of triaxial stress. This results ultimately in the loss of lattice cohesion. This loss of lattice cohesion facilitates crack nucleation and subsequent crack growth. The process continues until the crack growth is terminated due to the exhaustion of the hydrogen in the volume of material within possible diffusion distance from the crack-tip [Hardie and McIntyre, 1973]. The second mechanism deals with the other extreme, where a phase change occurs at the crack tip, i.e. a metal hydride is formed. Hydrides may also be stress-induced as observed by Grossbeck and his co-workers. Furthermore, hydrogen can migrate towards the crack tip under the influence of applied stress. Under
such conditions, a hydride may be formed at a temperature above the transition temperature
[Grossbeck and Birnbaum, 1977]. The hydrides are brittle, and they cleave to form
microcracks which coalesce to form larger cracks that can propagate readily when
remote loads are applied [Farahani et al., 1981].

Figure 2.14  (a) Fatigue Limit of Niobium as a Function of Temperature for Various
Oxygen Contents. (b) Fatigue Crack Growth Rate for Different Hydrogen
Concentrations in Nb-H Alloys
2.3.2. \textbf{Nb_3Al-xTi}

2.3.2.1 Introduction

Intermetallics are currently being considered as a candidate materials for high temperature applications due to their relatively low density, retention of high strength and oxidation resistance at elevated temperature. However, intermetallics are generally brittle at room temperature. Recent studies by Fraser and co-workers [Shyue, 1992, 1993] have shown that the addition of Ti can obtain stabilize the B2 phase and thus promote significant improvement in the ductility of Nb_3Al-xTi intermetallics [Menon et al., 1992]. Nb_3Al-xTi intermetallics may, therefore, be used as ductile phase reinforcements.

2.3.2.2 Microstructure and Deformation Mechanisms

Nb_3Al exhibits an A15 crystal structure at room temperature [Yasuda et al., 1991]. It is, therefore, very brittle at room temperature due to the limited number of slip systems that operate in this temperature regime. These have been identified to include dislocations of the <001>{210} type [Aindow et al., 1991]. Metastable B2 phases have been identified in rapidly solidified melt-spun ribbons, and the most recent work has demonstrated that the B2 phase can be stabilized under conventional casting conditions by the addition of titanium [Pan et al., 1975; Marieb et al., 1991]. Slip under compressive deformation has been reported to occur by the activation of <111> slip on \{101\}, \{112\}, and \{123\} slip planes [Shyue et al., 1993] in the 40Ti alloy(Nb-15Al-40Ti). Slip has also been observed to occur on \{101\} planes in Nb-15Al-10Ti and Nb-15Al-25Ti. Evidence of slip on \{112\} and \{123\} planes has also been found in some samples of the 10Ti alloy. However, \{101\} slip lane is the most common slip plane [Fraser, 1991].
The above slip systems provide the five independent deformation modes required for homogeneous plastic deformation. However, slip in the different Nb3Al-xTi alloys appears to be concentrated in the B2 phase. The contributions to slip from the other phases appear to be negligible even at higher temperatures. In fact, both the orthorhombic and A15 phases appear to impede slip, presumably as a result of their unfavorable crystal structures. It is also interesting to note that the <111> type dislocations in the B2 phases are actually present as dissociated superdislocations. The superpartials have a Burger's vector of 1/2<111>, and the APB energy appears to decrease with increasing Ti content.

Stress-induced martensite (pseudo-twins) was observed on Nb-15Al-10Ti and 25Ti alloys, but not 40Ti alloy. Pseudo-twin was found on {112} plane with Burger vector of 1/6<111> type. Orthorhombic phase was created by pseudo-twinning mechanisms in a B2 crystal. The occurrence of stress-induced martensite, or the intersection of two pseudo-twins, may produce crack nucleation sites. This can be used to explain the low ductilities exhibited by 10Ti and 25Ti alloys.

2.3.2.3 Mechanical Properties

Basic mechanical properties of niobium aluminide alloys are presented in Table 2.1. Compressive yield stresses have been obtained for the casted Nb3Al-10Ti, Nb3Al-25Ti Nb3Al-40Ti at temperatures up to 900°C [Shyue et al., 1993]. The compounds are remarkably strong in this temperature range, as shown in Figure 2.15. Nb-15Al-10Ti has greater absolute and specific strength than IN 718 at both room- and elevated-temperature. Nb3Al-10Ti also maintains a 150°C strength advantage over IN 718 which has approximately the same strength at a lower temperature of 750°C (Fig. 2.15a). The ductile
Nb₃Al-40Ti intermetallic has a lower strength than the brittle Nb₃Al-10Ti alloy (Fig. 2.15a and 2.15b). Also, both alloys have higher compressive strengths after heat treatment, as shown in Figure 2.15 in which the strengths of as-cast and cast + heat treated materials are compared.

<table>
<thead>
<tr>
<th></th>
<th>Nb-15Al-10Ti</th>
<th>Nb-15Al-25Ti</th>
<th>Nb-15Al-40Ti</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>As-Cast</td>
<td>Recrystallized</td>
<td>As-Cast</td>
</tr>
<tr>
<td>$\sigma_y$ (MPa)</td>
<td>730.9</td>
<td>767.4</td>
<td>710</td>
</tr>
<tr>
<td>$\varepsilon_{\text{Failure}}$ (%)</td>
<td>&gt;17.6</td>
<td>&gt;15.1</td>
<td>&gt;10</td>
</tr>
</tbody>
</table>

Table 2.1 RT Compression Deformation Properties of Alloys Studied

Tensile tests have been performed on the Nb-15Al-40Ti alloy to assess its room temperature ductility and strength. These have shown very favorable ductilities of about 20% after cold rolling to a reduction of 40% prior to annealing for 1 hour at 1100°C. The inherent ductility in this condition is associated with a ductile dimpled transgranular fracture mode in this alloy [Shyue et al., 1993]. However, a mixed intergranular + ductile dimpled fracture mode is observed in the Nb₃Al-10Ti intermetallic which fractured in a brittle manner before a tensile fracture test could be performed [Shyue, 1992]. This suggests that
the grain boundaries in this alloy may be embrittled since the five independent slip systems required for grain boundary compatibility have been observed in specimens deformed under compression [Shyue, 1992].

Figure 2.15  Compressive Yield Stresses in Nb-15Al-10Ti, Nb-15Al-25Ti and Nb-15Al-40Ti Alloys

2.3.2.4 Oxidation Behavior

Nb₃Al-xTi alloys have been shown to have better oxidation resistance than pure Nb at temperature regime 500-750°C, especially on those alloys with 5 atomic % Cr additions [Shyue, 1993]. Oxidation studies on Nb-15Al-40Ti at 1100°C by [Shyue, 1993] show that oxygen dissolution results in separation of initial B2 structure into α-Ti (Ti-15Nb-5Al) and A15 phases. Further oxygen penetration results in the internal oxidation of the A15 phase to form Al(Nb,Ti)O₄. The high temperature oxidation behavior of the Nb-15Al-40Ti
was also shown to be similar to that of pure titanium [Kofstad, 1988] because of the continuous nature of the Ti-containing phases within the oxide scale and underlying case layers.

2.3.3 Partially Stabilized Zirconia

2.3.3.1 Introduction

Pure ZrO₂ exists as a monoclinic phase at room-temperature. However, it transforms to a tetragonal phase at 1170°C, and a cubic phase (with the fluorite structure) at 2370°C. Unit cells of three polymorphs of ZrO₂ are shown in Figure 2.16. Metastable tetragonal phase or cubic phase can also be retained at room-temperature via addition of Y₂O₃, CeO₂, CaO and other stabilizers [Petrovic, 1990]. In any case, the metastable tetragonal phase of ZrO₂ can transform to a monoclinic phase upon the application stress. This transformation is associated with a 3-5% volume increase. This results in the application of compressive stress around the individual particles. Hence, as a crack propagates, a transformation zone is formed which is somewhat akin to a residual plastic wake. The closure tractions associated with the transformation zone are the primary causes of crack-tip shielding by transformation toughening.

2.3.3.2 Phase Transformation in Partially Stabilized ZrO₂

2.3.3.2.1 Phase Diagram

The equilibrium phase diagram for the ZrO₂-Y₂O₃ system is shown in Figure 2.17 [Ruh et al., 1984]. The tetragonal to monoclinic transformation temperature decreases as the yttria content is increased. The addition of yttria levels greater than ~7.8 mole% results
in the formation of the cubic phase at room-temperature. At temperature above 500°C, a two phase mixture of tetragonal solid solution+cubic solid solution exists in the composition range 1.5-7.5 mol % Y₂O₃. Under certain conditions, it is possible to retain a metastable microstructure consisting of tetragonal (t) precipitates within a cubic (c) matrix at room-temperature. This material frequently referred to as 'partially stabilized zirconia'.

Figure 2.16 Three Polymorphs of Zirconia

<table>
<thead>
<tr>
<th>Fm3m</th>
<th>P42/nmc</th>
<th>P21/c</th>
</tr>
</thead>
<tbody>
<tr>
<td>ac=5.124 Å</td>
<td>at=0.5094 Å</td>
<td>a=5.156 Å</td>
</tr>
<tr>
<td>ct=5.177 Å</td>
<td></td>
<td>b=5.191 Å</td>
</tr>
<tr>
<td></td>
<td></td>
<td>c=5.304 Å</td>
</tr>
<tr>
<td></td>
<td></td>
<td>b=98.9°</td>
</tr>
</tbody>
</table>

Figure 2.16 Three Polymorphs of Zirconia
Figure 2.17  Phase Diagram of the ZrO$_2$-Y$_2$O$_3$ System Near the ZrO$_2$ Rich End. [Ruh et al., 1984]
2.3.3.2.2 Metastability of t-ZrO_2

The addition of certain amounts of various divalent (e.g., Ca^{2+}, Mg^{2+}), trivalent (e.g., Y^{3+}, Sc^{3+}, Ln^{3+}) or tetravalent (e.g., Ce^{4+}) oxides of cubic symmetry allow the stabilization of t-ZrO_2 at low temperatures. The heterovalent cations replace a part of the Zr^{4+} ions and creates vacancies in the oxygen sublattice in order to maintain charge neutrality. The metastability of the high-temperature phases at low temperature was generally believed to be the result of a balance between chemical, strain, and interfacial energies \[ \text{Hannink et al., 1981} \].

Zirconia particle size was believed to have a considerable influence on the t→m transformation temperature \[ \text{Weber and Schwartz, 1957} \]. A concept of t-ZrO_2 metastability based upon surface free energy arguments was developed by Krauth and Meyer \[ \text{1965} \] and Garvie \[ \text{1965, 1970} \]. The free energy change in the t→m transformation can be described by \[ \text{Lange, 1982} \]:

\[
\Delta G_{t\rightarrow m} = \Delta G_c + \Delta G_{se} + \Delta G_s + \Delta G_m
\] ...(2.36)

where \( \Delta G_c \) is the chemical free-energy change associated with a change in structure from tetragonal to monoclinic phase, \( \Delta G_{se} \) the strain free-energy change and \( \Delta G_s \) the surface free-energy change (due to volume expansion and/or grain/twin boundary creation) for the phase transformation, and \( \Delta G_m \) is the change in surface energy associated with microcracking. \( \Delta G_c \) may be change by adding such stabilizers as CaO, MgO and Y_2O_3. At room temperature, \( \Delta G_c \) is always negative, but the magnitude \( |\Delta G^c| \) decreases with increasing Y_2O_3. \( \Delta G_{se} \) and \( \Delta G_s \) are functions of the elastic constants and the grain size of
zirconia, respectively. It was found that the critical grain size for the retention of the t-
phase increased from about 0.2 μm for ZrO₂ - 2 mol. % Y₂O₃ to about 1 μm for ZrO₂ - 3
mol. % Y₂O₃ at room temperature [Lange, 1982].

The residual state of stress acting on the particles. In the case of two phase systems,
the residual stress depends on the differential thermal expansion coefficients of the matrix
and inclusion. Since the t→m transformation results in a volume increase, a compressive
residual stress acting on the zirconia will favor the retention of the tetragonal phase. The
t→m transformation is also influenced by whether or not the constraints are relieved by
microcracking and/or twinning.

The difference in the free energies of the parent and product phases was calculated by
considering all the different components (chemical free energy difference, surface energy
contributions from internal surfaces like twins and microcracks and strain energy increases
due to matrix constraint). By setting the energy difference to zero, the critical grain size can
be given by the following expression [Lange, 1982]:

\[
\frac{1}{D_c} = \frac{1 + \left( \frac{\gamma_c g_c + \gamma_t g_T}{A_m \gamma_m - A_t \gamma_t} \right)}{1 - \left( \frac{\Delta U_{se} f c f_T}{\Delta G_c} \right)} \cdot \frac{6(A_m \gamma_m - A_t \gamma_t)}{\Delta G_c} \quad \text{...(2.37)}
\]

where \(\gamma_c\), \(\gamma_t\), and \(\gamma_m\) are the surface free energies of the crack, the tetragonal phase and the
monoclinic phase respectively, \(g_c\) and \(g_T\) are quantities that represent the areas of the crack
and twin boundaries normalized with respect to the surface area of the grains; \(A_m\) and \(A_c\) are
the surface areas of the product and parent phases; |ΔG_c| is the magnitude of the chemical
free energy of the transformation, $\Delta U_{se}$ is the increase in strain energy of the system per unit volume of the parent phase and $(1-f_c)$, $(1-f_t)$ are the fractions of the constraint that are relieved due to microcracking and twinning respectively.

Based on this expression, grain sizes less than $D_c$, the energy increases due to the creation of new surfaces and strain energy contributions prevented the transformation from occurring [Lange, 1982]. This analysis ignores nucleation-related kinetic barriers. It is also important to note that the analysis determines the condition where the t-ZrO$_2$ is energetically stable rather than being metastable with respect to the monoclinic phase.

2.3.4 MoSi$_2$

2.3.4.1 Introduction

Molybdenum disilicide (MoSi$_2$) has been used traditionally in heating elements due to its excellent oxidation resistance [Schlichting, 1978] and high temperature creep resistance [Sadananda et al., 1991]. However, the current interest in the development of transonic and hypersonic aerospace vehicles has stimulated considerable interest in the potential use of MoSi$_2$ as a structural high temperature material [Schlichting, 1978]. This interest has been due mainly to the attractive combinations of lower density (6.33 g/cc, 75% of that of conventional superalloys); excellent oxidation resistance due to the formation of a protective oxide film above 900°C [Meschter, 1992]; good elevated temperature strength retention at temperatures up to about 1200°C [Gac and Petrovic, 1985; Carter et al., 1989; Malloy et al., 1992]; high thermal conductivity [Petrovic and Honnell, 1990]; low coefficient of thermal expansion [Fitzer et al., 1973] and thermodynamic compatibility with most of the commonly used reinforcements such as SiC, Mo, W and Nb [Maloney and Hecht, 1992;
Deve and Maloney, 1991]. Unfortunately, however, the potential for near term structural applications of MoSi$_2$ is still limited by a severe pesting problem at intermediate temperatures (550-650°C) [Schlichting, 1978; Meschter, 1992] and its brittle characteristics at room temperature [Fitzer, 1973; Soboyejo, 1992, 1993]. There is, therefore, a need for the development of improved room temperature damage tolerance and intermediate temperature pest resistance in MoSi$_2$.

2.3.4.2. Microstructure and Slip Systems

MoSi$_2$ is nominally a line compound in the Mo-Si binary system with a small range of stoichiometry on the Mo-rich side, bordering the Mo$_5$Si$_3$-MoSi$_2$ phase field on the Mo-rich side and the MoSi$_2$-Si phase field on the Si side [Massalski, 1986]. The Mo-Si phase diagram is shown in the Figure 2.18.

![Figure 2.18 Phase Diagram of Mo-Si System [Massalski, 1986]](image-url)
The crystal structure of MoSi$_2$ is shown in Figure 2.19. It has a body centered tetragonal crystal structure, with space group I4/4mm and corresponding Strukturbericht notation of C11b. This is maintained up to the melting temperature of $\sim$ 2300 K [Vasudevan and Petrovic, 1992]. The primary slip system in MoSi$_2$ has been identified to be of the $<100>|011|$ type. The secondary slip system, $1/2<111> \{1\overline{1}0\}$, is active only above 600°C [Malloy et al., 1992]. Even when both the slip systems are operative, they account only four independent slip systems and cannot accommodate homogeneous plastic deformation [Von Mises, 1982]. At higher temperatures, several slip systems have been observed. It is interesting to note that climb of dislocations with $b=<100>$ and $b=<1/2<111>$ occurs in polycrystalline MoSi$_2$ at 1400°C [Ramamurthy et al., 1993]. This provides two additional slip systems for deformation above 1400°C. Slip systems in the single and polycrystalline MoSi$_2$ are summarized in Table 2.2 and Table 2.3.
Table 2.2. Slip Systems Observed in Single Crystal MoSi$_2$

<table>
<thead>
<tr>
<th>Slip Systems</th>
<th>Temperatures</th>
<th>Testing</th>
<th>Authors</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\frac{1}{2}&lt;331&gt;{110}$</td>
<td>900-1200°C</td>
<td>compression</td>
<td>Umakoshi et al. (1990)</td>
</tr>
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<td></td>
<td></td>
<td></td>
<td>Kimura et al. (1990)</td>
</tr>
<tr>
<td>$&lt;100&gt;, &lt;110&gt;$ on many planes</td>
<td>1300°C</td>
<td>compression</td>
<td>Umakoshi et al.</td>
</tr>
<tr>
<td>$1/4&lt;111&gt;$ connected by SISF on {110}</td>
<td></td>
<td></td>
<td>Kimura et al.</td>
</tr>
<tr>
<td>$&lt;100&gt;(011)$</td>
<td>room temp</td>
<td>indentation</td>
<td>Boldt et al. (1992)</td>
</tr>
<tr>
<td>$1/6&lt;331&gt;$, APBs</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$1/2&lt;331&gt;{013}$ decomposition and core spreading</td>
<td>1000°C</td>
<td>compression</td>
<td>Maloy et al. (1993)</td>
</tr>
<tr>
<td>$1/2&lt;111&gt;(011)$</td>
<td>1300-1600°C</td>
<td>compression</td>
<td>Maloy (1993)</td>
</tr>
<tr>
<td>$1/4&lt;111&gt;$ connected by SISF on {110}</td>
<td>1000-1200°C</td>
<td>compression</td>
<td>Maloy (1993)</td>
</tr>
<tr>
<td>$&lt;100&gt;$ on (013) and (011)</td>
<td>1200-1300°C</td>
<td>compression</td>
<td>Maloy (1993)</td>
</tr>
<tr>
<td>Slip Systems</td>
<td>Temperatures</td>
<td>Testing</td>
<td>Authors</td>
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<tr>
<td>$&lt;100&gt;,&lt;110&gt;,&lt;111&gt;$ on many planes</td>
<td>1200°C</td>
<td>4 point bend</td>
<td>Unal et al. (1990)</td>
</tr>
<tr>
<td>$&lt;100&gt;{011}$</td>
<td>room temp-1000°C</td>
<td>indentation</td>
<td>Maloy et al. (1992)</td>
</tr>
<tr>
<td>$1/2&lt;111&gt;{110}$</td>
<td>1300°C</td>
<td>compression</td>
<td>Kung et al. (1994)</td>
</tr>
<tr>
<td>$&lt;100&gt; {013}$, ${010}$, ${001}$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$1/2&lt;111&gt;{101}$</td>
<td>900°C</td>
<td>compression</td>
<td>Kung et al. (1994)</td>
</tr>
<tr>
<td>$1/2&lt;331&gt;{013}$</td>
<td></td>
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</table>

Table 2.3. Slip Systems Observed in Polycrystalline MoSi$_2$

2.3.4.3 Oxidation Resistance

MoSi$_2$ exhibits excellent oxidation resistance due to the formation of a protective silica film above 900°C [Meschter, 1992]. Unfortunately, however, the potential for near term structural applications of MoSi$_2$ is still limited by a severe pesting problem at intermediate temperatures (550-650°C) [Schlichting, 1978; Meschter, 1992]. The pest problem occurs largely as a result of slow SiO$_2$ formation kinetics in this regime. The pesting problem has been overcome to a large extent by the alloying of MoSi$_2$ with Ge and the use of halide...
crystals in coatings that are obtained via in-situ reactions in a pack cementation process [Cockeram et al., 1995, 1996]. The halide crystals appear to block the ingression oxygen into the bulk, thereby preventing the catastrophic oxidation reaction that leads to pesting by the reaction of Mo with O\textsubscript{2} gas to form MoO\textsubscript{3} [Cockeram et al., 1996]. The pest problem has also been overcome by the mixing in 30-50 vol.% of Si\textsubscript{3}N\textsubscript{4} with MoSi\textsubscript{2} to form Si\textsubscript{3}N\textsubscript{4}/MoSi\textsubscript{2} composites [Hebsur, 1995]. The MoSi\textsubscript{2}/Si\textsubscript{3}N\textsubscript{4} composites form protective silicon-oxynitride (Si-O\textsubscript{x}-N\textsubscript{y}) layers during thermal exposure in the pest temperature regime [Hebsur, 1995]. These layers prevent the ingression of oxygen into the bulk, and thus prevent the pesting problem discussed above.

