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TOUGHENING OF NICKEL ALUMINIDE (NiAl) COMPOSITES

DISSERTATION

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

By

Mingwei Li, B.S., M.S.

* * * * *

The Ohio State University
1999

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Nickel aluminide (NiAl) is a candidate material for high temperature (above 1000 °C) structural application in aerospace engine components due to its attractive properties such as high melting point (1638 °C), moderate density (5.85 g/cm³) and excellent oxidation and corrosion resistance up to 1300 - 1400 °C. However, NiAl exhibits brittle behavior with low ductility (less than 1 – 2 %) and fracture toughness (∼ 5 – 7 MPa√m) at room temperature. This makes NiAl unsuitable as a structural material. The principal objective of the current study was to improve the fracture toughness of NiAl by reinforcement with a second phase and to study the toughening mechanisms in general for brittle matrix composites. Three different kinds of reinforcement architectures were considered: NiAl composites reinforced with ductile layer (vanadium and Nb-15Al-40Ti), NiAl composites reinforced with partially stabilized zirconia (2 mole % yttria stabilized zirconia - YSZ), and hybrid NiAl composites reinforced with both YSZ and ductile phases (molybdenum particulates and vanadium layers). Ductile layers can improve the fracture toughness of brittle phase primarily by the crack bridging mechanism, while YSZ has the potential to improve the fracture toughness of the matrix through the mechanism of stress-induced transformation toughening. The effects of
thickness of two different ductile layers (vanadium and Nb-15Al-40Ti) on the resistance-curve behavior of the layered composites were studied. The results showed that steady-state toughness in these composites increases with the increasing thickness of ductile layer. Toughening analysis was performed in the framework of large-scale bridging toughening mechanisms, which provide good agreement between the experimental results and theoretical calculations. Different responses of the layered composites under monotonic loading and cyclic loading were compared. In addition to traditional analytic toughening models, finite element analysis was conducted to elucidate the crack/microstructure interactions in the layered NiAl/V composites. The resistance-curve behavior of the NiAl/YSZ composites was studied and significant toughening was achieved in these composites. The stress-induced transformation in the NiAl/YSZ composites was studied using Raman spectroscopy and the shielding contributions from transformation toughening were estimated using both dilatational and dilatational plus shear formulations. It was found the dilatational models alone usually underestimate the experimentally measured toughness increments. In the final part of the current study, synergistic toughening of NiAl composites was explored using two model hybrid toughened composites - NiAl/YSZ/Mo(p) composites and layered NiAl/YSZ/V composites. The significant improvement of initiation toughness and resistance-curve behavior was quantified using both linear superposition concepts and upper and lower bound synergistic toughening analysis. The results showed encouraging promise of engineering synergistic composites to achieve maximum toughening with optimal microstructure.
To My Parents and To My Wife
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CHAPTER 1

INTRODUCTION

1.1 BACKGROUND

There has been considerable interest in NiAl as a candidate material for high temperature applications in aerospace vehicles [1-3]. This interest has been due largely to its attractive combinations of excellent oxidation resistance, high melting point, moderate density, high specific modulus, and high thermal conductivity [1-3]. Unfortunately, however, the possible structural applications of NiAl have been limited by its low room-temperature fracture toughness (~5 - 7 MPa√m) [1-3]. This has stimulated extensive efforts aimed at toughening NiAl via intrinsic [4,5] and extrinsic [3,6-12] modification schemes.

1.2 OBJECTIVES

The principal objective of this study was to: (i) examine the effects of ductile layer reinforcements on the fracture and fatigue behavior of layered NiAl/V and NiAl/Nb-
1.3 APPROACH

Ductile phase reinforcement of brittle matrices has been shown to enhance fracture toughness of brittle materials by several mechanisms [3,6-12]. The most important mechanism is crack bridging. The fracture and fatigue 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 [3,13].

In the current study, the effects of ductile layer thickness on the resistance-curve behavior and fracture toughness were studied in NiAl composites reinforced with 20 vol.% V layers and Nb-15Al-40Ti layers. Toughening in the layered NiAl composites was analyzed using large scale bridging micromechanics models and finite element analysis (FEA).

Transformation toughening in NiAl composites reinforced with 20 vol.% YSZ transforming particles was also studied using dilatation and dilatation-shear
micromechanics models. The transformation zone size was characterized using Raman spectroscopy and the measured toughness levels were compared with theoretical predictions obtained from dilational and dilational plus shear models.

Following the studies of ductile layer toughening and transformation toughening, the possible design of synergy was explored in hybrid NiAl composites reinforced with both ductile reinforcements and transforming YSZ particles. Synergistic toughening was studied within a micromechanics framework established by Amazigo and Budiansky [14] for interacting transforming particles and bridging ductile particles. A model was also developed for the prediction of synergistic toughening due to interactions between transforming particles and ductile layer reinforcements. The predictions obtained from the models and compared with experimentally determined toughness levels.

1.4 MATERIALS SYSTEMS STUDIED

Materials systems studied include:

(i) Ductile layer toughening and effects of ductile layer thickness:
   (a) NiAl + 20 vol.% V (100 μm thick layer)
   (b) NiAl + 20 vol.% V (200 μm thick layer)
   (c) NiAl + 20 vol.% V (400 μm thick layer)
   (d) NiAl + 20 vol.% Nb-15Al-40Ti (100 μm thick layer)
   (f) NiAl + 20 vol.% Nb-15Al-40Ti (500 μm thick layer)
(g) NiAl + 20 vol.% Nb-15Al-40Ti (1000 μm thick layer)

(ii) Transformation toughening:
(a) NiAl + 20 vol.% YSZ (2 mole % yttria partially stabilized zirconia)

(iii) Synergistic toughening:
(a) NiAl + 20 vol.% YSZ + 20 vol.% Mo (particulate)
(b) NiAl + 20 vol.% YSZ + 20 vol.% V (200 μm thick layer)

1.5 ORGANIZATION OF THE THESIS

The thesis is organized into 7 chapters. Chapter 1 presents the background to the current study and outlines the objectives and the scope of the project. Chapter 2 reviews some basic fracture mechanics concepts, physical metallurgy of NiAl, and the most important toughening mechanisms for toughening of brittle materials including transformation toughening, ductile phase toughening and synergistic toughening. Materials processing and experimental details are described in Chapter 3. The effects of ductile layer (V and Nb-15Al-40Ti) toughening of NiAl, along with the toughening analysis, are discussed in Chapter 4. Results obtained for transformation toughening of NiAl are discussed in Chapter 5. Synergistic toughening concepts are explored and validated in Chapter 6, before summarizing some suggestions for future work in Chapter 7.
CHAPTER 2

LITERATURE REVIEW

2.1 FUNDAMENTALS OF FRACTURE AND FATIGUE

2.1.1 Fundamentals of Fracture

2.1.1.1 Griffith Fracture Theory

When subjected to increasing loads, solids may fracture. Modern theories of fracture find their origin in the pioneering work of Griffith [15] who formulated criteria for the unstable extension of a crack in a brittle solid in terms of a balance between changes in mechanical and surface energies.

Considering a through-thickness crack of length, 2a, located at the center of a large brittle plate of uniform thickness, B, and subjected to a constant far-field tensile stress, $\sigma$, Griffith used the stress analysis of Inglis [16] for an elliptical hole in an infinite elastic plate to derive that the net change in potential energy of the large plate to be (Figure 2.1):
\[ W_p = -\frac{\pi a^2 \sigma^2 B}{E} \quad (2.1) \]

and the surface energy for the crack shown in Figure 2.1 is given by:

\[ W_s = 4aB\gamma_s \quad (2.2) \]

where \( E' = \frac{E}{1 - \nu^2} \) for plane strain and \( E' = E \) for plane stress. Here \( E \) is the Young's modulus, \( \nu \) is the Poisson's ratio, and \( \gamma_s \) is the free surface energy per unit area.

The total system energy is then given by \( U = W_p + W_s \). Griffith noted that the critical condition for the onset of crack growth is [15]:

\[ \frac{dU}{da} = 0 \quad (2.3) \]

The resulting critical stress for fracture initiation is:

\[ \sigma_c = \sqrt{\frac{2E'\gamma_s}{\pi a}} \quad (2.4) \]
Griffith's work is limited to crack growth in the absence of plasticity. Orowan [17] modified Griffith's brittle fracture concept to metals by simply adding a plastic energy dissipation term to the surface energy term, giving the expression for critical stress as:

$$\sigma_c = \sqrt{\frac{E (2\gamma_s + \gamma_p)}{\pi a}}$$  \hspace{1cm} (2.5)

Strain energy release rate, G, first proposed by Irwin [18], is a measure of the rate of decrease of total potential energy, PE, with respect to crack length, a (per unit thickness of the crack front):

$$G = -\frac{\partial (\text{PE})}{\partial a}$$  \hspace{1cm} (2.6)

The Griffith criterion for fracture initiation in an ideally brittle solid can be rephrased in terms of G such that:

$$G = 2\gamma_s$$  \hspace{1cm} (2.7)

2.1.1.2 Linear Elastic Fracture Mechanics

There are three basic macroscopic modes of fracture (Figure 2.2). Mode I is the tensile opening mode in which the crack faces separate in a direction normal to the plane of the
crack. Mode II is the in-plane sliding mode in which the crack faces are mutually sheared in a direction normal to the crack front. Mode III is the tearing or anti-plane shear mode in which the crack faces are sheared (out of plane) parallel to the crack front.

Under conditions where the size of the plastic zone is much smaller than the length of cracks and the dimensions of the component, linear elastic fracture mechanics (LEFM) approaches can be applied. Irwin [19] quantified the near-tip fields for the linear elastic crack in terms of stress intensity factor, $K$. For plane problems, mode I stress fields in Cartesian coordinates (Figure 2.3) can be approximated as:

$$\begin{pmatrix}
\sigma_{xx} \\
\sigma_{yy} \\
\sigma_{xy}
\end{pmatrix} = \frac{K_I}{\sqrt{2\pi r}} \cos \theta \begin{bmatrix}
1 - \sin \frac{\theta}{2} \sin \frac{3\theta}{2} \\
\frac{\theta}{2} \sin \frac{3\theta}{2} \\
\frac{\theta}{2} \cos \frac{3\theta}{2}
\end{bmatrix}$$

(2.8)

where $\sigma_{xx}$, $\sigma_{yy}$, $\sigma_{xy}$, $r$, and $\theta$ are as shown in Figure 2.3, and $K_I$ is the applied stress intensity factor for mode I. Except at points very close to the crack tip, the crack-tip stress fields $\sigma_{ij} \approx \frac{1}{\sqrt{r}}$ stress singularity can be found to be true in many actual cases.

According to Equation 2.8, the stress fields of all cracks are identical, except for the scaling factor $K$. So $K$ can be used to represent the amplitude of the crack-tip fields. The stress intensity factor $K$ is generally given by the expression:
\[ K = f \left( \frac{a}{W} \right) \sigma \sqrt{\pi a} \quad (2.9) \]

where \( \sigma \) is the applied stress and \( f \left( \frac{a}{W} \right) \) is a function of the crack length, \( a \), and the width of the specimen, \( W \).

Since both \( G \) and \( K \) are measures of the crack driving force, they are related. For the general three-dimensional case involving plane strain [20]:

\[ G = \frac{(1-v^2)}{E} (K_I^2 + K_{II}^2) + \frac{(1+v)}{E} K_{III}^2 \quad (2.10) \]

and for plane stress:

\[ G = \frac{1}{E} (K_I^2 + K_{II}^2) \quad (2.11) \]

where \( K_I, K_{II}, \) and \( K_{III} \) are the stress intensity factors for mode I, mode II, and mode III, respectively.

The above linear elastic fracture mechanics parameters are applicable to crack growth under small scale yielding conditions (plastic zone size much smaller than crack length).
Elastic-plastic parameters such as the J-integral or crack-tip opening displacement may be used in cases where linear elastic fracture mechanics conditions are exceeded [20].

2.1.1.3 Fracture Toughness and Resistance Curve (R-Curve) Behavior

In linear elastic fracture mechanics, the initiation of crack advance under monotonic, quasi-static loading conditions is characterized by the critical value of the stress intensity factor, $K_c$. The value of $K_c$ is a function of the mode of loading, the chemical environment, the material microstructure, the test temperature, the stain rate, and the state of stress [20]. The critical value of the mode I stress intensity factor measured under plane strain conditions is commonly referred to as the fracture toughness, $K_{IC}$, of the material. The corresponding fracture toughness values in the sliding and tearing modes are designated as $K_{IIc}$ and $K_{IIIc}$, respectively. The standard test method for determining fracture toughness $K_{IC}$ is the ASTM E-399 standard for plane strain fracture toughness of metallic materials [21].

A resistance curve (R-curve) is a continuous record of toughness development in terms of $K$ or $J$ plotted against crack extension, $\Delta a$, in a material [21]. R-curve characterizes the resistance to stable crack growth under monotonic loading, which may result from crack/microstructure interactions when a crack intercepts a second phase in a composite. The fracture toughness value is the value of $K$ at the instability condition. This is
determined from the tangency between the R-curve and applied K curves, as shown in Figure 2.4. Applied K curves for a given configuration can be generated by assuming applied loads or stresses and calculating applied K as a function of crack length. In load control, K usually increases with crack extension and instability occurs at the maximum load, after which crack growth will become unstable and catastrophic failure will occur. The initial point on the R-curve, $K_{\text{init}}$, corresponds to the critical stress intensity factor for stable crack growth. In composite materials with second phase reinforcements, if the tip of the fatigue pre-crack in the specimen is a brittle matrix, $K_{\text{init}}$ is approximately equal to the matrix toughness. R-curve behavior is very important in determining component response since it indicates the resistance of the selected material to crack growth.

### 2.1.2 Fundamentals of Fatigue

#### 2.1.2.1 Introduction

Fatigue failure may occur as a result of crack initiation and propagation under cyclic loading conditions [20]. There are basically two different approaches to fatigue design [20]. Classical approaches to fatigue include total-life approaches involving the characterization of total fatigue life to failure as a function of the cyclic stress range (the S-N curve approach) or the strain range. In these methods, the number of stress or strain cycles necessary to induce fatigue failure in initially uncracked (and nominally smooth-
surfaced) laboratory specimens is estimated under controlled stress or strain amplitudes. The other approach is the defect-tolerant fracture mechanics approach. In this approach, the useful fatigue life is defined as the number of fatigue cycles to propagate the dominant crack from the initial size to some critical dimension. The different approaches to fatigue provide apparently different guidelines for the design of microstructural variables for optimum fatigue resistance [20].

2.1.2.2 Fatigue of Ductile Solids

Smooth, nominally defect-free specimens develop surface roughness when subjected to cyclic loading [20]. Persistent slip bands (PSB) are formed as a result of irreversibility of dislocation movement under cyclic loading. Intrusions and extrusions, developed within PSBs and the interface between PSB and matrix, eventually result in the nucleation of fatigue cracks [20].

The growth rate of a fatigue crack is expressed in terms of the crack length increment per cycle, \( da/dN \). The linear elastic fracture mechanics characterization of the rate of fatigue crack growth is based on the stress intensity factor range:

\[
\Delta K = K_{\text{max}} - K_{\text{min}}
\] (2.12)

where \( K_{\text{max}} \) and \( K_{\text{min}} \) are the maximum and minimum values, respectively.
Stable fatigue crack growth in ductile solid can be characterized by three distinct regimes [20], as shown in the schematic plot of log da/dN against log ΔK (Figure 2.5). Regime A is called the near-threshold regime and is associated with a threshold stress intensity factor range, ΔK\text{th}. Below this threshold, no crack propagation can be detected. In practice, ΔK\text{th} is typically defined as the ΔK corresponding to a crack growth rate of about 10^{-8} \text{ mm/cycle} (approximately one lattice spacing per cycle). This region corresponds to a cleavage-like growth mechanism where the crack follows preferred crystallographic directions.

Regime B (Paris Regime) is a linear regime of the plot which follows the Paris power law [20,22]:

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

(2.13)

where da/dN is the fatigue crack growth rate, C is a material constant that is often called the Paris coefficient, and m is another material constant called the Paris exponent. Typical values of m are between 2 and 4 in metallic materials [20]. However m may range between 10 and 50 in intermetallics, and between 10 and 100 in ceramics [20]. The slope of the line in the Paris regime is equal to m. Crack propagation usually proceeds by a mechanism of alternating slip and crack-tip blunting resulting in striation formation in
this regime [20]. Among several models proposed to explain the formation of fatigue striations [23, 24], an idealization of plastic blunting model by Laird [23] is widely accepted (Figure 2.6).

Regime C is called the high ΔK regime where crack growth rates increase rapidly causing catastrophic failure. Fatigue crack growth in this regime generally occurs by a combination of regime B mechanisms and static fracture modes [20]. Final fracture occurs when $K_{\text{max}}$ reaches approximately the fracture toughness, $K_{\text{IC}}$, of the material.

2.1.2.3 Fatigue of Brittle Solids

In highly brittle solids with strong covalent or ionic bonding and very little mobility of point defects and dislocations, no distinct differences are known to exist between static and cyclic loading conditions as far as the mechanisms of microscopic deformation or microcrack nucleation are concerned [20]. Crack nuclei can be introduced from microscopic Griffith flaws, atomically rough free surfaces, and microcracking during cooling from the processing temperature as a result of thermal contraction mismatch between adjacent grains or phases.

In transformation toughened ceramics, "plasticity" can be introduced by means of martensitic phase transformation under the influence of an applied stress. This phase change makes it possible for stable crack growth to occur under cyclic loading [20, 25].
Fatigue crack growth under tensile loading at room temperature is very difficult to monitor in most brittle solids. The typical Paris exponents, m, for brittle materials such as ceramics are very high. However, stable crack growth, attributable solely to cyclic variations in applied loads, can occur at room temperature in ceramics and ceramic composites under cyclic compression loading [20]. When notched plates of brittle solids are subjected to cyclic compression stress amplitude, confined microcracking occurs at the tip of the notch. If even a fraction of this microcracking deformation at the notch tip is permanent, residual tensile stresses are created within the microcrack zone upon unloading from the maximum far-field compression stress [20]. Fatigue pre-cracks sometimes can only be introduced in brittle materials under cyclic compression, prior to fracture toughness, R-curve, or fatigue crack growth tests.

2.2 PROPERTIES OF NiAl

2.2.1 Microstructure and Physical Properties

In the Ni-Al binary equilibrium phase diagram (Figure 2.7) [26], NiAl exhibits a wide single phase field, and the stoichiometric composition melts at 1911 K. NiAl has the ordered B2 (CsCl prototype) crystal structure, which consists of two interpenetrating primitive cubic cells (Figure 2.8). The lattice constant of the stoichiometric composition at room temperature (RT) is 0.28870±0.00001 nm [2]. The density of stoichiometric
NiAl at RT is 5.85 g/cm$^3$ [2]. Thermal conductivity of NiAl single crystal is 70 - 80 W/m·K, which is eight times larger than that of Ni-base superalloys [2]. Linear thermal expansion coefficient is $\sim 15.1 \times 10^{-6}$ K$^{-1}$ from 550 to 1290 K for stoichiometric NiAl [2]. Young's modulus, $E$, and Poisson's ratio, $\nu$, from RT to 1400 K are given by [2]:

$$E = 199.8 - 0.040(T)$$ \hfill (2.14a)

$$\nu = 0.307 + 2.15 \times 10^{-5}(T)$$ \hfill (2.14b)

where $E$ is in GPa and $T$ is in K.

2.2.2 Mechanical Properties and Deformation Behavior

2.2.2.1 Slip Systems, Ductility and Yield Strength

Operative slip systems observed in uniaxially deformed NiAl are listed in Table 2.1. Deformation behavior of NiAl single crystals strongly depends on crystal orientation [27]. Remarkably different behavior is observed between crystals tested along the <100> or "hard" orientation, and those tested along other non-<100> directions or "soft" orientations [1-3,28]. Yielding in the "hard" orientation at room temperature occurs at a stress that is several times higher than those in the "soft" orientations [1,2,28]. The dominant slip vector is <100> for "soft" orientations and a combination of <111>, <110>
and <100>, depending on temperatures, for "hard" orientation, as shown in Table 2.1.

Deformation in polycrystalline NiAl at low temperatures occurs mainly by <100>{011} type slip. As a consequence, only three independent slip systems are available for deformation [29,30], which is less than the five independent deformation modes considered necessary for extensive, uniform, and crack-free deformation of a polycrystalline material [29,30]. Thus, polycrystalline NiAl exhibits poor room-temperature ductility, ranging from zero to a maximum of 3 percent [1,3]. Due to insufficient slip systems, microcracks form at the grain boundaries arising from strain incompatibility and result in intergranular fracture [4].

NiAl is also brittle in single crystal form. Only 0.5 to 2.5 percent tensile ductility is generally observed below about 475 K in "soft" crystals and zero ductility up to approximately 600 K in stoichiometric NiAl of "hard" orientation [3]. The potential factors limiting ductility in single crystals may include insufficient dislocation sources, limited number of potential slip systems, low dislocation mobility, inhomogeneous slip, and low fracture stress [2,3].

NiAl undergoes a dramatic brittle-to-ductile transition (BDT) and increase in the ductility and fracture toughness in the intermediate temperature range of 550 - 700 K [1,2]. The BDT is thought to be due to the onset of localized diffusive processes such as dislocation climb in NiAl [4]. A combination of both glide and climb of <100> dislocations results
in the five independent slip systems required for bulk plastic deformation of polycrystalline NiAl [31].

The reported yield strength values for polycrystalline NiAl exhibit a remarkable variation. Some typical results are shown in Figure 2.9. The yield strength of NiAl decreases with increasing temperature. Deviation from stoichiometry results in an increase in both hardness and yield strength [1,2]. Stoichiometric and Ni-rich NiAl follow the Hall-Petch relationship [2,32]:

\[ \sigma_y = \sigma_0 + k_y d^{-1/2} \]  

(2.15)

where \( \sigma_y \) is the yield strength, \( \sigma_0 \) a measure of the lattice frictional stress, \( k_y \) a dislocation unpinning parameter, and \( d \) the mean grain diameter.

2.2.2.2 Fracture and Fatigue Behavior

The fracture mode observed in binary, polycrystalline NiAl is primarily intergranular at room temperature (RT) [1,2]. A transition to transgranular cleavage is reported at higher temperatures above 673 K [2,33,34]. The fracture toughness values (\( K_{IC} \)) of NiAl have been determined to be 4 - 7 MPa\( \sqrt{\text{m}} \) at RT for a wide range of grain sizes [2]. In BDT temperature range, the fracture toughness of NiAl approaches 20 to 50 MPa\( \sqrt{\text{m}} \) [2].
Few studies have been carried out to investigate the fatigue behavior of NiAl at RT and elevated temperatures [35,36]. An important conclusion that emerges from these studies is that monolithic, polycrystalline NiAl does not exhibit stable fatigue crack growth at RT. Once a crack of critical size nucleates at a pre-existing defect, final failure occurs rapidly. Thus the fatigue life of NiAl at RT is essentially the number of cycles required to nucleate a critical crack. At temperatures above BDT temperature, additional mechanisms of deformation, such as localized diffusion, allow for stable crack growth prior to the onset of catastrophic failure.