2.3.4.4 Mechanical Properties

2.3.4.4.1 Strength

The fracture toughness of monolithic polycrystalline MoSi\textsubscript{2} is approximately 4MPa $\sqrt{m}$ at room temperature. At room temperature, MoSi\textsubscript{2} exhibits highly brittle behavior, and failure occurs typically by transgranular cleavage. However, at elevated-temperature (above DBTT of ~1000-1200°C), MoSi\textsubscript{2} deforms plastically [Ramamurthy et al., 1993; Evans, 1994], although fracture still occurs predominantly by intergranular fracture modes. The 0.2% yield strengths of MoSi\textsubscript{2} are shown in Figure 2.20 for temperatures between 1200 and 1600°C. It should be readily apparent from this figure that yield strength of MoSi\textsubscript{2} drops very quickly as temperature increases from 1200°C to 1600°C. MoSi\textsubscript{2} is also very sensitive to strain rate in this temperature regime [Evans, 1994].
2.3.4.4.2 Creep

The creep behavior in MoSi₂ has received some attentions in recent years [Sadananda et al., 1992, 1993; Wiederhorn, 1992; Bose, 1992]. Studies of creep deformation in monolithic MoSi₂ at temperatures between 1100°C and 1450°C suggest that the creep mechanism at lower temperatures involves Newtonian viscous flow processes/self diffusion, although dislocation climb appears to dominate at higher temperatures [Sadananda et al., 1992, 1993]. In general, however, the above creep mechanisms are typically associated with grain boundary sliding mechanisms due to the flow of the intergranular glass phase. The creep exponents and activation energies are therefore not
comparable to those due to diffusion- or dislocation-controlled creep [Sadananda et al., 1992, 1993]. Monolithic MoSi$_2$ exhibits a secondary creep stress exponent of $\sim 2$ and an activation energy of approx. 380 kJ/mol [Ramamurty, 1993]. This is comparable to the activation energy for the diffusion of Mo atoms in MoSi$_2$. The latter are typically between 380 and 450 kJ/mol.

2.3.4.4.3 Crack Growth

Stable crack has not been obtained in monolithic MoSi$_2$ at room-temperature under tensile loading conditions. However, stable crack growth has been reported for monolithic MoSi$_2$ at room-temperature under far field compression [Soboyejo, 1992 & 1993]. Also, at elevated-temperature, stable creep-fatigue crack growth has been reported by Ramamurty et al. [1993] who performed systematic studies of creep-fatigue crack growth in MoSi$_2$. Stable creep and creep-fatigue crack growth was observed at 1200°C in monolithic MoSi$_2$ and an MoSi$_2$/SiC$_w$ composite. The observed elevated-temperature crack growth mechanisms are similar to those in monolithic and reinforced ceramics where pre-existing or in-situ formed glass phases at elevated-temperature can promote cavitation along interfaces [Berkowitz-Mattuck and Dils, 1965]. Glass phases are formed due to the oxidation of MoSi$_2$ according the following reaction:

$$5\text{MoSi}_2 + 7\text{O}_2 \rightarrow \text{Mo}_5\text{Si}_3 + 7\text{SiO}_2$$
2.3.5. MoSi$_2$ Composites

The room-temperature damage tolerance of MoSi$_2$ may be improved by intrinsic or extrinsic modification. Intrinsic modification can be accomplished by alloying to change the internal structure of MoSi$_2$ to one that is more favorable for multiple slip. Unfortunately, however, alloying of MoSi$_2$ has not been shown to result in significant improvements in mechanical properties [Vasudevan and Petrovic, 1992]. On the contrary, extrinsic modification via ductile [Liu et al., 1991; Shaw and Abbaschian, 1994; L. Xiao and Abbaschian, 1992] or brittle [Soboyejo et al., 1996; Gac and Petrovic, 1985; Petrovic and Honnell, 1990; Ramamurthy et al., 1993] reinforcement has been used to promote
significant improvements in individual properties, although the required balance of mechanical properties has not been achieved.

2.3.5.1 Brittle Reinforcement

2.3.5.1.1 Reinforced with SiC

SiC is considered as a potential brittle reinforcement material due to its excellent oxidation resistance and good elevated-temperature strength. SiC is also thermodynamically compatible with MoSi$_2$ [Ramamurty et al., 1993]. Previous studies have shown that MoSi$_2$/SiC composites have improved fracture toughness at room temperature. Fracture toughness levels of 5.3 MPa$\sqrt{m}$ have been obtained for SiC particulate composites [Ramamurty et al., 1993], while toughness levels of 6.6 MPa$\sqrt{m}$ have been reported for SiC whisker-reinforced composites produced by vapor-solid reactions [Carter et al., 1985]. Even toughness levels of 8.2 MPa$\sqrt{m}$ have been reported for SiC whisker-reinforced composites produced by vapor-liquid-solid reactions [Carter et al., 1985]. The addition of SiC to MoSi$_2$ has also been shown to promote significant improvements in high-temperature crack growth resistance at 1200°C [Ramamurty et al., 1993] (Figure 2.21). The improvement in fatigue crack growth resistance at elevated-temperature can be attributed primarily to the viscous flow of grain boundary glass phases that are formed by the following reaction:

$$2\text{SiC} + 3\text{O}_2 \rightarrow 2\text{SiO}_2 + 2\text{CO}$$
Such grain boundary flow processes (which dissipate energy by the nucleation and stable growth of cavities), result in the formation of stable microcrack zones. Some evidence of enhanced dislocation activity has also been observed during crack growth at elevated-temperature [Ramamurty et al., 1993].

2.3.5.1.2 Reinforced with Partially Stabilized ZrO$_2$ Particle

Partially stabilized ZrO$_2$ (PSZ) particles are very attractive reinforcement species for MoSi$_2$ due to their potential for both low temperature transformation toughening (tetragonal-to-monoclinic transformation) and possible elevated-temperature dispersion strengthening. Furthermore, the thermal expansion coefficient of PSZ is close to that of MoSi$_2$ [Petrovic and Honnell, 1990]. Hence, thermally-induced strains and residual stress levels in PSZ-reinforced composites are relatively low. Prior studies by Petrovic et al. [1990] have also shown that the fracture toughness of MoSi$_2$ can be increased to $\sim 6.6$ MPa/$\sqrt{\text{m}}$ by reinforcing with 30 vol. % of PSZ particles.

2.3.5.2 Ductile Reinforcements

Nb, Mo and W are considered as potential ductile reinforcements for toughening MoSi$_2$ due to their high strengths at intermediate temperatures and their thermodynamic compatibility with MoSi$_2$. The fracture toughness values of MoSi$_2$ composites reinforced with these reinforcements are summarized in Figure 2.22 [Soboyejo and Sastry, 1993].

Niobium-reinforced MoSi$_2$ composite have been studied by Soboyejo et al. [1992, 1993]. At elevated temperatures, Nb reacts with MoSi$_2$, forming other brittle intermetallic such as Nb$_5$Si$_3$ and (Mo, Nb)$_5$Si$_3$ at the interface [74] as shown on Figure 2.23. The
formation of the interfacial compounds at the expense of the ductile reinforcement not only degrades the toughening effect of the ductile phase, but also causes a notch effect on the ductile phase [Xiao and Abbaschian, 1992]. Therefore, the use of an inert diffusion barrier coating on the reinforcement is essential to decrease the extent of possible interfacial interactions that can occur during processing, and also to maintain the integrity of the ductile phase during potential service at elevated-temperature. ZrO$_2$ and Al$_2$O$_3$ coatings have been studied by Xiao et al [1992]. The results show that, at same processing condition, the interaction layer can be reduced from 30 µm to 6 µm for ZrO$_2$-coated samples, and 4 µm for Al$_2$O$_3$ coated sample. In addition, the composition of the interphase formed was determined to be Nb$_5$Si$_3$, instead of the predominantly (Mo,Nb)$_5$Si$_3$ observed in the uncoated samples. Y$_2$O$_3$ coatings have been studied by Liu et al [1991]. Their results show that the dense PVD Y$_2$O$_3$ coating is a very good diffusion barrier, although beneficial effects of this barrier can be negated when the coating is cracked. Furthermore, porosity in the sol-gel Y$_2$O$_3$ coating permits interdiffusion to proceed.
Figure 2.22 Summary of Particulate Reinforced MoSi$_2$ Composites.

Figure 2.23 Microstructures of Particulate MoSi$_2$/Nb Composites.
CHAPTER 3

EXPERIMENTAL PROCEDURES

3.1 Fracture Toughness Test

Fracture toughness tests were performed on Single Edge Notched (SEN) bend test samples with relatively deep notches (notch-to-width ratios of 0.4), as shown in Figure 3.1(a). The SEN specimens were produced by electro-discharge machining (EDM) techniques. The specimen dimensions were selected to promote plane strain conditions in accordance with the ASTM E399 code [Annual Book of ASTM Standards, 1993], which required that:

\[ a > 2.5 \left( \frac{K_{IC}}{\sigma_{YS}} \right)^2 \]

\[ B > 2.5 \left( \frac{K_{IC}}{\sigma_{YS}} \right)^2 \]  \ ...(3.1)

where \( a \) is the crack length, \( B \) is the specimen thickness, \( K_{IC} \) is the fracture toughness value and \( \sigma_{YS} \) is the 0.2% offset yield strength of the material.
The fracture toughness tests were performed in accordance with the ASTM E399 code. The specimens were initially pre-cracked under far-field compression loading [Brockenbrough and Suresh, 1988]. Precracking use a stress ratio $K_{\text{min}}/K_{\text{max}}$ of 0.1, to produce an atomistically 'sharp' crack-tip. This is required to ensure that sufficiently high crack-tip triaxiality levels were maintained during the tests. Fracture toughness tests were then carried out under three-point loading at a loading rate corresponding to a stress intensity factor increase rate of 0.92 MPa $\sqrt{m}$ s$^{-1}$. The failure modes in the fractured specimens were then examined using scanning electron microscopy (SEM) techniques.

Similar fracture toughness tests were performed on the double edge notched (DEN) bend specimens with two nominally identical notches, as shown on Figure 3.1(b). The two notches were located (on the same side) between the two inner rollers within the four-point bend loading configuration that was used. The notches, therefore, experienced the same nominal stress intensity factors during monotonic loading. However, in most cases, small local differences between the notches, induced as a result of machining and local microstructural features, typically resulted in the onset of unstable crack growth/catastrophic failure from one of the two notches. Such failure normally occurred after an initial phase of almost identical stable crack growth from both notches. The remaining unfractured halves of the double notched bend specimens, therefore, retained useful information on the extent stable crack growth and crack bridging prior to the onset of catastrophic failure.
3.2 Resistance Curve Behavior (R-Curve)

An R-curve behavior is a continuous record of toughness development in terms of $K_f$ plotted against crack extension in the material as the crack is driven under a continuously increased stress intensity factor, $K$ [Annual Book of ASTM Standards, 1993]. A typical R-curve is shown on Figure 3.2. R-curves characterize the resistance to crack growth in materials subjected to monotonic loading. R-curve behavior is an indication of plastic work or energy dissipation due to crack-tip shielding processes.

R-curve may therefore result from crack bridging or/and blunting when a crack intercepts a second phase. The fracture toughness value is the value of $K_f$ at instability condition. This is determined from the tangency between the R-curve and the applied $K$ curve, as shown on Figure 3.2. In this study, R-curve tests were performed on Single Edge Notched (SEN) bend test samples. The specimens were initially pre-cracked under
far-field compression loading [Brockenbrough and Suresh, 1988] to produce a sharp pre-crack. A load corresponding to lower stress intensity factor (below the initiation toughness) was applied and quickly removed. The specimen was then examined under an optical microscope. The applied loads were increased in steps of 5% if no crack growth was detected.

Figure 3.2  Schematic Representation of R-Curve and Applied K Curves Used to Predict The Conditions For Fracture Instability; \( (K_c, a_c) \). (Taken From The Annual Book of ASTM Standards, 1993)
3.3 Fatigue crack growth

Fatigue crack growth studies were carried out on similar single edge notched (SEN) bend specimens that were similar to those used in the fracture toughness testing. However, the initial notch-to-width ratios were 0.25 instead of 0.4. The SEN specimens were produced by electro-discharge machining (EDM) techniques. Prior to pre-cracking under far field compression, the sides of the specimens were metallographically polished to a mirror surface finish to facilitate visual observation. All the fatigue crack growth tests were carried out in a closed loop servohydraulic testing machine.

Fatigue crack growth tests were initially conducted under manual control at a constant stress amplitude. A cyclic frequency of 10 Hz was used in the test and a stress ratio ($R = K_{\min}/K_{\max}$) of 0.1 was employed. Low stress ranges (below the fatigue threshold) were applied initially. The applied load ranges were increased by 5-10% if no crack growth was detected after ~ $10^6$ cycles. Constant load ranges were then maintained throughout the tests which were stopped in the Paris regime. Automated fatigue crack growth tests were conducted during the final stages of the program. Crack growth in these tests were monitored using potential drop techniques [Donald, 1990] under three-point bend loading. With this technique, crack length is determined from electric potential difference (EPD) measurements. These rely on the fact that the resistance of the specimen changes significantly as a result of crack growth, i.e., cracks act as insulators. Hence, electric field in a cracked sample, with a current flowing through it, is a function of the sample geometry and crack length. For constant current flow, the electric potential or voltage drop across the crack plane will increase with increasing crack length due to modification of the electric filed and associated perturbation of the current flow field.
The change in voltage can be related to crack length through analytical or experimental calibrations. A schematic of a typical DC potential drop system is shown in Figure 3.3.

Fatigue crack growth experiments were started at mid-stress intensity factor ranges, ΔK, 10-20 MPa√m, depending on the fracture toughness of the materials that were tested. A load-shedding rate, C, of -2 (1/inch), was also employed in the automated fatigue crack growth tests. The load shedding rate, C, is given by following equation:

\[ K_{\text{max}} = K_{\text{max}0} \exp(C(a-a_0)) \] (3.2)

where \( K_{\text{max}} \) is the current stress intensity, \( K_{\text{max}0} \) is the initial stress corresponding to \( a_0 \), C is a constant with dimensions of 1/length: (represents the load shedding/increasing rate); \( a \) is current crack length, and \( a_0 \) is the initial crack length.

Fatigue crack growth was also monitored using a high resolution (2.5 μm) telescope connected to a video monitoring unit. Fracture mechanisms in selected specimens were studied by scanning electron microscopy after loading the samples to failure under monotonic loading.

3.4 Tensile Test

Tensile tests were performed on smooth dog-bone shaped specimens. The tensile specimens had gage length of 25.4 mm (1 inch), thicknesses of ~ 3 mm (0.125 inch) and width of gage is 12.7 mm (0.5 inch). The tensile tests were performed in air at room-temperature. A strain rate of \( 5 \times 10^{-4} \) s\(^{-1} \) was used for all tests. The displacements along the gauge section were measured using a contact extensometer that was mounted on the specimen with rubber bands. The extensometer had a gage length of 1 inch and a range +/-5% strain.
3.5 Fractography

The fracture surfaces of the tested fracture toughness, fatigue and tensile specimens were examined using scanning electron microscopy (SEM) techniques. In case of the SEN specimens that were used in the fatigue crack growth test, the fracture surfaces were examined in the precrack, near-threshold, Paris and high $\Delta K$ regimes. Representative photo micrographs of the fracture modes were obtained at each position along the fracture surface. SEM was carried out predominantly under secondary electron (SE) imaging.
mode. However back scattered (BS) electron imaging was used to distinguish between different phases in selected specimens where Z-contract imaging was deemed useful.

3.6 Optical Interference Microscopy (OIM) Techniques

Optical Interference Microscopy (OIM) techniques can be used to measure the widths of plastic process zone and transformation process zones in this study [Clarke, 1982]. This technique involves the use of a monochromatic light source and a prism arrangement to produce a pattern of linear interference fringes on the surface of a flat, polished specimen. Any variation in the surface topography of the specimen such as variations induced as a result of mechanical damage will cause deviations in the fringe patterns from their initial configurations. The extent of the damage may therefore be estimated from the deviations in the fringes. In this work, the crack was imaged in an optical interference microscope so that the fringe patterns produced around the crack was also used to estimate the size of the transformation zone. In particular, the width of the zone was determined by measuring the distance from the crack face to points where the optical interference fringes deviate from linearity.

3.7 X-ray Diffraction

X-ray diffraction was performed on the as-received MoSi$_2$/TZ-2Y composites at room temperature to measure the percentage of zirconia phases present, after a careful calibration. Ni-filtered Cu K-α X-rays (λ=1.5406 Å) were used as the source in a Scintag PAD diffractometer. X-ray diffraction was also used to determine the phase formed during fatigue crack growth test at elevated-temperature for Nb-15Al-xTi alloys.
3.8 Laser Raman Spectroscopy (LRS) Techniques

Laser Raman Spectroscopy (LRS) techniques [Bever, 1986] can be used to obtain quantitative estimate of the degree of transformation [Clarke, 1982]. Raman spectroscopy studies were conducted on the sides of the as-processed and fractured specimens. Studies were carried out on a Spex 1403 Scanning Raman Spectrometer. An argon ion laser beam (λ = 514.5 nm) was used to excite the specimen. In particular, LRS techniques can be used to estimates the monoclinic phase content in the regions surrounding the crack [Kontoyannis, 1984]. Laser Raman spectroscopy techniques may thus be used to estimate the variation of monoclinic phase content with increasing distance from the crack-face. The estimates of phase volume fraction may also be obtained with a high degree of spatial resolution (~ 1 µm).

The principle behind the use of Raman spectroscopy (to characterize the structure of zirconia) is based on the so-called Raman effect. Incident electromagnetic radiation is inelastically scattered and the frequency shift between the incident and the scattered radiation is characteristic of the structure of the material [Bever, 1986]. The Raman shifts can thus be measured to provide structural information. The Raman spectra for the tetragonal and monoclinic polymorphs of zirconia have been obtained by previous workers [Clarke, 1982]. Typical Raman spectra of tetragonal and monoclinic phases of ZrO₂ was shown in Figure 3.4.
Figure 3.4 Typical Raman Spectra of the Tetragonal and Monoclinic Phases of ZrO$_2$.
[Clarke and Adar, 1982]
Clarke and Adar [1982] have utilized a calibration procedure based on X-ray diffraction intensity measurements to arrive at an expression for the concentration of the monoclinic phase based on the Raman monoclinic and tetragonal peak intensities. The monoclinic concentration, \( c_m \), is expressed as:

\[
c_m = \frac{I_{181}^{m} + I_{192}^{m}}{F(I_{148}^{t} + I_{164}^{t}) + I_{181}^{m} + I_{192}^{m}}
\]  

\( (3.3) \)

where \( I \) refers to the integrated intensities, the superscripts refer to the Raman shift of the peaks and the subscripts \( m \) and \( t \) refer to the monoclinic and tetragonal phases respectively. \( F \) is an empirically determined factor close to unity [Clarke, 1982].
CHAPTER 4

FATIGUE AND FRACTURE OF MoSi$_2$ COMPOSITES

4.1 Effects of Reinforcement Morphology on the Fatigue and Fracture Behavior

4.1.1 Introduction

The concept of ductile phase toughening of brittle materials is not new. It was proposed originally by Kristic [1980, 1981 and 1983] as a means of increasing the energy dissipation (by plastic stretching of ductile materials) in brittle materials. Since the original work by Kristic, there have been considerable efforts to improve the fracture toughness of brittle materials by the incorporation of ductile phases [Smith, 1989; Flinn, 1989; Deve, 1990 and 1991; Lu, 1991; Kajuch, 1992; Alman, 1992 and 1995; Xiao, 1992; Shaw, 1994]. Unfortunately, however, very few of these studies have considered the role of reinforcement morphology and cyclic loading on the damage tolerance of ductile phase toughened composites [Ritchie et al., 1997; Sobevejo et al., 1996]. Our current understanding of the effects of reinforcement geometry is therefore insufficient for the design of composites with the desired combinations of fracture toughness and fatigue resistance. The effects of fiber and laminate reinforcement geometries on the
fatigue crack growth and fracture behavior of model MoSi₂/Nb composites are discussed in this section.

4.1.2 Materials and Processing

The -325 mesh (approx. 44 μm average diameter) MoSi₂ powder employed in this study was purchased from Cerac, Milwaukee, WI. The Cerac powder was found to be molybdenum rich relative to stoichiometric MoSi₂ which contains 36.92 wt. % Si. The 250 μm and 750 μm Nb wires were procured from G & S Titanium, Wooster, OH. The 200 μm Nb layer were purchased from Nuclear Metals, Henderson, NV. The monolithic MoSi₂ and MoSi₂ composites were made in similar way. The fiber and laminate-reinforced composites were produced by manual lay-up of 250, 750 and 200 μm diameter fibers/laminates on a Nb wire frame, evacuated (10⁻⁴ Pa) and sealed by electron beam welding. The canned materials was then hot isostatic pressed (HIPing) under 207 MPa pressure, at 1400°C for 4 hours. The resulting compact was cooled slowly (over a period of 10 hours) to room temperature to minimize thermal gradients and cracking.

The resulting microstructures of monolithic MoSi₂ or MoSi₂ matrix are shown on Figure 4.1a-4.1b. The monolithic MoSi₂ or MoSi₂ matrix contained some silica particles (light regions in Figure 4.1b) and 1-2% porosity (dark regions in Figure 4.1b). The Nb fiber reinforced composites are presented in Figures 4.2a-4.2d, and Nb laminate-reinforce composites are presented in Figures 4.3a-4.3b. All the composites, were reinforced with 20 volume percent of Nb reinforcement. The composites were fabricated at McDonnell Douglas, St. Louis, MO. Layered interfacial regions were observed in the interfacial regime between the fiber- and laminate-reinforced MoSi₂ (Figure 4.2b, 4.2d and 4.3b).
Figure 4.1 Microstructures of MoSi$_2$ Showing 97% Dense Structure with Equiaxed Grains (a) Low Magnification; and (b) High Magnification.
Figure 4.2  Microstructures of Fiber-Reinforced MoSi₂/Nb Composites: (a, b) 250 μm Diameter Fiber; (c, d) 750 μm Diameter Fiber;

(to be continued)
Figure 4.2 (Continued)

(c) 200 µm

(d) 50 µm
Figure 4.3  Microstructures of Laminated MoSi$_2$/Nb Composites:
(a) Laminate Distribution; and (b) Laminate/Matrix Interface.
Interfacial phases of MoSi$_2$/Nb composites under similar processing condition have been
determined by Liu et al. [74] to be Mo$_5$Si$_3$ and (Mo, Nb)$_5$Si$_3$ using TEM technique.
Similar composition was observed using energy dispersive X-ray analysis in this study.

For comparison, some efforts were made to study the fatigue crack growth behavior
in pure Nb produced from powder that was also supplied by Nuclear Metals, Henderson,
NV. The powders were poured into Nb cans, and electron beam welded after evacuating
the cans. The cans were then HIPed under the same processing conditions that were used
for the processing of the fiber- and laminate-reinforced composites. The same processing
conditions were used for the fabrication of the composites and monolithic materials in an
attempt to ensure that the interstitial contents of the fiber/laminated MoSi$_2$/Nb
composites were similar to those in the monolithic Nb compacts.