2.3 TOUGHENING MECHANISMS

2.3.1 Introduction

Two approaches have been explored in efforts to improve the room-temperature fracture toughness and ductility of polycrystalline NiAl. One is intrinsic toughening in which NiAl is alloyed with ternary elements (such as B and Zr) to improve grain boundary strength and activate additional slip systems [4,5]. Although intergranular fracture is suppressed and the yield strength is improved by such alloying additions, the fracture toughness and ductility is not improved due to solid-solution strengthening effects. Also, slip is not observed to occur on additional systems. The other approach is extrinsic toughening (composite approach) by the reinforcement of NiAl with brittle [37,38] or
ductile [6-12,38,39] second phases. This approach has been shown to improve the fracture toughness of NiAl composites by a variety of mechanisms that include crack bridging [6-12], crack trapping [38,39] and transformation toughening [40-43]. The relevant toughening mechanisms will be discussed in the next section.

2.3.2 Transformation Toughening

2.3.2.1 Introduction

Some researchers have attempted to improve the fracture toughness of NiAl composites by reinforcement with brittle ceramic $\text{Al}_2\text{O}_3$ whiskers or fiber reinforcements that tend to promote crack-tip shielding via crack bridging [37,38]. However, the toughening levels achieved via such reinforcements have been limited. In contrast, significant toughening levels have been achieved via transformation toughening with partially stabilized zirconia particles [40-43]. These promote toughening via tetragonal-to-monoclinic martensitic phase transformations that give rise to dilatation ($\sim$4 %) and shear ($\sim$16 % or less). The stress-induced phase transformation will be discussed in this section along with the common toughening models for the estimation of toughening increments due to stress-induced martensitic phase transformations.
2.3.2.2 Transformation Toughening with Partially Stabilized Zirconia (PSZ)

2.3.2.2.1 Tetragonal-to-Monoclinic Phase Transformation

Pure zirconia ($\text{ZrO}_2$) exists in three polymorphs: monoclinic (m), tetragonal (t), and cubic (c) [44]. At room temperature, pure zirconia has a monoclinic structure. At about 1150 °C, this structure transforms to the tetragonal structure. From above ~2350 °C to the melting point of 2650 °C, the cubic structure is stable.

The tetragonal crystal structure of zirconia can be retained at room temperature under certain conditions, provided the crystallite size is less than a critical value, which is of the order of a fraction of 1 μm [44-47]. The addition of some metal oxide solutes such as $\text{Y}_2\text{O}_3$, CaO, MgO, and CeO to zirconia stabilizes the tetragonal phase at lower temperatures. The stabilization is promoted by the reduction of the chemical driving force for the transformation from tetragonal to monoclinic phase. It is also clear from the equilibrium phase diagram for the ZrO$_2$-$\text{Y}_2\text{O}_3$ system (near the ZrO$_2$ rich end) that the temperature required for the tetragonal-to-monoclinic transformation decreases as the $\text{Y}_2\text{O}_3$ content increases (Figure 2.10) [48].

The metastable tetragonal phase can transform to monoclinic phase under an applied stress [44-55]. It has been discovered that this stress-induced martensitic transformation,
associated with a volume increase of approximately 3 - 5% (due to the lower density of
the monoclinic phase), can greatly enhance the fracture toughness of zirconia-containing
ceramics [44-47,49-55]. A transformation zone is created as a crack propagates through
a matrix reinforced with transforming particles, and a shielding stress is exerted on the
crack (Figure 2.11a). This reduces the local stress intensity level at the crack tip, and thus
improves the fracture toughness of the material, as shown in Figure 2.11c.

Lange [46] considered the thermodynamics of the constrained tetragonal-to-monoclinic
transformation. The free energy change associated with the transformation is:

\[
\Delta G_{\text{t} \rightarrow \text{m}} = \Delta G_c + \Delta U_{\text{se}} + \Delta U_s + \Delta U_{\text{mt}}
\]  

(2.16)

where \( \Delta G_c \) is the chemical free energy for the transformation from tetragonal to
monoclinic phase, \( \Delta U_{\text{se}} \) is the strain energy change, \( \Delta U_s \) is the change in energy
associated with the surface of inclusion particles, and \( \Delta U_{\text{mt}} \) is the additional surface
energy due to microcracking and twinning. Considering the case in which both
microcracking and twinning accompany the transformation, and by setting \( \Delta G_{\text{t} \rightarrow \text{m}} \) to
zero, Lange [46] obtained the following expression for the critical particle size, \( D_c \), for
the transformation:

\[
D_c = \frac{6(\gamma_C g_C + \gamma_T g_T + \gamma_m g_s) - g_s \gamma_t}{\Delta G_c - \Delta U_{\text{se}} f_C f_T}
\]  

(2.17)
where \( \gamma_m \), \( \gamma_t \), \( \gamma_C \), and \( \gamma_T \) are the specific surface free energies of the monoclinic phase, the tetragonal phase, the microcrack, and the twin boundary, respectively, \( g_C \) and \( g_T \) are numerical values that represent the area of the microcrack and twin boundary normalized with respect to the surface area of the particle, \( g_s = A_s/A_m \), where \( A_m \) and \( A_t \) are the surface areas of the product and parent phases, respectively, and \((1-f_C)\) and \((1-f_T)\) are the fractions of the constraint that are relieved due to microcracking and twinning, respectively. For the inclusion size (or grain size) less than \( D_C \), the energy increase due to the creation of new surfaces and the increase in strain energy prevent the transformation from occurring [46]. This analysis ignores kinetic nucleation barriers. Also, it essentially determines the condition where the tetragonal zirconia is energetically stable rather than being metastable with respect to monoclinic state.

2.3.2.2.2 Toughening due to Tetragonal-to-Monoclinic Phase Transformation

The degree of crack-tip shielding is related to the transformation zone size and the volume fraction of transforming particles. The transformation zone size associated with a mode I crack under small-scale transformation conditions has been studied [56,57]. Assuming that the transformation occurs when the mean stress level at the crack tip exceeds a critical stress value, \( \sigma_c^T \), Budiansky et al. [57] have derived the following equation for the size of the transformation zone for dilatational transformations (for an idealized case in which all the particles within the transformation zone are transformed):
\[ h = \frac{\sqrt{3}(1+\nu)^2}{12\pi} \left( \frac{K}{\sigma^T_c} \right)^2 \]  

(2.18)

where \( h \) is the half-height of the transformation wake (\( r_0 \) in Figure 2.11a), \( K \) is the far-field stress intensity factor, and \( \nu \) is the Poisson's ratio. The toughening due to the transformation can be expressed as \([56,57]\):

\[ \Delta K_t = \frac{0.22E_c\varepsilon^T\sqrt{h}}{1-\nu} \]  

(2.19)

where \( E_c \) is the elastic modulus of the composite, \( f \) is the volume fraction of transformed particles, \( \varepsilon^T \) is the transformation volume dilatational strain, which for the case of the tetragonal-to-monoclinic transformation in zirconia is approximately 0.04. This model assumes that the volume fraction of the transformed phase to be constant with the distance from the crack face, \( x \). However, in reality, the actual volume fraction of transformed phase varies with the distance from the crack face \([55,58,59]\). Equation 2.19 can, therefore, be expressed in integral form to account for the variation in the degree of transformation with the distance from the crack face \([55]\):

\[ \Delta K_t = \frac{0.22E_c\varepsilon^T}{1-\nu} \int_0^h \frac{f(x)}{2\sqrt{x}} \, dx \]  

(2.20)
where $f(x)$ is a function of $x$ that represents the fraction of transformed zirconia.

Although the purely dilatant transformation formulations [55-57] are convenient for modeling the deformation and fracture behavior, the neglect of shear effects may lead to a great underestimation of the actual toughness enhancement due to phase transformation [55,60-65]. Shear-induced phase transformations have been demonstrated by Chen and co-workers [61,62] in MgO-stabilized and CeO-stabilized zirconia. Budiansky and Truskinovsky [63], Simha and Truskinovsky [64] and Stam and van der Giessen [65] have also modeled the effects of shear of the transformation toughening of zirconia ceramics. However, with the exception of prior work by Chen and co-workers [61,62], there are no reported combined experimental and theoretical studies that explore the role of dilatation and shear in toughening of transformation toughened brittle matrix composites that do not have partially stabilized zirconia matrices.

The critical transformation stress necessary to achieve the transformation can be expressed as a function of the total Gibbs free energy associated with the transformation from tetragonal to monoclinic phase. This may be estimated from [54,66]:

$$\sigma_c^T = \frac{\Delta G}{\varepsilon_T}$$

(2.21)

where $\sigma_c^T$ is the critical stress and $\Delta G$ is the Gibbs free energy of the transformation.
The above expression does not account for the potential mean stresses due to the thermal expansion mismatch between matrix and PSZ particles after processing. Depending on the thermal expansion coefficients, the zirconia particles may be subjected to either mean tension or compression. The hydrostatic stress is given by [54]:

\[ \sigma_h = (\alpha_p - \alpha_m) \Delta T \left[ \frac{1 + \nu_m}{2E_m} + \frac{1 - 2\nu_p}{E_p} \right]^{-1} \]  

(2.22)

where \( \alpha \) is the linear thermal expansion coefficient, \( \nu \) is the Poisson's ratio, \( \Delta T \) is the difference between processing temperature and testing temperature, and the subscripts "m" and "p" denote matrix and particles, respectively. The total radial residual stress is given by [54]:

\[ \sigma_r = \sigma_h \left[ 1 + \frac{3V_f}{[(4\pi)^{1/3} - (3V_f)^{1/3}]^3} \right] \]  

(2.23)

where \( V_f \) is the volume fraction of second phase. If the hydrostatic stress is compressive, the far-field tensile stress necessary for transformation will increase. On the contrary, the existence of tensile hydrostatic stress will trigger the transformation at a lower applied tensile stress. As a result of this, the required applied stress, \( \sigma_a \), to induce the transformation of zirconia particles is modified by the radial residual stress [54]:

26
2.3.2.2.3. Characterization of Tetragonal-to-Monoclinic Phase Transformation

The conventional techniques to characterize the tetragonal-to-monoclinic transformation have been transmission electron microscopy (TEM) [67,68] and X-ray diffraction (XRD) [41,69]. XRD patterns of the tetragonal, monoclinic, and cubic phases are distinct. However, the size of transformation zone is generally too small for XRD characterization, and usually too large for TEM examination.

Raman microscope spectroscopy has therefore been used to determine the transformation zone size [43,58,59]. The high spatial resolution (~1 μm) of the technique, together with the fact that it can be used in conjunction with an optical microscope, makes it possible to identify the region of interest and to characterize the structure of that particular region, if it is Raman active. In the case of the polymorphs of zirconia which are all Raman active, the concentrations of the interested phase can be determined in a mixture of phases with an accuracy of a few volume percent, through external calibration.

During Raman spectroscopy, incident light is scattered by the molecules when it interacts with matter [70]. Incoherent scattering occurs when some fraction of the scattered light shows a constant shift in frequency from that of the incident beam. This change in

\[ \sigma_a = \sigma_c - \sigma_r \]  

(2.24)
frequency or wavelength (between the incident and scattered radiation) is referred to as the Raman shift, which is a characteristic of the material structure. Typically, a laser is used as the light source of a Raman spectroscopy system since it provides an intense, monochromatic source of illumination [70].

The Raman spectra of the tetragonal and monoclinic polymorphs of zirconia have been established [58], as shown in Figure 2.12. Clarke and Adar [58] used a calibration procedure based on X-ray diffraction intensity measurements to arrive at an empirical expression for the monoclinic phase concentration, \( c_m \), by measuring the Raman monoclinic and tetragonal peak intensities. \( c_m \) is expressed as [58]:

\[
c_m = \frac{I_{181}^{m} + I_{192}^{m}}{0.97(I_{148}^{t} + I_{264}^{t}) + I_{181}^{m} + I_{192}^{m}}
\]

(2.25)

where \( I \) is the integrated intensity, the superscripts refer to the Raman shift of the peaks (in cm\(^{-1}\)), and the subscripts m and t refer to the monoclinic and tetragonal phases, respectively. The variation of monoclinic phase content with distance from the crack face in the region surrounding the crack can be determined according to the above equation. It is then possible to estimate the size and shape of the transformation zone.

Optical interference microscopy has been suggested as another method to estimate the transformation zone size [71]. The height of the transformation zone can be determined
by identifying the points where the parallel interference fringe lines begin to deviate from linearity. The deviation is caused by topographical changes within the transformation zone, where a volume increase of the transformed particles occurs as a result of stress-induced martensitic transformation from tetragonal to monoclinic phase.

2.3.2.3 Transformation Toughening of NiAl

Transformation toughening of NiAl have been studied by Barinov et al. [40-42], who showed that the fracture toughness of NiAl can be improved from a matrix toughness of ~ 15 MPa√m to a toughness of ~ 25 MPa√m after reinforcement with PSZ particles. They argued that the fracture toughness increment was due to transformation toughening on the basis of XRD analysis of the fracture surfaces and residual stress analysis. However, they did not conduct Raman spectroscopy and crack-tip TEM studies to demonstrate conclusively the occurrence of the stress-induced phase transformation. Also, the NiAl matrix toughness was anomalously high (~ 15 MPa√m compared with typical values of ~ 4 - 7 MPa√m [1-3,39,43,72]) in their studies.

Ramasundaram et al. [43] studied NiAl composites reinforced with PSZ particles with different Y$_2$O$_3$ stabilization levels between 0 and 6 mole percent. They found significant toughness improvement (from a matrix value of 5.3 MPa√m to a maximum of 14.1 MPa√m), especially in the NiAl/TZ-2Y (2 mole % Y$_2$O$_3$) composite. They also used
Raman spectroscopy and TEM analysis to verify and quantify the occurrence of transformation toughening in the NiAl/TZ-2Y composite. The degree of transformation toughening was estimated using Raman spectroscopy measurements (of the spatial variation of the monoclinic phase content within the transformation zone) and micromechanics models (Equation 2.19). Transformation toughening was not detected in composites reinforced with unstabilized zirconia (no Y₂O₃), and PSZ containing 4 and 6 mole % Y₂O₃.

2.3.3 Ductile Phase Toughening

2.3.3.1 Introduction

Ductile phase reinforcements have been used to improve the fracture toughness and ductility of brittle materials including NiAl. Ductile phases have the potential to improve the fracture toughness of brittle matrices through mechanisms such as crack bridging, crack-tip blunting, crack deflection, and crack trapping [3,6,11,13,73-77]. In addition, the ductility of the matrix can be improved by promoting slip transfer processes from the ductile reinforcements to the brittle matrix [11,78]. The fracture and fatigue properties of the ductile phase reinforced composites are determined by the mechanical properties, morphology, and volume fraction of the reinforcement phase, and by the nature of interface between the matrix and the reinforcement [73-77].
2.3.3.2 Crack Bridging

The most important mechanism for ductile phase toughening is crack bridging, especially in composites reinforced with continuous ductile ligaments. During crack bridging (Figure 2.13a), a crack is intercepted by the ductile reinforcements. If the interface between the matrix and reinforcement is moderately strong, limited debonding may occur along the interface as the ductile reinforcements undergo plastic stretching, making further crack opening more difficult [3]. This will reduce the stress intensity at the crack tip and thus enhance the fracture toughness of the composite [79,80]. The reduction in stress intensity factor is caused by a distribution $\sigma(x)$ of closure stresses that are applied behind the crack tip and a steady-state bridging length, $L$. For small scale crack bridging, in which the bridging length is small relative to crack length, specimen dimensions, and the distance from the crack to the specimen boundaries, the toughening may be estimated from [81]:

$$\Delta K_{br} = \sqrt{\frac{2}{\pi}} V_f \int_0^L \frac{\sigma(x)}{\sqrt{x}} \, dx$$

(2.26)

where $V_f$ is the volume fraction of ductile reinforcements. When the normal stress supported by the bridging ligaments is assumed to be constant (equal to the yield strength of the particle, $\sigma_y$), the toughness increment due to crack bridging is given by:
\[ \Delta K_{br} = K - K_m = 2 \sqrt{\frac{2}{\pi}} V_f \sigma_y \sqrt{L} \]  \hspace{1cm} (2.27)

and the toughening ratio for crack bridging, \( \lambda_{br} \), is given by:

\[ \lambda_{br} = \frac{K}{K_m} = 1 + 2 \sqrt{\frac{2}{\pi}} \frac{V_f \sigma_y \sqrt{L}}{K_m} \]  \hspace{1cm} (2.28)

where \( K \) is the applied stress intensity factor and \( K_m \) is the matrix fracture toughness.

The ductile ligaments remain intact for a certain distance behind the crack tip and the length of the cracked surface which is bridged by the ductile phase is called the bridging zone. Toughening by this mechanism is enhanced if the ductile phase exhibits high strength and a large strain hardening exponent, and thus deforms uniformly instead necking easily [3]. The crack bridging effect is even greater if the reinforcement is continuous in nature. This is because the crack front is forced to intercept the ductile phase, which experiences extensive plastic strains in the region just behind the crack tip [82]. Growth of the bridging zone with crack extension results in resistance curve behavior [6,80,83,84]. Once the bridging ligaments furthest from the crack tip fracture or completely pull-out, the bridging zone reaches a steady-state value. Consequently, the resistance curve reaches a saturation level (Figure 2.14a).
Budiansky et al. [79] have modeled the toughening due to small scale crack bridging. They idealized the crack-bridging particles as elastic, elastic-perfectly plastic, or rigid-perfectly plastic springs that connect the bridged crack surfaces (Figure 2.15). The springs are assumed to break when the extension exceeds a critical crack opening displacement. Based on these assumptions, the modified toughening ratio due to crack bridging for the rigid-perfectly plastic case is:

\[
\Lambda_{br} = \frac{\lambda_{br}}{\sqrt{\omega(1-V_f)}} = \frac{K}{K_m \sqrt{\omega(1-V_f)}} = \left[1 + \frac{2V_f}{1-V_f} \frac{E_m \sigma_y \nu_p}{K_m^2 (1-V_m^2)} \right]^{1/2} \quad (2.29a)
\]

with

\[
\omega = \frac{E(1-v_m^2)}{E_m(1-v^2)} \quad (2.29b)
\]

where \(E\) and \(E_m\) are the Young's moduli of the composite and matrix, respectively, \(v\) and \(v_m\) are the Poisson's ratio of the composite and matrix, respectively, and \(\nu_p\) is the crack-face displacement at fracture. The relation between modified toughening ratio and bridging length is given by modifying Equation 2.27:

\[
\Lambda_{br} = 1 + \frac{V_f \sigma_y}{K_m} \sqrt{\frac{8L}{\pi \omega (1-V_f)}} \quad (2.30)
\]
The above two-dimensional model is quite general and of practical applications, but it does not take into account the effect of the crack front bowing between second phase particles.

Alternatively, crack bridging toughening may be explained using an energy approach, which attributes the toughening effect to the energy dissipation due to the plastic deformation of the constrained ductile ligaments [85-87]. The increase in fracture energy of the composite is given by [85]:

$$\Delta G_c = V_f \int_0^{u^*} \sigma(u) du$$  \hspace{1cm} (2.31)

where $u$ is the crack opening, $u^*$ is the crack opening at the point when the ductile material fails, as shown in Figure 2.16, $\sigma(u)$ is the nominal stress on the bridging ligament, and $V_f$ is the area fraction of reinforcements on the crack plane. Equation 2.31 indicates that the toughening depends on the stress-displacement function of constrained ductile ligament, $\sigma(u)$, which depends on the extent of decohesion at the matrix/reinforcement interface, properties and size of the ductile phase. Based on the observed stress-displacement relations, Equation 2.31 can be rewritten as [85]:

$$\Delta G_c = CV_f \sigma_0 a_0$$  \hspace{1cm} (2.32)
where \( \sigma_0 \) and \( a_0 \) are the unconstrained yield strength and representative cross-sectional radius of the ductile phase, respectively, and \( C \) is a dimensionless function representing the work of rupture, which is defined as:

\[
C = \int_0^u \frac{\sigma(u) du}{\sigma_0 a_0}
\]  

(2.33)

Depending on the degree of constraint, \( C \) varies from 1.6 for complete bonding to 6.0 for limited debonding [85]. It can be seen that the nature of the interface between the matrix and the reinforcement is an important variable since a limited amount of debonding promotes crack bridging, while excessive debonding results in a loss of strength. Based on Equation 2.32, the corresponding steady-state toughness, \( K_{ssb} \), is [88]:

\[
K_{ssb} = \sqrt{K_m^2 + E' CV_f \sigma_0 a_0}
\]  

(2.34)

where \( E' = \frac{E}{1 - v^2} \) for plane strain and \( E' = E \) for plane stress. Here \( E \) is the Young’s modulus and \( v \) the Poisson’s ratio of the ductile phase.

In the case of fiber or layer reinforced composites, the bridging zone length may be large compared with the crack length and specimen dimensions. Under such conditions, a continuously rising resistance curve may result due to the so-called large-scale bridging.
effects [84,88,89] (Figure 2.14b). Zok and Horn [84] have developed models for the estimation of the shielding due to large-scale crack bridging by taking into account the finite specimen dimensions. Odette et al. [88] have also developed a large-scale bridging model based on an independent evaluation of the fundamental composite properties that include stress-displacement function $\sigma(u)$, initiation toughness, and elastic constants. The large-scale bridging models by Zok and Horn [84] and Odette et al. [88] are generally in good agreement with experimental observations [84,88]. More rigorous self-consistent models have also been developed in recent years by Cox and Lo [89]. However, these large-scale bridging models generally require iterative methods/algorithms that may have convergence problems associated with them.

A simpler large-scale bridging model was proposed by Bloyer et al. [90-92] for ductile layer reinforced composites. This model utilizes weight functions by Fett and Munz [93], in the estimation of the weighted distributions of bridging traction across the individual reinforcements (Figure 2.17). The shielding due to large-scale bridging, $\Delta K_{lsb}$, may thus be expressed as:

$$\Delta K_{lsb} = \int_{L} \alpha \sigma(x) h(a, x) dx$$  \hspace{1cm} (2.35)

where $L$ is the length of the bridge zone, $\alpha$ a constraint/triaxiality factor, $\mathcal{H}(x)$ a traction function along the bridge zone, and $h(a, x)$ a weight function by Fett and Munz [93]:

36
where \( a \) is the crack length and \( W \) is the specimen width. The coefficients, \( A_{\nu\mu} \), are given in Table 2.2 for a single edge notched bend (SENB) specimen. The toughening may now be estimated by a simple application of the principle of linear superposition. This gives the following expression for the estimation of the stress intensity factors:

\[
K = K_i + \Delta K_{lsb}
\]

where \( K_i \) is the initiation toughness required for renucleation ahead of the first ductile layer encountered by the propagating crack, and \( \Delta K_{lsb} \) is given by Equation 2.35 for large-scale bridging.

2.3.3.3 Crack-Tip Blunting

Crack-tip blunting (Figure 2.13b) occurs when a crack propagating in a brittle matrix is impeded as it intersects a ductile phase. Through extensive localized plastic deformation of the second phase, the stresses at the crack tip are relaxed and thus the crack tip is blunted. The driving force for crack growth is thus reduced.
Chan [94] developed a micromechanics model to estimate the toughening due to crack-tip blunting in an α2-based Ti-24Al-11Nb alloy where the β phase is ductile and continuous. He assumed that fracture occurs when the strain at a characteristic distance ahead of the crack tip exceeds a critical value. In his model, he postulated that the near-tip effective strain distribution in the matrix and composite could both be described by Hutchinson-Rice-Rosengren (HRR) field expressions given below [95,96]:

\[
\bar{\varepsilon} = \alpha \varepsilon_y \left[ \frac{J}{\alpha \varepsilon_y \sigma_y I_n r} \right]^{n+1} \bar{\varepsilon}(\theta, n) \tag{2.38}
\]

where \( \varepsilon_y \) and \( \sigma_y \) represent yield strain and stress, respectively, \( J \) is the path independent parameter (J integral) that varies with the applied load, crack length, and the geometry of the specimen, \( I_n \) is a numerical constant that depends on the stress relation of the material, \( \bar{\varepsilon}(\theta, n) \) is also a numerical constant related to the angle away from the crack plane, \( \theta \), at a particular \( n \) value, \( \alpha \) and \( n \) are constants in the Ramberg-Osgood stress-strain relation which is given by:

\[
\frac{\varepsilon}{\varepsilon_y} = \frac{\sigma}{\sigma_y} + \alpha \left[ \frac{\sigma}{\sigma_y} \right]^n \tag{2.39}
\]
where \( n \) is the inverse of the strain hardening exponent, \( N \), and \( \alpha \) is a material constant.