4.1.3 Residual Stress Analysis

Since residual stress distributions may affect the fatigue and fracture behavior of the
composites, an attempt was made to quantify the residual stress levels in the composites.
It is also assume residual stresses in fiber- and laminate-reinforced composites occur
mainly as a result of the thermal expansion mismatch between the reinforcements and the
matrix materials. The residual stresses will be different for the fiber- and laminate-
reinforced composites due to differences in constraint levels.

In the case of the fiber-reinforced composites, the composites are initially stress free
at 1400°C. The matrix MoSi$_2$ has a higher thermal expansion coefficient than Nb fiber
[Metal Handbook, 1990]. Upon cooling, however, the matrix shrinks in all directions
relative to the fiber. As a result, the Nb fiber is subjected to residual compression, and
the MoSi$_2$ matrix is under tension. It is assumed that fibers are parallel, infinitely long
compared to the spacing, and perfectly bonded to the surrounding matrix. Furthermore,
the fibers are assumed to be periodically spaced, so that a representative "cell" containing
a single fiber may be used. The cell structure is shown in Figure 4.4(a).
The equilibrium equations and Hooke's law in the chosen axis-symmetric coordinate system are given by the following equations [Popov, 1990]:

\[
\frac{d\sigma_r}{dr} = \frac{1}{r}(\sigma_\theta - \sigma_r) \tag{4.1}
\]

\[
\varepsilon_\theta = \frac{u}{r} = \frac{1}{E_x} \left[(1 - \nu_x)(\sigma_\theta - \nu_x\sigma_r) + \alpha \Delta T \right] \tag{4.2}
\]
\[ \varepsilon_r^x = \frac{u}{r} = \frac{1}{E_x} \left[ (1 - \nu_x) \sigma_r^x - \nu_x \sigma_\theta \right] + \alpha \Delta T \] 

...(4.3)

where, \( x \) is replaced by \( f \) or \( m \) to denote either a fiber (\( f \)) or matrix (\( m \)), \( \sigma \) and \( \varepsilon \) respectively represent the stress and strain; subscripts \( r \) and \( \theta \) indicate the radial and tangential directions, respectively; \( u \) is the displacement in radial direction, \( E \) is the elastic modulus and \( v \) is the Possion's ratio. Stresses and displacement are given by [Povov, 1990]:

\[ \sigma_r = A + \frac{B}{r^2} \] 

...(4.4)

\[ \sigma_\theta = A - \frac{B}{r^2} \] 

...(4.5)

\[ u = \frac{1}{E} \left[ (1 - 2v) \cdot r \cdot A - \frac{1 + v}{2} \cdot \frac{B}{r} \right] + \alpha \cdot \Delta T \cdot r \] 

...(4.6)

where \( A \) and \( B \) are constants which will be determined later. Since the stresses cannot be infinite in Equations (4.4) and (4.5) when \( r = 0 \), it is clear that \( B \) must be equal to zero in Equations (4.4) - (4.6). Hence, we have

\[ \sigma_r = \sigma_\theta = \sigma_p = \sigma_0 \] 

...(4.7)

\[ u_p = \frac{1}{E_f} \left( 1 - 2\nu_f \right) \cdot r \cdot A_f + \alpha_f \cdot \Delta T \cdot r \] 

...(4.8)
where, $\sigma_0$ is the residual stress due to an individual fiber in the matrix, $E_f$ is the Young's modulus of the fiber and $\nu_f$ is the Possion's ratio of the fiber. In the matrix region, the stresses and displacements are given by:

$$\sigma_r = A_m - \frac{B_m}{r^2}$$  \hspace{1cm} (4.9) \\

$$\sigma_\theta = A_m - \frac{B_m}{r^2}$$  \hspace{1cm} (4.10) \\

$$u_m = \frac{1}{E_m} \left[ (1-2\nu_m) \cdot \frac{1}{r} \cdot A_m - \frac{1+\nu_m}{2} \cdot \frac{B_m}{r} \right] + \alpha_m \cdot \Delta T \cdot r$$  \hspace{1cm} (4.11) \\

where, $A_m$ and $B_m$ are constants to be determined, and $E_m$ and $\nu_m$ are the elastic modulus and Possion's ratio of the matrix, respectively. Boundary conditions take the form:

$$\sigma_r\big|_{r=a}^- = \sigma_r\big|_{r=a}^+ = (\sigma_0)_i$$  \hspace{1cm} (4.12) \\

$$u\big|_{r=a}^- = u\big|_{r=a}^+$$  \hspace{1cm} (4.13) \\

$$\sigma_r\big|_{r=R} = 0$$  \hspace{1cm} (4.14)
where $a$ is the radius of the fiber, $R$ is the radius of the matrix, $\alpha_f$ and $\alpha_m$ are the thermal expansion coefficients of the fiber and the matrix, respectively, $\Delta T = T_0 - T$, $T_0$ is the fabrication temperature, and $T$ is the temperature at which the stress is determined.

Combining equations (4.6) - (4.8) and (4.11) - (4.14), we have

$$\sigma_0 = \frac{E_m (\alpha_f - \alpha_m) \Delta T}{E_f (1 - 2v_f) + \frac{1}{1 - V_f} \left[ (1 - 2v_m) V_f + \frac{1}{2} (1 + v_m) \right]} \quad \text{(4.15)}$$

where, $V_f$ is the volume fraction of the fiber. When $V_f$ approaches zero, we have the solution for the special case of a single fiber in an infinite matrix. The residual hydrostatic stress is independent of coordinate system. Local variations in residual stress associated with the angular dependence of residual stress with $\theta$ and $\varphi$ away from the composite are neglected by such hydrostatic stresses. Nevertheless, the residual hydrostatic stresses will be used as average measures of residual stress in this study.

Using equation 4.15, the residual stress in Nb fiber-reinforced MoSi$_2$ composites was estimated to be about ~ 8 MPa, which is not very significant. A schematic illustration of residual stress distribution in and around a fiber is shown in Figure 4.4 (b).

Residual stress levels in the laminate-reinforced composites will be even less compare to fiber-reinforced composites, since residual stress in the direction perpendicular to the laminates can be released by contraction of entire specimen. However, the residual stress in the direction parallel to laminates can not be released. Assuming that no debonding occurs, for this Nb laminate-reinforced MoSi$_2$ composites (MoSi$_2$ has higher thermal...
expansion coefficient), the axial stresses in Nb layer will be compressive and have maximum magnitude at the interface.

4.1.4 Bend Strength

Duplicate four-point (pure) bend tests were carried out on 25.4 mm long composite bars with square cross sections (0.25 mm x 0.25 mm). The tests were conducted in vacuum (approx. 10^-6 Pa) due to the susceptibility of Nb reinforcements to interstitial pick-up and oxidation at elevated temperature. The bend tests were carried out at temperatures between 1000 and 1500°C. The specimens were soaked at temperature for 30 minutes prior to bend testing at a maximum flexural strain rate of approx. 5 x 10^-4 s^-1. The initial flexural loading axis was parallel to the fiber direction, and the specimens were mounted on SiC rollers. Ultimate tensile strengths were determined from the peak loads when the specimens did not exhibit any plastic strains prior to failure. However, 0.2% offset yield stresses were estimated for the specimens that exhibited at least 0.2% plastic strain prior to failure.

The bend strengths of the different composites are compared in Figure 4.5. The room-temperature strength of the Nb laminates was much higher than that of all the other systems. However, the Nb laminates had lower strengths than those of the other high-temperature materials at elevated temperature. The results presented in Figure 4.5 show that the strengths of the fiber-reinforced composites were generally lower than those of monolithic MoSi2 at elevated-temperature, presumably as a result of the lower strengths of the Nb reinforcements at elevated temperature. The larger diameter fiber-reinforced composite also had lower bend strengths than the small diameter fiber-reinforced
composite at temperatures below 1100°C, although it was stronger at higher temperatures. A significant rise in bend strength was typically observed in MoSi₂ and its composites with increasing temperature, and the strengths of all the composites decreased with increasing temperature, at temperatures above 1100°C.

Figure 4.5 Effects of Temperature on Bend Strength

86
Reasons for the trends in the bend strength data with increasing temperature are difficult to identify due to the extreme flaw sensitivity of the materials. Nevertheless, it is interesting to note that the bend strength data is generally not predicted by constant strain simple rule-of-mixtures. The significant deviation from simple rule-of-mixtures may be attributed partly to the high flaw sensitivity (low fracture toughness) and the presence of a relatively high density of flaws in the MoSi$_2$ matrix (Figures 4.1-4.3). Premature crack initiation may therefore occur before the true ultimate tensile stress is reached. Similarly, the microcracks or Kirkendall voids within the layered interfacial regions in the different composites may also promote premature crack initiation in the composites. Further work is clearly needed to improve our basic understanding of elevated-temperature strengthening mechanisms in Nb-reinforced MoSi$_2$.

4.1.5 Fracture Toughness

4.1.5.1 Monolithic MoSi$_2$

The average fracture toughness data obtained from the monolithic MoSi$_2$ are compared with those obtained from MoSi$_2$ composites in Figure 4.6. Also included in Figure 4.6, are data from previous studies on Nb, Mo and W particulate reinforced MoSi$_2$ composites [Soboyejo et al., 1993] and structural aluminum alloys which typically have anisotropic fracture toughness value between 15 and 25 MPa$\sqrt{m}$ [Metal handbook, 1990]. Monolithic MoSi$_2$ has a low fracture toughness of $\sim$3.6 MPa$\sqrt{m}$. The typical fracture mode observed in monolithic MoSi$_2$ at room-temperature is cleavage fracture, as shown on Figure 4.7.
4.1.5.2 Fiber-Reinforced Composites

The 250 and 750 μm diameter composites had fracture toughness values of 9.1 and 14.1 MPa√m, respectively. These were associated respectively with approx. 2.1 and 2.8 mm of stable crack growth in the 250 and 750 μm diameter composites. The fracture toughness of the fiber-reinforced composites can be rationalized by assessing the implications of the typical failure mechanisms shown in Figures 4.8a-4.8d for composites with fiber diameters of 250 μm and 750 μm. Failure in the Nb fibers in the composites reinforced with 250 μm diameter fibers occurred by a combination of cleavage and ductile dimpled transgranular fracture (Figures 4.8a and 4.8b). Some evidence of debonding was also observed (Figure 4.8b) at the fiber/matrix interface. This was typically associated with ductile dimpled fracture modes in the surrounding Nb fibers, presumably as a result of the relaxation of constraint that can occur in the fibers due to debonding [Ashby, 1989].

Figure 4.6 Comparisons of Fracture Toughness Data
Figure 4.7 Typical Fracture Modes in Particulate-Reinforced Composites Under Monotonic Loading (a,b) Mixed Cleavage+Intergranular Fracture in Matrix
Figure 4.8  Typical Fracture Modes in Fiber-Reinforced Composites Under Monotonic Loading (a, b) 250 μm Nb Fiber; (c, d) 750 μm Nb Fiber
Figure 4.8 (Continued)

(c)

(d)
Figure 4.9 Interactions of Cracks in Double Notched Specimen With the Underlying Microstructure: (a) 250 μm Nb Fiber; and (b) 750 μm Nb Fiber.
<table>
<thead>
<tr>
<th>Property</th>
<th>MoSi₂</th>
<th>Nb</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density (g/cm³)</td>
<td>5.60</td>
<td>8.57</td>
</tr>
<tr>
<td>Crystal Structure</td>
<td>bct (ordered C11b)</td>
<td>bcc</td>
</tr>
<tr>
<td>Melting point (°C)</td>
<td>2050</td>
<td>2468</td>
</tr>
<tr>
<td>Elastic modulus, E (GPa)</td>
<td>380</td>
<td>103</td>
</tr>
<tr>
<td>Poisson's ratio, ν</td>
<td>0.17</td>
<td>0.38</td>
</tr>
<tr>
<td>Ductile-to-brittle transition temperature (°C)</td>
<td>~925</td>
<td>~450</td>
</tr>
</tbody>
</table>

(a) Physical and Mechanical properties [Metal Handbook, 1990]:

<table>
<thead>
<tr>
<th>MoSi₂</th>
<th>(m/m·°C)·10⁻⁶</th>
<th>Nb</th>
<th>(m/m·°C)·10⁻⁶</th>
</tr>
</thead>
<tbody>
<tr>
<td>20°C</td>
<td>6.8</td>
<td>100°C</td>
<td>7.10</td>
</tr>
<tr>
<td>400°C</td>
<td>8.3</td>
<td>200°C</td>
<td>7.21</td>
</tr>
<tr>
<td>800°C</td>
<td>9.2</td>
<td>400°C</td>
<td>7.42</td>
</tr>
<tr>
<td>1000°C</td>
<td>9.5</td>
<td>800°C</td>
<td>7.85</td>
</tr>
<tr>
<td>1200°C</td>
<td>9.8</td>
<td>1000°C</td>
<td>8.06</td>
</tr>
<tr>
<td>1400°C</td>
<td>10.0</td>
<td>1200°C</td>
<td>8.27</td>
</tr>
</tbody>
</table>

(b) Thermal Expansion Coefficients [Metal Handbook, 1990]

Table 4.1 Contituent Property Data
The brittle cleavage fracture modes observed in the vicinity of regions without debonding in Figure 4.8b are attributed to the effects of the high stress triaxiality induced in these regions. It is important to note, however, that both the brittle and ductile fiber fracture modes were preceded by fiber yielding. In the case of the large diameter fiber composite, however, fiber fracture occurred predominantly by ductile dimpled transgranular failure (Figures 4.8c and 4.8d). There was also some evidence of debonding and crack-tip blunting at the fiber/matrix interfaces of the 250 and 750 μm diameter fibers.

The double notched specimens revealed that the fiber-reinforced composites were bridged (Figures 4.9a and 4.9b). The debonding at the fiber-matrix interfaces can also be considered as evidence of toughening by crack-tip blunting [Chan, 1992]. The toughening due to crack bridging may be expressed in terms of the stress intensity factor. The toughening ratio due to crack bridging under monotonic loading may thus be expressed as:

\[
\lambda_b = \frac{K}{K_m} = 1 + \frac{1}{K_m} \sqrt{\frac{\pi}{2}} \int_0^L \frac{\sigma_y}{\sqrt{x}} dx
\]

...(4.16)

where \(K_m\) is the matrix fracture toughness, \(x\) is the distance behind the crack-tip, \(L\) is the bridge length, which is equal to the distance between the crack-tip and the last unfractured row of fibers behind the crack-tip.
<table>
<thead>
<tr>
<th>Type of Reinforcement</th>
<th>$V_f$</th>
<th>$L$(mm)</th>
<th>$\lambda_b$</th>
<th>$\Delta K_b$ $(\text{MPa}\sqrt{\text{m}})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>250 µm Fiber</td>
<td>0.08</td>
<td>2.1</td>
<td>1.8</td>
<td>2.7</td>
</tr>
<tr>
<td>750 µm Fiber</td>
<td>0.12</td>
<td>2.8</td>
<td>2.4</td>
<td>4.6</td>
</tr>
<tr>
<td>200 µm Laminate</td>
<td>0.20</td>
<td>3.5</td>
<td>2.7</td>
<td>8.2</td>
</tr>
</tbody>
</table>

Table 4.2 Crack Bridging In MoSi$_2$/Nb Composites

The toughening due to crack bridging can be estimated from Equations 4.16 using the property data shown in Table 4.1. The resulting estimates (Table 4.2) generally indicate that bridging alone cannot account for the toughness levels in the fiber-reinforced composites. It is therefore important to analyze the shielding effects due to crack-tip blunting. To access the degree of toughening due to crack-tip blunting, Chan [1992] propose a model based on the assumption that the HRR field can be used to describe the near tip strain field both in the composite and the matrix. However, it may not be fully valid in MoSi$_2$/Nb composite case. In fact, due to the brittle nature of the matrix, an elastic crack-tip stress field is more likely to describe the stress distribution in the matrix [Soboyejo, Aswath and Xu, 1997]. In the plastic region, the strain field in the composite can be described by the HRR expression given by equation 4.17:
\[ \bar{\varepsilon}_c = \alpha_c e_c^y \left[ \frac{J_c}{\alpha c e_c^y \sigma_c^y I_{n_c} r} \right]^{n_c/n_c+1} \bar{\varepsilon}(\theta, n_c) \] ...(4.17)

In the elastic region, the strain in the composite is:

\[ \bar{\varepsilon}_c = \frac{K_c}{E_c} \frac{1}{(2\pi r)^{1/2}} \bar{\varepsilon}(\theta) \] ...(4.18)

where \( K_c \) and \( E_c \) are the stress intensity factor and Young's modulus of the composite, \( \bar{\varepsilon}(\theta) \) is a function of orientation, and \( r \) is the distance from the crack-tip. Equation 4.17 and 4.18 can be reformulated as:

\[ \left( \frac{\bar{\varepsilon}_c}{\alpha_c e_c^y} \right)^{(n+1)/n} = \frac{J_c}{\alpha c e_c^y \sigma_c^y I_{n_c} r} \left[ \bar{\varepsilon}(\theta, n_c) \right]^{(n+1)/n} \] ...(4.19)

and

\[ (\bar{\varepsilon}_c)^2 = \left( \frac{K_c}{E_c} \right)^2 \frac{1}{2\pi} [\bar{\varepsilon}_c(\theta)]^2 \] ...(4.20)

At the junction between the elastic and plastic regions, \( \bar{\varepsilon}_c = e_c^y \). Equation 4.19 and 4.20 can be combined with:
\[ J_c = \frac{(1 - \nu_c^2)K_c^2}{E_c} \] ... (4.21)

leading to:

\[ \frac{[\epsilon_c(\theta, n_c)]^{(n+1)/n}}{[\epsilon_c(\theta)]^2} \frac{1}{I_n \tau} \frac{(1 - \nu_c^2)}{\alpha_c(1/\alpha_c)^{(n+1)/n}} = \frac{1}{2\pi} \] ... (4.22)

For the matrix, the near-tip strain field can be express as:

\[ (\bar{\epsilon}_m)^2 = \left( \frac{K_m}{E_m} \right)^2 \frac{1}{2\pi} [\bar{\epsilon}_m(\theta)]^2 \] ... (4.23)

Since \( \bar{\epsilon}_m(\theta) = \bar{\epsilon}_c(\theta) \), combining Equations 4.19-4.23 gives:

\[ \frac{K_c}{K_m} = \frac{E_c}{E_m} \frac{(\bar{\epsilon}_c)^{(n+1)/2n}}{\bar{\epsilon}_m} \left( \frac{\epsilon^y}{\epsilon_c} \right)^{(n-1)/2n} \] ... (4.24)

Hence, the modified blunting toughening ratio is given by:

\[ \lambda_b = \frac{K_m}{K_m} = \frac{K_c}{K_m} = \frac{E_c}{E_m} \frac{(\bar{\epsilon}_c)^{(n+1)/2n}}{\bar{\epsilon}_m} \left( \frac{\epsilon^y}{\epsilon_c} \right)^{(n-1)/2n} \] ... (4.25)
Toughening ratio estimates obtained from the modified crack-tip blunting model are slightly higher than those predicted by the Chan's model. This result is intuitively obvious since the HRR field expressions may overestimate the crack-tip field in an elastic material. Conversely, the assumption of purely elastic behavior in the brittle matrix material is likely to underestimate the actual crack-tip fields in nearly elastic materials. The most representative toughening ratios are therefore likely to be in between those predicted by the Chan's model and the new model. Nevertheless, the new model will be used in subsequent discussion. Since it is likely to provide a better representation of the crack-tip stress field in the brittle matrix MoSi$_2$ than the Chan's model.

Using data summarized in Table 4.1, the toughening ratio due to crack-tip blunting can be obtained relatively easily. The predicted toughening levels are summarized in Table 4.2. These show that toughening due to blunting alone cannot account for the overall toughness of the composites.

<table>
<thead>
<tr>
<th>Type of Reinforcement</th>
<th>$\varepsilon_{yd} / \varepsilon_{ym}$</th>
<th>$\sigma_{yd} / \sigma_{ym}$</th>
<th>$\lambda_{bl}$</th>
<th>$\Delta K_{bl}$ (MPa\sqrt{m})</th>
</tr>
</thead>
<tbody>
<tr>
<td>250 $\mu$m Fiber</td>
<td>12</td>
<td>1.8</td>
<td>1.3</td>
<td>3.0</td>
</tr>
<tr>
<td>750 $\mu$m Fiber</td>
<td>15</td>
<td>1.8</td>
<td>1.5</td>
<td>3.6</td>
</tr>
<tr>
<td>200 $\mu$m Laminate</td>
<td>20</td>
<td>1.8</td>
<td>1.8</td>
<td>4.6</td>
</tr>
</tbody>
</table>

Table 4.3 Crack-Tip Blunting In MoSi$_2$/Nb Composites
The overall toughening increment, \( \Delta K_{\text{tot}} \), must therefore account for the combined effects of bridging and toughening. This may now be estimated if we neglect the potential interactions between crack-tip blunting and crack bridging mechanisms. The estimate of the overall toughening due to crack bridging and crack-tip blunting mechanisms is obtained simply by applying the principle of linear superposition. This yields:

\[
\Delta K_{\text{tot}} = \Delta K_{\text{b}} + \Delta K_{\text{bl}} \tag{4.26}
\]

The predicted overall fracture toughness is generally small than the measured toughness (Table 4.3). The discrepancy between the measured and predicted fracture toughness values is greater than the experimental error in the fracture toughness measurement, and it may be due to possible interactions between crack-tip blunting and bridging mechanisms and neglecting constraint effects. The constraint effects will be discussed later. The predictions also show that the higher fracture toughness values of the larger diameter fiber composites (Table 4.3). Table 4.3 also shows clearly that the toughening levels in the fiber-reinforced composites are much less than those in the laminated composites.
<table>
<thead>
<tr>
<th>Type of Reinforcement</th>
<th>Bridging $\Delta K_b$ (MPa$\sqrt{m}$)</th>
<th>Blunting $\Delta K_{bl}$ (MPa$\sqrt{m}$)</th>
<th>Total $K_{total}$ (MPa$\sqrt{m}$)</th>
<th>Measured $K_{exp}$ (MPa$\sqrt{m}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>250 $\mu$m Fiber</td>
<td>2.7</td>
<td>3.0</td>
<td>9.3</td>
<td>9.1</td>
</tr>
<tr>
<td>750 $\mu$m Fiber</td>
<td>4.6</td>
<td>3.6</td>
<td>11.8</td>
<td>14.1</td>
</tr>
<tr>
<td>200 $\mu$m Laminate</td>
<td>8.2</td>
<td>4.6</td>
<td>16.4</td>
<td>18.0</td>
</tr>
</tbody>
</table>

Note that matrix toughness = 3.6 MPa$\sqrt{m}$

Table 4.4 Overall Toughening In MoSi$_2$/Nb Composites
4.1.5.3 Laminated Composites

The measured fracture toughness values obtained from the laminated composites were between 16 and 20 MPa\(\sqrt{\text{m}}\). These were associated with approx. 3.0 mm of stable crack growth. The fracture toughness levels are clearly much higher than those of the particulate and fiber-reinforced composites (Figure 4.7 and 4.8). It is therefore important to try to understand why the laminated composites are so tough. As in the previous sections, the relatively high fracture toughness of the laminated MoSi$_2$/Nb composite can be understood in evaluating the contributions from crack-tip shielding after careful consideration of the relevant fracture/toughening mechanisms. Unlike the particulate (Figures 4.7) and fiber-reinforced (Figures 4.8) composites, fracture in the laminated composites occurred completely by plastic stretching and ductile dimpled failure of the Nb layers (Figures 4.10a and 4.10b). Extensive matrix cracking was also observed in the laminated composites (Figure 4.10c), along with evidence of crack bridging and crack-tip blunting (Figures 4.10d). The laminated composites therefore exhibited the clearest evidence of ductile fracture and ductile phase toughening (Figures 4.10a-4.10d).

Evidence of multiple matrix cracking on the sides the double edge notched specimens is presented in Figures 4.10c and 4.10d. The average saturation matrix crack spacing observed in the double notched specimens was ~ 1.3 mm after fracture of one of the notches. Bridge lengths were also estimated by careful examination of the sides of the double edge notched specimens. The average bridging length in the laminated composites was also determined to be ~ 2.9 mm. The toughening increments due to crack bridging and crack-tip blunting can therefore be calculated using equations presented earlier. The results are given in Tables 4.2 and Table 4.3 in which the predicted toughening levels are
Figure 4.10  Typical Deformation and Fracture Modes in Laminated Composites:
(a) Ductile Dimpled Fracture of Nb Layer; (b) Extensive Plastic Stretching of Nb Layers;
(c, d) Multiple Matrix Cracking, Crack Bridging and Crack-tip Blunting by Nb Layers.
Figure 4.10 (Continued)

(c) Notch

(d) Nb layer

103
compared with the measured values. The results show that neither crack bridging nor crack-tip blunting can account solely for the overall toughness of the composites.

The overall fracture toughness of the bridged laminated MoSi$_2$/Nb composites must therefore assess the contributions from crack bridging and crack-tip blunting. This can be achieved by applying the principle of linear superposition. The resulting predictions obtained from Equation 4.16 and 4.25 are summarized in Table 4.3. The overall laminated composite toughness is estimated to be approx. 16.4 MPa√m. This is lower than the measured toughness values of approx. 18 MPa√m that was obtained from the laminated composites (Table 4.3). The differences between the measured and predicted toughness levels in the laminated composites are greater than the experimental scatter in the measured fracture toughness data (Figure 4.6). This suggests that the overall toughening (Table 4.3) may be enhanced by interactions between crack bridging and blunting. However, such analysis is beyond the scope of the present study.

Finally in this section, it is important to discuss the implications of the current results for potential structural applications. Structural aluminum alloys have orientation dependent fracture toughness levels that are typically between 15 and 25 MPa√m. The lower fracture toughness levels are typically observed in the short transverse orientations, especially in forged and/or rolled products. The fracture toughness levels in the laminated MoSi$_2$/Nb composites are therefore close to those of structural aluminum alloys that are currently used in a wide range of structural applications. However, unlike structural aluminum alloys, the fracture toughness of the MoSi$_2$/Nb laminates do not appear to be very orientation dependent. Preliminary average fracture toughness values of approx. 16 MPa√m have been obtained from specimens with cracks parallel to the Nb layers. These are only 11% lower than the average fracture toughness obtained from
MoSi\(_2\)/Nb laminates with cracks perpendicular to the laminae. The MoSi\(_2\)/Nb laminates therefore appear to be tough when the cracks are parallel or perpendicular to the Nb layers. The constraint effects will be discussed next, to give better prediction.

4.1.6 Constraint Effects

The constrained stretching of Nb fiber and layers is discussed in this section. For simplicity, the behavior of rows of fibers or layers is idealized by the constrained behavior of a single layer or fiber with relative dimensions that are consistent with the reinforcement volume fraction. The constrained plastic deformation of the reinforcement may therefore be idealized by the tensile deformation of a single fiber or a single layer. The restraining stress at the interface are due to the effects of residual stresses induced as a result of the thermal expansion mismatch between Nb and MoSi\(_2\).

For simplicity, we will consider two types of deformation schemes: (i) elastic-perfectly plasticity and (ii) piece-wise linear elastic-plastic behavior. These are shown in Figure 4.11.

![Figure 4.11 Schematic Illustration of Strain-Stress Behavior of (a) elastic-perfectly plasticity, and (b) Elastic-ideally plastic.](image)
The elastic and plastic deformation of the ductile phase can be translated into the amount of work done in terms of toughness, which is associated with the integrated area of the strain vs. stress curve as shown in Figure 4.11. The amount of toughening can be assessed using the model developed by Budiansky et al. [1988] which gives:

$$\Delta K = 2 \sqrt{\frac{2}{\pi}} V_f \int_{0}^{L} \frac{\sigma_y}{\sqrt{x}} \, dx$$

...(4.27)

$$\sigma_y' = \alpha \cdot \sigma_y$$

...(4.28)

where $V_f$ is the volume fraction of ductile phase, $x$ is the distance behind the crack-tip, and $L$ is the bridge length, $\sigma_y$ is the yield strength of ductile phase and $\alpha$, a constant, depends on constraint, which is given by:

$$\alpha = \frac{H_{ud}}{H_d} = \frac{\sigma_{yd}}{\sigma_{yu}}$$

...(4.29)

where $H$ is the hardness, $\sigma_y$ is the yield stress, and subscripts $d$ and $u$ denote deformed and undeformed reinforcements, respectively. The degree of hardening due to the constrained yielding of the ductile phase reinforcements can be estimated by measuring the Vickers microhardness values at several points along fibers in undeformed specimens, and within the fibers/laminates in the unfractured halves of the double edge notched specimens that were examined after monotonic loading to failure. Average values of the
reinforcement microhardness were thus obtained from undeformed and deformed fibers/laminate using 20 measurements per fiber.

It has been shown by Ashby et al. [1989] that the force-displacement curve is strongly influenced by the constrain. A set of simple models have been proposed to give insight into the ways in which the shape of the force-displacement curve is influence by decohesinon, work hardening, wire dimension and so forth.

Typical values of a obtained for the fiber and layer geometry are summarized in Table 4.4. The average stress, $\sigma_y$, can be estimated from $\sigma_y = \alpha \sigma_y$. The estimated values are summarized in Table 4.5. Note that these will affect the predicted shielding levels due to bridging (Equation 4.16). The adjusted values of the associated toughening ratios are presented in Table 4.6. The predicted toughening levels are somewhat higher than those obtained from the analysis in which hardening and constraint effects were ignored (Table 4.3). By consider the constrain effect, we can predict the toughening level more accurately.
<table>
<thead>
<tr>
<th>Type of Reinforcement</th>
<th>$V_f$</th>
<th>$L$(mm)</th>
<th>$\alpha$</th>
<th>$\lambda_b$</th>
<th>$\Delta K_b$ (MPa $\sqrt{m}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>250 $\mu$m Fiber</td>
<td>0.08</td>
<td>2.1</td>
<td>1.3</td>
<td>1.8</td>
<td>3.5</td>
</tr>
<tr>
<td>750 $\mu$m Fiber</td>
<td>0.12</td>
<td>2.8</td>
<td>1.6</td>
<td>2.4</td>
<td>7.4</td>
</tr>
<tr>
<td>200 $\mu$m Laminate</td>
<td>0.20</td>
<td>3.5</td>
<td>1.4</td>
<td>2.7</td>
<td>11.5</td>
</tr>
</tbody>
</table>

Table 4.5 Modified Crack Bridging In MoSi$_2$/Nb Composites

<table>
<thead>
<tr>
<th>Type of Reinforcement</th>
<th>Bridging $\Delta K_b$</th>
<th>Blunting $\Delta K_{bl}$</th>
<th>Total $K_{total}$ (MPa $\sqrt{m}$)</th>
<th>Measured $K_{exp}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>250 $\mu$m Fiber</td>
<td>3.5</td>
<td>3.0</td>
<td>10.1</td>
<td>9.1</td>
</tr>
<tr>
<td>750 $\mu$m Fiber</td>
<td>7.4</td>
<td>3.6</td>
<td>14.6</td>
<td>14.1</td>
</tr>
<tr>
<td>200 $\mu$m Laminate</td>
<td>11.5</td>
<td>4.6</td>
<td>19.7</td>
<td>18.0</td>
</tr>
</tbody>
</table>

Note that matrix toughness $= 3.6$ MPa $\sqrt{m}$

Table 4.6 Modified Overall Toughening In MoSi$_2$/Nb Composites
4.1.7 Resistance Curve Behavior

4.1.7.1 Experimental Results and Discussion

Resistance curve (R-curve) behavior were also studied in MoSi$_2$ Composites. R-curve characterize the resistance to fracture of materials during incremental slow-stable crack extension. In ductile materials, R-curve behavior generally resulted from the growth of the plastic zone, as a crack extends from a sharp notch. In ductile phase reinforced composites, such as the MoSi$_2$/Nb composite, R-curve behavior results mainly from crack bridging or/and crack-tip blunting when a crack intercepts a second phase. Typical R-curves obtained from this study are presented in Figure 4.12. All of the composites exhibit an initiation toughness of $\sim$ 3.5 MPa$\sqrt{m}$. This is close to the fracture toughness of $\sim$ 3.6 MPa$\sqrt{m}$ obtained for the MoSi$_2$ matrix. The strongest R-curve behavior is observed in the layered MoSi$_2$/Nb composite. The fiber-reinforced composites also exhibit strong R-curve behavior. However, no effect of fiber diameter was observed in the resistance curve experiments, although the measured fracture toughness levels were different in these composites. The resistance curve behavior was due largely to the effects of ductile phase toughening by bridging and blunting mechanisms.
Figure 4.12 Effects of Reinforcement Morphology on The Resistance Curve Behavior of MoSi$_2$/Nb Composites (Experimental vs. Predicted)
Figure 4.13 Schematic Illustration of Crack/Microstructure Interaction in a 250 μm Nb Fiber-Reinforced MoSi$_2$ Composite.
4.1.7.2 R-curve Prediction

It is apparent from the experimental observations that the increase in crack growth resistance is due primarily to the effects of crack bridge and crack-tip blunting. Using the models described earlier, the R-curve can be predicted by estimating the shielding effects of crack bridging and crack-tip blunting. A schematic illustration of the observed crack/microstructure interactions are presented in Figures 4.13a-d. The initial pre-cracked composite sample is shown in Figure 4.13a. The initial cracks propagate rapidly through the MoSi$_2$ matrix until they intercept a ductile Nb reinforcement. Subsequent crack growth reinitiates in the matrix on the other side of the reinforcement. Since crack growth in the MoSi$_2$ matrix is very rapid, the propagating crack is essentially always bridged and blunted. The shielding due to crack-tip blunting was estimating using the modified blunting toughening model described earlier:

$$\lambda_b = \frac{K_\infty}{K_m} = \frac{K_c}{K_m} = \frac{E_c}{E_m} \left( \frac{\bar{\varepsilon}_c}{\bar{\varepsilon}_m} \right)^{(n+1)/2n} \left( \frac{\bar{\varepsilon}_c}{\bar{\varepsilon}_m} \right)^{(n-1)/2n}$$  \hspace{1cm} (4.25)

where $K_c$ and $K_m$ is the fracture toughness for composite and matrix, respectively; $E_c$ and $E_m$ is Young's modulus for composite and matrix, respectively; $\bar{\varepsilon}_c$ and $\bar{\varepsilon}_m$ is the near tip strain field for composite and matrix, respectively; and $\varepsilon_c^Y$ is yielded strain for composite.

The Shielding due to crack bridging was estimated using a model developed originally by Budiansky et al. [1983]. This gives:

$$\lambda_b = \frac{K_c}{K_\infty} = 1 + \frac{2}{K_m} \sqrt{\frac{2}{\pi}} \alpha V_i \int_0^b \frac{\sigma_i}{\sqrt{x}} dx$$  \hspace{1cm} (4.16)
where $K_C$ and $K_m$ is the matrix fracture toughness for composite and matrix, respectively; $x$ is the distance behind the crack-tip, $\alpha$ is the constrain parameter, $V_t$ is the volume fraction of ductile reinforcement phase, and $L$ is the bridging length.

The overall effects of bridging and blunting may thus be estimated by superposing the toughening increments due to both mechanisms. The predicted and measured $R$-curves are qualitatively similar.

4.1.8 Fatigue Crack Growth

4.1.8.1 Monolithic MoSi$_2$

Stable fatigue crack growth rate data was not obtained in the monolithic MoSi$_2$ that was tested under three-point bend loading after compression pre-cracking. However, room- and elevated-temperature monolithic MoSi$_2$ fatigue crack growth rate data, taken from Ramamurthy et al. [1993], is included in Figure 4.14 for comparison. The fatigue crack growth rates were very fast compared to those in monolithic materials. The Paris exponent was $-9.4$, compared to typical values between 2 and 4 in monolithic metals [Ritchie, 1979], and values between 15 and 50 in ceramics [Dauskardt, 1989, 1990]. Unlike monolithic MoSi$_2$, in which relatively straight crack paths were observed under compression fatigue loading (Figure 4.15a), Fatigue crack growth in the monolithic MoSi$_2$ matrix occurred mainly by a transgranular cleavage fracture mode that was very similar to the cleavage fracture mode observed under monotonic loading (Figure 4.7).
Figure 4.14 Summary of Fatigue Crack Growth Rate Data
4.1.8.2 Fiber-Reinforced Composites

The interaction of the fatigue cracks with the underlying microstructure of a typical fiber-reinforced composites is illustrated in Figure 4.15b. Fatigue damage initiated from the notch, and propagated into the first row of fibers, prior to some debonding at the first fiber/matrix interface. Subsequent crack extension then occurred from the other side of the fiber, thus resulting in the formation of a bridging zone in the regime between the crack-tip and the first row of Nb fibers ahead of the crack-tip. No evidence of fiber rupture was observed until very high ΔK levels were reached. This is in contrast with the high incidence of fiber rupture that was observed in the double-notched specimens which were deformed under monotonic loading. The lower levels of debonding and fiber fracture observed under cyclic loading are attributed to the lower crack opening displacements at relatively low ΔK levels under cyclic loading.

Fatigue fracture mechanisms in the fiber-reinforced composites (Figures 4.16a and 4.16b) were similar to those observed in the particulate-reinforced composites [Soboyejo et al., 1993]. The Nb fibers therefore failed by cleavage fracture mechanisms under cyclic loading. This is in contrast to the mostly ductile modes observed in the fiber-reinforced composites under monotonic loading (Figures 4.8a-4.8d). Reasons for the occurrence of cleavage fracture in the Nb reinforcements deformed under cyclic loading are unclear at present. However, it is possible to speculate that the brittle cleavage fracture modes are due to high strain rates associated fatigue loading.

Crack growth in the fiber-reinforced composites was intermittent in the fiber/matrix interface regime. Nevertheless, average fatigue crack growth rate data was obtained for comparison of fatigue crack growth resistance. Note that the data includes some
components of intermittent crack growth. Typical average fatigue crack growth rate data obtained for the fiber-reinforced composites are presented in Figure 4.14. The fiber-reinforced composites with the smaller diameter (250 μm) fibers are more resistant to fatigue crack growth than the fiber-reinforced composites with the larger diameter (750 μm) fibers. This is due largely to the smaller distances between the rows of fibers in the smaller diameter composite. The reduction in the average fatigue crack growth rates induced as a result of the greater number of crack-tip interactions in the composite reinforced with the smaller diameter fibers. This is in contrast with the behavior under monotonic loading (Figure 4.8a and 4.8b).

Finally in this section, it is important to note that crack bridging did not appear to have a significant effect on the fatigue crack growth rate data that was obtained from the fiber-reinforced composites. This was confirmed by assessing the role of crack bridging using the method proposed by McMeeking and Evans [1990]. This gives the following expression for the stress intensity factor at the crack-tip of a bridged crack subjected to cyclic loading:

\[ \Delta K_{\text{tip}} = 2K_{\text{tip}}(\Delta \sigma/2) \]  

...(4.30)

where \( K_{\text{tip}}(\Delta \sigma/2) \) is the near-tip stress intensity factor at the cyclic mean stress, \( \Delta \sigma/2 \), for a bridged crack subjected to a maximum stress of \( \Delta \sigma \) at a stress ratio, \( R = K_{\min}/K_{\max} \), of zero. The plots of fatigue crack growth rate versus the effective crack-tip stress intensity factor range are presented in Figure 4.14. These are very close to the plots of fatigue crack growth rate versus the applied stress intensity factor range, i.e., the effects of crack
bridging are relatively small under cyclic loading conditions. The Paris coefficients are also very similar for the fatigue crack growth rate data obtained from the applied and effective ΔK values.

4.1.8.3 Laminated Composites

The fatigue crack growth rate data for the laminated composites are presented in Figure 4.14. The laminates have much slower fatigue crack growth rates than the particulate- and fiber-reinforced composites. The laminate fatigue crack growth rates were also significantly greater than those in the pure Nb compacts, and crack growth in the laminated composites was intermittent. The intermittent nature of crack growth was due to the interactions of the cracks with the ductile Nb layers. The fatigue crack paths in the laminated composites (Figure 4.15c) were similar to those obtained under monotonic loading at lower stress intensity factor ranges (Figures 4.10a and 4.10b). Toughening in the laminated composites therefore occurred by a combination of crack-tip blunting and crack bridging in the low/mid ΔK regime. However, crack bridging was not observed in the high ΔK regime because the cracks extended into the Nb reinforcements in this regime. Stable fatigue crack growth in the Nb laminae occurred by a combination of flat cleavage-like (Figure 4.17a-d) and shear modes (Figure 4.17a). The observed crack-tip shielding mechanisms (crack bridging and crack-tip blunting) in the different fatigue crack growth regimes are difficult to model due to complex load reversal effects that occur under cyclic loading. Also, the levels of crack-tip plasticity in the Nb layers are expected to be relatively small in the low-mid ΔK regime. The shielding effects due to crack-tip blunting should therefore be very small, except in the high ΔK regime where the
levels of crack-tip plasticity may be significant in the Nb layers. The shielding effects due to crack-tip blunting were therefore not modeled under cyclic loading. However, the shielding due to crack bridging was modeled using an approach proposed originally by McMeeking and Evans [1990]. The possible role of crack closure was ignored in this analysis. The effective stress intensity factor, $\Delta K_{eff}$, was thus equated to $\Delta K_{up}$, which is given by Equation 4.30. The resulting plots of fatigue crack growth rate versus effective stress intensity factor ranges are similar to the plots of fatigue crack growth rate versus applied stress intensity factor range (Figure 4.14), i.e., the shielding contributions from crack bridging are very limited under cyclic loading.

Finally, it is of interest to compare the fatigue crack growth rate data of the MoSi$_2$/Nb composites with those of alternative metallic and ceramic materials [Ramamurthy, 1993; Dauskardt, 1989, 1990]. Most metallic materials have much slower fatigue crack growth rates and Paris exponents (typically between 2 and 4 [Richie, 1989]) than the composites examined in this study. However, the Nb fiber-reinforced and laminated MoSi$_2$/Nb composites have Paris exponents close to 1, while the particulate-reinforced MoSi$_2$/Nb composites have Paris exponents close to 9. The fatigue crack growth rates in the MoSi$_2$/Nb composites are also slower than those in many of the alternative ceramic materials which tend to have Paris coefficients between 15 and 20. The fatigue crack growth resistance of the model Nb-reinforced composites examined in this study are therefore intermediate between those of alternative ceramic and metallic materials.
Figure 4.15 Interaction of Fatigue Cracks With Microstructure:
(a) Compression Precrack in Monolithic MoSi$_2$
(b) Bridging and Blunting in Fiber Composite.
(c) Multiple Cracks in Laminated Composite.
Direction of crack growth

200 μm

(b)
Figure 4.16 Typical Fatigue Fracture Modes Observed in Fiber-Reinforced Composite: (a, b) 250 μm Diameter Fiber
Figure 4.17 Typical Fatigue Fracture Modes Observed in Laminate-Reinforced Composite: (a) Typical Fracture Surface; (b) Two Different Failure Mode in Nb Layer; (c) Crack Growth From Matrix to Nb Layer; (d) Crack Growth From Nb Layer to Matrix; (e) Evidence of Striations in Nb Layers.
Figure 4.17 (Continued)

[Image of microscopic crack growth pattern]

direction of crack growth

(e)
4.1.9 Effects of Annealing

4.1.9.1 Experimental Procedures

Effects of annealing on the fracture behavior was studied on the MoSi$_2$ composite reinforced with 200 $\mu$m Nb layer. The layered MoSi$_2$/Nb composite was annealed in a vacuum furnace ($10^{-6}$ Pa) at 1400°C for 24 hours to coarsen the interface. Single-Edge-Notched (SEN) bend specimens of the layered MoSi$_2$/Nb composite were also annealed at 1400°C for 24 hours under the same conditions. The effects of interfacial coarsening on fracture was thus investigated by performing resistance curve experiments on the SEN specimens. Fracture toughness tests were also conducted on SEN specimens using similar conditions to those described earlier.