By assuming that the stress-strain behavior is the same in both the matrix and composite, the toughening ratio due to crack-tip blunting, which is defined as the ratio of the applied stress intensity factor to the stress intensity factor in the matrix, can be expressed as:

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

(2.40a)

with

\[
\Sigma = \frac{\sigma_d^y}{\sigma_m^y}
\]

(2.40b)

and

\[
\Gamma = \frac{\varepsilon_d^f}{\varepsilon_m^f}
\]

(2.40c)

where \( \varepsilon^f \) is the fracture strain, \( V_f \) is the volume fraction of reinforcement, \( E \) is the elastic modulus, and subscripts m, d, and c denote matrix, ductile reinforcement, and composite, respectively.
Due to the brittle nature of the matrix, the assumption that HRR field can be used to describe the near-tip strain field in both the composite and the matrix may not be fully valid. Soboyejo et al. [76] modified Chan's model by describing the stress distribution in the matrix with an elastic crack-tip stress field. The near-tip strain field in the matrix can be expressed as:

$$\epsilon_m = \frac{K_m}{E_m} \frac{1}{\sqrt{2\pi r}} \epsilon_m(\theta)$$

(2.41)

Hence, the blunting toughening ratio in this case is given by:

$$\lambda_{bl} = \frac{E_c}{E_m} \left( \frac{\epsilon_f}{\epsilon_m} \right)^{\frac{n+1}{2n}} \left( \frac{\epsilon_f'}{\epsilon_m} \right)^{\frac{n-1}{2n}}$$

(2.42)

The toughening ratio estimates obtained from the modified crack-tip blunting model are slightly higher than those predicted by Chan's model [76]. The most representative toughening ratios are likely to be in between those predicted by these two models [76].

2.3.3.4 Crack Deflection

Any second phase that exhibits a weak bond with the matrix has the potential to increase the fracture toughness of the system through crack deflection processes (Figure 2.13c).
The crack is redirected during the deflection process and the stress intensity factor at the crack tip becomes reduced [97]. 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. For pure deflection of a mode I two-dimensional crack by a deflection angle, $\phi$, $K_I$ and $K_{II}$ are given by [97]:

$$K_I = \cos^3\left(\frac{\phi}{2}\right)K_\infty$$  \hspace{1cm} (2.43)

and

$$K_{II} = \sin\left(\frac{\phi}{2}\right)\cos^2\left(\frac{\phi}{2}\right)K_\infty$$  \hspace{1cm} (2.44)

where $K_\infty$ is the applied stress intensity factor. The effective stress intensity factor, $K$, is:

$$K = \sqrt{K_I^2 + K_{II}^2} = \cos^2\left(\frac{\phi}{2}\right)K_\infty$$  \hspace{1cm} (2.45)

The toughening ratio due to deflection is therefore given by:

$$\lambda_d = \frac{K_\infty}{K} = \frac{1}{\cos^2\left(\frac{\phi}{2}\right)}$$  \hspace{1cm} (2.46)
It is important to note here that the above two-dimensional analysis indicates that only large angles of deflection will result in significant improvements in fracture toughness.

Faber and Evans [98,99] used a fracture mechanics approach to predict the fracture toughness increase due to crack deflection by tilting and twisting around second phase particles. The variables found to be important in determining the toughness increase include the volume fraction of second phases, the particle morphology and aspect ratio, and the distribution of particle spacing. They showed that deflection toughening is most effective for reinforcements with large aspect ratios (i.e. rod shaped or whisker reinforcements).

2.3.3.5 Crack Trapping

Crack trapping (Figure 13d) can occur in particulate or fiber reinforced composites, when crack front reaches reinforcements of higher toughness and are pinned at these locations [6,7,86]. The remainder of the crack front continues to propagate and bows out, causing the stress intensity factor to be larger at the pinned points. The crack can then cut through the reinforcements when the stress intensity factor at those points exceeds the fracture toughness of the reinforcements. For this case, the toughening ratio due to crack trapping was expressed by Bower and Ortiz [100] to be:

42
where $K_\infty$ is the applied stress intensity factor, $K_m$ is the fracture toughness of the matrix, $K_p$ is the toughness of reinforcements, $R$ the radius and $L$ the spacing of the reinforcements. Although the nature of crack trapping is quite complex, this three-dimensional model [100] provides a simple formulation to estimate the toughening due to crack trapping.

2.3.3.6 Ductile Phase Toughening of NiAl

The fracture toughness of brittle intermetallics can be improved significantly by the incorporation of ductile phase reinforcements [72-80,82-94,101,102]. Previous studies [13,39,72,90-92] have shown that ductile particulate and fiber reinforced intermetallic composites have lower fracture toughness levels than those with ductile layer reinforcements of the same volume fractions. The higher fracture toughness levels in the layered composites (compared with those in the particulate and fiber reinforced composites) are generally attributed to higher levels of crack bridging [13,39,72,90-92].

There have been several studies of ductile phase reinforced NiAl composites [6-12,39]. One candidate reinforcement is Ni$_3$Al ($\gamma'$), which is a ductile phase in equilibrium with
NiAl in the binary Ni-Al system [103]. Other ductile phases used are refractory metals including Mo [6-10,39], Cr [6,10-12], and V [7,10]. Most of the studies focus on in situ composites based on pseudo-binary NiAl-X eutectic systems where X is Cr, Mo, or V [6-12]. The typical microstructures of these systems with eutectic composition consist of fine, uniformly distributed ductile rods or alternating layers in the matrix. The fiber and layer morphologies of ductile phases have been shown to result in optimal toughening in intermetallics [3,65]. Due to the narrow range of sizes of the reinforcement phase and the low solubility of the refractory elements in NiAl, these microstructures tend to be stable at high temperatures [9]. NiAl-X alloys can be fabricated by conventional casting [9] or by directional solidification [6,7,10-12]. The latter has the advantage of producing reinforcement phases that are continuous and aligned.

Artificial composites, fabricated by the hot isostatic pressing (HIPing) of NiAl with Mo powders or fibers have been studied by Ramasundaram et al. [39]. It was found that the NiAl/Mo composites were significantly tougher than the binary NiAl (fracture toughness up to ~17.0 MPa√m in the fiber reinforced composite), mainly due to the effects of crack trapping. Stable fatigue crack growth was also observed in the NiAl/Mo composites under cyclic loading. However, Ramasundaram et al. [39] failed to provide critical evidence of the occurrence of crack trapping.

Listed in Table 2.3 is a summary of reported data for most of the ductile phase reinforced NiAl composites considered in the literature. The table includes the room-temperature
fracture toughness values. Most of the toughness values are much higher than those of monolithic NiAl, but are in general less than 20 MPa√m.

2.3.4 Synergistic Toughening

In the case where multiple toughening mechanisms operate, the total toughening can be estimated from the sum of the contributions due to each mechanism. Such linear superposition concepts neglect the possible interactions between individual mechanisms. However, synergistic interactions between individual toughening mechanisms may promote a greater degree of toughening than the simple sum of the toughening components [104-106].

Amazigo and Budiansky [14] conducted an original theoretical study of the possible interactions between toughening effects of crack bridging and transformation toughening. They showed that it is possible to induce synergy depending on the parametric ranges of bridging and transformation toughening. In cases where the interaction is synergistic, the overall increase in toughness is greater than the sum of the toughening due to crack bridging and transformation toughening alone. The interaction of crack bridging and transformation toughening is characterized in terms of the following key parameters:

(i) The modified toughening ratio due to particulate crack bridging:
\[ \Lambda_p = \frac{\lambda_p}{\sqrt{1-c}} = \frac{K_p}{K_m \sqrt{1-c}} \]  \hspace{1cm} (2.48)

where \( \lambda_p \) is the toughening ratio due to crack bridging by ductile particles, \( c \) is the volume concentration of ductile particles, \( K_p \) is the increased toughness due to bridging by ductile particulate reinforcements, and \( K_m \) is the fracture toughness of the matrix.

(ii) The toughening ratio due to transformation toughening:

\[ \lambda_T = \frac{K_T}{K_m} \]  \hspace{1cm} (2.49)

where \( K_T \) is the increased toughness from transformation toughening.

(iii) The combined modified toughening ratio:

\[ \Lambda = \frac{K}{K_m \sqrt{1-c}} \]  \hspace{1cm} (2.50)

where \( K \) is the total increased toughness of the composite system.

(iv) The coupling parameter, \( \rho \):
where \( v \) is the Poisson's ratio, \( S \) is the strength of the ductile particle, and \( \sigma_m^c \) is the mean stress in transformation zone. This coupling parameter governs the interaction between particulate and transformation toughening when they occur simultaneously during steady crack growth. Representative numerical results are presented in Figures 2.18a-c for \( \Lambda \) versus \( \lambda_T \), for \( \Lambda_p = 2, 3, 4 \), respectively. The individual curves in each figure are for selected values of the coupling parameter in the range \([0, \infty]\). The limiting results for \( \rho = \infty \) and 0 are of special interest:

\[
\Lambda = \Lambda_p \lambda_T \quad \text{for} \quad \rho \to \infty
\]  

(2.52)

and

\[
\Lambda = \left[ \Lambda_p^2 + \lambda_T^2 - 1 \right]^{1/2} \quad \text{for} \quad \rho \to 0
\]  

(2.53)

The anticipated product rule \( \lambda = \lambda_p \lambda_T \) for the combined toughening ratio holds in the first limiting case. For sufficiently large finite values of \( \rho \), bridging and transforming particles interact synergistically, producing a larger increase in the fracture toughness than the sum of the individual contributions from crack bridging and transformation.
toughening. On the other hand, for \( p \) near zero, the combined toughness can be substantially less than the cumulative.

(v) Due to difficulties in obtaining sufficient information to calculate the above coupling parameter, \( p \), a second coupling parameter, \( \eta \), has also been proposed by Amazigo and Budiansky [14]. This gives:

\[
\eta = \frac{H_T(1-c)}{L_p}
\]  

(2.54)

where \( H_T \) is the transformation zone height and \( L_p \) is the bridging length for pure particulate toughening. The counterpart to Figure 18 is shown in Figure 19, with curves showing \( \Lambda \) for various values of \( \eta \). An appropriate choice for \( \eta \) can then be made on the basis of observations of separate toughening mechanisms. For quite small values of \( \eta \), it is enough to provide results close to those for \( \eta = p = \infty \), for which the synergistic product rule applies. It means that synergism is not precluded despite the fact that transformation toughening zone heights tend to be smaller than bridging lengths.

Another study by Cui [107] has also shown that transformation particles and aligned fibers may interact synergistically to increase the effective fracture toughness of a brittle matrix containing a long, initially unbridged crack. The results obtained from this analysis are qualitatively similar to those obtained by Amazigo and Budiansky [14].
Table 2.1 Observed Slip Systems in Uniaxially Deformed NiAl [1,3]

<table>
<thead>
<tr>
<th>Material</th>
<th>Temperature Range, (K)</th>
<th>Slip Vector</th>
<th>Slip Plane</th>
<th>Analysis Technique</th>
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</thead>
<tbody>
<tr>
<td>Polycrystalline NiAl</td>
<td>300-900</td>
<td>&lt;100&gt;</td>
<td>{011}</td>
<td>TEM</td>
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<tr>
<td>Single Crystal NiAl</td>
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<td>&quot;Soft&quot; Orientations:</td>
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<td></td>
</tr>
<tr>
<td>[111]</td>
<td>77-1373</td>
<td>&lt;100&gt;</td>
<td>{011}</td>
<td>TEM/SSTA</td>
</tr>
<tr>
<td>[122]</td>
<td>77-300</td>
<td>&lt;100&gt;</td>
<td>{011}</td>
<td>SSTA</td>
</tr>
<tr>
<td>[123]</td>
<td>77-873</td>
<td>&lt;100&gt;</td>
<td>{011}</td>
<td>TEM</td>
</tr>
<tr>
<td>[110]</td>
<td>77-300</td>
<td>&lt;100&gt;</td>
<td>{011}</td>
<td>TEM/SSTA</td>
</tr>
<tr>
<td>[110]</td>
<td>300-1373</td>
<td>&lt;100&gt;</td>
<td>{001}</td>
<td>TEM/SSTA</td>
</tr>
<tr>
<td>[227]</td>
<td>573</td>
<td>&lt;100&gt;</td>
<td>{011}</td>
<td>SSTA</td>
</tr>
<tr>
<td>[112]</td>
<td>77-873</td>
<td>&lt;100&gt;</td>
<td>{011} or {001}</td>
<td>TEM/SSTA</td>
</tr>
<tr>
<td>&quot;Hard&quot; Orientation</td>
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<td>&lt;100&gt;</td>
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<tr>
<td></td>
<td>77-600</td>
<td>&lt;111&gt;</td>
<td>{112}, {011}, or {123}</td>
<td>TEM/SSTA</td>
</tr>
</tbody>
</table>

a TEM - Transmission Electron Microscopy Investigation
b SSTA - Surface Slip Trace Analysis

Table 2.2 Coefficients of Fit Polynomial for (SENB) Specimen [90-93]

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<thead>
<tr>
<th>v</th>
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<th>2</th>
<th>3</th>
<th>4</th>
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<td>-10.986</td>
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</table>

Table 2.2 Coefficients of Fit Polynomial for (SENB) Specimen [90-93]
<table>
<thead>
<tr>
<th>Composite</th>
<th>Reinforcement Morphology</th>
<th>Volume Fraction (%)</th>
<th>Fracture Toughness (Steady State Toughness) (MPa(\sqrt{m}))</th>
<th>Reference</th>
</tr>
</thead>
</table>
| NiAl/Mo (DS\(^a\))  
NiAl/Cr(Mo) (DS) | Fine Mo Rod  
Fine Cr(Mo) Layer | 12  
30 | 15  
22 | 6         |
| NiAl-9Mo (AC\(^b\)+HIP\(^c\)+HT\(^d\))  
NiAl-9Mo (AC+Forged+HT)  
NiAl-12Mo (AC+HIP+HT)  
NiAl-12Mo (AC+Extruded+HT)  
NiAl-23Mo (AC+HIP+HT)  
NiAl-38Mo (AC+HIP+HT)  
NiAl-36Mo-2Ti (AC+HIP+HT) | Fine Mo Fiber  
Mo Dendrite and Fine Mo Fiber  
Mo Dendrite and Fine Mo Fiber  
Mo Dendrite and Fine Mo Fiber  
Primary Mo Dendrite  
Primary Mo Dendrite | 11  
16  
16  
44  
50  
50 | 9.4  
13.6  
16.6  
11.3  
11.7  
17.1 | 9         |
| NiAl-9Mo (DS)  
NiAl-12Mo (DS)  
NiAl-15Mo (DS)  
NiAl-40V (DS)  
NiAl-33.3Cr-11.1Nb (DS) | Fine Mo Rod  
Fine Mo Rod  
Fine Mo Rod  
Fine V Layer  
Fine Cr Rod | N/A  
N/A  
N/A  
N/A  
N/A | 15.2  
15.5  
13.2  
30.7  
11.6 | 10        |
| NiAl-28Cr-6Mo (DS)  
NiAl-34Cr (DS) | Fine Cr(Mo) Layer  
Fine Cr Fiber | N/A  
34 | 21  
11 | 11        |
| NiAl/Mo (HIP)  
NiAl/Mo (HIP)  
NiAl/Mo (HIP)  
NiAl/Mo (HIP) | Mo Particle  
Mo Particle  
Mo Particle  
Mo Fiber | 10  
20  
30  
20 | 12.3  
14.4  
14.0  
16.7 | 39        |

\(^a\) DS - Direct Solidification  
\(^b\) AC - As Cast  
\(^c\) HIP - Hot Isostatic Pressing  
\(^d\) HT - Heat Treatment

Table 2.3 Fracture Toughness of Ductile Phase Reinforced NiAl-Based Composites
Figure 2.1 A large plate of an elastic material containing a crack of length 2a [20].

Figure 2.2 Three basic modes of fracture [20]. (a) Tensile opening (mode I), (b) in-plane sliding (mode II), and (c) anti-plane shear (mode III).
Figure 2.3 Coordinate system and stresses in the near-tip region of a crack in a plate [20].

Figure 2.4 Schematic representation of R-curve and applied K curves to predict instability; $K_C$, $P_3$, $a_c$, corresponding to an initial crack size, $a_0$ [21].
Figure 2.5 Schematic illustration of the different regimes of stable fatigue crack propagation [20].

Figure 2.6 An idealization of plastic blunting and re-sharpening model in fully-reversed fatigue [20,23]. (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 directions.
Figure 2.7 The Ni-Al binary phase diagram [26].

Figure 2.8 The B2 crystal structure of NiAl, with the observed a<100>, a<110>, and a<111> slip vectors shown on the (011̅) plane [2].
Figure 2.9 The yield stress of nominally stoichiometric polycrystalline NiAl [2].

Figure 2.10 The phase diagram of the ZrO$_2$-Y$_2$O$_3$ system near the ZrO$_2$ rich end [48].
Figure 2.11 Schematic illustration of (a) transformation zone around a crack induced by the tetragonal-to-monoclinic phase transformation, (b) the typical stress-strain behavior for the transformation, and (c) the modified stress field ahead of a crack tip in the presence of a transformation zone [50]. $p_c^A$ is the critical stress needed to induce the transformation.
Figure 2.12 Typical Raman spectra of (a) tetragonal and (b) monoclinic phases of zirconia [58].
Figure 2.13 Schematic illustration of extrinsic toughening mechanisms [3,39]. (a) Crack bridging, (b) crack-tip blunting, (c) crack deflection, and (d) crack trapping.
Figure 2.14 Schematic diagram showing resistance curve behavior due to (a) small scale bridging and (b) large scale bridging [84].

Far-field: $\sigma_{\alpha\beta} = \frac{K_1\alpha\beta(\theta)}{\sqrt{2\pi r}}$

Figure 2.15 Schematic illustration of bridging-spring model [79].
Figure 2.16 Schematic illustration of a crack in a brittle matrix, intersected by ductile particles [85]. The particles stretch and fail as the crack opens.

Figure 2.17 Schematic representation of a large-scale bridging model [91].
Figure 2.18 Modified toughening ratio for various values of coupling parameter $\rho = \frac{(1 + \nu)cS}{\sigma_m}$ [14]. (a) $\Lambda_p = 2$, (b) $\Lambda_p = 3$, and (c) $\Lambda_p = 4$. 
Figure 2.19 Modified toughening ratio for various values of coupling parameter
\[ \eta = \frac{H_T (1 - c)}{L_p} \] [14]. (a) \( \Lambda_p = 2 \), (b) \( \Lambda_p = 3 \), and (c) \( \Lambda_p = 4 \).
CHAPTER 3

MATERIALS AND EXPERIMENTAL PROCEDURES

3.1 MATERIALS PROCESSING AND SPECIMEN PREPARATION

3.1.1 NiAl + 20 vol. % YSZ (2 mole % Yttria Stabilized Zirconia) Composites

The -325 mesh (25 - 30 μm average particle size) NiAl powders were procured from Homogeneous Metals, Inc., Clayville, NY. The 2 mole % yttria stabilized zirconia (YSZ) powders were obtained from Zirconia Sales, Marietta, GA. The average particle size was approximately 0.35 μm. The NiAl and zirconia powders were mixed in suitable proportions, and ball milled using zirconia milling media for 24 hours. The resulting mixtures were transferred into stainless steel cans, before the cans were evacuated and sealed by electron beam welding. The evacuated and sealed cans were then hot isostatic pressed under 207 MPa pressure at 1100 °C for 4 hours.
3.1.2 Layered NiAl + 20 vol. % V and NiAl + 20 vol. % Nb-15Al-40Ti Composites

The -325 mesh (25 - 30 μm average size) NiAl powders that were used in this study were procured from Homogeneous Metals, Inc., Clayville, NY. The vanadium strips with thickness of 100, 200 and 400 μm were supplied by Fine Metals Corp., Ashland, VA, while the Nb-15Al-40Ti strips with thickness of 100 μm, 500 μm and 1000 μm were produced by Teledyne Wah Change, Albany, OR. Model NiAl composites reinforced with 20 vol.% of V or Nb-15Al-40Ti layers were produced by manual lay-up of NiAl powders on the layered reinforcements inside stainless steel cans. After manual lay-up, the cans were evacuated and sealed by electron beam welding. The evacuated cans were then hot isostatic pressed under 207 MPa pressure at 1100 °C for 4 hours.

3.1.3 NiAl + 20 vol. % YSZ + 20 vol. % Mo(p) (Particulate) Composites

The -325 mesh (25 - 30 μm average size) NiAl powder was procured from Homogeneous Metals, Inc., Clayville, NY. The -325 mesh molybdenum (Mo) powder was obtained from CERAC, Milwaukee, WI. The 2 mole % Y₂O₃ partially stabilized zirconia (YSZ) powder was obtained from Tosoh Corp., Bound Brook, NJ. The average particle size was approximately 0.7 μm. The NiAl was dry phase blended with 20 vol.% Mo powder and 20 vol.% YSZ particles for 24 hours in a ball mill. After dry phase blending, the powder mixtures were poured into stainless steel cans which were subsequently evacuated, electron beam sealed and hot isostatically pressed at 1100 °C for 4 hours.
3.1.4 Layered NiAl + 20 vol. % YSZ + 20 vol. % V Composites

The -325 mesh (25 - 30 μm average size) NiAl powders that were used in this study were procured from Homogeneous Metals, Inc., Clayville, NY. The 200 μm thick vanadium strips were supplied by Fine Metals Corp., Ashland, VA. The 2 mole % yttria stabilized zirconia (YSZ) powders were obtained from Zirconia Sales, Marrietta, GA. The average particle size was approximately 0.35 μm. The NiAl powder was dry phase blended with 20 vol.% YSZ particles for 24 hours. Hybrid NiAl composites reinforced with 20 vol.% YSZ particles and 20 vol.% of V layers were then produced by manual lay-up of the mixture of NiAl and YSZ powders on the V layer reinforcements inside stainless steel cans. After manual lay-up, the cans were evacuated and sealed by electron beam welding. The evacuated cans were then hot isostatic pressed under 207 MPa pressure at 1100 °C for 4 hours.

3.2 FRACTURE TOUGHNESS TEST

To obtain the composite matrix fracture toughness, fracture toughness tests were performed on monolithic NiAl using single edge notched bend (SENB) specimens with rectangular cross sections. The specimens were fabricated via electro-discharge machining (EDM) initial notch-length-to-width ratios of ~0.4. The fracture toughness tests were performed in accordance with the ASTM E399 code [21]. The SENB
specimens were initially pre-cracked under far-field compression loading [20]. Fatigue pre-cracking was carried out at a stress ratio, \( R = \frac{\sigma_{\text{min}}}{\sigma_{\text{max}}} \) of 0.1 to produce an atomistically 'sharp' crack (Figure 3.1). This was 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\(\sqrt{\text{m}}\).s\(^{-1}\).