4.1.9.2 Microstructure

The effects of annealing on the microstructure of the layered MoSi$_2$/Nb composite are shown in Figure 4.18. Annealing at 1400°C for 24 hour was found to promote the coarsening of the layered interface. The thickness of interface was found to be $\sim$ 16 $\mu$m for the annealed MoSi$_2$/Nb composite compared to 10 $\mu$m for the as-received one. Composition profile obtained by EDX of as-received and annealed composite were shown in Figure 4.19. A single interfacial layer (Figure 4.18), consisting predominantly of Nb$_5$Si$_3$ was also observed after annealing at 1400°C. In contrast, a graded interfacial layer, consisting of at least two distinct layers, (Nb, Mo)$_5$Si$_3$ and Mo$_5$Si$_3$ [74] was observed before annealing at 1400°C (Figure 4.3b). Prolonged annealing at the processing temperature of 1400°C therefore results in the homogenization and coarsening of the interface. However, the microstructures of the MoSi$_2$ and Nb layers are not significantly affected by annealing.
Figure 4.18 Microstructure of Annealed MoSi$_2$/Nb Composite
Figure 4.19 Composition Profiles of MoSi$_2$/Nb Composites at Interface (a) As-received (b) Annealed
4.1.9.3 Results and Discussion

The resistance curve obtained for the annealed layered composites is compared with the resistance curve of the as-received one. The annealed layer composite also exhibits slightly lower initiation toughness and somewhat weaker R-curve (for $\Delta a$ levels < 1 mm) behavior than the as-received composite. However, the annealed composite also exhibits a slightly higher fracture toughness of $\sim 21 \text{ MPa m}$. The improved fracture toughness may be associated with lower interfacial strength after annealing. However, further work is required to verify this speculation.

In any case, it is of interest to try to predict the resistance curve behavior of the layered composite after annealing. As in the earlier analysis, toughening was due to bridging and blunting was analyzed using Equation 4.16 and 4.25, respectively. However, the layer volume fraction was adjusted to account for the increased thickness of the interface, i.e., the depletion of the Nb layer. The overall composite was thus given by superposition to be the sum of the matrix toughness, $K_m$, and the shielding contributions due to crack bridging, $\Delta K_b$, and crack-tip blunting, $\Delta K_{bl}$, for given $\Delta a$ levels on the R-curve. Because of the decrease in effective Nb layer thickness is small (about 5%), the predicted resistance curve will be very close to the prediction for the as-received one. Therefore, previous prediction on the as received composite can also be used as prediction for the annealed composite.

The predictions and the experimental results are compared in Figure 4.20. This shows that there is generally good agreement between the experimental and predicted R-curves. However, it is clear that further work is needed to fully assess the effects of interfacial thickness on fracture toughness. Finally, it is of interest to note that multiple
matrix cracks were observed in the MoSi$_2$ matrix in all of the R-curve specimens. Such multiple cracks may give rise to shielding/anti-shielding, depending on the spatial distributions and sizes of the cracks. However, the shielding/anti-shielding contributions are difficult to quantify due to the complex nature of the microcrack distribution (Figure 4.21).

![Figure 4.20 Effects of Annealing on the Resistance Curve behavior of MoSi$_2$/Nb Composites](image)

Figure 4.20 Effects of Annealing on the Resistance Curve behavior of MoSi$_2$/Nb Composites
Figure 4.21 Crack/Microstructure Interaction and Multiple Matrix Cracking in Annealed MoSi₂/Nb Composite
4.2 Transformation Toughening

4.2.1 Introduction

The room-temperature fracture toughness and stress-induced transformation behavior of MoSi$_2$ composites reinforced with yttria partially stabilized zirconia (Y-PSZ) polycrystals are described in this section. The phenomenon of transformation toughening in zirconia was reviewed in chapter 2. To summarize briefly, stress-induced martensitic transformation of zirconia occurs from the tetragonal phase to the monoclinic phase, in the region surrounding a growing crack [Evans and Cannon, 1986; Budiansky et al., 1983]. This transformation is associated with volume increase of $\sim 4\text{-}6\%$. This volume increase induces closure tractions (within a transformation zone) that lead to the reduction of the effective stress intensity factor at the crack-tip. The fracture toughness is thus enhanced as a result of crack-tip shielding.

The possibility of toughening MoSi$_2$ with partially stabilized zirconia has been previously studied by Soboyejo et al. [1995]. Transformation toughening was observed in MoSi$_2$ reinforced with 2 mole $\%$ Y$_2$O$_3$ stabilized ZrO$_2$. In the following sections, the results obtained from a detailed study of the MoSi$_2$/TZ-2Y composite will be presented. The bulk phase content will be determined by XRD and the transformation zone will be analyzed using a Raman spectroscopy methods and optical interference techniques.
4.2.2 Materials and Microstructures

The molybdenum disilicide that was used in this study was procured from Cerac, Milwaukee, WI, in the form of -325 mesh powder (44 μm average diameter). The MoSi₂ powder was 99.5 % pure. Zirconia powder with 2 mole % yttria stabilization was procured from Tosoh Corporation, Bound Brook, NY. The average particle size of the 99% pure yttria particles was 0.7 μm. Mixtures consisting of 80 vol. % MoSi₂ and 20 vol. % zirconia particles were dry phase blended by ball milling with zirconia media for 24 hours. The phase blended powders were then poured into Nb cans, vacuum sealed by electron beam welding and hot isostatically pressed (HIPed) at 1400°C under 207 MPa pressure for 4 hours.

Optical micrographs that show the microstructures of the resulting materials are presented in Figures 4.22(a) and 4.22(b). These show a relatively uniform distribution agglomerated TZ-2Y particles in a matrix of MoSi₂. The average grain size of the MoSi₂ grains was close to the average powder particle size of ~ 44 μm. However, size of the agglomerated TZ-2Y particles were typically between 10 and 20 μm.

4.2.3 X-ray Diffraction Analysis

Knowledge of the volume fractions of tetragonal and monoclinic phase in the different composites is required before an assessment of the shielding contributions from transformation toughening can be made. As in previous studies [Marshal et al. 1990], estimates of the bulk levels of monoclinic and tetragonal phase were obtained using X-ray diffraction techniques, which rely on a calibration curve that is obtained by plotting
the ratios of X-ray peaks in powder mixtures of known proportions of tetragonal and monoclinic phase against the known volume fractions of monoclinic or tetragonal phase. Since the TZ-0Y reinforcements are fully monoclinic and the TZ-6Y reinforcements are fully tetragonal [Soboyejo and Brooks, 1996], the phase contents in the powder calibration mixtures were varied by mixing various proportions of the TZ-0Y and TZ-6Y powders. The existence of the monoclinic phase is indicated by the strong doublet peaks for (111) at 2θ = 31.4° and (111) planes at 2θ = 28.2° (Figure 4.23a). The tetragonal phase has its strongest peak at 2θ = 30.5° which corresponds to (111) (Figure 4.23b). Such a clear-cut difference of monoclinic phase content made these two powders ideal materials to calibrate the relationship between the volume fraction of transformable zirconia in the composites and the X-ray diffraction intensity.

A sample diffraction pattern obtained from the MoSi_2/TZ-2Y powder mixture is compared with the diffraction patterns for the MoSi_2/TZ-0Y and MoSi_2/TZ-6Y in Figures 4.23(a)-4.23(c). The {111} diffraction peak of tetragonal ZrO_2 overlaps with the (101) peak of MoSi_2. Instead the (220) diffraction peak of tetragonal phase at 2θ = 50.4° and (111) peak for monoclinic ZrO_2 (111) was chosen for the calibration.

Differences between the bulk levels of monoclinic zirconia phase and the volume fractions of monoclinic zirconia phase with the transformation zones may also be used to infer the volume fractions of monoclinic phase produced as a result of stress-induced martensitic transformations.

The TZ-2Y composite was found to contain 7 vol. % monoclinic phase and 13% tetragonal phase. It was therefore apparent that only about 13 vol. % of the 20 vol. % of
TZ-2Y composite had the potential to undergo stress-induced phase transformations from the tetragonal to the monoclinic phase.

4.2.4 Fracture

Fracture toughness tests were also performed under three-point bend (with an inner span 12.7 mm) in air at room temperature using single edge notched (SEN) bend bars with square (6.35 mm x 6.35 mm) cross sections. Notches of 1.9 mm in depth were produced by electro-discharge machining (EDM).

A fracture toughness value of $\sim 5.0 \text{ MPa}\sqrt{\text{m}}$ was obtained for MoSi$_2$ reinforced with 20 vol. % TZ-2Y. Fracture occurred predominantly by cleavage of the MoSi$_2$ matrix and intergranular fracture of the zirconia particles, as shown in Figures 4.24.

4.2.5 Laser Raman Spectroscopy

After fracture testing, laser Raman spectroscopy analysis was performed on the sides of the fractured SEN specimens to determine the volume fractions of monoclinic/tetragonal phase as a function of distance from the crack faces (up to 500 µm). The Raman spectroscopy examination was performed by SPEX Industries, Inc., Edison, NJ, using a Raman 500 microprobe under the same conditions that were used to obtain the LRS calibrations. The volume fractions of monoclinic phase were estimated from a calibration that was obtained under the following conditions: 488 nm laser excitation, 100 mW of power at the laser head ($\sim 10$ mW at specimen), 80 X objective, monochromator entrance width of 100 µm, and a probe diameter of $\sim 1$ µm. The typical
time for spectra collection was approximately 4 minutes. Intensity ratios of the Raman shifts/peaks (181 and 192 cm\(^{-1}\) for the monoclinic phase; 148 and 264 cm\(^{-1}\) for the tetragonal phase) were used to estimate the volume fractions of monoclinic phase before and after fracture toughness testing. The size of the transformation zone was estimated to be equal to the distance from the crack face to the point where the volume fraction of monoclinic phase was equal to that in the bulk.

Optical interference microscopy techniques were also used to obtain independent checks of the transformation zone dimensions around the cracks in the fractured specimens. The zones were examined using a Zeiss interference microscope. Interference phenomena produced by a monochromatic green light from a thallium light source, resulted in fringes on the sides of the specimens (near the fracture surface) when the fracture stresses were sufficient to induce the transformation from tetragonal-to-monoclinic phase. The heights of the transformation zones were determined by identifying the points where the parallel fringe lines in the elastic regions, or the polished flat surfaces outside the transformation zones, deviated from linearity (Fig. 4.25). The deviation is caused by topographical changes that occur in the highly stressed regions within the transformation zones, where a volume increase of the transformed particles occurs as a result of stress-induced martensitic transformations. Further details of the optical interference technique are given in a recent paper by Soboyejo and Mercer [1994].

The Raman spectroscopy analysis of the sides of the TZ-2Y fracture specimen revealed an increase in the volume fraction of monoclinic phase from bulk average values (away from the fracture surface) to higher levels within the transformation zone.
typical plot of the volume fraction of monoclinic phase against distance from the crack face is presented in Figure 4.26. This shows that the maximum volume fraction of monoclinic phase occurs in the region that is closest to the fracture surface. A discernible drop in the volume fraction of monoclinic phase is then observed with increasing distance from the crack face, presumably as a result of lower stress concentrations. The volume fraction of monoclinic phase reduces to an asymptotic value that corresponds to the average volume fraction of monoclinic phase in the bulk. This occurs at a distance of approximately 120-125 μm from the fracture surface, which is consistent with the zone size inferred from the points where the optical interference fringes deviate from linearity (Figures 4.25). The optical interference transformation zone size measurements are therefore in good agreement with those obtained from the LRS analysis (120 μm) of the TZ-2Y specimen.

The volume fraction of monoclinic phase was estimated by subtracting the bulk average monoclinic zirconia levels from those within the transformation zone. The average amount of monoclinic zirconia in the transformation zone was thus estimated by integration to be approx. 3 vol. %.
Figure 4.22 Typical Microstructure of As-Hipped MoSi$_2$/TZ-2Y Composite
(a) Optical Photomicrograph and (b) SEM Photomicrograph
Figure 4.23  XRD Patterns Obtained from As-Processed Composites.  
(a) MoSi$_2$/TZ-0Y and (b) MoSi$_2$/TZ-6Y
Figure 4.23 (continued); (c) MoSi$_2$/TZ-2Y

Figure 4.24 Typical Fracture Modes in MoSi$_2$/TZ-2Y Composite
Figure 4.25  Typical Optical Interference Micrograph Showing Fringes Near the Fracture Surfaces of MoSi$_2$/TZ-2Y Composite

Figure 4.26  Volume Fraction of Monoclinic Zirconia as a Function of Distance from the Crack-Tip in MoSi$_2$+20 vol. % TZ-2Y Composite.
4.2.6 Analysis of Toughening

The contribution of stress-induced transformation to toughening can be estimated using the model by Budiansky et al. [1983]:

$$\Delta K_t = \frac{0.22E_c f e_C^T \sqrt{f}}{1 - \nu}$$

where $E_c$ is the elastic modulus of the composite, $f$ is the volume fraction of transformed particles, $e_C^T$ is the transformation volume strain and $\nu$ is poisson ratio.

From the Raman spectroscopy analysis, the zone height, $h$, was estimated to be 120 $\mu$m and volume fraction of particles that undergo stress-induced transformation was estimated to be $\sim$ 3%. The degree of transformation toughening in MoSi$_2$/TZ-2Y composite is thus estimated to be 1.2 MPa$\sqrt{m}$. Hence, for a matrix toughness of approx. 3.8 MPa$\sqrt{m}$, the fracture toughness of the TZ-2Y composite is estimated to be approx. 5.0 MPa$\sqrt{m}$. This is in exact agreement with the fracture toughness data obtained from the experimental fracture toughness measurements.

The model by Budiansky et al. [1983] therefore appears to provide very good estimates of the degree of transformation toughening in the TZ-2Y composite. This is in spite of the fact that it neglects to effects of shear in its formulation, i.e., it assumes that the transformations are induced purely by dilatational stresses. Similar agreement between theoretical estimates obtained from the analysis of Budiansky et al. [1983] and measured fracture toughness values have also been obtained by Marshall et al. [1983] in prior studies on transformation toughened ceramics. The role of shear stresses in the stress-induced martensitic transformation processes therefore appears to be relatively small in the systems that have been studied so far. The dilational-stress-controlled transformation toughening model by Budiansky et al. [1983] therefore appears to be adequate for the estimation of transformation toughening.
4.3 Synergistic Toughening

4.3.1. Introduction

The synergistic toughening concept was first proposed by Amazigo and Budiansky [1988]. In their original paper, they studied the combined toughening due to crack-bridging by ductile particles and transforming toughening by particles that undergo purely dilational stress-induced phase transformations in a brittle matrix. In their studies, they found that interactions between transformation toughening and crack bridging mechanisms may promote synergy in certain parametric ranges of constituents. Under such conditions, they predicted that the overall toughening is greater than the sum of the individual toughening components.

The objective of this study is to develop synergistically toughened MoSi$_2$ composites reinforced with transforming partially stabilized zirconia particles and bridging Nb reinforcements. Attempts were made to engineer synergy by promoting interactions between crack bridging and transformation toughening. Since, the results from the earlier studies showed that transformation toughening occurred only in the composite reinforced with 2 mole% yttria particles with an average particle size of ~0.7 μm [Soboyejo et al., 1995], TZ-2Y particles were used to induce transformation toughening. Furthermore, since Nb laminates were observed to have the higher fracture toughness levels (~18-20 MPa√m) than Nb fiber-reinforced (9-15 MPa√m) and Nb particulate-reinforced (~5-6 MPa√m) composites, Nb laminates were used to promote crack bridging in the hybrid/synergistically toughened composites that were examined in this study. In addition to promoting crack bridging, Nb layers are shown to promote significant
toughening via crack-tip blunting in the composites reinforced with 20 vol.% Nb layers and 20 vol.% TZ-2Y particles with an average size of ~ 0.7 μm. A limited amount of transformation toughening was also shown to occur, especially in the regions of high stress concentration close to the interface between Nb and MoSi$_2$.

4.3.2 Materials and Processing

In order to study the effects synergistic toughening, MoSi$_2$ composites reinforced with 20 vol.% of Nb layers and 20 vol.% zirconia particles stabilized with 2 mole% yttria (TZ-2Y) were fabricated. Nb foils thickness of ~ 200 μm were procured from G & S Titanium, Worcester, OH. The MoSi$_2$ powder, -325 mesh (approx. 44 μm average diameter), and TZ-2Y power with average diameter of 0.7 μm were purchased from Cerac, Milwaukee, WI. MoSi$_2$ and TZ-2Y are baked and mixed in mill for 48 hours. The Nb layers and MoSi$_2$-TZ-2Y were manually deposited in Nb cans that were vacuum (10$^{-4}$ Pa) sealed by electron beam welding prior to hot isostatic pressing (HIPing) at 1400°C under a pressure of 207 MPa. The microstructure of the resulting composites are shown in Figures 4.27a and 4.27b. These show the uniform distribution of TZ-2Y grains in MoSi$_2$ and the Nb layers very clearly. A layered interfacial structure consisting of (Mo,Nb)$_5$Si$_3$ and Nb$_5$Si$_3$ [74] layers is also observed in the higher magnification photomicrograph shown in Figure 4.7(b). Similar structures have been reported in the earlier studies on MoSi$_2$/Nb laminates. The morphology of the TZ-2Y particles is also comparable to that observed in the MoSi$_2$ composites reinforced only with 20 vol.% of TZ-2Y particles.
Figure 4.27  Microstructure of Synergistically Toughened MoSi$_2$+20 vol.% Nb + 20 vol.% TZ-2Y Composite.
4.3.3 Fracture Toughness

Single Edge Notched (SEN) bend specimens with a square cross sections (6.02 x 6.02 mm) and a length of ~ 38 mm were fabricated by electro-discharge machining (EDM) techniques. The specimens had initial notch-length-to-width ratios of ~0.4. The SEN specimens were deformed continuously to failure under monotonic loading that resulted in a stress intensity factor increase rate of ~ 0.92 MPa\sqrt{m} s^{-1}. The fractured specimens were then examined under a scanning electron microscope to determine the failure modes in the composite.

The fracture toughness of the as-fabricated synergistically toughened composite (~ 21\pm1.0 MPa\sqrt{m}) is compared with previously reported data toughness data for MoSi$_2$ (~ 3.6 MPa\sqrt{m}) and MoSi$_2$ composites (~ 4-18 MPa\sqrt{m}) in Figure 4.28. Also included in Figure 4.28 is the range of fracture toughness data that is typically obtained from structural aluminum alloys [ASM Handbook, 1990] which have typical toughness values between 20 and 25 MPa\sqrt{m}. The synergistically toughened composites therefore have fracture toughness levels that are comparable to those of structural aluminum alloys. However, it is important to note that the measured fracture toughness values correspond to an instability point along a rising resistance curve. The initiation toughness values of the synergistically toughened are thus likely to correspond to the toughness levels of ~ 5 MPa\sqrt{m} obtained from previous studies of TZ-2Y reinforced MoSi$_2$ [Soboyejo et al., 1995]. The synergistically toughness may therefore have relatively low initiation fracture toughnesses compared to existing structural aluminum alloys. Nevertheless, the
measured fracture toughness of $21\pm1.0$ MPa$\sqrt{m}$ is clearly remarkable. It is clearly the highest fracture toughness that has been reported for any MoSi$_2$ composite. It is therefore exciting to imagine the fracture toughness improvements that can be achieved through further optimization of the layered synergistically toughened composite structure.

Crack bridging and crack-tip blunting by debonding of interface was observed and shown on Figure 4.29. Fracture of the MoSi$_2$ occurred by a combination of intergranular and cleavage fracture (Figure 4.30). A flat featureless fracture surface was also observed in the zirconia grains, while the Nb layers failed by a combination of cleavage and ductile dimpled fracture modes. A limited amount of debonding was also observed to occur between the Nb layers and the MoSi$_2$/TZ-2Y layers. Such debonding may be associated with crack-tip blunting mechanisms observed in earlier studies on layered MoSi$_2$/Nb composites [Soboyejo et al., 1996].
Figure 4.28 Fracture Toughness Data
Figure 4.29 Interaction of Crack and Microstructure in SEN Specimen Before Final Fracture. (a) Crack Bridging and Blunting, and (b) Multiple Cracks in Matrix
Figure 4.30  Typical Fracture Modes in Fracture Toughness Specimen of MoSi$_2$+ TZ-2Y+Nb Composite. (a) Matrix and (b) Nb Layer.
After fracture testing, laser Raman spectroscopy analysis was performed on the sides of the fractured specimens to determine the volume fraction of monoclinic/tetragonal phase as a function of distance from the crack faces, and distance from the Nb layer. The results are presented in Figure 4.31. The typical Raman spectra obtained from the deformed and undeformed composites are also shown in Figure 4.32 for comparison. It is apparent from these figures that the extent of transformation is greater in the region close to crack and Nb laminates. The increased level of transformation in the regions close to Nb layer are attributed to the effects of interfacial tractions. Such tractions may also be enhanced by debonding as shown in Figure 4.29. By careful analysis of the above Raman plots, the transformation zone was estimated to be ~150 µm, with an average of about 4.5% of the zirconia grains undergoing stress-induced transformation. Using equation 4.31, the toughening due to transformation was thus estimated to be about 0.4 MPa√m in the synergistically toughened composite.

Toughening due to crack bridging and crack-tip blunting can be estimated by equation 4.16 and 4.25, respectively. The amount of toughening due to crack bridging is estimated to be about 7.8 MPa√m. The amount of toughening due to crack-tip blunting is estimated to be about 4.5 MPa√m. These give the estimated toughness of MoSi2/Nb-TZ-2Y to be about 16.3 MPa√m, which is lower than the experimental value of about 21 MPa√m.
Figure 4.31  Volume Percentage of Monoclinic Phase Obtained Under Monotonic Loads on the Side of Deformed SEN Fracture Toughness Specimen
Figure 4.32 Typical Raman Spectra Observed in MoSi$_2$/TZ-2Y/Nb Composite
(a) Transformed Region of Deformed Materials
(b) Untransformed Regions of Undeformed Materials
Figure 4.32 (continued)

(b)
Finally in this section, it is of interest to examine the current results within the context of prior model by Budiansky and Amazigo [1988]. The coupling parameter $\rho$ in the model by Amazigo and Budiansky [1988] described in chapter 2, is given by:

$$\rho = \frac{(1+\nu)vS}{\sigma_m^c} \quad \text{...(4.32)}$$

where $\nu$ is Poisson's ratio, $v$ is the volume fraction of ductile reinforce phase, $S$ is the strength of reinforcement and $\sigma_m^c$ is the mean stress in the transformation region. The latter can be estimated from the terms of the elastic stress fields near the crack-tip. These are given by:

$$\begin{bmatrix}
\sigma_{xx} \\
\sigma_{yy} \\
\sigma_{zz}
\end{bmatrix} = \frac{K_1}{\sqrt{2\pi r}} \cos \frac{\theta}{2} \begin{bmatrix}
1 - \sin \frac{\theta}{2} - \sin \frac{3\theta}{2} \\
\theta \\
\sin \frac{\theta}{2} - \cos \frac{3\theta}{2}
\end{bmatrix} \quad \text{...(4.33)}$$

Since the mean stress exhibits a $1/\sqrt{r}$ singularity, it is apparent that the mean stress in the transformation zone is much greater than the strength of the Nb layer (249 MPa). Hence, the coupling parameter given by Equation 4.32 is close to zero. The toughening ratio for the limiting case in which $\rho \to 0$ is thus obtained from the analysis of Budiansky and Amazigo (1988) to be $\lambda = (\lambda_b^2 + \lambda_T^2 - 1)^{1/2}$. In the current study, $\lambda_b$ was estimated to be $\sim 3.16$, while $\lambda_T$ was estimated to be $\sim 1.11$. The overall value of $\lambda$ for $\rho \to 0$ is thus given by $\lambda = (\lambda_b^2 + \lambda_T^2 - 1)^{1/2}$ to be $3.19$. This is very close to the
toughening due to crack bridging along. However, the synergistic toughening due to bridging and stress-induced transformation is given by $\lambda K_m$ which is equal to 11.5 MPa/\(\sqrt{m}\). This is 3.28 MPa/\(\sqrt{m}\) greater than the sum of the individual toughening contributions of bridging and transformation toughening. The toughening contribution due to synergy are thus estimated to be $-3.28$ MPa/\(\sqrt{m}\). If this is included in the overall estimation of the composite toughness along with the shielding contributions due to crack-tip blunting, the overall composite toughness $K$ is estimated to be $K_m + \lambda K_m + \Delta K_{blunting}$ which is equal to $3.6+11.5+4.5=19.6$ MPa/\(\sqrt{m}\). This is very close to the measured toughness of $21\pm1.0$ MPa/\(\sqrt{m}\). The above estimates of the shielding contribution due to synergy are very encouraging in spite of the limited contributions from transformation toughening. They show clearly that synergistic toughening components can significantly enhance the fracture toughness even when the shielding contributions from transformation toughening are limited. It is also apparent from the current analysis that the extent of synergy may be further optimized by increasing the zirconia volume fraction and/or using zirconia reinforcements that undergo higher levels of transformation than those employed in this study. Further work is clearly needed for the optimization of synergistically toughened composites.

4.3.4 Resistance Curve Behavior

Resistance curves behavior of synergistically toughened composites obtained from this study are presented in Figure 4.33. R-curve behavior results mainly from crack bridging, crack-tip blunting and transformation toughening. An initiation toughness of $-
4.5 MPa√m was observed on this composite, which is slightly smaller than the matrix toughness of 5.0 MPa√m. This may due to difference in stress distribution of composite and monolithic materials. The prediction was shown to overestimated the resistance behavior in some degree. Due to complex stress redistribution in a cracked composite, finite element method may be needed in further study to try to characterize the driving force for such composite structure.

Figure 4.33 Effect of Transformation Toughening on the Resistance Curve Behavior of MoSi₂ Composites
4.3.5 Fatigue Crack Growth

The fatigue crack growth rates in the synergistic toughened composites are compared with corresponding fatigue crack growth rate data obtained from pure monolithic Nb and other composites in Figure 4.34. Fatigue crack growth rate data reported for monolithic MoSi$_2$ [Kajuch et al., 1992] is also included in Figure 4.34 for comparison. Unlike monolithic MoSi$_2$ in which stable fatigue crack growth was difficult to obtain at stress intensity factor levels below the fracture toughness [Rao et al., 1992; Soboyejo et al., 1993; Ramamurthy et al., 1994], stable fatigue crack growth occurred readily in the MoSi$_2$/Nb composites that were examined in this study. However, the initial crack growth rates were high in all the composites. Stable crack growth in the MoSi$_2$/Nb composites was also intermittent due to the interactions of the fatigue cracks with the Nb layers. The crack growth rates were generally very fast in the MoSi$_2$/TZ-2Y layers and slow in Nb layers.

The interaction of fatigue cracks with the underlying composite microstructure are illustrated in Figure 4.35. It is apparent from this figure that the cracks were both bridged and blunted by the ductile Nb layers. The cracks were also observed to reinitiate on the other side of the layers, thereby giving rise to bridged crack configurations of low and intermediate $\Delta K$ values. This is shown in Figure 4.35. However, at higher $\Delta K$ values, the cracks were observed to propagate through the Nb layers (Figure 4.36). Bridged layers were also fractured as the crack opening displacements increased. In general, however, crack growth in the MoSi$_2$ matrix occurred predominantly by transgranular cleavage (Figure 4.30a). Similar to the MoSi$_2$ composite reinforced only with Nb layers,
the Nb layers failed by cleavage fracture mode under cyclic loading. Typical Nb fracture modes are shown in Figure 4.37. The incidence of cyclic cleavage may be due to the high strain rates associated with reversed plasticity under cyclic loading [Ritchie et al., 1997; Soboyejo et al., 1993 and 1997].

It is of interest to compare the extent of transformation toughening that under monotonic and under cyclic loading. Typical Raman results obtained from the fatigue crack growth specimens are presented in Figure 4.38. These are similar in character to the Raman results presented earlier for monoclinic loading. As in the earlier case, the extent of transformation was greater in the regions close to the layers and the crack faces. However, the overall volume fraction of transformed zirconia was generally less than the levels observed under monotonic loading. The transformation zone size (~ 120 μm) obtained under cyclic loading was also somewhat smaller than the transformation zone size (~ 150 μm) that was observed under monoclinic loading. The lower levels of transformation and the smaller transformation zone are attributed to the lower stress levels associated with subcritical fatigue crack growth. Further work is clearly needed to determine additional effects of cyclic loading on the critical condition required for stress-induced phase transformations.
Figure 4.34 Summary of Fatigue Crack Growth Rate Data on MoSi$_2$/TZ-2Y/Nb Composites
Figure 4.35 Interaction of Fatigue Crack and Underlying Microstructure in Synergistic Toughened MoSi$_2$+20 vol.% Nb + 20 vol.% TZ-2Y Composite
Figure 4.36  Fatigue Crack Growth Through Nb Layer
Figure 4.37 Typical Fatigue Fracture Mode in (a) Nb Layer and (b) Matrix
Figure 4.38  Volume Percentage of Monoclinic Phase in a Typical Fatigue Specimen of the MoSi$_2$/TZ-2Y/Nb Composite
Nevertheless, it is of interest to compare the shielding contributions from the transformation toughening and ductile phase toughening under cyclic loading. Using Raman estimates of $V_t = 5 \%$, $h = 120 \mu m$ and material constants listed in Table 4.1, the shielding due to transformation is estimated from Equation 4.31 to be $0.4 \text{ MPa}\sqrt{m}$. Similarly, the shielding due to ductile phase toughening may be estimated from Equations 4.28 and 4.29 for crack-tip blunting and crack bridging, respectively. However, the effects of cyclic loading must be included in the analysis of ductile phase toughening. In the case of crack bridging, the approach proposed by McMeeking and Evans [1990] was used to estimate the $\Delta K_{\text{eff}}$ from the bridging estimates at the mean stress. This approach applies strictly to crack growth at a stress ratio, $R = K_{\text{min}}/K_{\text{max}} = 0$. However, it is being used in current study for a stress ratio, $R = 0.1$. This gives:

$$\Delta K_{\text{tip}} = 2K_{\text{tip}}(\Delta \sigma/2)$$  \hspace{1cm} (4.30)

where $K_{\text{tip}}(\Delta \sigma/2)$ is the near-tip stress intensity factor at the cyclic mean stress, $\Delta \sigma/2$, for a bridged crack subjected to a maximum stress of $\Delta \sigma$ at a stress ratio, $R = K_{\text{min}}/K_{\text{max}}$, of zero. The toughening due to bridging and blunting may therefore be estimated from equations 4.28 and 4.29. The synergy due to interactions between transformation toughening and crack bridging may also be estimated using the approaches developed by Budiansky and Amazigo [1988].

The $\Delta K_{\text{eff}}$ vs. $da/dN$ plot in Figure 4.34 shows that the effective $\Delta K$ plots are shifted somewhat to the left of the applied $\Delta K$ plots. An indication of the additional shielding
due to synergy is provided by the difference between the $\Delta K_{\text{eff}}$ plots obtained for the hybrid (layered Nb+MoSi$_2$+TZ-2Y) and layered (MoSi$_2$+Nb). This shows clearly that synergistic toughening has a beneficial effect, in spite of the limited shielding contributions from transformation toughening. Further work is clearly need to optimize the design of synergistically toughened composites.
CHAPTER 5

FATIGUE AND FRACTURE OF NIOBIUM ALUMINIDES

5.1 Introduction

The has been considerable interest in the development of high temperature intermetallics with the potential to replace nickel, titanium and cobalt base alloys [Lipsitt, 1985]. However, most of the efforts have focused on the aluminides of nickel and titanium which appear to have very limited prospects for near term structural applications largely as a result of their brittle behavior at room temperature. In contrast, recent studies by Fraser and co-workers [Hou, 1994; Shyue et al., 1993; Fraser, 1996] has shown that the addition of Ti to Nb3Al (which has the A15 crystal structure and is brittle at room temperature) can stabilize the B2 crystal structure, which has five independent slip systems required for homogeneous plastic deformation [Von Mise, 1928]. The resulting alloys have ductilities of ~ 3-30 % and fracture toughness levels of ~ 60-100 MPa√m. Niobium aluminide base alloys also retain attractive combinations of strength retention and oxidation resistance at temperature up to 750-800°C.
In this chapter, the effects of alloying with Ti are examined in three different alloys: Nb-15Al-10Ti (10Ti), Nb-15Al-25Ti (25Ti) and Nb-15Al-40Ti (40Ti). The fatigue and fracture behavior of all the alloys were examined at room-temperature. Fatigue crack growth was also studied in the 40Ti alloy at 750°C. Slower near-threshold elevated-temperature (750°C) fatigue crack growth rates are attributed to the combined effects of oxide-induced crack closure and crack-tip blunting.

5.2 Materials

The alloys that were examined in this study were produced by Teledyne Wah Chang, Albany, OR. Nominal and actual compositions are summarized in Table 5.1. Melted ingots were produced by triple vacuum arc remelting (VAR) in a 11.4 cm diameter x 25.4 cm high mold. Typical microstructures of the cast alloys are presented in Figure 5.1a-5.1f. As cast 10Ti and 25Ti alloys retained their B2 structure after heat treatment at 750°C for 25 hours (Figure 5.1a and 5.1c). However, the same heat treatment resulted in a duplex (orthorhombic + B2) structure in the 40Ti alloy (Figure 5.1e). The three alloys were also heat treated at 1150°C for 2 hours or 50 hours, followed by furnace cooling. Second phase precipitates were observed in the 10Ti and 25Ti alloys (Figure 5.1b and 5.1d) after annealing at 1150°C. These have the A15 crystal structure which has been shown by Shyue et al. (1993). The second phase present in the 40Ti alloy has an orthorhombic crystal structure. The presence of orthorhombic phase has also been reported in the 25Ti alloy [Hou, 1994]. A higher volume fraction of precipitates were observed in the samples that were heat treated for 50 hours.
<table>
<thead>
<tr>
<th>Alloy</th>
<th>Nb</th>
<th>Al</th>
<th>Ti</th>
<th>O</th>
<th>N</th>
<th>H</th>
<th>C</th>
<th>Cu</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nb-15Al-10T</td>
<td>Balance</td>
<td>12.54</td>
<td>8.71</td>
<td>0.131</td>
<td>0.033</td>
<td>0.040</td>
<td>0.016</td>
<td>0.008</td>
</tr>
<tr>
<td>Nb-15Al-25T</td>
<td>Balance</td>
<td>15.12</td>
<td>25.12</td>
<td>0.250</td>
<td>0.021</td>
<td>0.085</td>
<td>0.016</td>
<td>0.004</td>
</tr>
<tr>
<td>Nb-15Al-40T</td>
<td>Balance</td>
<td>14.55</td>
<td>40.20</td>
<td>0.146</td>
<td>0.019</td>
<td>0.058</td>
<td>0.038</td>
<td>&lt;0.01</td>
</tr>
</tbody>
</table>

Table 5.1 - Compositions of Alloys in Atomic Percent
Figure 5.1  Typical Microstructures of Niobium Aluminide Alloys: (a) Nb-15Al-10Ti (As-Cast); (b) Nb-15Al-10Ti (1150°C/2hrs/FC); (c) Nb-15Al-25Ti (As-Cast); (d) Nb-15Al-25Ti (1150°C/2hrs/FC); (e) Nb-15Al-40Ti (As-Cast); (f) Nb-15Al-40Ti (1150°C/2hrs/FC)
Ingots of the 40Ti alloys were reduced to billet form by conventional upset forging steps as shown in Table 5.2. However, the 10 and 25Ti alloys were processed using isothermal forging conditions. The resulting microstructures are presented in Figures 5.2a-5.2e. Forged 10Ti and 25Ti have microstructures consisting of B2 and A15 phases (Figure 5.2a and 5.2b). The forged 10Ti and 25Ti alloys were tested in the as-forged condition and after annealing at 750°C for 25 hours. The 750°C anneal was used to stabilize the microstructure at the potential service temperature. The as-forged microstructure of the 10Ti and 25Ti alloys consist of elongated B2 grains. The grains are elongated in the direction perpendicular to the forging direction. A small fraction of A15 precipitates were observed in the as-forged 10 and 25Ti alloys (Figure 5.2a and 5.2b). The 10 and 25Ti alloys retained their elongated grain structure along with a small fraction of A15 precipitates, following the 750°C stabilization anneal.
Figure 5.2 Typical Microstructures of Niobium Aluminide Alloys: (a) Nb-15Al-10Ti (As-Forged); (b) Nb-15Al-25Ti (As-Forged); (c,d) Nb-15Al-40Ti (As-forged+750°C/25hrs); and (e) Nb-15Al-40Ti (S & A)
<table>
<thead>
<tr>
<th>STEP #</th>
<th>DESCRIPTION</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Triple vacuum arc remelt into 4.5&quot; (114 mm) diameter ingot.</td>
</tr>
<tr>
<td>2.</td>
<td>Machine to 4.2&quot; (107 mm) diameter and saw in half (about 4&quot; (102 mm) long for each pieces)</td>
</tr>
<tr>
<td>3.</td>
<td>Preheat 1.5 - 2 hours at 1150°C</td>
</tr>
</tbody>
</table>
| 4.     | Forge to rectangular bar  
(a) Upset to 3.0" (76 mm)  
(b) Reheat 10 min.  
(c) Forge to 3" x 4" x L (76 mm x 102 mm x L)  
(d) Reheat 10 min  
(e) Forge to 2.5" x 4.0" x L (64 mm x 102 mm x L)  
(f) Reheat 10 min  
(g) Forge to 1.75" x 4.0 x L (44 mm x 102 mm x L)  
(h) Forge to 1.5" x 4.5" x L (38 mm x 114 mm x L)  
(i) Reheat 10 min  
(j) Forge to 1.25" x 4.5" x 9"L (32 mm x 114 mm x L) |

Table 5.2 - Summary of Forging Steps for Nb-15Al-40Ti

The heat treatments for the forged 40Ti alloy consisted of a direct age (DA) and a solution and age (S&A) treatment. The DA specimens were stabilization annealed at 750°C for 25 hours followed by a furnace cool. This resulted in the formation of a two phase microstructure consisting of orthorhombic platelets in a B2 matrix. Typical optical and transmission electron micrographs of the heat treated material are presented in Figure 5.2c and 5.2d, respectively. Note the large size (~200 μm) prior B2 grains in Figure 5.1c. Orthorhombic platelets are also clearly evident within the prior B2 grains in the TEM photomicrograph (Figure 5.1d). Such microstructures are intended to simulate the actual microstructures that might exist in the potential service temperature regime (~750°C).
The S&A specimens were recrystallized at 1150°C for 8 hours followed by an aging treatment at 750°C for 25 hours. This resulted in a recrystallized microstructure consisting of orthorhombic platelets in a B2 matrix.

The tensile properties of forged 10Ti, 25Ti and 40Ti are summarized in Table 5.3. The results show that the 10Ti and 25Ti alloy exhibit very limited ductility and very low fracture stress. Note that the 10Ti and 25Ti alloys also failed by brittle cleavage fracture modes (Figure 5.3a-b). In contrast, the 40Ti alloy exhibits extensive tensile ductility and high yield strengths (Figure 5.3c and 5.3d). However, 40Ti alloys exhibit strain softening during yielding under monotonic loading. Hence, the forged 40Ti alloy does not have a true ultimate tensile strength in the as-forged and DA treated conditions. In any case, the as-forged and DA treated 40Ti alloy failed by ductile dimpled fracture with splitting occurring along the grain boundaries of the elongated B2 grains.

<table>
<thead>
<tr>
<th></th>
<th>10Ti</th>
<th>25Ti</th>
<th>40Ti</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>as forged</td>
<td>DA</td>
<td>as forged</td>
</tr>
<tr>
<td>E (GPa)</td>
<td>125±3.0</td>
<td>77.4±1.5</td>
<td>106±2.5</td>
</tr>
<tr>
<td>σ_y (MPa)</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>σ_{UTS} (MPa)</td>
<td>200±19</td>
<td>97.8±17</td>
<td>193±21</td>
</tr>
<tr>
<td>ε_{Max} (%)</td>
<td>0.17±0.2</td>
<td>0.15±0.3</td>
<td>0.19±0.3</td>
</tr>
</tbody>
</table>

Table 5.3 - Room-Temperature Tensile Properties of Forged Nb-15Al-xTi alloys
Figure 5.3 Typical tensile fracture modes in: brittle cleavage in (a) as-forged 10Ti; (b) as-forged 25Ti; ductile dimple fracture in (c) as-forged 40Ti and (d) DA treated 40TiT
5.3 Fracture Toughness

5.3.1 Cast Nb-15Al-xTi

The results of the fracture toughness tests are summarized in Table 5.4. Fracture toughness is higher in the 40Ti alloy. The as-cast 40Ti alloy also has the highest fracture toughness of ~ 110MPa√m. The as-cast 10Ti and 25Ti alloys have lower fracture toughness of 27 MPa√m and 34 MPa√m, respectively. The fracture toughness seems to increase with the amount of Ti added in. Also, the A15 phase significant decrease in the fracture toughness. Hence, in the case of the Nb-15Al-10Ti alloy, fracture toughness drops from 27 MPa√m to 9.2 MPa√m, after recrystallization at 1150°C for 2 hours. The drop in toughness is clearly associated with the precipitation of a greater fraction of A15 second phase (Figure 5.1b and 5.1d). A further drop in fracture toughness (to 8.2 MPa√m) was also observed after annealing at 1150°C for 50 hours. This drop was associated with a significant increase in B2 grain size and the volume fraction of A15 phase.

The DA treatment (750°C/25hrs) appears to have only a small effect on the 10Ti alloy. However, the effect of the DA treatment on the 40Ti is quite significant, especially after the precipitation of orthorhombic phase which degrades the ductility and the fracture toughness values. The fracture surfaces of the 10Ti and 25Ti alloys exhibit brittle cleavage and intergranular fracture modes (Figure 5.4a-h). However, fracture in the 40Ti alloy occurs mainly by ductile dimple fracture (Figure 5.4i-l). A notable exception to this is the 40Ti alloy that was heat treated at 1150°C for 50 hours. This heat treatment resulted in a combination of ductile dimpled fracture and transgranular fracture as shown in Figure 5.4(l)
<table>
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<th>Material</th>
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<th>Phase</th>
<th>Fracture Toughness (MPa(\sqrt{m}))</th>
<th>Fracture Mode</th>
</tr>
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<tr>
<td>Nb-15Al-10Ti</td>
<td>as-cast</td>
<td>B2</td>
<td>27</td>
<td>intergranular</td>
</tr>
<tr>
<td></td>
<td>as-cast+750°C/25hrs</td>
<td>B2</td>
<td>23</td>
<td>intergranular</td>
</tr>
<tr>
<td></td>
<td>as-cast+1150°C/2hrs</td>
<td>B2+A15</td>
<td>9.2</td>
<td>intergranular</td>
</tr>
<tr>
<td></td>
<td>as-cast+1150°C/50hrs</td>
<td>B2+A15</td>
<td>8.3</td>
<td>intergranular</td>
</tr>
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<td>Nb-15Al-25Ti</td>
<td>as-cast</td>
<td>B2</td>
<td>34</td>
<td>intergranular</td>
</tr>
<tr>
<td></td>
<td>as-cast+750°C/25hrs</td>
<td>B2</td>
<td>25</td>
<td>intergranular</td>
</tr>
<tr>
<td></td>
<td>as-cast+1150°C/2hrs</td>
<td>B2+A15</td>
<td>13.5</td>
<td>intergranular</td>
</tr>
<tr>
<td></td>
<td>as-cast+1150°C/50hrs</td>
<td>B2+A15</td>
<td>10.8</td>
<td>intergranular</td>
</tr>
<tr>
<td>Nb-15Al-40Ti</td>
<td>as-cast</td>
<td>B2</td>
<td>110</td>
<td>ductile dimple</td>
</tr>
<tr>
<td></td>
<td>as-cast+750°C/25hrs</td>
<td>B2+O</td>
<td>90</td>
<td>ductile dimple</td>
</tr>
<tr>
<td></td>
<td>as-cast+1150°C/2hrs</td>
<td>B2</td>
<td>88</td>
<td>ductile dimple</td>
</tr>
<tr>
<td></td>
<td>as-cast+1150°C/50hrs</td>
<td>B2</td>
<td>82</td>
<td>ductile dimple  +transgranular</td>
</tr>
</tbody>
</table>

Table 5.4 Summary of Fracture Toughness Values Obtained for Cast Nb-15Al-xTi
Figure 5.4   Typical Fracture Modes in SEN Fracture Toughness Specimens: Brittle Fracture in 10 Ti (a) as-cast, (b) as-cast+750°C/25hrs, (c) as-cast+1150°C/2hrs and (d) as-cast+1150°C/50hrs; 25Ti (e) as-cast, (f) as-cast+750°C/25hrs, (g) as-cast+1150°C/2hrs and (h) as-cast+1150°C/50hrs; 40 Ti (i) as-cast, (j) as-cast+750°C/25hrs, (k) as-cast+1150°C/2hrs and (l) as-cast+1150°C/50hrs;
Figure 5.4 (Continued);
Figure 5.4 (Continued)
5.3.2 Forced Nb-15Al-xTi

The fracture toughness data obtained from the forged alloys are summarized in Table 5.5. Fracture toughness increases from 10-20 MPa√m in the 10Ti and 25Ti alloys, to as high as about 100 MPa√m in the 40Ti alloy. The DA treated 10Ti and 25Ti alloys exhibit a significant increase in fracture toughness from about 18 to 28 MPa√m. Nevertheless, fracture in the 10Ti and 25Ti alloys occurred by transgranular cleavage (Figure 5.5a-d). In contrast, the as-forged and DA treated 40Ti alloys exhibit ductile dimpled fracture modes (Figure 5.5e and 5.5f). Ductile dimpled fracture in the forged 40Ti alloy also occurred along with secondary splitting along the boundaries between the elongated grains that were present after DA heat treatment (Figure 5.5f).