3.3. RESISTANCE CURVE (R-CURVE) TEST

The initiation fracture toughness and the resistance-curve behavior of all the NiAl composites were studied using single edge notched bend (SENB) specimens with rectangular cross sections. For NiAl/YSZ composites, layered NiAl/V composites, layered NiAl/Nb-15Al-40Ti composites, and layered NiAl/YSZ/V composites, the specimen dimensions are ~38.1 mm long with a width of ~15.24 mm and a thickness of ~6.35 mm. For NiAl/YSZ/Mo\(_{(p)}\) composites, the specimens are ~20 mm long with a width of ~8.8 mm and a thickness of ~6.7 mm. All the specimens were fabricated via electro-discharge machining (EDM) with initial notch-length-to-width ratios of ~0.25. The sides of the specimens were diamond polished prior to pre-cracking under cyclic compression. After pre-cracking, the SENB specimens were loaded in incremental stages under three-point bending until crack initiation was observed from the pre-cracks. The loads were then increased in ~2 - 5 % increments to promote stable crack growth until specimen fracture occurred. The crack/microstructure interactions associated with stable
crack growth were monitored with an optical microscope before each load increment. This was continued until unstable crack growth/fracture occurred during incremental loading. As a control, the fracture toughness of monolithic NiAl was always measured using SENB specimens of the same dimensions.

3.4 FATIGUE CRACK GROWTH TEST

For layered NiAl/V and NiAl/Nb-15Al-40Ti composites, fatigue crack growth tests were conducted on SENB specimens (~38.1 mm long with a width of ~15.24 mm and a thickness of ~6.35 mm) with initial notch-to-width ratios of ~0.25. The specimens were pre-cracked under far-field compression fatigue, and then subjected to constant amplitude cyclic tensile loading at a stress ratio, \( R = \frac{K_{\text{min}}}{K_{\text{max}}} \), of 0.1. A cyclic loading frequency of 10 Hz was used in the fatigue experiments. Low initial stress ranges corresponding to a stress intensity factor range of about 1 MPa√m were applied initially for incremental loading stages of \( 10^4 \) cycles. The stress ranges were then increased in incremental stages of ~10 % until crack growth was detected after \( 10^4 \) cycles under an optical microscope. Upon the detection of crack growth, the stress amplitudes were maintained constant, except in cases where the cracks stopped growing due to interactions with the ductile layers. Load increments of 5 % were typically needed for continued crack growth in such cases. The interactions of the cracks with the underlying composite microstructures were monitored using an optical microscope.
3.5 TENSILE TEST

Tensile tests were performed on vanadium thin foils in an effort to determine the constitutive laws for the different layer thickness. The thin foils were gripped between aluminum tabs with wedge action grips. They were then deformed continuously to failure at strain rate of $5 \times 10^{-4}$ s$^{-1}$. Strain was measured across the gauge sections using an extensometer with a gauge length of 25.4 mm.

3.6 FRACTOGRAPHY

The fracture surfaces of the fracture toughness, resistance-curve, fatigue and tensile tested specimens were examined using a scanning electron microscope (SEM). In order to characterize the fracture surface morphology, secondary electron imaging mode was used primarily. Occasionally, back-scattered electron imaging mode was used to distinguish the different phases in the composite systems. Electron dispersive spectroscopy (EDS) was also used to characterize the compositions of interfaces between two different composite constituents during SEM examination.

3.7 RAMAN SPECTROSCOPY

After catastrophic failure of SENB specimens that were used in the resistance-curve experiments on NiAl/YSZ, NiAl/YSZ/Mo(p) and layered NiAl/YSZ/V specimens, micro
Raman spectroscopy analysis was performed on the zirconia regions from the polished sides of the fractured specimens [43]. This was used to determine the volume fractions of monoclinic and tetragonal phases as functions of distance from the crack faces (up to a distance of ~500 μm) [43]. Calibration procedures developed by Clarke and Adar [58] were used for the measurements of the volume fraction of the monoclinic phase. These utilize X-ray diffraction intensity measurements to arrive at an expression for the concentration of the monoclinic phase based on the monoclinic and tetragonal Raman peak intensities. The monoclinic phase concentration, \( c_m \), is thus given by:

\[
\frac{c_m}{181} = \frac{I_{181}^{m} + I_{192}^{m}}{I_{181}^{t} + I_{192}^{t}}
\]

(3.1)

where \( I \) refers to the integrated intensities of the peaks, the superscripts refer to the Raman shift of the peaks, and the subscripts \( m \) and \( t \) refers to the monoclinic and tetragonal peaks, respectively. Based on this expression, the volume fraction of monoclinic zirconia was determined as a function of distance from the fracture surface.

The Raman spectroscopy examinations were performed partly at the Instruments S.A., Inc., Edison, NJ, and also in the Department of Chemistry at The Ohio State University, Columbus, OH. An argon ion laser beam with a probe diameter of ~1 μm was used to excite the specimen. The microscope was equipped with a motion system and the scattered radiation was collected using a triple spectrometer. The initial Raman spectra
were obtained from spots (on the sides of the specimens) that were very close to the fracture surfaces. The motion system was then used to guide the collection of spectroscopy data from points that were ~2 - 3 μm apart. In this way, the volume fraction of transformed monoclinic phase was measured as a function of distance from the crack faces. The size of transformation zone was also estimated from the distance at which the volume fraction of transformed monoclinic phase was comparable to that in the bulk.

3.8 X-RAY DIFFRACTION

X-ray diffraction was performed on the as-received and heat-treated YSZ powders, and consolidated blocks to obtain phase content information of partially stabilized zirconia at room temperature. Cu-Kα radiation was used in a Scintag PAD diffractometer.
Figure 3.1 Fatigue pre-cracks in monolithic NiAl obtained by far-field compression cyclic loading.
4.1 INTRODUCTION

Since the pioneering work of Krstic and co-workers [108,109], there have been considerable efforts to utilize the concept of ductile phase toughening in the design of toughened composite systems [7,9,11,38,39,73-76,80,82,85-88,90-92,101,102,106]. Much of the early work was performed on composites reinforced with ductile particles [13,39,73,86] or fibers [6,13,80,85,86,88,102] that were chosen to promote toughening largely by crack bridging. The early studies showed that fiber-reinforced composites generally promote greater levels of toughening than particulate-reinforced composites. However, subsequent work on ductile layer-reinforced composites [7,9,11,13,83,90-92,87,88,101,106] soon revealed that such composites architectures result in even greater levels of toughening than ductile fiber-reinforced brittle matrix composites. The interest, in recent years, has therefore shifted towards the understanding of the effects of ductile layer reinforcements on the fracture toughness of brittle matrix composites composites [7,9,11,13,83,90-92,87,88,101,106].
The current study presents the results of fundamental studies of the effects of ductile layer thickness on the fracture initiation toughness and resistance-curve behavior of nickel aluminide microlaminates. Model composites reinforced with 20 vol.% of ductile vanadium layers (100, 200 and 400 µm thickness) or ductile Nb-15Al-40Ti layers (100, 500 and 1000 µm thickness) were used in this study. The ductile phase reinforcements were selected due to their compatibility with NiAl in the processing temperature regime (~1100 °C). The vanadium and Nb-15Al-40Ti were also investigated since they exhibit essentially elastic-perfectly plastic behavior. Furthermore, the Nb-15Al-40Ti intermetallic layers exhibit attractive combinations of damage tolerance and oxidation resistance in the intermediate-temperature regime (650-850 °C) [110,111].

As in recent studies by Bloyer et al. [90-92] on similar layered composites, fracture initiation toughness and resistance-curve behavior in the model composite systems are shown to improve with increasing layer thickness in the crack-arrestor orientation. The intrinsic steady-state toughness values are also shown to increase with increasing ductile layer thickness. However, the results indicate that fracture instability is more likely to occur at smaller crack extensions, as the ductile layer thickness is increased. The initiation toughness, resistance-curve behavior and steady-state toughness levels are also predicted with micromechanics models. The implications of the results are then discussed for the design and potential applications of brittle matrix composites reinforced with ductile layers. The results of finite element simulations are used to explain the re-
nucleation of cracks in adjacent NiAl layers after crack retardation by the vanadium layers.

4.2 MICROMECHANICAL MODELING

Following the example of Budiansky et al. [79] and Rose [112], the individual ductile layers within a bridged crack may be modeled as springs (Figure 2.15) with effective spring stresses that are given by:

\[ \sigma = \frac{kE\nu}{1 - \nu^2} \]  \hspace{1cm} (4.1)

where \(\nu\) is the crack-face displacement, \(E\) is the Young's modulus, \(\nu\) is the Poisson's ratio, and \(k\) is the spring-stiffness coefficient. The effective spring constant for the bridged layer configurations may be estimated by considering the pinning of the crack by a single isolated layer in a dilute composite with relatively low volume fraction, \(c\), of layers in which interactions between individual layers can be neglected (Figures 4.1a and 4.1b). The remote displacement of the crack in Figure 4.1a may be estimated by invoking the analogy between the crack opening profile and the displacement profile due to a smooth punch. This is given by Johnson [113] to be:

\[ \nu = \frac{\alpha\sigma_p \left(1 - \nu_m^2\right)}{E_m} \]  \hspace{1cm} (4.2)
where

\[
\alpha = \frac{(a + b) \ln \left(1 + \frac{b}{a}\right)^2 + (a - b) \ln \left(1 - \frac{b}{a}\right)^2}{\pi}
\]  

(4.3)

where \(a\) is the half thickness of the ductile layer and \(b\) is chosen to satisfy \(a/b = c\), \(E_m\) and \(\nu_m\) are the Young's modulus and Poisson's ratio of the matrix, respectively, and \(\sigma_p\) is the average layer stress. Equation 4.2 corresponds essentially to a layer/crack configuration in a half-space for which \(c \rightarrow 0\) (Figures 4.1a and 4.1b). Note that \(c\) also corresponds to the layer volume fraction for the unit cell shown in Figure 4.1b. Following the methods of Budiansky et al. [79], the average crack opening displacement, \(u_{ave}\), may also be estimated for arbitrary values of \(c\) to be:

\[
u_{ave} = \beta(c) \frac{\alpha \sigma_p \left(1 - \nu_m^2\right)}{E_m}
\]  

(4.4)

where \(\beta(c)\) is a correction factor for the solution of a crack in a half space (Figure 4.1a) presented in Equation 4.2. The variations of \(\beta(c)\) with ductile layer volume fraction may be estimated using stress intensity factor solutions for a double edged crack solid provided by Tada et al. [81]. This gives:
\[ K_i = \sigma \sqrt{\pi (b - a)} F \left( 1 - \frac{a}{b} \right) \]  

(4.5)

where

\[ F \left( 1 - \frac{a}{b} \right) = \frac{1.122 - 0.561 \left( 1 - \frac{a}{b} \right) - 0.205 \left( 1 - \frac{a}{b} \right)^2 + 0.471 \left( 1 - \frac{a}{b} \right)^3 - 0.190 \left( 1 - \frac{a}{b} \right)^4}{\sqrt{\frac{a}{b}}} \]  

(4.6)

where \( \sigma = c\sigma_p \) is the applied stress. The energy released, \( R \), by cutting the crack into the block (Figure 4.1b) in the presence of constant \( \sigma \) is given by:

\[ R = \int_b^a \frac{K_i^2 (1 - \nu_m^2)}{E_m} B dx \]  

(4.7)

where \( B \) is the thickness of the block. \( R \) may also be equated to \( 2Bb\sigma u_{ave} \). Hence, \( u_{ave} \) may be found by equating the above expression to Equation 4.7:

\[ u_{ave} = \frac{\int_a^b \frac{K_i^2 (1 - \nu_m^2)}{E_m} dx}{2b\sigma} \]  

(4.8)

By equating \( u_{ave} \) from Equation 4.8 to Equation 4.4, \( \beta(c) \) is found to be:
Substituting $\nu = \nu_{\text{ave}}$ into Equation 4.1 gives the following relationship for the spring constant $k$:

$$k = \frac{c}{\beta \alpha} \frac{E_m}{1 - \nu^2} \frac{1 - \nu^2}{E_m}$$  \hspace{1cm} (4.10)$$

where $E$ and $\nu$ are the effective Young's modulus and Poisson's ratio of the composite materials, respectively.

The above derivation for elastic springs may be extended to the case of elastic-plastic springs by assuming elastic-perfectly plastic behavior of ductile layer for which (Figure 4.2):

$$\sigma = \frac{kE\nu}{1 - \nu^2} \quad \text{for} \quad \nu \leq \nu_y = \frac{\sigma_y (1 - \nu^2)}{kE}$$

$$= \sigma_y \quad \text{for} \quad \nu \geq \nu_y$$  \hspace{1cm} (4.11)
Hence, if $u(L)$ at the end of the bridged zone exceeds $u_y$, the J-integral result for the toughening due to crack bridging generalizes to [79]:

$$\frac{(1-v^2)K^2}{E} = \frac{(1-v_m^2)K_m^2}{E} + \frac{(1-v^2)v_y^2}{kE} + 2\sigma_y [u(L) - u_y]$$ (4.12)

If failure of the last spring is assumed to occur when $u(L) - u_y$ reaches a critical plastic value $u_p$, the toughening ratio, $\lambda$, becomes [79]:

$$\lambda = \frac{K}{K_m} = \left[1 + \frac{\sigma_y^2}{kK_m^2} \left(1 + \frac{2u_p}{u_y}\right)^{\frac{1}{2}}\right]$$ (4.13)

where $K_m$ is the matrix toughness. The result can be rearranged to obtain an estimate of the toughness increment, $\Delta K_b$, due to ductile layer bridging:

$$\Delta K_b = (\lambda - 1)K_m$$ (4.14)

Equations 4.13 and 4.14 can be used to estimate the steady state fracture toughness of brittle matrix reinforced with ductile layers. However, the above modeling framework cannot be used readily to predict the resistance-curve behavior due to crack bridging since it does not include a bridging length scale. This can be accomplished by
considering the work required for the elastic and plastic stretching of bridging phases to failure. This may be estimated using a physically appealing analytical model proposed originally by Ashby et al. [88]. This model, which emerged from some early work on the deformation of the lead/glass system, established a methodology for the estimation of the change in the energy release rate due to the highly constrained plastic stretching of ductile wires. This gave the following expression for the estimates of the change in the energy release rate, $\Delta G_b$, due to the constrained plastic stretching of ductile reinforcements:

$$\Delta G_b = f r \sigma_0 \chi$$

(4.15)

where $f$ is the volume fraction of ductile phase, $r$ is the characteristic length of the ductile phase, $\sigma_0$ is the unconstrained yield stress and $\chi$ is a non-dimensional work of rupture parameter that is given by [85,86,88]:

$$\chi = \int_{r}^{u^*} \sigma \left( \frac{u}{r} \right) d\left( \frac{u}{r} \right)$$

(4.16)

where $\sigma(u)$ is a stress-displacement function often determined from experiments, $u$ is the displacement of the ductile phase, and $u^*$ is the displacement at the point of failure of the ductile phase. The toughening in the above models was associated largely with the
additional energy required for the plastic deformation of the bridging ductile phases that
deform plastically to fracture during crack opening under monotonic loading in a fracture
toughness test. However, it is often more convenient to express the improvements in
fracture toughness in terms of the stress intensity factor, $K$. This enables the toughening
problem to be quantified in terms of a shielding stress intensity factor, $K_b$, or a
toughening ratio, $\lambda_b$, due to crack bridging.

The problem of small-scale bridging (small bridging zone compared to crack size) was
modeled analytically by Budiansky et al. [79]. Assuming either rigid/perfectly plastic, or
elastic perfectly plastic behavior, they obtained a number of solutions for the estimation
of toughness due to crack bridging by ductile particles. As in the solutions presented
earlier in Equations 4.13 and 4.14, most of the expressions in Ref. [79] do not include a
bridging length scale. However, one of the equations, which was obtained essentially
from Tada et al. [81], did include a bridging length scale. This gives the toughening ratio
due to crack bridging, $\lambda_b$, to be:

$$\lambda_b = \frac{K}{K_m} = 1 + \sqrt{\frac{2}{\pi}} \frac{f}{K_m} \int_0^L \frac{\sigma(x)}{\sqrt{x}} \, dx$$

(4.17)

where $\alpha$ is a constraint/triaxiality factor, $\sigma(x)$ represents the bridging traction across the
ductile reinforcements, $x$ is the distance from the crack face behind the crack-tip, and $L$ is
bridging length, which is equal to the distance from the crack-tip to the last unfractured
reinforcement (Figure 2.15). The above analysis applies largely to the problem of small-scale bridging, which is generally encountered in particulate-reinforced composites [13,73,79]. However, in the case of ductile fiber-reinforced and ductile layer-reinforced composites, the lengths of bridging zones are generally observed to be comparable to the overall crack dimensions [88,90-92,106]. Under such conditions, large-scale bridging models [84,88-92] are needed to estimate the shielding contributions from crack bridging.

The early large-scale bridging models were first formulated by Odette et al. [88] and Zok and Hom [84]. Subsequent work by Cox and co-workers [89] also established self-consistent methods for the analysis of large-scale crack bridging. However, these large-scale bridging models often require iterative methods/algorithms that may have convergence problems associated with them.

A simpler large-scale bridging model was, therefore, employed in the current study. This model, which was first proposed by Bloyer et al. [90-92], utilizes weight functions by Fett and Munz [93], in the estimation of the weighted distributions of bridging traction across the individual reinforcements (Figure 2.17). The shielding due to large-scale bridging, \( \Delta K_{bb} \), may thus be expressed as:

\[
\Delta K_{bb} = f \int_0^L \alpha \sigma(x) h(a, x) \, dx
\]

(4.18)
where $L$ is the length of the bridge zone, $\alpha$ is a constraint/triaxiality factor, $\sigma(x)$ is a traction function along the bridge zone, and $h(a,x)$ is a weight function given by Fett and Munz [93]:

$$h(a,x) = \sqrt{\frac{2}{\pi a}} \frac{1}{\sqrt{1 - \frac{x}{a}}} \left[ 1 + \sum_{(\nu,\mu)} A_{\nu\mu} \left( \frac{a}{W} \right) \left( 1 - \frac{a}{W} \right)^\nu \right]$$

where $a$ is the crack length and $W$ is the specimen width. The coefficients, $A_{\nu\mu}$, are given in Table 2.2 for a single edge notched bend (SENB) specimen. The resistance-curve behavior may now be estimated by a simple application of the principle of linear superposition. This gives the following expression for the estimation of the stress intensity factors along the resistance-curve:

$$K = K_i + \Delta K_{sb}$$

where $K_i$ is the initiation toughness required for renucleation ahead of the first ductile layer encountered by the propagating crack, and $\Delta K_{sb}$ is given by Equation 4.18 for large-scale bridging.
4.3 MICROSTRUCTURE

Typical microstructures of the NiAl/V microlaminates are presented in Figures 4.3a - 4.3d. These show relatively uniform distributions of vanadium layers in a matrix of NiAl. The average size of NiAl grains, measured by image analysis, was about 25 μm. A small interfacial layer was also observed to form between the NiAl and vanadium layers (Figure 4.3d). Semi-quantitative energy dispersive X-ray (EDX) spectroscopy revealed that this layer consisted of ~11.8 at.% Ni, ~11.6 at.% Al and ~76.6 at.% V. The interfacial layers were approximately 5 - 10 μm thick in all the composites that were produced.

Typical microstructures of the NiAl/Nb-15Al-40Ti composites are presented in Figures 4.4a - 4.4d. As in the NiAl/V composites (Figures 4.3a - 4.3d), the microstructures are relatively uniform. However, a more complex reaction zone of approximately 15 - 20 μm thick was observed to form between the NiAl and the Nb-15Al-40Ti layers (Figure 4.4d). EDX analyses showed that the average composition of the reaction interface is ~5.9 at.% Ni, ~23.8 at.% Al, ~45.8 % Nb and 24.5 at.% Ti.

Constituent mechanical properties (which were assumed to be isotropic) that were used in the shielding estimations are summarized in Table 4.1.
4.4 RESULTS

4.4.1 NiAl/V Composites

4.4.1.1 Crack/Microstructure Interactions and Resistance-Curve Behavior

In all NiAl/V composites, matrix crack initiation occurred in the NiAl at the matrix toughness level of ~6.6 MPa√m. However, the propagating cracks in the NiAl layers were retarded by the ductile vanadium layers (Figures 4.5a - 4.5b). Subsequent crack growth, therefore, involved the re-initiation of cracks in the adjacent interfacial layers, as shown in Figure 4.5b. Note that the cracks were bridged by the vanadium layers as they propagated through the NiAl/V composites. Also, although the vanadium layers were deformed plastically, none of them were observed to fracture during the development of large-scale bridging zones. Furthermore, fracture of the vanadium layers was only observed to occur at the onset of catastrophic failure.

A similar sequence of events was observed in all the composites (100, 200 and 400 μm layers) that were examined (Figures 4.6a - 4.6c). The crack/microstructure interactions illustrated in Figures 4.5a - 4.5b are, therefore, comparable to those of all the other composites. It is also important to note here that propagating cracks stopped when they reached the vanadium layers (Figure 4.5a). The measured resistance-curves therefore correspond to the interceptions of the propagating cracks with the ductile vanadium
layers. Furthermore, a small plastic zone and some debonding were then observed in the vanadium, as the load was increased in an effort to re-initiate crack growth in the composites (Figure 4.5a). Slip bands were observed to form along the ~45° orientation on both sides of the vanadium layers, as the load was increased further (Figure 4.5b). Eventually, stable crack growth was observed to re-nucleate from the slip bands into the adjacent interfacial layers, as shown in Figure 4b. In all cases, re-initiation occurred at a point that is offset somewhat from the initial mode I direction (Figure 4.5b). This offset position, corresponding to an angle of ~45° to the initial mode I direction, is consistent with the positions of peak maximum shear strain that were computed in the detailed finite element simulations of the same NiAl/V composite systems [106]. These will be discussed in detail in Section 4.6.

Subsequent crack growth occurred along the deflected direction (~30° from the pure mode I direction), as shown in Figures 4.6a and 4.6b, for composites reinforced with 100 and 200 μm thick vanadium layers. Unfortunately, however, re-nucleation in the case of the composites containing 400 μm thick layers (Figure 4.6c) resulted in unstable crack growth and catastrophic failure. Also, the onset of unstable crack growth and catastrophic failure in the composites reinforced with 400 μm thick vanadium layers was associated with relatively high load increments (compared to those in the composites reinforced with 100 and 200 μm thick vanadium layers where re-nucleation of stable crack growth occurred in NiAl layers adjacent to the vanadium layers). The rates of change of crack driving force (with respect to crack length) were, therefore, close to the levels required
for unstable crack growth upon re-nucleation of crack growth in the layers adjacent to the 400 µm thick vanadium layers.

Final failure of the vanadium layers in all the specimens that were examined occurred predominately by cleavage fracture, with some ductile dimpled fracture occurring in regions close to debonds (Figures 4.7a - 4.7c). It is postulated that the occurrence of cleavage in the middle of the vanadium layers was due to the relatively high levels of stress triaxiality while the higher incidence of ductile dimpled fracture in the vicinity of the debonds was associated with the relaxation of constraints, i.e., lower levels of stress triaxiality. In contrast, the NiAl matrix failed primarily by brittle intergranular fracture (Figure 4.7d).

The resistance-curves obtained from experiments for NiAl composites reinforced with 100 and 200 µm vanadium layers are shown in Figures 4.8a and 4.8b, respectively. Each data point on the resistance curves corresponds to the position of a vanadium layer in front of the notch tip of the specimens. In both cases, resistance-curves increase significantly beyond the matrix toughness.