The S&A heat treatment also resulted in a mixed fracture mode, consisting predominantly of intergranular facets (Figure 5.5g), with some incidence of ductile dimpled fracture (Figure 5.5h). However, unlike the 10Ti and 25Ti alloys, the occurrence of stable intergranular crack growth is associated with significantly lower fracture toughness levels in the solution treated and aged 40Ti alloy tested in the S&A condition, which is about 40 MPa√m. It is possible that such intergranular failure modes may be associated with grain boundary diffusion processes. Significant amount of plasticity was also observed on the S & A treated 40Ti alloys as shown in Figure 5.5 (i), which clearly shows that the crack was bridged by grain and the grain deformed plastically before a final intergranular fracture. This can, to some degree, explain the relatively high toughness of 40 MPa√m and stable crack growth for an intergranular fracture. Several effects to characterize the surface compositions of the intergranular facets did not yield
any conclusive results. However, it is possible that intergranular crack growth may be due to the formation of submicroscopic grain boundary oxide precipitates, as suggested by Johnson [1997] in a recent Auger study of the 40Ti alloy.

<table>
<thead>
<tr>
<th>Material</th>
<th>Processes</th>
<th>Phase</th>
<th>Fracture Toughness (MPa√m)</th>
<th>Fracture Mode</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nb-15Al-10Ti</td>
<td>as-forged</td>
<td>B2+A15</td>
<td>17</td>
<td>transgranular</td>
</tr>
<tr>
<td></td>
<td>as-forged+750°C/25hrs</td>
<td>B2+A15</td>
<td>27</td>
<td>transgranular</td>
</tr>
<tr>
<td>Nb-15Al-25Ti</td>
<td>as-forged</td>
<td>B2+A15</td>
<td>18</td>
<td>transgranular</td>
</tr>
<tr>
<td></td>
<td>as-forged+750°C/25hrs</td>
<td>B2+A15</td>
<td>29</td>
<td>transgranular</td>
</tr>
<tr>
<td>Nb-15Al-40Ti</td>
<td>as-forged</td>
<td>B2</td>
<td>110±10</td>
<td>ductile dimple</td>
</tr>
<tr>
<td></td>
<td>as-forged+750°C/25hrs</td>
<td>B2+O</td>
<td>88.5-115</td>
<td>ductile dimple</td>
</tr>
<tr>
<td></td>
<td>as-Forged+1150°C/2hrs+750°C/25hrs</td>
<td>B2+O</td>
<td>41</td>
<td>intergranular</td>
</tr>
</tbody>
</table>

Table 5.5 Summary of Fracture Toughness Values Obtained for Forged Nb-15Al-xTi
Figure 5.5 Typical Fracture Modes in SEN Fracture Toughness Specimens:
Cleavage in forged 10 Ti (a) as-forged, (b) as-forged + 750°C/25hrs;
Cleavage in forged 25 Ti (c) as-forged, (d) as-forged + 750°C/25hrs;
Ductile Fracture in 40Ti Alloy (e) as-forged, (f) as-forged + 750°C/25hrs;
Intergranular Fracture in S&A Treated 40Ti (g), (h) and Evidence of Plasticity (i)

(to be continued)
Figure 5.5 (Continued)

(e)  (f)  

(g)  (h)
5.4 Fatigue Crack Growth

5.4.1 Room-Temperature Fatigue Crack Growth Behavior

5.4.1.1 Cast Nb-15Al-xTi

The fatigue crack growth rates in the cast niobium aluminide alloys are compared with those of mill annealed Ti-6Al-4V [Dubey et al., 1997] in Figure 5.6(a)-(g). The fatigue threshold and Paris exponent, C, are summarized in Table 5.6. The 10Ti and 25Ti alloys have faster crack growth rates than the 40 Ti alloys, which have comparable growth rates to those observed in mill annealed Ti-6Al-4V. The fatigue crack growth threshold, $\Delta K_{th}$ levels obtained for the 25Ti alloy are lower than those obtained for 10Ti and 40Ti alloys. However, the 25Ti and 40Ti alloys that were heat treated at 1150°C exhibited much faster crack growth rates than the as-cast alloys. Annealing at 750°C for 25 hours also found to have a stronger effect on the 40Ti alloy than the 10 and 25Ti alloys. Annealing at this temperature generally resulted in faster crack growth rates which were associated with the formation of orthorhombic phase in the 40Ti alloy (Figure5.2d). Nevertheless, fatigue crack growth in the 10Ti and 25Ti alloys occurred mainly by cyclic cleavage which are shown in Figure 5.7(a)-(h), while crack growth in the 40Ti alloy occurred by crystallographic crack growth mechanisms at lower $\Delta K$ levels and classical striation mechanisms at high $\Delta K$ levels (Figure 5.7i-l).
<table>
<thead>
<tr>
<th>Material</th>
<th>Processes</th>
<th>Phase</th>
<th>m</th>
<th>C (mm/cycle- (MPa√m)^m)</th>
<th>ΔKth (MPa√m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nb-15Al-10Ti</td>
<td>as-cast</td>
<td>B2</td>
<td>16</td>
<td>6.2x10^-22</td>
<td>8.6</td>
</tr>
<tr>
<td></td>
<td>as-cast+750°C/25hrs</td>
<td>B2</td>
<td>21</td>
<td>3.2x10^-28</td>
<td>9.5</td>
</tr>
<tr>
<td></td>
<td>as-cast+1150°C/2hrs</td>
<td>B2+A15</td>
<td>7.6</td>
<td>9.7x10^-14</td>
<td>8.5</td>
</tr>
<tr>
<td></td>
<td>as-cast+1150°C/50hrs</td>
<td>B2+A15</td>
<td>12.5</td>
<td>2.5x10^-17</td>
<td>8.0</td>
</tr>
<tr>
<td>Nb-15Al-25Ti</td>
<td>as-cast</td>
<td>B2</td>
<td>17</td>
<td>8.3x10^-23</td>
<td>8.9</td>
</tr>
<tr>
<td></td>
<td>as-cast+750°C/25hrs</td>
<td>B2</td>
<td>13</td>
<td>1.35x10^-18</td>
<td>8.4</td>
</tr>
<tr>
<td></td>
<td>as-cast+1150°C/2hrs</td>
<td>B2+A15</td>
<td>5.8</td>
<td>2.3x10^-11</td>
<td>8.2</td>
</tr>
<tr>
<td></td>
<td>as-cast+1150°C/50hrs</td>
<td>B2+A15</td>
<td>14.3</td>
<td>1.1x10^-18</td>
<td>7.3</td>
</tr>
<tr>
<td>Nb-15Al-40Ti</td>
<td>as-cast</td>
<td>B2</td>
<td>9.7</td>
<td>1.4x10^-16</td>
<td>9.6</td>
</tr>
<tr>
<td></td>
<td>as-cast+750°C/25hrs</td>
<td>B2+O</td>
<td>4.8</td>
<td>1.3x10^-10</td>
<td>6.9</td>
</tr>
<tr>
<td></td>
<td>as-cast+1150°C/2hrs</td>
<td>B2</td>
<td>4.4</td>
<td>2.1x10^-10</td>
<td>9.9</td>
</tr>
<tr>
<td></td>
<td>as-cast+1150°C/50hrs</td>
<td>B2</td>
<td>4.5</td>
<td>1.0x10^-10</td>
<td>9.0</td>
</tr>
</tbody>
</table>

Table 5.6 Summary of Paris Exponents, m, and Constant, C, and Fatigue Threshold ΔK_th for Cast Nb-15Al-xTi
Figure 5.6 Summary of Fatigue Growth Rate Data Obtained For:
(a) Cast Nb-15Al-10Ti Alloys; (b) Cast Nb-15Al-25Ti Alloys;
(c) Cast Nb-15Al-40Ti Alloys; (d) As-cast Nb-15Al-xTi Alloys;
(e) As-cast+750°C/25hrs Nb-15Al-xTi Alloys;
(f) As-cast+1150°C/2hrs Nb-15Al-xTi Alloys
(g) As-cast+1150°C/50hrs Nb-15Al-xTi Alloys
Figure 5.6 (continued)

Fatigue Crack Growth Rate, da/dN (mm/cycle) vs. Stress Intensity Factor Range $\Delta K$ (MPa$\sqrt{m}$)

- As-cast
- As-cast+750°C/25hrs
- As-cast+1150°C/2hrs
- As-cast+1150°C/50hrs
- Ti-6Al-4V (mill annealed)
Figure 5.6 (continued)

Fatigue Crack Growth Rate, $\frac{da}{dN}$ (mm/cycle) vs. Stress Intensity Factor Range $\Delta K$ (MPa$\sqrt{m}$)

- As-cast
- As-cast+750°C/25hrs
- As-cast+1150°C/2hrs
- As-cast+1150°C/50hrs
- Ti-6Al-4V (mill annealed)
Fatigue Crack Growth Rate, \( \frac{da}{dN} \) (mm/cycle)

Stress Intensity Factor Range \( \Delta K \) (MPa\( \sqrt{m} \))

Figure 5.6 (continued)
Figure 5.6 (continued)

Fatigue Crack Growth Rate, da/dN (mm/cycle)

Stress Intensity Factor Range ΔK (MPa√m)

(e)
Figure 5.6 (continued)

Fatigue Crack Growth Rate, $d_a/dN$ (mm/cycle) vs. Stress Intensity Factor Range $\Delta K$ (MPa$\sqrt{m}$)

- **Nb-15Al-10Ti**
- **Nb-15Al-25Ti**
- **Nb-15Al-40Ti**
- **Ti-6Al-4V (mill annealed)**
Figure 5.6 (continued)

Stress Intensity Factor Range $\Delta K$ (MPa$\sqrt{m}$)

Fatigue Crack Growth Rate, $da/dN$ (mm/cycle)
Figure 5.7 Typical Fracture Modes in Fatigue Crack Growth Specimens: Transgranular Fracture in Cast 10 Ti (a) as-cast, (b) as-cast + 750°C/25hrs; (c) as-cast + 1150°C/2hrs, (d) as-cast + 1150°C/50hrs; Cast 25 Ti (e) as-cast, (f) as-cast + 750°C/25hrs, (g) as-cast + 1150°C/2hrs, (h) as-cast + 1150°C/50hrs; Cast 40 Ti (i) as-cast, (j) as-cast + 750°C/25hrs; (k) as-cast + 1150°C/2hrs, (l) as-cast + 1150°C/50hrs;
Figure 5.7 (Continued):
Figure 5.7 (Continued);
5.4.1.2 Forged Nb-15Al-xTi

The fatigue crack growth rates in the forged Nb-15Al-xTi are compared with those of mill annealed Ti-6Al-4V [Dubey et al., 1997] in Figure 5.8(a)-(d). The fatigue threshold and Paris exponent, C, are summarized in Table 5.7. The 10Ti and 25Ti alloys have faster crack growth rates than the 40 Ti alloy, which has comparable fatigue crack growth resistance to annealed Ti-6Al-4V. The fatigue threshold, $\Delta K_{th}$, levels in the as-forged 25Ti and 10Ti alloys (6.4 and 7.1 MPa$\sqrt{m}$, respectively) are greater than that of the 40Ti alloy (5.1MPa$\sqrt{m}$) in the as-forged condition. However, the fatigue crack growth rates in the 40Ti alloy are generally slower than those obtained for the 10Ti and 25Ti alloys. The DA treatment appears to have limited effects on the fatigue crack growth behavior of 10Ti and 25Ti. However, DA treatment has a significant effect on 40Ti. The fatigue threshold drop from 8.6 MPa$\sqrt{m}$ to 6.7 MPa$\sqrt{m}$ after DA treatment.

Inspection of the fracture surfaces of the fatigue samples reveals faceted cleavage fracture modes in the 10Ti and 25Ti alloys (Figure 5.9a-d). The DA treated 40Ti alloy exhibits crystallographic fracture modes in the low- and mid-$\Delta K$ regimes, and striations in the high $\Delta K$ regime (Figures 5.9e and f). Careful examination of the polished sides of the as-forged 40Ti specimen revealed the formation of slip bands in areas around the crack tips of the specimen, as shown in Figure 5.10(a) and (b). The crack profile on the sides of the specimens also showed that fatigue crack growth in the ductile 40Ti alloy occurred by the extension of the "unzipping" of crack into slip bands. The mechanism of crack extension is, therefore, similar to the "unzipping" mechanism proposed originally by Neumann [1974] for crack growth in single crystal copper alloys. The unzipping crack growth mechanisms is illustrated schematically in Figure 2.6.
<table>
<thead>
<tr>
<th>Material</th>
<th>Processes</th>
<th>Phase</th>
<th>m</th>
<th>C  (mm/cycle-(MPa(\sqrt{m}))(^{-m}))</th>
<th>ΔK(\text{th}) (MPa(\sqrt{m}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nb-15Al-10Ti</td>
<td>as-forged</td>
<td>B2+A15</td>
<td>13.7</td>
<td>4.3 \times 10^{-19}</td>
<td>7.2</td>
</tr>
<tr>
<td></td>
<td>as-forged+750°C/25hrs</td>
<td>B2+A15</td>
<td>19.6</td>
<td>7.0 \times 10^{-24}</td>
<td>7.0</td>
</tr>
<tr>
<td>Nb-15Al-25Ti</td>
<td>as-forged</td>
<td>B2+A15</td>
<td>10.4</td>
<td>1.5 \times 10^{-15}</td>
<td>6.4</td>
</tr>
<tr>
<td></td>
<td>as-forged+750°C/25hrs</td>
<td>B2+A15</td>
<td>8.5</td>
<td>7.6 \times 10^{-14}</td>
<td>6.4</td>
</tr>
<tr>
<td>Nb-15Al-40Ti</td>
<td>as-forged</td>
<td>B2</td>
<td>9.7</td>
<td>5.0 \times 10^{-16}</td>
<td>8.6</td>
</tr>
<tr>
<td></td>
<td>as-forged+750°C/25hrs</td>
<td>B2+O</td>
<td>4.4</td>
<td>1.7 \times 10^{-10}</td>
<td>6.7</td>
</tr>
<tr>
<td></td>
<td>as-Forged+1150°C/2hrs+750°C/25hrs</td>
<td>B2+O</td>
<td>2.2</td>
<td>3.7 \times 10^{-8}</td>
<td>5.1</td>
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</table>

Table 5.7 Summary of Paris Exponents, m, and Constant, C, and Fatigue Threshold ΔK\(\text{th}\) for Forged Nb-15Al-xTi
Figure 5.8 Summary of Fatigue Growth Rate Data Obtained For:
(a) Forged 10Ti and 25Ti Alloys; (b) Forged Nb-15Al-40Ti Alloys;
(c) As-forged Nb-15Al-xTi Alloys; (d) As-forged+750°C/25hrs Nb-15Al-xTi Alloys
Figure 5.8 (continued)

![Graph showing Stress Intensity Factor Range $\Delta K$ (MPa\(\sqrt{m}\)) vs Fatigue Crack Growth Rate, $da/dN$ (mm/cycle) for different conditions: As-forged, As-forged+DA, As-forged+S&A, Ti-6Al-4V (mill annealed).]
Figure 5.8 (continued)

![Graph showing fatigue crack growth rate vs. stress intensity factor range.](image)

- Nb-15Al-10Ti
- Nb-15Al-25Ti
- Nb-15Al-40Ti
- Ti-6Al-4V (mill annealed)

Fatigue Crack Growth Rate, da/dN (mm/cycle)

Stress Intensity Factor Range ΔK (MPa√m)

(c)
Figure 5.8 (continued)

Fatigue Crack Growth Rate, da/dN (mm/cycle) vs. Stress Intensity Factor Range ΔK (MPa√m)

- Nb-15Al-10Ti
- Nb-15Al-25Ti
- Nb-15Al-40Ti
- Ti-6Al-4V (mill annealed)
Figure 5.9  Typical Fatigue Fracture Modes in Forged (a) 10Ti and (b) 25Ti; As-forged+750°C/25hrs (c) 10Ti and (d) 25Ti; Forged 40Ti (e) low ΔK (f) high ΔK; (e) striation and secondary cracking in 40Ti (DA) and (h) 40Ti (S & A)
Figure 5.9 (Continued):
Figure 5.10 Crack/Microstructure Interactions in Nb-15Al-40Ti: (a) Crack Growth Profile of 40Ti (As-cast) Showing Unzipping Along Slip Bands; (b) SEM Photomicrograph Shows Crack Grow into Slip Bands
5.4.2 High Temperature Fatigue

The fatigue crack growth rate data obtained for the DA heat treated 40Ti alloys at 750°C are presented in Figure 5.11. The near-threshold crack growth rates obtained at 750°C were slower than those obtained in air at 25°C. Higher thresholds at 750°C (8.2 MPa√m) compared with corresponding fatigue threshold values of 5.1 MPa√m at 25°C. The relatively high elevated-temperature fatigue thresholds are attributed to the effects of the oxide-induced crack closure. Evidence of the possible role of oxide-induced closure was obtained from the fractographic analysis and the examination of the crack profiles shown in Figures 5.12(a) and (b). The show clearly that oxide debris (Fig. 5.12a) and an oxide layer (Fig. 5.12b) are formed on the fracture surfaces of the fatigue specimen that was tested at 750°C. Such oxide layers and debris can induce crack closure when the debris/oxide thicknesses are comparable to crack-tip opening displacements. To explore this possibility, oxide-induced closure levels were estimated using a modified Dugdale-Barenblatt closure model [Suresh and Ritchie, 1984]. The model accounts for the wedging induced by an oxide layer that forms behind the crack-tip (Figure 5.13). Since the composition and thickness of the oxide layer must be known in any detailed oxide-induced closure analysis. The Oxide layer was shown to consist solely of TiO₂ in X-ray analysis and energy dispersive X-ray analysis of the fracture surfaces. The excess oxide thicknesses and the wedge lengths of the oxide films were estimated by careful analysis of the crack profiles (Fig.5.12). The closure stress intensity factor, $K_{cl}$, was thus estimated from the following expression due to Suresh and Ritchie [1984].
\[ K_{cl} = \frac{dE}{4(\pi l)^{1/2}(1-\mu^2)} \]  

where \( d \) is the excess oxide thickness, \( 2l \) is the wedge length of the oxide film, \( \mu \) is Poisson's ratio, and \( E \) is the Young's modulus. The excess oxide thickness was measured from the crack profiles of the 40Ti specimen. An average oxide of thickness of \(-5 \, \mu m\) was measured in the 40Ti alloy following the threshold test. The wedge length, \( 2l \), was also measured at the end of the test. This was shown to be \(-4.3 \, mm\). With Young's modulus, \( E=105 \, GPa \), and Poisson's ratio assumed to be 0.3, the closure stress intensity level, \( K_{cl} \), is estimated to be \(1.8 \, MPa\sqrt{m} \) in 40Ti alloy at 750°C. Hence, the effective fatigue threshold, \( \Delta K = \Delta K_{app} - \Delta K_{cl} = 6.6 \, MPa\sqrt{m} \). This is close to the room-temperature fatigue threshold obtained for the 40Ti alloy at room-temperature. This suggests that the differences between the thresholds and near-threshold crack growth rates at 25 and 750°C are due largely to the effects of oxide-induced closure.

However, the crack growth rates in the mid-\( \Delta K \) and high \( \Delta K \) regimes were comparable to those at room-temperature where oxide-induced closure was not observed. This suggests that oxide-induced closure does not occur in mid-\( \Delta K \) and high-\( \Delta K \) regimes where the crack opening displacements are much greater than the excess oxide thickness levels. The ineffectiveness of oxide-induced closure in this regime may also be attributed partly to the limited time available for surface oxidation at mid and high-\( \Delta K \) levels.
In addition to the retarding effects of oxide-induced wedging, evidence of crack-tip blunting was observed in the crack/microstructure profiles (Figure 5.12b). This was associated with limited debonding along the grain boundaries that intersected the crack path. This is shown clearly in Figure 5.12(b). Such debonding can reduce the mode I components of the dominant crack. The debonding is also associated with the migration of oxygen into the grain boundaries. However, the extent of debonding is limited (Figure 6), and the possible shielding effects of crack-tip blunting do not appear to be significant since the elevated-temperature crack growth rates are comparable to those in the mid- and high-ΔK regimes at room-temperature where splitting was not observed to occur along grain boundaries.
Figure 5.11 Fatigue Growth Rate at Elevated Temperature for As-forged+DA Treated Nb-15Al-40Ti
Figure 5.12  Fatigue Crack Growth in The 40Ti Alloy at 750°C (a) Oxidation Debris and Striations on The Fracture Surface; (b) Crack Profile Showing Evidence of Oxide Layer and Secondary Splitting Along Intersecting Grain Boundary
Figure 5.13 Schematic Illustration of Oxidation Induced Closure.

\[
K_{el} = \frac{dE}{4(\pi t)^{1/2}(1-\mu^2)}
\]
5.5 Effect of Reinforcement Thickness on the Fatigue and Fracture Behavior of MoSi$_2$/Nb-15Al-40Ti Composites

5.5.1 Introduction

One approach to the engineering of improved oxidation resistance of Nb$_3$Al-xTi alloys is to use of an oxidation resistant coating, such as MoSi$_2$, to protect the Nb$_3$Al-xTi intermetallic. However, the oxidation problem may occur again upon cracking of the MoSi$_2$. A more realistic approach to the design of improved oxidation resistance could therefore rely on a layered arrangement of Nb$_3$Al-xTi and MoSi$_2$. The life of such a system will thus depend on the time required for progressive oxidation of the Nb$_3$Al-xTi layers, and the cracking of the MoSi$_2$ layers. Also, unlike coated Nb$_3$Al-xTi alloys, the layered Nb$_3$Al-xTi/MoSi$_2$ composites are more likely to fail progressively at elevated temperature once the integrity of the outermost oxidation resistant coating has been violated. The fatigue and fracture behavior of layered MoSi$_2$/Nb-15Al-40Ti composites will be discussed in this section.