4.4.1.2 Fatigue Crack Growth Behavior

Stable fatigue crack growth was also observed in the layered NiAl/V composite. Such stable crack growth is difficult to achieve in monolithic NiAl under tensile loading or
bending configurations [39,106]. However, in contrast to the crack propagation in the NiAl/V composite under monotonic loading, the fatigue crack growth occurred continuously across the V layers and the adjacent NiAl matrix layers (Figures 4.9a and 4.9b). There was no evidence of crack bridging under cyclic loading (even at low ∆K levels) although evidence of crack-tip blunting was observed (Figures 4.9a and 4.9b). Fatigue crack growth in the V layers was also quite slow compared to fast growth rates in the NiAl matrix. Typical fatigue fracture modes are presented in Figures 4.10a and 4.10b. Finely spaced fatigue striations were evident along the direction perpendicular to the crack growth direction in the V layers (Figure 4.10b). Some ridges were also observed along the crack growth direction (Figure 4.10a). However, the NiAl matrix still failed predominantly by intergranular fracture (Figure 4.10a).

It is also of interest to present some of the fatigue crack growth rate data obtained from the current study. The data is presented on plots of da/dN versus ∆K in Figure 4.11. Two distinct trends are apparent in the plot. The faster fatigue crack growth rates are associated with crack growth in the NiAl layers. The fatigue crack growth rates in the V layers are substantially below those in the NiAl layers, and increase with the increasing stress intensity factor range ∆K. Further work is clearly needed to improve our basic understanding of fatigue crack growth mechanisms in the NiAl/V composite. Nevertheless, the preliminary results reported in this study suggest stable crack growth and significant toughening can be engineered in NiAl composites by the use of ductile V layer reinforcement.
4.4.2 NiAl/Nb-15Al-40Ti Composites

4.4.2.1 Crack/Microstructure Interactions and Resistance-Curve Behavior

The crack/microstructure interactions in the NiAl/Nb-15Al-40Ti microlaminates were somewhat complex due to the polycrystalline nature of the Nb-15Al-40Ti layers. Unlike the V layers, the Nb-15Al-40Ti layers were prone to grain boundary cracking during interactions with propagating cracks. This is shown clearly in Figures 4.12a - 4.12b for a specimen containing 100 μm thick Nb-15Al-40Ti layers. The initial fatigue pre-crack appears to be on the left hand side of the first layer (Figure 4.12a). However, it is possible that some segments of the crack have already intercepted the first Nb-15Al-40Ti layer across the thickness of the specimen. Consequently, the initiation toughness obtained after fatigue pre-cracking is somewhat ill-defined since it depends largely on the extent of the crack interactions with the first ductile layer ahead of the initial crack-tip. A renucleation toughness, K_i, was therefore defined in an effort to identify a crack initiation condition that was not subject to arbitrary differences in the initial crack/microstructure interactions. This was taken to correspond to the stress intensity factor at which crack renucleation was observed ahead of the first ductile layer ahead of the initial crack-tip.

Subsequent crack growth resulted in a bridged crack configuration (Figure 4.12a). However, unlike the bridging zones in the NiAl/V composites, the bridging zones in the
NiAl/Nb-15Al-40Ti composites were degraded by intergranular cracking across the Nb-15Al-40Ti layers (Figure 4.12b). The overall bridging lengths in the NiAl/Nb-15Al-40Ti composite were, therefore, much less than those in the NiAl/V composites in which the V layers remained intact prior to the onset of the catastrophic failure (Figure 4.13). Similar intergranular cracking phenomena in Nb-15Al-40Ti were observed in NiAl composites reinforced with 500 and 1000 µm thick layers (Figure 4.14b), although crack growth did not occur completely across the Nb-15Al-40Ti layers before the onset of catastrophic failure (Figure 4.14b). Crack bridging was also observed in the composites reinforced with 500 µm thick Nb-15Al-40Ti layers (Figure 4.14a), but not in those with 1000 µm thick Nb-15Al-40Ti layers. In the latter case, the crack re-nucleation from the first intercepting layer resulted in unstable crack growth and catastrophic failure. Prior to final fracture, there was considerable evidence of plastic stretching and slip bands in the Nb-15Al-40Ti layers (Figure 4.15). Furthermore, final fracture occurred by mixed cleavage, ductile dimpled, and intergranular fracture in the Nb-15Al-40Ti layers (Figures 4.16a and 4.16b).

It is interesting to relate the above crack/microstructure interactions to the measured resistance curves presented in Figures 4.17a and 4.17b. Only limited data are presented due to the tendency of the specimens to undergo unstable crack growth after a limited amount of crack extension. It is also important to note that each point on the resistance curves corresponds to the intersection of a propagating crack with an Nb-15Al-40Ti layer, or re-nucleation from the other side of the ductile layer. Furthermore, the Nb-15Al-
40Ti layers are fractured (behind the crack-tip), as the cracks propagate through subsequent NiAl layers. The measured resistance-curves are, therefore, attributed largely to bridging by Nb-15Al-40Ti layers followed by intergranular fracture (behind the crack-tip) with increasing bridge length. This is in contrast to the NiAl/V composites in which the V layers remained intact prior to the onset of the catastrophic failure.

4.4.2.2 Fatigue Crack Growth Behavior

Stable fatigue crack growth was observed in the NiAl composites reinforced with 500 μm thick Nb-15Al-40Ti layers. The fatigue crack was bridged by the Nb-15Al-40Ti layers during the initial stage of crack growth (Figure 4.18a). However, subsequent fatigue crack growth occurred across the Nb-15Al-40Ti layers from both sides of the layers, and led to the degradation of bridge zone (Figures 4.18b). Well defined fatigue striations were evident in the Nb-15Al-40Ti layers along the direction perpendicular to the crack growth (Figure 4.19b). In any case, the NiAl matrix failed predominantly by intergranular fracture (Figure 4.19a).
4.5 DISCUSSION

4.5.1 Large-Scale Bridging Modeling

It is clear from the microscopic examination of the crack/layer interactions that crack-tip shielding in NiAl/V and NiAl/Nb-15Al-40Ti composites occurred predominantly via crack bridging (Figures 4.5, 4.6, 4.12 and 4.14). It is, therefore, of interest to examine the shielding effects due to crack bridging.

The large-scale bridging framework accounts for the weighted distribution of the bridging traction along a bridge zone (Equations 4.18 and 4.20). The remote stress intensity factor, $K_{\text{lb}}$, required to cause crack growth under large-scale bridging conditions may thus be estimated by applying the principle of linear superposition to be:

$$K_{\text{lb}} = K_i + \Delta K_{\text{lb}}$$

(4.20)

where $K_i$ is the stress intensity factor required for re-nucleation from the first layer that intercepts the propagating crack. This is used instead of the matrix toughness, $K_m$, because bridging does not occur prior to matrix crack re-nucleation from the first layer that intercepts the crack. Furthermore, the variabilities in the measured values of $K_i$ are generally significantly less than those in the initiation toughness values associated with compression pre-cracks whose positions are less well defined across the specimen.
thickness, as shown in the case of NiAl/Nb-15Al-40Ti composites. This again indicates that $K_i$ is a more appropriate term to use in Equation 4.20. The values of $K_i$ obtained for the three layer thickness in each composites are summarized in Tables 4.2 and 4.3, respectively. This shows that $K_i$ increases with increasing layer thickness.

The prediction of $K_{lb}$ employs the traction function, $\sigma(x)$, which depends on the stress-stretch relationships determined from the experiments on the single layer composite tensile tests. Here, $\sigma(x)$ is assumed as a constant and be equated to the yield stresses of the monolithic V and Nb-15Al-40Ti foils. The predicted large-scale bridging resistance-curves are presented in Figures 4.8 and 4.17. Note that no large-scale bridging predictions were obtained for composites with 400 µm thick vanadium layers and 1000 µm Nb-15Al-40Ti layers since bridging was not observed in these specimens. As in prior studies on other intermetallic composite systems [88,90-92,114], the large-scale bridging predictions are comparable to the measured resistance-curves. Similar large-scale bridging results have been reported in previous studies on other ductile phase toughened intermetallic matrices such as MoSi$_2$/Nb[114], Nb$_3$Al/Nb [90-92] and TiAl/TiNb [88].

Since neither the measured resistance-curves nor the large-scale bridging resistance-curves exhibit steady-state toughness values. An attempt has been made to obtain the specimen independent steady-state toughness, $K_{ss}$, from Equations 4.19 and 4.20 by assuming a specimen width that is significant greater than the length of bridge zone, i.e., simulating small-scale bridging conditions artificially. This approach, which was first
applied by Bloyer et al. [90-92] to Nb3Al/Nb layered composites, has the advantage of providing intrinsic toughness values that are essentially independent of specimen geometry differences. The calculated steady-state toughness values for NiAl/V and NiAl/Nb-15Al-40Ti composites are listed in Tables 4.2 and 4.3, respectively. Note that the values of $K_{ss}$ increase with increasing layer thickness.

It is interesting to compare the above predicted steady-state toughness with theoretical estimates of $\Delta K_b$ from Equations 4.13 and 4.14. The results are also shown in Tables 4.2 and 4.3. The materials parameters that were used in the modeling are summarized in Table 4.1. The analysis assume that the ductilities of the ductile layers are somewhat degraded due to interdiffusion phenomena and constrained yielding. In any case, the predicted steady-state toughness levels from Equations 4.13 and 4.14 are generally comparable to those extrapolated from weight function method (Equations 4.19 and 4.20). The modeling framework presented in Equations 4.13 and 4.14, therefore, appears to provide reasonably accurate estimates of the fracture toughness of the model microlaminates that were examined in this study.

4.5.2 Comparison with Other Layered Systems

The current results are consistent with the results of Bloyer et al. [90-92] who also show that the intrinsic steady state toughness values increase with increasing layer thickness in ductile layer toughened brittle matrix composites. The above trends, therefore, appear to
apply generally to brittle matrix composites (microlaminates) reinforced with ductile layers. However, they may not apply to nanolaminates in which toughening may be controlled by dislocation/boundary interactions and pile-ups at interfaces [115,116]. Such nanoscale composites may offer some opportunities for toughening by layer refinement. However, the limited amount of experimental data for such systems [117,118] suggest that the fracture toughness levels in nanolaminates are limited to levels between $-1 - 5 \text{ MPa}\sqrt{\text{m}}$. Microlaminate architectures, therefore, appear to offer greater opportunities for the design of tough composites than nanolaminates, at least within the near term. This is particularly encouraging since the microlaminates are relatively easy to fabricate compared to nanolaminates. The larger dimensions in microlaminates can also be controlled easily by varying the foil dimensions or the amount of powder that is used in the lay-up of the composites.

### 4.5.3 Implications for Damage Tolerant Design

The two model systems examined in the current study show consistently that significant resistance-curve behavior can be engineered in brittle NiAl composites reinforced with ductile layers with thickness in the range between 100 to 1000 $\mu$m. Similar improvements in microlaminate fracture toughness have also been reported by Kajuch et al. [87] for niobium silicide composites reinforced with ductile Nb layers. Ye et al. [105, 114] and Shaw and Abbaschian [101] have also demonstrated that MoSi$_2$/Nb microlaminates exhibit large improvements in fracture toughness/resistance-curve
behavior that are comparable to those observed in this study on NiAl microlaminates. However, none of the above systems are suitable for applications as structural materials in high temperature systems. This is due largely to the fact that their "true" initiation toughness (from the pre-cracks) levels are still close to those of the brittle matrix materials. Subsequent resistance-curve behavior is also associated largely with intermittent crack/layer interactions in which relatively fast crack growth rates occur between the individual ductile layers [13,92]. This is especially true under cyclic loading where the crack growth rates are particularly fast, compared to those in ductile layers [13,92]. One example of the relatively fast growth rates in the brittle NiAl layers is shown in Figure 4.11 in which fatigue crack growth rate data obtained for NiAl/V microlaminates are compared. The fatigue crack growth rates are relatively slow in the ductile vanadium layers where fatigue crack growth occurs by classical crack-tip blunting mechanisms [23] that give rise to striation formation (Figure 4.10b). In contrast, fast fatigue crack growth rates occur in the NiAl layers where crack growth occurs predominantly by intergranular fracture, as shown in Figure 4.10a.

The very fast crack growth rates in the brittle matrix materials, therefore, result in average fatigue crack growth rates in the composites/microlaminates that are too fast for damage tolerant structural applications in high temperature systems such as aeroengines and land-based engines. However, it is possible that the layered composite architectures (microlaminates) may be used in the design of damage tolerant coatings that undergo progressive, but controlled degradation, due to combinations of cracking and oxidation.
phenomena (Figure 4.20) [119]. The lives of such coatings would, therefore, depend on the time required for "failure" to occur from these two mechanisms. Further work is needed to explore the possible design of novel multilayered coatings within this framework.

4.6 FINITE ELEMENT ANALYSIS

4.6.1 Modeling Technique

For layered NiAl/V composites, the crack driving forces and local strain distributions associated with the observed crack/microstructure configurations were modeled using the finite element package ABAQUS produced by Hibbitt, Karlsson & Sorensen, Inc., Pawtucket, RI. A plane strain assumption was made in all the analysis, and approximately 90,000 eight-node isoparametric elements were used to model the individual NiAl, V and interfacial layers (which were assumed to have properties similar to those of NiAl), as shown in Figure 4.21.

Special collapsed crack-tip elements were used to model the crack-tip regions. These are special quarter-point elements that are standard features within the ABAQUS software package. They are used to model the singularity at the crack-tip. Mode I J-integral, \( J_I \), and stress intensity factors, \( K_I \), were calculated for all the observed crack/microstructure combinations, which generally correspond to stable/stationary configurations in which
the cracks were in contact with the vanadium layers. It is important to note here that crack growth was generally unstable in the NiAl layers, except under cyclic compression. Furthermore, the constituent mechanical properties of the individual layers were assumed to be isotropic. The constituent mechanical properties that were used in the finite element simulations are summarized in Table 4.1. Interfacial properties are not presented since the results presented in the current study were actually obtained from finite element simulations in which the interfaces were assumed to have similar elastic properties to the matrix material NiAl.

4.6.2 Resistance-Curves Calculated from Finite Element Modeling

Before presenting the resistance-curves calculated from finite element modeling, it is important to note here that all the stress intensity factors, K, presented in this section were computed using finite element methods described earlier, i.e., the crack driving force estimates were obtained from finite element idealizations of the observed crack/layer configurations. As in previous studies by other researchers [84,88,90-92,114], the mode I stress intensity factor was used to describe the crack driving force, although it is recognized that the crack-tip fields in the multilayered specimens are inherently mixed mode in nature, especially when the cracks are deflected at an angle of ~30°. Also, stress intensity factors are only presented after verifying that small-scale yielding conditions apply to the specific crack configurations, i.e., the plastic zone sizes estimated from the Von Mises yield criterion were much smaller than the crack lengths.
The resistance-curves obtained from the detailed finite element computations of each crack configuration are presented in Figures 4.22 for three different layer thickness (100, 200 and 400 μm). The initiation toughness was \(-6.5 \text{ MPa}\sqrt{\text{m}}\) in all the three composites that were examined. This is close to the matrix toughness of \(-6.6 \text{ MPa}\sqrt{\text{m}}\). Also, the resistance-curve behavior was almost identical in the composites containing 100 and 200 μm thick vanadium layers, although the steady-state fracture toughness of the composite reinforced with 200 μm thick vanadium layers is greater than that of the composite reinforced with 100 μm thick vanadium layers. The resistance-curves in these composites were associated with large-scale bridging, as shown in Figures 4.6a and 4.6b. In contrast, a much steeper resistance-curve was observed in the composite that was reinforced with 400 μm thick vanadium layers. Furthermore, catastrophic failure always initiated in this composite after the interaction of the cracks with the first row of intersecting vanadium layers (Figure 4.6c). The steep resistance-curve behavior of the composite containing 400 μm thick vanadium layers is, therefore, associated with the transmission of strain across the first intersecting vanadium layer.

4.6.3 Finite Element Modeling of Crack/Microstructure Interactions

The finite element simulations discussed above provide some useful insights into the observed crack/microstructure interactions. Peaks are observed in the maximum shear strain distributions along the interfaces between the vanadium and the NiAl layers for all
the vanadium layer thickness (100, 200 and 400 μm), as shown in Figure 4.23. The position of peaks corresponds to an angle of ~45° to the initial mode I direction on the other side of the vanadium layers. The elevated interfacial strain levels are thought to be responsible for the small amount of interfacial debonding and the re-nucleation of crack growth in the adjacent interfacial layers (Figures 4.5 and 4.6). As shown in Figures 4.5 and 4.6, the crack re-nucleation always occurs at a point that is offset somewhat from the initial mode I direction. This offset position, corresponding to an angle of ~45° to the initial mode I direction, is consistent with the positions of the peak maximum engineering shear strain that were computed in the finite element analyses (Figure 4.23). Finally in this section, it is important to note that the predicted loads (from the finite element analysis) at which the cracks were observed to re-nucleate in the adjacent interfacial layers were comparable to the measured loads (Table 4.4).

4.7 CONCLUSIONS

The fracture toughness/resistance-curve behavior of two model microlaminates (NiAl/V and NiAl/Nb-15Al-40Ti) systems has been investigated in this study. The salient conclusions arising from the study are summarized below:

1. The specimen-independent intrinsic steady-state fracture toughness of ductile layer reinforced microlaminates increases with increasing thickness of the ductile layers. The improved intrinsic toughness values and the observed resistance-curve behavior are
attributed largely to the shielding effects of crack bridging by the ductile layers. Estimates of the resistance curves obtained from layer bridging models are also in general agreement with the measured resistance curves.

2. The crack/layer interactions in the NiAl/V composites are similar for the three vanadium layer thickness (100, 200 and 400 μm) examined in this study. Resistance-curve behavior in these systems is associated with the following sequence of events: crack retardation by the ductile vanadium layers; slip band nucleation ahead of the crack-tip in the vanadium layers; renucleation of crack growth in adjacent NiAl layers, and crack bridging by the uncracked vanadium layers behind the crack-tip. The above sequences is repeated until unstable crack growth occurs during crack re-nucleation occurs in the adjacent NiAl layers. The increase in the stress intensity factor required for renucleation also increases with increasing ductile vanadium layer thickness. However, renucleation is most likely to be followed by unstable crack growth/catastrophic failure in the case of the composite reinforced with the thicker layers.

3. Similar phenomena are observed in the NiAl/Nb-15Al-40Ti composites. However, the crack/layer interactions in these systems are more complex due to the polycrystalline nature of the Nb-15Al-40Ti layers and the interfacial reaction that occurs between the NiAl and Nb-15Al-40Ti layers. The former give rise to intergranular crack growth across the Nb-15Al-40Ti layers, while the latter gives rise to limited debonding. The intergranular crack growth across the Nb-15Al-40Ti layers also tends to decrease the
sizes of the bridging zones since they lead to premature failure of the Nb-15Al-40Ti layers. Nevertheless, the NiAl/Nb-15Al-40Ti composites exhibit significant resistance-curve behavior. The measured resistance-curves are also predicted by fracture mechanics models in which the actual bridging and crack/layer dimensions are used.

4. In spite of the observed and predicted resistance curve behavior, the model microlaminate systems investigated in this study are not recommended for future consideration for possible structural applications in high temperature systems. This is due largely to the relatively low "initiation" toughness levels and the fast crack growth rates in the brittle NiAl layers. The average crack growth rates in the composites/microlaminates are considered to be too fast for potential structural applications. However, it is possible that the layered composite configurations in high temperature coatings, especially in systems where the model ductile layers are replaced by oxidation resistant alloys such as nickel-base superalloys. Further work is clearly needed to explore such possibilities.

5. The initiation toughness levels for pre-cracks in the NiAl layers are close to the NiAl matrix fracture toughness. However, these initiation toughness levels are below the stress intensity levels required to re-nucleate cracks ahead of the front row of ductile layers that intercept the propagating cracks during the resistance-curve experiments. Since the re-nucleation processes occur just prior to the development of a bridging zone, the re-nucleation toughness, $K_i$, is proposed as a measure of the initiation toughness in
the analysis to estimate the resistance-curve behavior. Also, $K_I$ increases with increasing ductile layer thickness.

6. In layered NiAl/V composites, the re-nucleation of cracks always occurs at an offset position corresponding to an angle of $\sim 45^\circ$ to the initial mode I direction. The re-nucleation of cracks in adjacent NiAl layers occurs at positions of maximum engineering shear strain at the interface between NiAl and vanadium. The subsequent crack growth occurred along the deflected direction ($\sim 30^\circ$ from the pure mode I direction), as they extend further into the NiAl layers. Similar re-nucleation phenomena are observed in the composites with the different layer thickness. However, re-nucleation is followed by catastrophic failure in the composites reinforced with 400 $\mu$m thick vanadium layers.
Table 4.1 Material Properties of NiAl, V and Nb-15Al-40Ti

<table>
<thead>
<tr>
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<tr>
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<td>103</td>
<td>101</td>
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<tr>
<td>Possion's Ratio ν</td>
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Table 4.2 Comparison of Initiation Toughness and Steady-State Toughness for NiAl/V Laminate

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<tr>
<th>V Layer Thickness (μm)</th>
<th>Initiation Toughness K_i (MPa√m)</th>
<th>Steady-State Toughness K_ss (MPa√m)</th>
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<td>200</td>
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<td>400</td>
<td>20.9</td>
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<tr>
<td>Nb-15Al-40Ti Layer Thickness (µm)</td>
<td>Initiation Toughness $K_i$ (MPaVm)</td>
<td>Steady-State Toughness $K_{ss}$ (MPaVm)</td>
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<td>---------------------------------</td>
<td>-------------------------------------</td>
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Table 4.3 Comparison of Initiation Toughness and Steady-State Toughness for NiAl/Nb-15Al-40Ti Laminate

<table>
<thead>
<tr>
<th>100 µm V laminate</th>
<th>200 µm V laminate</th>
<th>400 µm V laminate</th>
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<td>$\Delta a$ (µm)</td>
<td>$P_{EX}$ (N)</td>
<td>$P_{FEM}$ (N)</td>
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<tr>
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<tr>
<td>1700</td>
<td>4360</td>
<td>4805</td>
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</table>

$\Delta a$: Crack increment, $P_{EX}$: Experimental data, $P_{FEM}$: FEM prediction

Table 4.4 Applied Loads Calculated from FEM vs. Experimental Results
Figure 4.1 Idealization of crack opening profile due to ductile layer bridging: (a) $c \to 0$ and (b) $c = a/b$.

Figure 4.2 Stress vs. average displacement showing elastic-perfectly plastic behavior of ductile layer (after Budiansky et al. [25]).
Figure 4.3 Typical microstructure of NiAl/V composites: Optical micrograph of NiAl composites reinforced with (a) 100 µm thick V layer, (b) 200 µm thick V layer, and (c) 400 µm thick V layer, and (d) SEM micrograph of the interface between NiAl and V layers.

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<td>Al</td>
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<tr>
<td>V</td>
<td>0      78.8 74.5 99.2</td>
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106
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<th>4</th>
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Figure 4.4 Typical microstructure of NiAl/Nb-15Al-40Ti (40Ti) composites: Optical micrograph of NiAl composites reinforced with (a) 100 μm thick Nb-15Al-40Ti layer, (b) 500 μm thick Nb-15Al-40Ti layer, and (c) 1000 μm thick Nb-15Al-40Ti layer, and (d) SEM micrograph of the interface between NiAl and Nb-15Al-40Ti layers.
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Figure 4.12 Crack/microstructure interactions in NiAl composites reinforced with 100 μm thick Nb-15Al-40Ti (40Ti) layer: (a) Crack bridging and (b) bridging degradation by intergranular fracture across Nb-15Al-40Ti layers.
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Figure 4.15 Extensive plastic deformation observed in 500 μm thick Nb-15Al-40Ti (40Ti) layers after the failure of NiAl/Nb-15Al-40Ti composites.

Figure 4.16 Typical fracture modes in layered NiAl/Nb-15Al-40Ti (40Ti) composite: (a) 100 μm thick Nb-15Al-40Ti layer and (b) 500 μm thick Nb-15Al-40Ti layer.
Figure 4.17 Resistance-curves obtained for NiAl/Nb-15Al-40Ti composites from experiments and estimated from large-scale bridging model (LSB): (a) 100 μm and (b) 500 μm Nb-15Al-40Ti laminates. Kss is the steady-state toughness extracted from the weight function method.
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Figure 4.23 Maximum shear strain distribution along interface between NiAl and vanadium layers for NiAl/V composites reinforced with vanadium layers of three thickness.
CHAPTER 5

TRANSFORMATION TOUGHENING OF NiAl

5.1 INTRODUCTION

Since the pioneering work of Garvie et al. [49], transformation toughening in partially stabilized zirconia and zirconia toughened ceramics has been a subject of intensive study [44-69]. The studies have shown that the metastable tetragonal phase of zirconia can transform martensitically to monoclinic phase under an applied stress [44-69]. This stress-induced martensitic transformation is associated with a volume increase of approximately 3 - 5% (due to the lower density of the monoclinic phase) and can greatly enhance the fracture toughness of partially stabilized zirconia (PSZ), and brittle matrix composites reinforced with PSZ [40-71]. In both cases, a transformation zone is created as a crack propagates through a matrix reinforced with transforming particles, and a shielding stress is exerted on the crack (Figure 5.1). This reduces the local stress intensity level at the crack tip, and thus improves the fracture toughness of the material.
Transformation toughening of NiAl has been studied by Barinov et al. [40-42], who showed that the fracture toughness of NiAl can be improved from a matrix fracture toughness of ~15 MPa√m to a fracture toughness of ~25 MPa√m after reinforcement with partially stabilized zirconia (PSZ) particles. They argued that the fracture toughness increment was due to transformation toughening on the basis of X-ray diffraction (XRD) analysis of the fracture surfaces and residual stress analysis. However, they did not conduct Raman spectroscopy and crack-tip transmission electron microscopy (TEM) studies to demonstrate conclusively the occurrence of the stress-induced phase transformation. Also, the NiAl matrix toughness that they measured in their studies was anomalously high (~15 MPa√m compared with typical values of ~4 - 7 MPa√m reported by other researchers [1-3,38,39,43,72]).

Ramasundaram et al. [43] have also studied the NiAl composites reinforced with PSZ particles with different Y₂O₃ stabilization levels between 0 and 6 mole percent. They found significant toughness improvement (from a matrix value of 5.3 MPa√m to a maximum of 14.1 MPa√m), especially in the NiAl/TZ-2Y (PSZ with 2 mole % Y₂O₃) composite. They also used Raman spectroscopy and TEM analysis to verify and quantify the occurrence of transformation toughening in the NiAl/TZ-2Y composite. The degree of transformation toughening was estimated using Raman spectroscopy measurements (of the spatial variation of the monoclinic phase content within the transformation zone) and micromechanics models that considered only dilatational stress-induced phase transformations. The predictions obtained from these models were generally lower than
the measured toughening levels [43]. Also, transformation toughening was not detected in composites reinforced with unstabilized zirconia (no \(Y_2O_3\)), and PSZ containing 4 and 6 mole % \(Y_2O_3\) [43].

Zeng et al. [120] have developed discrete finite element models for the estimation of toughening due to purely dilatational stress-induced phase transformations. They modeled the same NiAl/TZ-2Y composite that was studied by Ramasundaram et al. [43], and predicted somewhat higher toughening levels than those obtained from the smeared-out dilatational models [56,57] that were used in the studies of Ramasundaram et al. [43]. However, they were unable to fully account for the measured toughening levels in the NiAl/TZ-2Y composites, as shown in Table 5.1. Similar problems have been encountered by other researchers who have often found that the dilatational toughening models may not fully predict the measured toughening levels [55,60-65]. This suggests that the effects of shear stresses may also be important in the estimation of toughening due to stress-induced phase transformations.

Shear-induced phase transformations have been demonstrated by Chen and co-workers [61,62] in MgO-stabilized and CeO-stabilized zirconia. Budiansky and Truskinovsky [63], Simha and Truskinovsky [64] and Stam and van der Giessen [65] have also modeled the effects of shear on the transformation toughening of zirconia ceramics. However, with the exception of prior work by Chen [61,62], there are no combined experimental and theoretical studies that explore the role of dilatation and shear in
toughening of transformation toughened brittle matrix composites that do not have partially stabilized zirconia matrices.

The current study presents the results of a combined experimental and theoretical study of transformation toughening on the fracture toughness/resistance-curve behavior of a model NiAl composite reinforced with 20 vol. % of 2 mole % yttria-partially stabilized zirconia (YSZ). The extent of stress-induced phase transformation is characterized using laser Raman spectroscopy. The shielding effects of the stress-induced phase transformations are also estimated with analytical micromechanics models that assess the effects of dilatation and shear. As in previous studies [55,60-65], approximate dilatational models (with truncations of Taylor series expansions) are shown to underpredict the overall levels of transformation toughening. However, untruncated dilatational solutions provide better estimates of the overall toughening levels due to purely dilatational stress-induced martensitic phase transformations. Furthermore, the predictions obtained from untruncated dilatational plus shear solutions are shown to be in good agreement with experimentally-determined toughening levels.

5.2 MICROSTRUCTURE

The microstructure of the NiAl/YSZ composites is presented in Figure 5.2. The zirconia phase occupied the grain boundary regions defined by the NiAl grains due to the large differences between the starting particles sizes of the NiAl (~25 μm) and the zirconia.
(~0.3 μm) powders. No porosity was observed. X-ray spectroscopy (XRD) and Raman spectroscopy analyses showed the zirconia phase in the composites was almost completely tetragonal. It is also important to note that all the YSZ particles were polycrystalline in nature. This has been demonstrated in prior TEM analysis of similar NiAl/YSZ composites which revealed that each of the YSZ agglomerates consists of particles/grains that are approximately 0.3-0.5 μm in diameter [43]. The YSZ particle sizes, which are the important microstructural scale for transformation toughening [44-47, 51-55], were, therefore, much less than the agglomerate sizes in Figure 5.2.

5.3 RESULTS AND DISCUSSION

5.3.1 Resistance-Curve Behavior and Crack/Microstructure Interactions

The measured resistance-curve obtained for the NiAl/YSZ composite is presented in Figure 5.3. This shows that the composite has an initiation toughness of ~7.8 MPa√m. This initiation toughness is slightly higher than the matrix toughness, $K_m$, of NiAl of ~6.6 MPa√m. The increase is due to the closure tractions associated predominantly with stress-induced phase transformations in the transformation zone behind the crack-tip of the fatigue pre-crack. These closure tractions give rise to an increase in the initiation toughness prior to the onset of crack growth. Subsequent resistance-curve behavior is strong, and the stress intensity factor required to promote stable crack growth increases rapidly until a steady-state toughness, $K_{ss}$, of ~11.8 MPa√m is approached. However,
unstable crack growth and catastrophic failure ensued after ~260 μm of stable crack growth.

The crack/microstructure interactions associated with the measured resistance-curve behavior are presented in Figure 5.4. Stable crack growth and catastrophic failure of NiAl grains occurred predominantly by transgranular fracture, as is also evident from the fracture surface presented in Figure 5.5. It is important to note here that stable crack growth (of the type observed in this study) has not been reported in monolithic NiAl, which generally undergoes unstable crack growth and intergranular fracture at an initiation toughness of ~6-7 MPa√m [1-3,43,72]. The occurrence of stable crack growth in the NiAl/YSZ composite was therefore attributed to the beneficial effects of transformation induced "plasticity". Failure of YSZ particles occurred primarily by intergranular fracture of the very fine zirconia grains (Figure 5.5).

5.3.2 Raman Spectroscopy Analysis

In an effort to distinguish between monoclinic zirconia phase produced by the stress-induced transformation and that in the bulk, Raman spectroscopy analysis was performed on the bulk material far away from the crack faces, as well as material close to crack/fracture faces. The bulk volume fraction of transformed phase was thus determined using Equation 2.15. This was subtracted from the total volume fraction of monoclinic phase in the transformation zone, to obtain an estimate of the volume fraction of
monoclinic phase produced by stress-induced phase transformation. The volume fraction of transformed phase, c, was thus estimated as a function of the distance from the crack face. The height of the transformation zone, h, was also estimated from the distance at which the volume fraction of transformed phase was found to be equal to the bulk volume fraction of tetragonal zirconia. In this way, two of the parameters that are critical to the modeling of transformation toughening were determined for use in subsequent micromechanical modeling.

The Raman spectroscopy analysis revealed that stress-induced phase transformations (from tetragonal to monoclinic phase) occurred in the zirconia particles close to the crack face. Typical Raman spectra obtained from the material close to crack/fracture faces and the bulk material far away from the crack faces are shown in Figure 5.6a and 5.6b, respectively. Note the intense tetragonal zirconia peaks in Figure 5.6a. The volume fraction of monoclinic phase is plotted as a function of distance from the crack face in Figure 5.7. As usual in transformation toughened materials [55,60-62], there is a region of saturation close to the crack faces, and the volume fraction of transformed monoclinic phase decreases with increasing distance from the crack face (Figure 5.7). Since the average volume percentage of transformed monoclinic phase in the bulk was ~2 %, we may estimate the size of the transformation zone to be ~30 μm from Figure 5.7. The average volume percentage of transformed monoclinic phase within the transformation zone may also be estimated to be ~30 %. Thus, the volume fraction of the zirconia undergoing transformation was estimated to be 0.06 (this is equal to the total volume
fraction of zirconia of 0.2 multiplied by 30 % of the particles that undergo stress-induced phase transformation in the transformation zone). These measured values will be used in the estimation of toughening components in the next section.

5.3.3 Toughening Analysis

The toughening due to stress-induced martensitic transformations in YSZ particles, $\Delta K_T$, may be estimated using the well known analysis of McMeeking and Evans [56] and Budiansky et al. [57]. For purely dilatational transformations, this gives [56,57]:

$$\Delta K_T = \frac{0.22 E_c f e_c^T \sqrt{h}}{1 - \nu}$$

(5.1)

where $E_c$ is the composite modulus (~191 GPa), $f$ is the volume fraction of the zirconia undergoing transformation (~0.06), $e_c^T$ is the transformation strain (~4 %), $h$ is the height of the transformation zone (~30 µm) and $\nu$ is the Poisson's ratio (~0.3). Substituting the above data into Equation 4.1, we may estimate the shielding contributions, $\Delta K_T$, due to transformation toughening to be ~0.8 MPa/√m. This clearly underestimates the overall toughening that was determined in the fracture toughness/resistance curve experiments, $\Delta K_{ex}$, given by:

$$\Delta K_{ex} = K_{ss} - K_m$$

(5.2)
Since $K_{ss}$ is 11.8 MPa\(\sqrt{m}\) and $K_m$ is 6.6 MPa\(\sqrt{m}\), the overall toughness increment, $\Delta K_{ex}$, is 5.2 MPa\(\sqrt{m}\). Similar discrepancies have been reported by Ramasundaram et al. [43] and Zeng et al. [120] for NiAl/TZ-2Y (PSZ with 2 mole % Y\(_2\)O\(_3\)) composites when toughening estimates were obtained using purely dilatational models as shown in Equation 5.2. A number of other researchers [55,60-65] have also reported that the overall levels of transformation toughening in zirconia-toughened ceramics cannot be fully accounted for by micromechanical models that only account for the dilatational effects associated with volume changes due to the tetragonal-to-monoclinic stress-induced phase transformations.

This suggests than the role of shear must also be accounted for in the estimation of the overall toughening due to stress-induced phase transformations. The role of shear was neglected in much of the prior work because the orientations of the different shear variants were thought to effectively cancel each other out. However, work by Chen and co-workers [61,62], Simha and Truskinovsky et al. [64], and Stam and van der Giessen [65] has shown that it is important to account for shear in the estimation of the overall toughening levels due to stress-induced phase transformations from tetragonal phase to monoclinic phase. The current study will, therefore, explore a micromechanical modeling framework in which the roles of dilatational and shear stresses/strains will be investigated.
The approach that will be utilized is based on the work of Chen and co-workers [61,62] and Evans et al. [60] who developed much of the fracture mechanics framework (for the estimation of transformation toughening) that is used in this thesis. The work by Chen and co-workers [61,62] established the basic mechanisms approach to the modeling of shear, while Evans et al. [60] proposed the use of the Hutchinson-Rice-Rosengreen (HRR) field expressions in the characterization of the complex stress and strain fields in the transformation zone.

Transformation toughening in this work is attributed largely to the shielding effects provided by closure tractions in the transformation zone behind the crack-tip. These closure tractions can give rise to an increase in the fracture initiation toughness to levels that are greater than the matrix fracture toughness. This has been discussed in Section 5.3.1. The closure tractions associated with an evolving transformation zone can also give rise to resistance-curve behavior, as shown in Figure 5.2, for the NiAl/PSZ composite that was examined in this study.

Furthermore, it is important to note here than the resistance-curve approaches a steady-state toughness, $K_{ss}$, as the crack length increases. This is associated with the evolution of a steady state process zone with a height, $h_0$ (Figure 5.8). The process zone also includes a region with height $h_i$, where the transformation is saturated, and a partially transformed region between $h_i$ and $h_0$ [62].
The overall toughening due to stress-induced phase transformations may be estimated from a simple energy balance [57]. This gives:

\[ J = J_m + \Delta J = J_m + 2 \int_{y} U(y)dy \]  

(5.3)

where \( J \) is the J-integral, \( U(y) \) is the energy per unit volume associated with loading and unloading cycle and \( \Delta J \) represents the toughness increment due to stress-induced phase transformations.

As discussed earlier, Evans et al. [60] have proposed that the stress-strain field within the transformation zone may be approximated with HRR field expressions. Hence, assuming a stationary crack (this is not really true for a growing crack in a resistance-curve test), \( \Delta J \) may be estimated to be [62]:

\[ \Delta J = f \frac{2n}{n+1} h_0 \sigma_0 \varepsilon_0 \ln \left( \frac{h_0}{h_i} \right) \]  

for dilatational transformations \hspace{1cm} (5.4)

or

\[ \Delta J = f \frac{2n}{n+1} h_0 \tau_0 \gamma_0 \ln \left( \frac{h_0}{h_i} \right) \]  

for shear transformations \hspace{1cm} (5.5)
where $n$ is the inverse of the strain hardening exponent, $\sigma_0$ and $\tau_0$ are the yield stresses in pure dilatation and pure shear, respectively, and $\varepsilon_0$ and $\gamma_0$ are the yield strains in pure dilatation and pure shear, respectively. Furthermore, from the strain expressions in the Ref. [62], we may obtain the following expressions:

$$\frac{h_i}{h_0} = \left( \frac{\sigma_0}{B\varepsilon_m^*} \right)^{\frac{n+1}{n}}$$  \hspace{1cm} (5.6)$$

and

$$\frac{h_i}{h_0} = \left( \frac{\tau_0}{G\gamma_c^*} \right)^{\frac{n+1}{n}}$$  \hspace{1cm} (5.7)$$

Substituting Equations 5.6 and 5.7 into Equations 5.4 and 5.5, respectively, gives:

$$\Delta J = 2f_{h_0}\sigma_0 \left( \frac{\sigma_0}{G} \right) \ln \left( \frac{B\varepsilon_m^*}{\sigma_0} \right) = 2f_{h_0}\sigma_0 \left( \frac{\sigma_0}{G} \right) \ln \left( 1 + \frac{B\varepsilon_m^*}{\sigma_0} \right)$$  \hspace{1cm} (5.8)$$

and

$$\Delta J = 2f_{h_0}\tau_0 \left( \frac{\tau_0}{G} \right) \ln \left( \frac{G\gamma_c^*}{\tau_0} \right) = 2f_{h_0}\tau_0 \left( \frac{\tau_0}{G} \right) \ln \left( 1 + \frac{G\gamma_c^*}{\tau_0} \right)$$  \hspace{1cm} (5.9)$$
For a weak transformation, we may estimate the overall toughening by considering only the first term in the Taylor series expansion for the logarithmic functions. This gives:

\[ \Delta J = 2fh_0 \sigma_0 \varepsilon_m^T \quad \text{for dilatational transformations} \quad (5.10) \]

and

\[ \Delta J = 2fh_0 \tau_0 \gamma_e^T \quad \text{for shear transformations} \quad (5.11) \]

Equations 5.10 and 5.11 are equivalent to relationships obtained from prior work by Budiansky et al. [57], and Chen and Reyes-Morel [61].

The toughness increments may be expressed in terms of the stress intensity factor, \( K \), by using the standard relationship:

\[ J = \frac{K^2}{E'} \quad (5.12) \]

where \( E' = E \) for plane stress and \( E' = E/(1-\nu^2) \) for plane strain conditions, \( E \) is the Young's modulus and \( \nu \) is the Poisson's ratio. The resistance curve behavior may thus be estimated from:
\[ K_c = K_m + \Delta K_T \]  \hspace{1cm} (5.13)

where \( \Delta K_T \) is the increment in fracture toughness due to stress-induced phase transformations, and \( K_c \) is the fracture toughness of the composite material.

Finally, for the current composite in which the transitional zone has been squeezed out, Chen [62] has shown that the overall toughening increment, \( \Delta K \), for weak transformations reduces to:

\[ \Delta K = fE_c e_m^T \sqrt{\alpha_m h_0} \] for dilatational transformations \hspace{1cm} (5.14)

and

\[ \Delta K = fE_c \gamma_c^T \sqrt{\alpha_c h_0} \] for shear transformations \hspace{1cm} (5.15)

where

\[ \alpha_m = \frac{\sqrt{3(1 + \nu)^2}}{12\pi} \] \hspace{1cm} (5.16)

and
Equation 5.14 is identical to prior expressions obtained by McMeeking and Evans [56] and Budiansky et al. [57] for pure dilatational transformations (Equation 5.1), while Equation 5.15 is equivalent to a prior expression by Chen and Reyes-Morel [61]. Substituting Equation 5.17 into Equation 5.15 gives the following equation for soft shear toughening:

\[
\Delta K_T = \left[ \frac{0.1614}{1 - v} \right] \gamma_c^T E_c \sqrt{h} \quad \text{for plane strain} \quad (5.18)
\]

Substituting \( \gamma_c^T = 0.16 \) into Equation 5.18, we may estimate the shielding contributions \( \Delta K_T \) due to shear transformation toughening to be \( \sim 2.4 \text{ MPa}\sqrt{\text{m}} \). Hence, the soft shear toughening model does not fully account for the measured toughening of \( \sim 5.2 \text{ MPa}\sqrt{\text{m}} \) in the NiAl/YSZ composites. Similarly, as stated earlier, the soft dilatational model estimates the overall toughening to be \( \sim 0.8 \text{ MPa}\sqrt{\text{m}} \), which is well below the measured toughening level of \( \sim 5.2 \text{ MPa}\sqrt{\text{m}} \).
In contrast, the assumption of a strong transformation and the complete use of the terms in the logarithmic expressions in Equations 5.4, 5.5 and 5.12 leads to improved estimates of the overall toughening levels. From Figure 5.6, the size of the saturated zone close to the crack-tip, \( h_i \), can be estimated to be \( \sim 3 \, \mu m \), while the overall size of the transformation zone, \( h_0 \), is \( \sim 30 \, \mu m \). In the case of dilatational transformations, the overall composite steady-state toughness, \( K_c \), may be estimated from Equations 5.4 and 5.12 (using data obtained by Chen for MgO-stabilized and CeO-stabilized zirconia [61,62]: \( \varepsilon_0 = 0.04, \sigma_0 = 500 \, MPa, \gamma_0 = 0.16, \tau_0 = 350 \, MPa, \) and \( n = 10 \)) to be \( \sim 8.8 \, MPa\sqrt{m} \). This is closer to the measured steady state toughness of \( \sim 11.8 \, MPa\sqrt{m} \) at the end of the resistance-curve tests.

Similarly, in the case of dilation plus shear, the overall prediction of composite toughness may be estimated from Equations 5.5 and 5.12 to be \( 11.5 \, MPa\sqrt{m} \). This is in almost exact agreement with the measured steady state toughness of \( \sim 11.8 \, MPa\sqrt{m} \) at the end of the resistance-curve tests. Therefore, the introduction of shear contributions to transformation toughening does give a much better prediction of overall toughening levels obtained for NiAl/YSZ composites. In any case, the predicted composite fracture toughness values are closer to the measured fracture toughness levels when the complete expression for the toughening increments, \( \Delta J \), are used in the estimation of toughening instead of the approximations from the Taylor series expressions. This indicates that some of the prior problems in the predictions of the overall shielding contributions from transformation toughening may be associated partly with the approximate nature of the
expressions (truncated Taylor series etc.) that were used for the estimation of toughening [62]. The complete expressions for toughening due to strong transformations may, therefore, be recommended for future modeling efforts.

5.4 CONCLUSIONS

A combined experimental and theoretical study of transformation toughening of a NiAl/TZ-2Y composite has been carried out in this study. The following conclusions have been reached:

1. Stress-induced phase transformation occurs in the NiAl/YSZ composite during monotonic loading in resistance-curve experiments. The size of the saturated zone close to the crack-tip is ~3 μm, while the overall size of the transformation zone is ~30 μm. Laser Raman spectroscopy also provides estimates of the overall volume fraction of transformed monoclinic phase (due to stress-induced phase transformations) to be ~0.06.

2. A simple analytical micromechanics framework is presented for the estimation of toughening due to dilatation, or dilatation plus shear. The framework includes approximate solutions (for weak transformations) obtained from Taylor series truncations, and complete analytical solutions obtained from "smeared-out" models (for strong transformation).
3. The overall toughening due to stress-induced phase transformations in the NiAl/YSZ composite can only be fully predicted when the strong nature of the transformation is assessed within a micromechanics framework that does not include truncated Taylor series approximations. Predicted toughening levels from the untruncated dilatation plus shear solutions are in closest agreement with the measured steady-state toughening levels. This indicates the importance of incorporating shear in the prediction of transformation toughening in NiAl/YSZ composites.
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Table 5.1 Toughness Increment Associated with Transformation Toughening in NiAl/TZ-2Y Composites (after Zeng et al. [120])
Figure 5.1 Schematic illustration of transformation toughening.

Figure 5.2 Typical microstructure of NiAl/YSZ composites.
Figure 5.3 Experimental resistance-curve for NiAl/YSZ composites.

Figure 5.4 Stable crack growth in NiAl/YSZ composites.
Figure 5.5 Typical fracture modes for NiAl/YSZ composites.
Figure 5.6 Typical Raman spectra obtained from the material (a) very close to crack faces and (b) far away from crack faces. t — Tetragonal Zirconia Phase and m — Monoclinic Zirconia Phase.
Figure 5.7 Volume fraction of monoclinic zirconia phase as a function of distance from crack face after final fracture.