5.5.2 Materials

The laminate-reinforced composites were prepared from MoSi$_2$ power and Nb-15Al-40Ti foils with different thicknesses. The -325 mesh (approx. 44 μm average diameter) MoSi$_2$ powder that was used in this study was procured from Cerac, Milwaukee, WI. The Nb-15Al-40Ti foils were produced by Teledyne Wah Chang (TWC), Albany, OR. The foils were obtained from triple melted ingots which were produced by multi-step
cold/hot rolling after vacuum arc casting (in a 11.4 cm diameter x 25.4 cm high mold), conventional upset forging and soaking at 1150 °C for 1.5 hours. The wrought processing sequence consisted of upsetting and squaring through five forging steps to produce a final rectangular billet with dimensions 3 cm x 24 cm x 15 cm. The forged ingot was then hot and cold rolled in Zenzeimer Mill a TWC to produce foils with different thickness as shown on Figure 5.14. The rolling steps are shown in Table 5.8.

The laminated composites were produced by hot isostatic pressing (HIPing) of MoSi2 powder and foils. The composite constituents were arranged manually in layers within evacuated (10^-4 Pa) Nb cans at McDonnell Douglas, St. Louis, MO. HIPing was conducted at ABB Autoclave, Columbus, OH, at 1400°C, under 207 MPa pressure for 4 hours. The resulting microstructures are shown in Figures 5.15a-5.15d. The layered interfacial reaction zones consist predominantly of Mo5Si3. The total interfacial reaction zone thickness was approx. 25-35 μm. All of the composites were reinforced with 20 volume percent of Nb-15Al-40Ti layers with thicknesses of 100, 500 and 1000 μm.

Evidence of extensive diffusion was observed in the composite reinforced with 100 μm thick Nb-15Al-40Ti layers. The diffusion profiles are shown in Figure (5.16a-5.16e). This shows that the diffusion distance for MoSi2 is about 50 μm in the 100 and 500 μm Nb-15Al-40Ti layer. This results in the formation of a yet unidentified phase. As a result of this phase, the Nb-15Al-40Ti layers are embrittled, especially in the case of the composites reinforced with thinner 100 μm Nb-15Al-40Ti layers. It is also possible that embrittlement may occur during processing above 1150°C. However, the reasons for the embrittlement observed after exposure to elevated-temperature above ~1150°C are yet to
be established. Finally in this section, it is also interesting to note that severe interfacial debonding and matrix cracking are also observed in the composites reinforced with 500 and 1000 μm layers of Nb-15Al-40Ti.

Figure 5.14 Photograph of Nb-15Al-40Ti Sheet Materials
<table>
<thead>
<tr>
<th>Step #</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Blast, pickle and surface condition forged ingot for hot rolling (1.17&quot;x4.1&quot;x9&quot;L)</td>
</tr>
<tr>
<td>2.</td>
<td>Preheat 45 min. at 1150°C</td>
</tr>
</tbody>
</table>
| 3.     | Hot roll (mill setting not actual thickness)  
(a) Roll to 1.0"  
(b) Roll to 0.85"  
(c) Reheat 6 min.  
(d) Roll to 0.7"  
(e) Roll to 0.62"  
(f) Reheat 6 min.  
(g) Roll to 0.55"  
(h) Roll to 0.5"  
(i) Reheat 6 min.  
(j) Roll to 0.45"  
(k) Roll to 0.40"  
(l) Reheat 5 min.  
(m) Roll to 0.35"  
(n) Roll to 0.31"  
(o) Reheat 5 min.  
(p) Roll to 0.27" (Measured size = 0.30"x10"x16"L) |
| 4.     | Blast and pickle, trim edges to square |
| 5.     | Trial roll piece of edge trim at 850°C (rolled well to 0.06" thick) |
| 6.     | Preheat 15 min. at 1000°C  
(a) Roll to 0.25"  
(b) Reheat 3 min.  
(c) Roll to 0.21"  
(d) Reheat 3 min.  
(e) Roll to 0.18"  
(f) Reheat 3 min.  
(g) Roll to 0.15"  
(h) Reheat 3 min.  
(i) Roll to 0.12"  
(j) Reheat 3 min.  
(k) Roll to 0.10" (Measured size = 0.17"x10"x26") |
| 8.     | Blast, pickle and cut edges to square off 9"x13" piece for further cold rolling |
| 9.     | Vacuum anneal 9"x13" piece for 2Hrs at 927°C |

Table 5.8 - Summary of Rolling Steps
Fig. 5.15  Microstructure of MoSi$_2$ Composites Reinforced with Nb-15Al-40Ti Laminates With Thickness of (a), (b) 100 µm layers, (c) 500 µm layers, (d) 1000 µm layers.
Figure 5.16. Diffusion Profile of MoSi$_2$/Nb-15Al-40Ti Laminated Composites. (a) Mo, (b) Si, (c) Nb, (d) Al and (e) Ti
Figure 5.16 (continued)

(c) Composition of Nb (atom %) vs. Distance from interface (μm)

(d) Composition of Al (atom %) vs. Distance from interface (μm)
Figure 5.16 (continued)

![Graph showing the composition of Ti as a function of distance from the interface. The graph compares MoSi$_2$ Matrix and Nb-15Al-40Ti Layer with different layer thicknesses: 100 μm, 500 μm, and 1000 μm. The x-axis represents distance from the interface (μm), and the y-axis represents the composition of Ti (atom %).](Image)

(e)
5.5.3. Results and Discussion

5.5.3.1 Tensile Deformation of Nb-15Al-40Ti Foils

The stress-strain curves obtained from the Nb-15Al-40Ti foils with different thicknesses are presented in Figure 5.17. The 100 µm thick foil exhibits high strength of ~1000 MPa. However, this foil fails at a relatively low plastic strain level (~2%), although catastrophic failure occurs by ductile dimpled fracture and shear lips associated presumably with plane stress components (Figure 5.18a). The 500 µm and 1000 µm thick foils both exhibit ductile behavior, as shown in Figure 5.17. However, both foils exhibit almost no hardening and lower strength levels of ~800 MPa. The 500 µm thick foil exhibits a lower plastic strain to failure of ~17% compared to the 1000 µm thick foil in which a plastic to failure of ~31% was measured. Final fracture in both of the thicker (500 and 1000 µm) foils occurred predominantly by ductile dimpled failure, as shown in Figures 5.18(b) and (c).

Fundamental reasons for the thickness dependence of the tensile properties are not well understood at present. However, it is possible to speculate that the differences are induced as a result of the differences in the stress states associated with the different foil thicknesses. Further studies are clearly needed to improve our basic understanding of the deformation mechanisms in the Nb-15Al-40Ti foils. Nevertheless, it is encouraging to note that the 500 and 1000 µm thick foils do exhibit good ductility and strength combinations.
Figure 5.17 Strain vs. Stress Curves for Nb-15Al-40Ti Foils
Figure 5.18  Typical Tensile Fracture Modes Observed in Nb-15Al-40Ti Foils
(a) 100 μm Foil; (b) 500 μm Foil and (c) 1000 μm Foil
5.5.3.2 Fracture Toughness

The composite fracture toughness data obtained from the current study are summarized in Figure 5.19. The laminated composites reinforced with the 500 µm and 1000 µm thick layers have fracture toughness levels of ~ 10 MPa√m. These toughness levels are greater than the MoSi$_2$ fracture toughness of ~ 4 MPa√m obtained from previous studies [Venkateswara-Rao et al., 1991; Soboyejo et al., 1993]. However, the fracture toughness of the layered composite reinforced with 100 µm Nb-15Al-40Ti layers was only ~ 4 MPa√m. This is consistent with the brittle behavior of the 100 µm layers discussed earlier in the previous section (Figure 5.18a). The fracture toughness levels of the composites reinforced with 500 and 1000 µm thick foils were also lower than those obtained from previous studies on layered MoSi$_2$/Nb composites in which typical fracture toughness values were between 18 and 24 MPa√m [Soboyejo et al., 1996]. The crack-tip blunting and crack bridging toughening mechanisms observed in MoSi$_2$/Nb composites are therefore more effective in toughening MoSi$_2$ than the toughening mechanisms in the composites reinforced with 500 and 1000 µm Nb-15Al-40Ti layers.

Fractographic (SEM) studies of the failure modes in the composites show that the MoSi$_2$ matrix and all the reinforcement layer exhibit brittle failure modes (Figures 5.20a-5.20d). The 40Ti foil of 100 µm was difficult to distinguish from the MoSi$_2$ matrix under SEM. As shown before in Figure 5.16, the diffusion distance was ~ 50 µm. As result of this, the whole 100 µm layer has not longer had the balance Nb-15Al-40Ti composition. Fracture of the 500 and 1000 µm layers occurs by a combination of transgranular and intergranular cleavage. The failure modes in the MoSi$_2$ matrix are consistent with previous reports of fracture modes in monolithic MoSi$_2$ and MoSi$_2$ composites at room-
temperature [Soboyejo and Sastry, 1992; Alman and Stolof, 1990]. However, the brittle fracture modes observed in the 500 and 1000 μm layers were somewhat surprising given the extensive ductility of the 500 and 1000 μm thick foils discussed earlier (Figure 5.18b-c). The loss of ductility appears to be due to the interdiffusion of constituent elements (Si and Mo diffuse mostly into the Nb-15Al-40Ti layers) during HIPing at 1400°C. This can be confirmed by examining the chemical composition profiles obtained from HIPed specimen after processing at 1400°C which induces considerable interdiffusion of the constituent elements (Figure 5.16a-5.16e). Lower processing temperatures are clearly needed to reduce the amount of interdiffusion that can occur during composite fabrication.

![Figure 5.19](image)

**Figure 5.19** Summary of Fracture Toughness of Nb-15Al-40Ti Laminate-Reinforced MoSi$_2$ Composites
Figure 5.20 Typical fracture modes in Nb-15Al-40Ti laminate reinforced composite. (a) Intergranular fracture of MoSi2 matrix; (b), (c) and (d) cleavage on the 100, 500 and 1000μm layers
5.5.3.3 Resistance Curve Behavior

Resistance curves behavior of MoSi$_2$/Nb-15Al-40Ti composites was studied on the MoSi$_2$ reinforced with 100 μm and 500 μm layer composites. Typical resistance curve obtained from this study are presented in Figure 5.21. Significant resistance to crack growth was observed in the MoSi$_2$ reinforced with 500 μm 40Ti layer. However, no resistance was observed in the one with 100 μm. Among the MoSi$_2$ composites shown in Figure 5.21, reinforced with 500 μm 40Ti layer appears to have the highest resistance. This is probably due to the high stiffness and thicker geometry of 40Ti alloy. Further study on the effect of reinforcement properties on the resistance behavior is needed by using finite element method.

![Figure 5.21 R-Curve Behavior of Laminate MoSi$_2$/Nb-15Al-40Ti Composite](image)

Figure 5.21 R-Curve Behavior of Laminate MoSi$_2$/Nb-15Al-40Ti Composite
5.5.3.4. Fatigue Crack Growth

Results obtained from fatigue crack growth studies show that stable crack growth can occur in MoSi$_2$/Nb-15Al-40Ti composites at room-temperature (Figure 5.22). Unlike monolithic MoSi$_2$, stable fatigue crack growth is observed in the MoSi$_2$ composite reinforced with 500 μm thick Nb-15Al-40Ti layers. However, no stable crack growth was observed on the one reinforced with 100 μm 40Ti layer. Typical fracture modes observed under cyclic loading were similar to those under monotonic loading. The MoSi$_2$ matrix failed by intergranular fracture and the 40Ti layer failed by cyclic cleavage as shown in Figure 5.23. The Fatigue crack growth occurs at relatively slow rates in the MoSi$_2$ matrix during near-threshold fatigue crack growth. Crack growth is also retarded as the crack-tips approach the MoSi$_2$/Nb-15Al-40Ti layer interfaces. The interactions of the propagating crack with the layer interfaces promote crack-tip shielding via debonding, crack-tip blunting and crack bridging mechanisms. The fatigue crack growth rates was faster than those in metals [Ritchie, 1979] but slower than those in other brittle materials [Dauskardt et al., 1989, 1990; Han and Suresh, 1989; Reece et al., 1989].
Figure 5.22  Fatigue Growth Rate of Nb-15Al-40Ti Laminate-Reinforced MoSi₂ Composites
Figure 5.23  Typical Fatigue Fracture Modes in Nb-15Al-40Ti Laminate-Reinforced MoSi$_2$ Composites.
CHAPTER 6

CONCLUSIONS AND SUMMARIES

6.1 MoSi$_2$ Composites

1. Ductile phase toughened Nb fiber-reinforced MoSi$_2$ composites exhibit rising elevated-temperature flexure strengths at temperatures below 1100°C. However, the strengths of the composites decrease with increasing temperature above 1100°C. Reasons for above trends are not fully understood at present. Also, the composite strengths are not predicted by constant stress/strain simple rule-of-mixtures, presumably as a result of the strong flaw sensitivity of the composites.

2. Fracture of "ductile" Nb reinforcements may occur by ductile or brittle fracture modes. Cleavage fracture is promoted by faster strain rates and cyclic loading in particulate- and fiber-reinforced composites. The incidence of ductile dimpled fracture increases with increasing fiber diameter under monotonic loading. However, Nb layers in the laminates fail by ductile dimpled fracture under monotonic loading.

3. Significant improvements in fracture toughness (100-300%) are obtained via fiber-reinforcement, and the fracture toughness values of the fiber-reinforced composites increase with increasing fiber diameter. The most significant improvements in fracture
toughness (400-500%) are obtained from laminated composites reinforced with 200 µm thick laminae.

4. Toughening in the Nb fiber- and laminate-reinforced composites occurs by crack-tip blunting and crack bridging. The toughening mechanisms are similar under monotonic and cyclic loading, and the shielding effects of individual toughening mechanisms can be estimated using existing micromechanics models.

5. Fatigue crack growth rates in composites reinforced with 750 µm diameter Nb fibers are about an order-of-magnitude faster than those in composites reinforced with the 250 µm diameter Nb fibers, and two order of magnitudes faster than those in laminated composites reinforced with 200 µm thick Nb laminae. The laminated composites have similar crack growth resistance to the particulate composites in near-threshold regime. However, crack growth rates in the composites are much faster than those in monolithic Nb. Fatigue crack growth in the composites is intermittent.

6. The interface was coarsened after annealing at 1400°C for 24 hours. The coarsened interface may promote debonding and thus affect the properties. Annealed MoSi2 composite shown lower crack growth resistance at early part of crack growth.

7. The highest fracture toughness levels were observed in the MoSi2 composite reinforced with 20 vol. Nb and 20 vol. TZ-2Y. The improved toughness was due to shielding contributions from crack bridging (~ 7.8 MPa/m), crack-tip blunting (~ 4.5 MPa/m), transformation toughening (~0.4 MPa/m) and synergistic interactions (~ 3.3 MPa/m). The predicted toughness of the synergistic toughened composite (~19.5
MPa$\sqrt{m}$) was close to the measured fracture toughness of $\sim 20.5 \pm 1.0$ MPa$\sqrt{m}$ that was obtained from the synergistically toughened composite.

8. Stable fatigue crack growth was observed in the layered MoSi$_2$/Nb composite and the synergistically toughened MoSi$_2$/Nb/TZ-2Y composite at room temperature. However, the crack growth was intermittent in nature due to crack/microstructure interactions. The occurrence of stable crack growth is attributed to the combined effects of kinematic irreversibility due to plasticity in the Nb layer and stress-induced phase transformations in the zirconia particles.

9. Stable crack growth occurs predominantly by cleavage fracture mechanisms in the MoSi$_2$ matrix and the TZ-2Y particles under monotonic and cyclic loading conditions. However, fracture of the Nb occurs predominantly by cleavage under cyclic loading conditions, and mixed ductile dimpled fracture/cleavage under monotonic loading conditions. Similar fracture modes are observed in the simple (MoSi$_2$+Nb; MoSi$_2$+TZ-2Y) and hybrid (MoSi$_2$+TZ-2Y+Nb) composites.

6.2 Nb$_3$Al-$x$Ti Intermetallics

1. The fatigue thresholds are higher in the 10Ti and 25Ti alloys. However, fatigue crack growth resistance is greater in the 40Ti alloys than in the 10Ti and 25Ti alloys. The fatigue crack growth rates of the ductile 40Ti alloys are comparable to those of mill-annealed Ti-6Al-4V.
2. Fracture in the brittle 10Ti and 25Ti alloys occurs by cleavage fracture modes under monotonic loading. Ductile dimpled tear regions (similar to those in metallic materials) are observed under monotonic loading in the stable crack growth regimes in the ductile 40Ti alloys. However, catastrophic failure of the 40Ti alloy occurs by intergranular fracture after the S&A heat treatment, or a combination of ductile dimpled fracture and secondary cracking along grain boundaries after DA heat treatment.

3. Crack tip deformation in cyclically deformed 40Ti specimens occurs by slip band formation. Fatigue crack growth in these ductile alloys occurs by the extension of cracks into these slip bands immediately ahead of the crack tip. The mechanism of crack extension is similar to the "unzipping" crack growth model proposed originally by Neumann for single crystal copper.

4. Thick oxide scales were observed within the crack profiles of fatigue crack growth specimen of the 40Ti alloys after testing at 750°C. Oxide-induced closure retards fatigue crack growth in the near-threshold regime. Since the crack opening displacements are comparable to the measured oxide thicknesses in the near-threshold regime, we attribute the slower near-threshold fatigue crack growth rates partly to the effects of oxide-induced closure. Evidence of debonding is also observed to occur along oxidized B2 grain boundaries at 750°C. However, crack-tip blunting does not appear to significantly impede fatigue crack growth rate in the 40Ti alloy at 750°C.
5. The tensile properties of Nb-15Al-40Ti foils appear to be dependent on foil thickness. However, the reasons for the thickness effect are not well understood at present, although it is possible to speculate that the thickness effects are due to differences in stress state.

6. A 100-150% improvement in fracture toughness is observed in the toughness of the MoSi$_2$/Nb-15Al-40Ti microlaminates reinforced with 500 $\mu$m and 1000 $\mu$m thick layers. However, the toughness of the composite reinforced with 100$\mu$m thick layers is close to that of MoSi$_2$. In any case, the mechanical properties (ductilities) of all the layers in the different composites appear to be degraded by interdiffusion that occur during processing at 1400°C for 4 hours.

7. Preliminary studies show that stable fatigue crack growth can occur in MoSi$_2$ composites reinforced with 500 $\mu$m thick Nb-15Al-40Ti layers. Further work is needed to determine the fatigue crack growth mechanisms in MoSi$_2$/Nb-15Al-40Ti layered composites.
CHAPTER 7

SUGGESTIONS FOR FUTURE WORK

1. The current study on the effects of reinforcement morphology was based mainly on the experimental data and analytical models. However, the possible effects of interactions between different toughening components, such as crack bridging and crack-tip blunting, are difficult to assess using analytical models. For example, finite element methods may be needed to assess the variations in the shielding levels induced by stress redistribution after bridging and blunting. Finite element methods may also be used to assess the crack driving force in the composite systems.

2. Alternative high temperature composite systems (other the MoSi$_2$ based composites) should be explored in future studies since the MoSi$_2$ composites in this study have low initiation toughness. This may involve the use of other metal/intermetallic matrices with the potential for plasticity at room-temperature. Matrix materials that promote much higher levels of transformation and synergistic toughening may also be selected for future studies. Toughening may also be enhanced by heat treatment to reduce the transformation barrier, and thus promote higher levels of transformation toughening.
3. Explore the potential use of NiAl in the development of synergistically toughened composites that are reinforced with zirconia particles and layer reinforcements. These composite can be processed at lower temperatures (~1100°C). NiAl composites may therefore provide an alternative to MoSi2 composites which have to be processed at a temperature of ~ 1400°C.

4. In situ tensile or bending tests in SEM, TEM and atomic simulation can be used to study the deformation mechanisms in niobium aluminides. The in-situ studies may provide evidence of the dislocation substructures that may lead to an understand of why the Nb-15Al-40Ti alloy is tougher than other two alloys.

5. Since the niobium aluminides are intended for intermediate temperature applications (~750°C), where creep deformation may become life limiting, it is important to study the creep deformation behavior as a function of stress and temperature. Creep crack growth mechanisms should also be investigated as a function of temperature and environment. The fundamental understanding of these mechanisms will facilitate the development of mechanistically-based life prediction models.

6. The oxidation resistance of the current generation of niobium aluminide alloys limits their possible applications to temperatures below ~ 750°C. This temperature limit may be increased by alloying or coating development. Future work may explore the effects of alloying with Cr on isothermal/cyclic oxidation behavior. In-situ coating concepts may also be developed for the formation of protective NiAl layers on niobium aluminide substrates. The isothermal and cyclic oxidation behavior of niobium aluminide alloys should also be explored along with the fatigue behavior of in-situ coated specimens.
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238


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243