Figure 5.8 Crack-tip configuration showing the crack encircled by an inner zone of saturated transformation and an outer transitional zone of partial transformation (after Chen [22]). The outmost radius $r$ is denoted by $R$, which coincides with $h$ at $\theta = \theta^*$. 
CHAPTER 6

SYNERGISTIC TOUGHENING OF NiAl

6.1 INTRODUCTION

The potential for the design of synergistically toughened brittle matrix composites was first suggested by Evans [121] who recognized that interactions could occur between ductile bridging particles and transforming particles. Subsequent work by Amazigo and Budiansky [14] later confirmed Evans' suggestions that synergistic interactions could occur between crack bridging particles and transformation toughening particles, leading to overall toughening levels that are greater than the sum of the individual toughening levels. Their models presented a number of closed form analytical solutions which were later validated by Li and Soboyejo [106] for NiAl composites reinforced with partially stabilized zirconia particles and bridging Mo particles. Becher and Tiegs [104] have also presented experimental evidence of synergistic toughening in ceramic matrix composites reinforced with bridging whiskers and transforming particles.
The interactions of bridging fibers and transforming particles have also been modeled in theoretical studies by Cui [107] who also demonstrates that synergistic interactions can occur between these two toughening mechanisms. Theoretical work by Stump [122] and Stump and Budiansky [123] has also demonstrated the potential opportunities for synergistic interactions between crack bridging and transformation toughening. However, there are no prior studies of the possible interactions between ductile layer toughening and transformation toughening by stress-induced martensitic transformation. Since bridging ductile layer reinforcement generally has a greater toughening effect than particulate or fiber reinforcement [13,91], the opportunities are explored for the synergistic toughening of model hybrid composites reinforced with ductile bridging layers and particles that undergo stress-induced martensitic phase transformations.

This chapter is divided into two sections. In the first section, the results of an effort to engineer synergistic toughening in a hybrid NiAl composite reinforced with 20 vol. % yttria stabilized zirconia (YSZ) and 20 vol. % molybdenum particles (NiAl/YSZ/Mo(p)) are presented. The composite is shown to exhibit strong resistance-curve behavior and toughness levels that are intermediate between the minimum and maximum levels suggested by Amazigo and Budiansky [14]. The overall toughening levels are quantified within the framework of superposition and synergistic toughening models. The implications of the results are also examined for the design of tough intermetallics and ceramics.
In the second section of the chapter, crack bridging by ductile layer reinforcements is considered before a review of relevant theory on transformation toughening in the first part. The possible interactions between crack bridging and transformation toughening are also considered in the first part of the section before presenting the microstructure of the hybrid NiAl composites reinforced with 20 vol. % yttria stabilized zirconia particles and 20 vol. % 200 μm thick vanadium layers (NiAl/YSZ/V) in the second part. The experimental evidence of synergistic toughening in the hybrid NiAl/YSZ/V composites, along with the implications of the theoretical and experimental results, is discussed in the third part of the section. The conclusions are then given in the fourth part.

6.2 NiAl/YSZ/Mo(p) COMPOSITES

6.2.1 Microstructure

The microstructure of the NiAl/YSZ/Mo(p) composites is presented in Figure 6.1. This shows a relatively uniform distribution of Mo particles in a hybrid matrix of NiAl + YSZ. Note that the YSZ particles were distributed largely along the boundaries of the NiAl grains. This is due largely to the large difference between the NiAl and YSZ particle sizes. Nevertheless, the model microstructure presented in Figure 6.1 is thought to provide an adequate framework for the basic study of synergistic toughening that is reported in the current study. Future work will clearly require microstructure development to produce structures with more uniform distributions of YSZ.
6.2.2 Results and Discussion

6.2.2.1 Resistance-Curve Behavior and Raman Spectroscopy Analysis

The measured resistance-curve behavior for the hybrid composite is presented in Figure 6.2. This shows that the hybrid NiAl/YSZ/Mo(p) composite has an initiation toughness of \( \sim 5.8 \text{ MPa}\sqrt{\text{m}} \). This is equal to the matrix toughness of NiAl, \( K_m \), measured using specimens of same dimensions in the current study. Subsequent resistance-curve behavior is strong, and the composite rapidly approaches a steady-state toughness of \( \sim 11.5 \text{ MPa}\sqrt{\text{m}} \). However, the true steady-state was not reached prior to the onset of catastrophic failure.

The crack/microstructure interactions associated with the measured resistance-curve behavior are illustrated in Figure 6.3a. This shows clearly that the composite exhibits ductile particle bridging during stable crack growth. This is a happy result that is not easy to accomplish in hybrid composites of this type [104,105]. It is also important to note that evidence of ligament bridging was observed prior to final fracture (Figure 6.3b). However, further work is needed to optimize the microstructure of hybrid toughened composites. Final failure occurred by cleavage of the NiAl and Mo grains and intergranular fracture of YSZ particles (Figure 6.4), as in prior studies of NiAl/YSZ and NiAl/Mo composites by Ramasundaram et al. [39,43].
The laser Raman spectroscopy analysis revealed that stress-induced phase transformations (from tetragonal to monoclinic phase) occurred in the zirconia particles. The results are shown in Figure 6.5 in which the volume fraction of monoclinic phase is plotted as a function of distance from the crack face. As usual in transformation toughened materials [58,59,105,106], the volume fraction of transformed monoclinic phase decreases with increasing distance from the crack face (Figure 6.5). Since the volume fraction of transformed monoclinic phase in the bulk was ~ 0, we may estimate the size of the transformation zone to be ~ 150 μm from Figure 6.5. The average volume percent of transformed monoclinic phase within the transformation zone may also be estimated to be ~ 20%. Thus the volume fraction of the zirconia undergoing transformation was estimated to be 0.04 (this is equal to the total volume fraction of zirconia of 0.2 multiplied by 20% of the particles that undergo stress-induced phase transformation in the transformation zone). These measured values will be used in the estimation of toughening components in the next section.

6.2.2.2 Toughening Analysis

The toughening due to stress-induced martensitic transformations in YSZ particles, $\Delta K_T$, may be estimated using the analysis of McMeeking and Evans [56] and Budiansky et al. [57]. This gives:
\[
\Delta K_T = \frac{0.22E_c f \varepsilon T \sqrt{h}}{1 - \nu}
\] (6.1)

where \( E_c \) is the composite modulus (~ 200 GPa), \( f \) is the volume fraction of the zirconia undergoing transformation (~ 0.04), \( \varepsilon T \) is the transformation strain (~ 4 %), \( h \) is the height of the transformation zone (~150 \( \mu \m) and \( \nu \) is the Poisson's ratio (~ 0.3). Substituting the above data into Equation 6.1, we may estimate the shielding contributions for transformation toughening.

Similarly, we may estimate the toughening due to crack bridging from the analysis of Budiansky, Amazigo and Evans [79]. This gives the toughness increment, \( \Delta K_b \), due to small-scale bridging (Figures 6.2 and 6.3) to be:

\[
\Delta K_b = 2 \sqrt{\frac{2}{\pi}} V_f \alpha \int \frac{\sigma(x)}{\sqrt{\pi}} dx
\] (6.2)

where \( \sigma(x) \) is the traction distribution across the bridge zone (approximately equal to the yield stress of Mo particles of 914 MPa), \( V_f \) is the volume fraction of ductile particles (0.2), \( \alpha \) is a constraint/triaxiality parameter which we equate to 1, \( x \) is the distance from the crack face and \( L \) is the bridge length, which was equated to the distance from the last unfractured Mo particle observed on the polished sides of the specimens to the crack-tip. The bridge length was measured to be ~ 255 \( \mu \m \) from the resistance-curve tests. Since
the bridge zone size is small compared to crack length (Figure 6.3a), small-scale bridging estimation obtained from Equation 6.2 is applicable in the current study.

Implicit within the above measurements of crack bridging and transformation toughening are the effects of the interactions between these mechanisms. Hence, it is possible to assess the effectiveness of the combined effects of these two mechanisms simply by applying the principle of linear superposition [105,106]. This gives the overall toughening, $\Delta K_{\text{tot}}$, as:

$$\Delta K_{\text{tot}} = \Delta K_\tau + \Delta K_b$$  \hspace{1cm} (6.3)

Alternatively, we may explore the possible interactions between $\Delta K_\tau$ and $\Delta K_b$ within the framework established by Amazigo and Budiansky [14]. This gives two coupling parameters for assessing the overall levels of synergism between the two toughening mechanisms.

The first coupling parameter, $\rho$, is given by [14]:

$$\rho = \frac{(1 + \nu)V_T \sigma_p}{\sigma^c_m}$$  \hspace{1cm} (6.4)
where \( \sigma_p \) is the strength of the ductile particle (~914 MPa) and \( \sigma_m^e \) is the mean stress in transformation zone (~500 MPa). It is important to note here that there are two limiting values of the overall toughening ratio, \( \Lambda \), corresponding to the upper and lower bounds in \( \rho \). The first corresponds to the maximum level of synergy which occurs when \( \rho = \infty \).

This gives the maximum toughening ratio, \( \Lambda_{\text{max}} \), as [14]:

\[
\Lambda_{\text{max}} = \Lambda_p \lambda_T \tag{6.5}
\]

where \( \lambda_T \) is the transformation toughening ratio and \( \Lambda_p \) the modified bridging toughening ratio. These are given by:

\[
\lambda_T = 1 + \frac{\Delta K_T}{K_m} \tag{6.6}
\]

and

\[
\Lambda_p = \frac{\lambda_b}{\sqrt{1-V_f}} = \frac{1 + \frac{\Delta K_b}{K_m}}{\sqrt{1-V_f}} \tag{6.7}
\]

The lower bound value of the toughening ratio corresponds to a \( \rho \) of 0. This gives an overall toughening ratio, \( \Lambda_{\text{min}} \), of [14]:

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\[ \Lambda_{\text{min}} = \left[ \Lambda_p^2 + \Lambda_T^2 - 1 \right]^{1/2} \]  \hspace{1cm} (6.8)

Substituting the appropriate values into Equations 6.4 - 6.8, \( \rho \), \( \Lambda_{\text{max}} \) and \( \Lambda_{\text{min}} \) are estimated to be 0.475, 2.4 and 2.1, respectively. The overall toughening ratio, \( \Lambda \) (including the effects of synergistic interactions), may be estimated from Figure 8 in Ref. 14 to be 2.1.

A similar set of results may also be obtained using an alternative coupling parameter, \( \eta \), which was also proposed by Amazigo and Budiansky [14]. This gives [14]:

\[ \eta = \frac{h(1 - V_f)}{L} \]  \hspace{1cm} (6.9)

Substituting the appropriate values into Equation 6.9 gives a value of \( \eta \) of 0.471. The overall level of toughening ratio, \( \Lambda \), may also be estimated from Figure 11 in Ref. 14 to be 2.2, which is between \( \Lambda_{\text{max}} \) and \( \Lambda_{\text{min}} \).

Estimates of the overall toughening obtained from Equations 6.3, 6.5 and 6.8 are compared with the experimental resistance-curve in Figure 6.2. This shows that the experimental resistance-curves are intermediate between the maximum and minimum possible levels suggested by the models. The agreement between the measured and
estimated resistance curves is remarkable given the simplicity of the above formulation. However, it is important to note that due to the difficulties in material fabrication, it is not possible to explore the statistics on the measured resistance-curves in the current study. Clearly, further tests are needed to explore the statistical variations that can occur due to microstructural inhomogeneity and other factors. Nevertheless, the consistency of the experimental results with the theoretical predictions does suggest that measured trends in the resistance-curve behavior are close to the mean values that would be expected from multiple values that would be expected from multiple experiments. Further work is clearly needed to fully establish the statistical variations that can occur around these "mean" resistance curves. Furthermore, it is exciting to note the synergistic toughening theory suggests that even higher levels of synergy may be engineered by the design of composites with higher levels of $\lambda_T$ and $\Lambda_p$. This possibility has been explored in hybrid composites reinforced with ductile layers and transforming zirconia particles in NiAl matrix, as discussed in the next section of the thesis. The potential promise of such systems is particularly exciting since the indication that toughening ratios of up to 10 may be achieved in intermetallic and ceramic matrix composites reinforced with transforming particles and bridging reinforcements. However, it is important to note here that the existing synergistic toughening theory has only been developed for particulate [14] or fiber-reinforced [107] hybrid composites. There is, therefore, a need to develop a modeling framework for the analysis of ductile layer-reinforced composites reinforced with particles that can undergo stress-induced phase transformations.
Finally, it is of interest to discuss the implications of the current work for the design of damage tolerant high temperature structural materials. The model systems examined in this study are clearly not serious candidates for near-term applications. However, they do provide some insights that are needed for the design of toughened brittle matrix composites in which synergistic interactions can be engineered between transformation toughening and crack bridging. The theories [14,107] indicate that toughening ratios of ~8 can be engineered due to such interactions. In the case of synergistically toughened NiAl composites with matrix toughness levels of ~5-7 MPa√m [43,72], this would suggest that synergistically toughened composites with fracture toughness levels of ~40-50 MPa√m may be engineered by the judicious selection of transforming particles and ductile bridging reinforcements. Such toughnesses are greater than those of structural aluminum alloys [13,124], and somewhat less than those of nickel [121] and titanium [124,125] base alloys. They indicate some potential for applications of synergistically toughened intermetallic composites in long-range applications in future high temperature engine systems.

6.2.3 Conclusions

The following conclusions have been reached in a study of a model hybrid NiAl composite reinforced with 20 vol. % of Mo particles and 20 vol. % of 2 mole % YSZ particles:
1. Synergistic toughening can be engineered by promoting interactions between transformation toughening and crack bridging, as suggested by Amazigo and Budiansky [14]. The overall levels of synergy in the above composite are somewhat intermediate between the maximum and minimum levels that are suggested by the theory.

2. The estimates of the overall toughening obtained by linear superposition are in good agreement with the measured resistance curves. This suggests that the measured transformation toughening and crack bridging parameters implicitly include the effects of the synergistic interactions. However, it is difficult to decouple the contributions from synergy within the linear superposition framework.

3. In contrast, the two coupling ratios proposed by Amazigo and Budiansky [14] provide a useful framework for the assessment of the possible synergistic interactions between crack bridging and transformation toughening. Both coupling parameters were computed to be ~ 0.5 in the hybrid composite that was examined in the current study. The estimates of resistance-curve behavior obtained from these models were also in good agreement with the experimental resistance curves.
6.3 NiAl/YSZ/V COMPOSITES

6.3.1 Micromechanical Modeling

6.3.1.1 Crack Bridging and Transformation Toughening

The micromechanical modeling of ductile layer crack bridging is discussed in Section 4.2 of Chapter 4. The steady state fracture toughness, $K_c$, of brittle composites reinforced with ductile layers can be estimated from Equation 4.13 to be:

$$K_c = \left[1 + \frac{\sigma_y^2}{kK_m^2} \left(1 + \frac{2\mu_p}{\mu_y}\right)\right]^{1/2} K_m$$  \hspace{1cm} (6.10)

and from Equation 4.18 to be:

$$K_c = K_i + \Delta K_{sb} = K_i + \int_{L} \alpha \sigma(x) h(a,x) dx$$  \hspace{1cm} (6.11)

The meaning of different symbols in Equations 6.10 and 6.11 can be referred to Chapter 4.

In the studies of transformation toughening by McMeeking and Evans [56] and by Budiansky et al. [57], it was assumed that during steady crack propagation, martensitic-
type transformations occur in particles when they are subjected to a critical mean stress $\sigma_m^c$. In the so-called supercritical case, the full volumetric transformation strain, $\varepsilon_c^T$, is approximately 0.04 in each transformation particle in a zone ahead of the crack tip as well as in its wake [57]. Along the curved front boundary of this region, the mean stress $\sigma_m^c$ is attained, and the dilations produced persist in a wake of height $H_T$ on each side of the crack [57]. With $V_t$ defined as the volume fraction of transformed particles, which were assumed by Budiansky et al. [57] to have the same elastic moduli as the matrix, the key parameter governing transformation toughening emerges as:

$$\omega = \frac{1 + v_c \frac{E_c V_e e_c^T}{\sigma_m^c}}{1 - v_c}$$

(6.12)

where $E_c$ and $v_c$ is the Young's modulus and Possion's ratio of the transformation toughened composite, respectively. The toughening ratio $\lambda_T$ is thus given by [57]:

$$\lambda_T = \left[1 + 2 \omega g(\omega)\right]^{\frac{1}{2}}$$

(6.13)

or

$$\lambda_T = \left[1 - 2 \omega f(\omega)\right]^{\frac{1}{2}}$$

(6.14)
where

\[ g(\omega) = \frac{H_T}{\left(1 + \nu\right)\frac{K_m}{\sigma_m}} \]  \hspace{1cm} (6.15) \]

and

\[ f(\omega) = \frac{H_T}{\left(1 + \nu\right)\frac{K_c}{\sigma_c}} \]  \hspace{1cm} (6.16) \]

For sufficiently small values of \( \omega \), the increase in toughness, \( \Delta K_T = K_T - K_m \), is given by [57]:

\[ \Delta K_T = \frac{E_c \sqrt{H_T V_c \varepsilon_c}}{1 - \nu} \frac{\sqrt{g(0)}}{\sqrt{\sigma_m}} \]  \hspace{1cm} (6.17) \]

where \( g(0) = \frac{1}{4\pi\sqrt{3}} = 0.214 \), as also shown in prior work by McMeeking and Evans [56] (Equation 5.1 in Chapter 5).
For sufficiently large values of \( \omega \), i.e., strong transformations, the increment in fracture toughness due to stress-induced martensitic transformations, \( \Delta K_T \), may be given by Equation 5.4 and Equation 5.12 in Chapter 5 [62]. The above modeling framework for transformation toughening has been restricted to the transformations that are dilatational in nature. However, it is recognized that shear components may also be important (Chapter 5). These are not considered in the current study for the sake of simplicity and clarity.

6.3.1.2 Linear Superposition

Before presenting the section on synergistic toughening, it is important to present a brief description of linear superposition concepts that may also be applied to the estimation of the overall toughening. For the case where the crack-tip stresses are essentially in the small-scale yielding regime, linear elastic fracture mechanics conditions prevail, and the overall toughness, \( K_{\text{tot}} \), may be estimated simply by the application of the linear superposition law. This gives:

\[
K_{\text{tot}} = K_m + \Delta K_b + \Delta K_T
\]  

(6.18)

where \( K_m \) is the matrix fracture toughness, \( \Delta K_b \) is the toughness increment due to crack bridging, and \( \Delta K_T \) is the toughness increment due to transformation toughening. Note that the volume fractions of transformation toughening and crack bridging are not...
included separately in Equation 6.18 since they have already been considered in the derivation of the appropriate relationships for $\Delta K_b$ and $\Delta K_T$, both of which may be estimated using various combination of the expressions presented earlier in prior sections of this thesis.

The above superposition framework may be used to assess the role of synergy since the volume fraction of transformed phase, $V_T$, the height of the transformation zone, $H_T$, and bridging length, $L$, may also be significantly affected by the interactions between crack bridging and transformation toughening. Hence, in cases where these parameters can be measured in the hybrid composites, the synergistic toughening is implicit within the linear superposition framework presented above. The same arguments pertain to the case of weak transformations in hybrid composites. However, in such cases the extent of the interactions would be expected to be weaker except for the areas close to the layers where the layer tractions could induce additional stress-induced phase transformations (Figure 6.6). In the case of weak transformations in hybrid composites, the total composite fracture toughness is now given by Equations 5.1 and 6.10 to be:

$$K_{t_{\text{tot}}} = K_m + \left[ 1 + \frac{\sigma_y^2}{kK_m^2 \left( 1 + \frac{2\nu_p}{\nu_y} \right)} \right]^{1/2} + \left[ \frac{0.22E_c \sqrt{H_T} V_{\text{T}} \varepsilon_c^T}{1 - \nu} \right]$$

(6.19)

where the variables have their usual meaning. It is important to note that the above Equation 6.19 can only be used to predict the $K_{t_{\text{tot}}}$ at the onset of fracture instability. This
is because of the fact that they do not include an evolving bridging length scale. Furthermore, the spring stiffness, $k$, includes a critical value of $v_{\text{ave}}$ that is only applicable at a given condition. There is, therefore, a need for a somewhat different approach for the estimation of resistance-curve behavior in the hybrid composite. This can be achieved by the use of the small- and large-scale bridging expressions presented in Section 4.2 in Chapter 4, which include an evolving bridging length scale. The overall toughness, $K_{\text{tot}}$, may thus be estimated as a function of the evolving bridge length. For transformation toughening and large scale-bridging conditions, which are generally applicable to the case of ductile layer toughened materials, the total composite fracture toughness, $K_{\text{tot}}$, is thus given by linear superposition of Equations 5.1 and 6.11 to be:

$$K_{\text{tot}} = K_1 + \int_0^L a\sigma(x) h(a, x) dx + \frac{0.22E_c\sqrt{H_T}V_c\varepsilon_c^T}{1-\nu}$$  \hspace{1cm} (6.20)

where the constants have their usual meaning. In the cases where $V_c$, $H_T$ and $L$ can be measured in the hybrid composite, the superposition approach provides a basis for the estimation of the interactions between crack bridging and transformation toughening. In cases where such measurements are not easily available, the interactions may be investigated within an analytical framework presented originally by Amazigo and Budiansky [14].
6.3.1.3 Synergistic Toughening

The combined toughening due to crack bridging and transformation toughening has been analyzed for particulate bridging [14] and fiber bridging [107]. However, the authors are unaware of prior work on the modeling of synergy due to layer bridging and transformation toughening. The current study explores the opportunities for synergism due to interactions between small or large scale bridging and dilatational transformation toughening. Following the approach of Budiansky and Amazigo [14], the overall toughening ratio, $\Lambda$, is expressed as:

$$\Lambda = \frac{K_c}{K_m \sqrt{1 - V_l}}$$  \hfill (6.21)

where $V_l$ is the volume fraction of ductile layer reinforcements. The toughening ratio may also be related to a coupling parameter that provides bounds for overall toughening ratio in terms of the individual toughening ratios, $\Lambda_I$ and $\lambda_T$. This gives (Appendix B):

$$\Lambda = \left[ \frac{E_c}{E_m} \frac{1 - \nu_m^2}{1 - \nu_c^2} \right]^{1/2} \Lambda_I \lambda_T$$  \hfill (6.22)

for $\rho \rightarrow \infty$
\[
\Lambda = \left[ \frac{E_c}{E_m} \frac{1 - \nu_m^2}{1 - \nu_c^2} \right] \left[ \Lambda_1^2 + \lambda_T^2 - 1 \right]^{1/2}
\]
for \( \rho \to 0 \) (6.23)

where \( \rho \) is a coupling parameter that is given by:

\[
\rho = \frac{(1 + \nu)V_i S}{\sigma^c_m}
\]
(6.24)

where \( \sigma^c_m \) is the critical transformation stress and \( S \) is the average layer traction that is applied over the bridging zone. This is given by:

\[
S = \alpha \sigma_y
\]
(6.25)

where \( \alpha \) is a constraint/triaxiality factor that may also include the effects of the weighted distributions of layer tractions across the bridging zone (Figure 2.17).

Equations 6.22 and 6.23 are similar to those derived earlier by Amazigo and Budiansky [14] for interacting transforming particles and ductile particulates. For the case of composites with identical elastic properties to the matrix materials \( (E_m = E_c \text{ and } \nu_m = \nu_c) \), the limiting conditions are given by [14]:

\[
\Lambda = \Lambda_1 \lambda_T
\]
for \( \rho \to \infty \) (6.26)
and

$$\Lambda = \left[ \lambda_t^2 + \lambda_T^2 - 1 \right]^{\frac{1}{2}}$$

for $\rho \rightarrow 0$ (6.27)

Equation 6.24 or 6.26 provides upper bound estimates of the overall toughening that is generally greater than the sum of the individual toughening components. Also Equation 6.25 or 6.27 provides estimates of the lower bound toughening for which for $\rho \rightarrow 0$. They may result in overall toughening levels that are less than the cumulative values.

Finally, it is important to note that the current results for bridging ductile layers are completely analogous to those reported earlier for ductile particles. However, the spring constants, crack opening displacement functions, and the unit cells for the layered composites are different from those employed for ductile particulate composites (see prior sections on ductile layer bridging in Chapter 4).

Since the parameters in Equation 6.24 are often difficult to obtain for composites of interest, Amazigo and Budiansky [14] have also proposed the use of an alternative coupling ratio that relates the height of the transformation zone, $H_T$, and the bridge length, $L_t$. The alternative coupling parameters, $\eta$, is now defined as:
\[ \eta = \frac{H_T (1 - V_t)}{L_t} \]  

(6.28)

It may be shown from Appendix A that [14]:

\[ \eta = \frac{4p^2 (\lambda^2 - 1)}{\pi \omega (\Lambda^2 - 1)} \]  

(6.29)

### 6.3.2 Microstructure

The microstructure of the NiAl/YSZ/V layered composites is presented in Figures 6.7a and Figure 6.7b. This shows a relatively uniform distribution of V layers (200 μm thick) in a hybrid "matrix" of NiAl + YSZ. As in NiAl/V layered composites, an interfacial layer of 10 - 15 μm thick formed between the NiAl + YSZ "matrix" and vanadium layers (Figure 6.7b). In contrast to those in NiAl/YSZ/Mo(p) composites, the YSZ particles were distributed largely in the NiAl grains (~25 μm average size) as agglomerates of an average size of ~50 μm (Figures 6.7a and 6.7b). The agglomerates were in circular shape and there were some NiAl grains inside them. Future work is clearly needed to produce microstructures with more uniform distributions of YSZ particles.
6.3.3 Results and Discussion

6.3.3.1 Initiation Toughness and Resistance-Curve Behavior

The initiation toughness and resistance-curve behavior in the hybrid NiAl/YSZ/V composite are compared with data for transformation toughened and ductile vanadium layer toughened NiAl composites in Figure 6.8. The hybrid composite exhibits a remarkable high initiation fracture toughness of ~14.8 MPa√m, compared to initiation toughness levels of ~6.6 MPa√m in the NiAl matrix and NiAl/V composite. The initiation toughness in the hybrid composite is also much greater than observed in the NiAl composite reinforced with yttria-partially stabilized zirconia. The latter has an initiation toughness of ~7.8 MPa√m which is somewhat greater than the toughness of the NiAl matrix. The increase in the initiation toughness of the hybrid composite is attributed to the increased volume fraction of transformed tetragonal phase, which is due presumably to the interactions between transformation toughening and crack bridging.

Beyond the fracture crack initiation toughness, the hybrid composite exhibits very strong resistance-curve behavior to a peak toughness of ~36.4 MPa√m. The resistance-curve behavior is associated with crack/ductile layer interactions and stress-induced phase transformations, as shown in Figures 6.9a and 6.9b. The evidence of crack/vanadium layer interactions is particularly interesting since it provides some key insights into the ductile toughening mechanisms that provide most of the toughening (on a fractional
basis) in the hybrid NiAl/YSZ composites. As in the simpler NiAl/V layered composite [72], the cracks initiate in the “matrix” and propagate rapidly to the first row of ductile V layers where they are stopped (Figure 6.9a). Subsequent increments in load then result in interfacial debonding (Figure 6.9b) and plastic deformation in the V layers prior to re-nucleation of crack growth in the adjacent hybrid NiAl/YSZ layers (Figure 6.9b). The re-nucleated cracks propagate rapidly to the next vanadium layer (Figure 6.9b) and the above sequence of events is repeated, until catastrophic failure of the specimen occurred.

It is also interesting to examine the mechanisms of final fracture. Typical SEM photomicrographs of the fracture surface are presented in Figures 6.10a to 6.10e. Fracture of the NiAl occurred predominantly by cleavage, as shown in Figure 6.10a in which river lines and clam shell markings that are indicative of this fracture mode are apparent. Final failure of the vanadium layers occurred predominantly by cleavage fracture, although some incidence of ductile dimpled fracture is also evident (Figure 6.10b). A large amount of debonding was also observed at the interface between the NiAl + YSZ layers and the vanadium layers (Figure 6.10c). Fracture of YSZ particles in the “matrix” occurred intergranularly (Figure 6.10d), although the whole YSZ agglomerates appeared to fail by cleavage-like fracture (Figure 6.10e).
6.3.3.2 Raman Spectroscopy Analysis

In addition to the crack/vanadium layer interactions, the resistance-curve behavior is also due partly to the stress-induced phase transformations that occur in the hybrid NiAl/YSZ/V layered composites. The occurrence of such stress-induced phase transformation is demonstrated by the laser Raman Spectroscopy results that are presented in Figure 6.11. These show the volume fraction of transformed monoclinic phase as a function of the distance from the crack face and also the distance from a ductile vanadium layer. As in prior studies on another synergistically toughened composite MoSi2/YSZ/Nb [105], the volume fraction of transformed monoclinic phase decreases with increasing distance from the vanadium layer, and also increasing distance from the crack face (Figure 6.11). It is particularly important to note that the measured increase in the volume fraction of transformed monoclinic phase in the vicinity of the vanadium layers (average ~45 % transformed zirconia compared to average ~30 % in NiAl/YSZ composites) is one indication of the interactions between crack bridging and transformation toughening. These interactions are associated with debond crack-tip fields and layer tractions in the regions close to the ductile V layers. These may induce additional transformations (increased $V_t$) compared to those in the simple NiAl/V composite. However, the height of the transformation zone in the hybrid composite is not significantly greater than that of the simple NiAl composite reinforced with only YSZ particles (~30 μm).
6.3.3.3 Toughening Analysis

The shielding contributions from crack bridging and transformation toughening may be analyzed within the framework of linear superposition models or synergy models presented earlier. The predictions based on the linear superposition model (Equation 6.20) and synergy model (Equations 6.22 and 6.23) are presented in Figure 6.12. Since large-scale bridging was observed in the resistance-curve experiments, the predictions are based on the superposition of large-scale bridging increments, $\Delta K_p$, and transformation toughening increments, $\Delta K_T$ (Equation 6.20). The trends in the predictions are in good agreement with the experimental resistance curves. However, the theoretical predictions for the initiation toughness and resistance-curve behavior are generally below the measured values when the simple dilatational toughening model based on Equation 5.1 [56,57] is used to estimate the transformation toughening ratio, $\lambda_T$. This is not surprising since these expressions underestimate the extent of transformation toughening in the hybrid composite, as shown in Chapter 5. In contrast, much better agreement is obtained between the measured and predicted resistance curves when the actual values of $\lambda_T$ corresponding to the measured initiation fracture toughness values are used in the analysis. This is shown in Figure 6.13 using results from the superposition (Equation 6.18) and synergistic toughening models (Equations 6.22 and 6.23). The experimental resistance-curve is in very good agreement with the theoretical predictions obtained from the linear superposition model and the lower bound synergistic toughening model. However, the measured resistance curves are well below the maximum possible
resistance-curves predicted from the synergistic toughening model. In an effort to further explore the synergistic toughening in the NiAl/YSZ/V composites, the coupling parameters, $\rho$ and $\eta$, were estimated from Equations 6.24 and 6.28, respectively to be 0.232 and 0.0068. The coupling ratios are therefore close to zero, compared to the maximum possible values of infinity. This would explain the overall levels of synergy that are close to the lower bound predictions that are predicted by the synergistic toughening model (Figure 6.13).

The above discussion has focused on the comparison of specimen-dependent resistance-curve behavior. It is also important to consider the intrinsic steady-state toughness of the layered hybrid composites exhibits large-scale bridging phenomena, as demonstrated in Chapter 4 of the thesis. Assuming an infinite specimen width and using $K_i = 22.6$ MPa$\sqrt{m}$ (corresponding to the renucleation toughness from the first row of V layers), steady-state fracture toughness of the NiAl/YSZ/V composites can be estimated to be ~27.8 MPa$\sqrt{m}$ from Equations 6.11, 4.19 and 4.20. Steady-state fracture toughness from layer bridging can also be estimated from analytical models presented in Equations 6.10, 4.13 and 4.14 to be ~27.0 MPa$\sqrt{m}$. Here, the matrix toughness, $K_m$, is assumed to be the initiation toughness on the resistance-curve (i.e., the toughness of NiAl/YSZ “matrix”). The steady-state fracture toughness values obtained from the above two methods are therefore in close agreement. Please note that both estimates already incorporate the synergy between layer bridging and transformation toughening. This is because the contributions from transformation toughening and the interactions between two
mechanisms are included in the measured values of $K_i$ and $K_m$. The intrinsic toughness (> 27.0 MPa$\sqrt{m}$) of the hybrid/synergistically toughened composite is, therefore, greater than that of the simple NiAl/V composite reinforced with 200 $\mu$m thick V layers, which was estimated to be 19.8 or 23.6 MPa$\sqrt{m}$, depending on the formulations used (Table 4.2).

It is also worth noting that in contrast to the layered NiAl/V composites, debonding along the vanadium layers and the NiAl + YSZ “matrix” occurred considerably more extensively when crack growth was retarded by the vanadium layers in the NiAl/YSZ/V composites. The delamination phenomena might provide additional source of toughening, as demonstrated by Chan et al. [126] and Bretz and Hertzberg [127]. Also, the crack-tip fields associated with the debonding cracks might have induced additional transformation of the YSZ particles, resulting in higher levels of transformation toughening in the hybrid NiAl/YSZ/V composites.

6.3.3.4 Implications

The experimental results presented in the previous section suggest that the synergistic toughening model and the linear superposition model both provide reasonable estimates of the resistance-curve behavior of the NiAl/YSZ/V layered composite that was examined in this thesis. This was expected in the case of the synergistic toughening model, and somewhat surprising in the case of the linear superposition model. However, it is important to note here that, implicit within the linear superposition framework are the
interactions that give rise to the synergy via higher levels of $V_t$ in the hybrid composite (compared to those in the simple transformation toughened composite). The summation of $\Delta K_T$ and $\Delta K_b$, therefore, provides a good estimate of the overall toughening in the hybrid NiAl/YSZ/V composite. The linear superposition model may not work as well when the coupling ratios are much greater than the values (close to zero) obtained in this study. In such cases, the synergy model would be recommended for the estimation of the overall toughening due to interactions between crack bridging and transformation toughening.

Finally in this section, it is of interest to compare the measured peak fracture toughness data (~ 36.4 MPa$\sqrt{m}$) with fracture toughness data from structural materials. Aluminum alloys typically have fracture toughness levels between 20 and 30 MPa$\sqrt{m}$ [13,124] while gamma-based titanium aluminide intermetallics have fracture toughness levels between 15 and 35 MPa$\sqrt{m}$ [110]. Titanium and nickel-base alloys have fracture toughness levels between ~ 40 and 100 MPa$\sqrt{m}$ [124,125], while steels have typical fracture toughness levels between 50 and 200 MPa$\sqrt{m}$ [124]. The measured fracture toughness levels are, therefore, somewhat below those of existing structural materials. However, the synergistic toughening analysis does indicate the possibility for the engineering of toughened systems with fracture toughness levels that are comparable to those of structural materials. Further work is clearly needed to explore these exciting possibilities.
6.3.4 Conclusions

A combined theoretical and experimental study of synergistic toughening of an NiAl composite reinforced with 2 mole % yttria partially stabilized zirconia (YSZ) and ductile V layers has been carried out. The following conclusions have been reached.

1. The initial formulation of Amazigo and Budiansky [14] is applicable to the analysis of synergy in hybrid composites reinforced with ductile layers and transforming particles. The bounds in the toughening suggested by Amazigo and Budiansky [14] are also applicable in general to problems involving transforming particles interacting with ductile particles or layers.

2. A linear superposition of toughening increments due to crack bridging and stress-induced phase transformation may also be used to estimate the overall toughening in hybrid NiAl/YSZ/V composite. Implicit within the formulation are the interactions (between crack bridging and transformation toughening) which give rise to a higher volume fraction of stress-induced transformation. The trends in the measured specimen-dependent resistance-curves for the hybrid NiAl/YSZ/V composite are predicted by the linear superposition and synergistic toughening models. Furthermore, the "intrinsic" specimen-independent steady-state toughness of the layered hybrid NiAl/YSZ/V composite is greater than that of the simple layered NiAl/V composite.
3. The coupling parameters obtained from hybrid NiAl/YSZ/V composite are close to the lower bounds predicted by the theoretical mechanics model. The measured peak toughness and resistance-curve behavior are therefore close to the lower bounds predicted by the synergistic toughening and linear superposition models. Hybrid synergistically toughened composites with even greater fracture toughness levels may be engineered by the selection of reinforcements that will give rise to higher coupling parameters.
Figure 6.1 Microstructure of NiAl/YSZ/Mo(p) composites.

Figure 6.2 Experimental and estimated resistance-curves for NiAl/YSZ/Mo(p) composites. (a) Experimental, (b) linear superposition of crack-bridging and transformation toughening (Equation 6.3), (c) maximum possible toughening predicted from synergistic toughening model (Equation 6.5), and (d) minimum toughening predicted from synergistic toughening model (Equation 6.8).
Figure 6.3 Crack/microstructure interactions during resistance-curve testing before final failure. (a) Ductile particles crack bridging and (b) ligament bridging.
Figure 6.4 Typical fracture modes for NiAl/YSZ/MO(ρ) composites.

Figure 6.5 Volume fraction of monoclinic zirconia phase as a function of distance from crack face after final fracture of NiAl/YSZ/MO(ρ) composites.
Figure 6.6 Schematic illustration of synergistic toughening by ductile layer and transforming particles.
Figure 6.7 Microstructure of layered NiAl/YSZ/V composites: (a) Distribution of V layers in a matrix of NiAl + YSZ and (b) interface between V layers and NiAl + YSZ matrix.
Figure 6.8 Comparison of experimental resistance-curves obtained for NiAl/YSZ/V hybrid composites, NiAl/YSZ composites and NiAl/V composites.
Figure 6.9 Crack/microstructure interactions in NiAl/YSZ/V hybrid composites: (a) Crack initiation and retardation and (b) crack debonding, crack bridging and crack renucleation. (Continued on the next page...)

Direction of Crack Propagation

200 µm
Figure 6.9 Crack/microstructure interactions in NiAl/YSZ/V hybrid composites: (a) Crack initiation and retardation and (b) crack debonding, crack bridging and crack renucleation. (...continued from the previous page)
Figure 6.10 Typical fracture modes in layered NiAl/YSZ/V composites: (a) Transgranular cleavage fracture of NiAl gains, (b) cleavage and ductile dimpled fracture of V layers, (c) debonding at the interfaces between V layers and NiAl + YSZ matrix, (d) intergranular fracture of YSZ gains and interfaces between NiAl and YSZ, and (e) cleavage-like characteristics of YSZ agglomerates. (Continued on the next page...)

Direction of Crack Propagation
Figure 6.10 Typical fracture modes in layered NiAl/YSZ/V composites: (a) Transgranular cleavage fracture of NiAl gains, (b) cleavage and ductile dimpled fracture of V layers, (c) debonding at the interfaces between V layers and NiAl + YSZ matrix, (d) intergranular fracture of YSZ gains and interfaces between NiAl and YSZ, and (e) cleavage-like characteristics of YSZ agglomerates. (…continued from the previous page)
Figure 6.10 Typical fracture modes in layered NiAl/YSZ/V composites: (a) Transgranular cleavage fracture of NiAl gains, (b) cleavage and ductile dimpled fracture of V layers, (c) debonding at the interfaces between V layers and NiAl + YSZ matrix, (d) intergranular fracture of YSZ gains and interfaces between NiAl and YSZ, and (e) cleavage-like characteristics of YSZ agglomerates. (...continued from the previous page)
Figure 6.11 Volume fraction of monoclinic zirconia phase vs. distance from crack face in NiAl/YSZ/V layered composites.
Figure 6.12 Resistance-curves for layered NiAl/YSZ/V hybrid composites: (a) Resistance-curve obtained from experiments for NiAl/YSZ/V hybrid composites, (b) linear superposition of large-scale bridging model and weak transformation model (Equation 6.20), (c) maximum possible toughening predicted from synergistic toughening model (Equation 6.22), and (d) minimum toughening predicted from synergistic toughening model (Equation 6.23).
Figure 6.13 Resistance-curves for layered NiAl/YSZ/V hybrid composites: (a) Resistance-curve obtained from experiments for NiAl/YSZ/V hybrid composites, (b) linear superposition of large-scale bridging model and actual value of transformation toughening, $\Delta K_T$, corresponding to the measured initiation fracture toughness value (Equation 6.18), (c) maximum possible toughening predicted from synergistic toughening model using actual value of transformation toughening, $\Delta K_T$, corresponding to the measured initiation fracture toughness value (Equation 6.22), and (d) minimum toughening predicted from synergistic toughening model using actual value of transformation toughening, $\Delta K_T$, corresponding to the measured initiation fracture toughness value (Equation 6.23).
CHAPTER 7

SUGGESTIONS FOR FUTURE WORK

1. The current study on the layered NiAl/YSZ/V composites does not give rise to high enough coupling parameters described in micromechanical models of synergistic toughening. The measured peak toughness and resistance-curve behavior are, therefore, close to the lower bounds predicted by the synergistic toughening and linear superposition models. To achieve significant synergy, the microstructure of NiAl/YSZ/V composites should be further optimized. If the very fine YSZ particles can be distributed more uniformly in the composite matrix (through processing control), a higher degree of transformation toughening may promote higher levels of synergy. From Equations 6.24, it is apparent that the higher the strength of the ductile reinforcements, the higher the coupling parameter, ρ. Thus, by choosing compatible high strength ductile layer, it is possible to achieve higher levels of synergy. Also, by increasing the volume fraction of partially stabilized zirconia in the composite systems, higher toughening ratios from transformation toughening can be achieved. This will therefore produce
higher levels of synergistic toughening ratios, as shown in Figures 2.18 and 2.19. Hence, it would be useful to study the synergistic toughening effects in the partially stabilized zirconia composites reinforced with ductile layers. There is also a need to study the effects of reinforcement morphology on synergistic toughening. In particular, it would be of interest to study the artificial hybrid NiAl composites reinforced with YSZ and V particulates or fibers.

2. In the current study of NiAl/YSZ composites, existing models for estimation of the shielding contributions from transformation toughening somehow cannot fully explain the toughness increment measured experimentally. More complete toughening models that include both contributions from dilatation and shear need to be developed. Finite element models can also be used efficiently to predict the contributions from individual particles to the overall transformation toughening. In addition, more refined analytical solutions are needed to address the individual contributions from uniformly or randomly distributed transforming particles.

3. A significant result of the current study is that the fracture toughness of the NiAl/YSZ composites is substantially greater than that of the monolithic NiAl. Besides fracture toughness, another property of interest is the response of the composite to cyclic loading. Subcritical fatigue crack growth at room
temperature has been reported in a magnesia partially stabilized zirconia [128]. In such cases, the tetragonal to monoclinic transformation provides the 'kinematic irreversibility' required for the stable crack growth. It would be of interest to determine whether stress-induced transformation is significant during fatigue crack growth, and what the transformation zone size is relative to that obtained under monotonic loading.

4. The degree of transformation toughening in NiAl/YSZ composites is influenced by materials processing parameters such as powder mixing conditions, processing temperature, pressure and cooling rate. Therefore, it would be very useful to investigate the effects of different processing parameters in an effort to obtain the optimal processing conditions for maximum stress-induced transformation at room temperature.

5. In brittle matrix composites reinforced with ductile layers, one important group of models that is used to estimate toughening by crack bridging utilizes the work of rupture parameter (Equation 4.15). These models are particularly applicable to problems involving large-scale bridging by ductile fibers and layers [83-88]. However, in order to use these models, constrained stress-displacement functions (Equation 4.16) \( \sigma(u) \) have to be determined through tensile tests on sandwich single foil specimens (Figure 7.1). It would be useful to fabricate such specimens (such as NiAl/V/NiAl specimens) to
measure the $\sigma(u)$ functions. It can be expected the foils will exhibit much higher peak stresses under constrained conditions than their yield stresses under unconstrained condition.
Figure 7.1 Schematic illustration of single foil sandwich specimens used to determine stress-displacement functions for ductile foil constrained by brittle composite matrix.
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APPENDICES

APPENDIX A

Interaction Analysis of Crack Bridging and Transformation Toughening

Let us consider the case of a steady-state crack subjected to the combined effects of crack bridging and transformation toughening. We assume that $\sigma_m = \sigma_m^c$ along the leading edge of the transformed zone (Figure A1) when $K_{up} = K_m \sqrt{1 - V_i}$ [14].

The crack-tip field is given by:

$$\sigma_{ap} = \frac{K_c}{\sqrt{2\pi R}} f_{ap}(\phi) \quad (f_{22}(0) = 1) \quad (A1)$$

where $\phi$ corresponds to the standard Muskhishvili potential:

$$\phi_K = \frac{K_c}{\sqrt{2\pi}} \sqrt{Z} \quad (A2)$$
The magnitude of the uniformly distributed plane-strain dilatation, \( \Omega \), is given by Budiansky et al. [57] to be:

\[
\Omega = \frac{2}{3} (1 + \nu) V \varepsilon_c^T
\]  \hspace{1cm} (A3)

and the field due to the transforming particles is given by:

\[
\phi_T = \frac{E_c \Omega}{4\pi(1 - \nu^2)} \int_C \log\left[ \left( \frac{1}{Z^2} + \frac{1}{Z_0^2} \right) \left( \frac{1}{Z^2} + \frac{1}{Z_0^2} \right) \right] dY_0 \]  \hspace{1cm} (A4)

The above integral is for the upper half \( C^+ \) of the curved front boundary \( C \) of the transformed region (Figure A1). Also, the elastic field associated with the smeared-out crack face tractions under small or large scale bridging conditions are given by:

\[
\frac{\partial \phi_i(Z)}{\partial Z} = \frac{V_s S}{\pi} \left[ -\frac{L}{Z} + \frac{1}{2} \log \left( \frac{\sqrt{Z} - i\sqrt{L}}{\sqrt{Z} + i\sqrt{L}} \right) \right] \]  \hspace{1cm} (A5)

The combined potential, \( \phi \), due to the applied stress field, \( \phi_K \), bridging potential, \( \phi_1 \), and transformation potential, \( \phi_T \), are thus given by linear superposition to be:
\[ \phi = \phi_K + \phi_I + \phi_T \quad \text{(A6)} \]

\[ u^+(X) = \frac{2(1 - v_s^2)}{iE_c} \left[ \phi(X) \right]^\dagger \quad \text{(A7)} \]

Substituting Equation A6 into Equation A7 gives the displacement of the upper crack-face along \( X < 0 \), and the mean stress outside region A (Figure A1) is given by:

\[ \sigma_m = \frac{4(1 + v_m)}{3} \text{Re} \left( \frac{\partial \phi}{\partial Z} \right) \quad \text{(A8)} \]

Assuming that during steady state crack growth, the displacement at \( X = -L \) is \( u_f \), and \( \sigma = \sigma_m^c \) at the boundary as \( Z \) approaches \( C \) from the exterior of \( A \) (Figure A1), we get:

\[ u_f = \frac{4(1 - v_s^2)K_e \sqrt{L}}{E_c \sqrt{2\pi}} - \frac{4V_s(1 - v_s^2)L}{\pi E_c} - \frac{2(1 + v_s)v_c^T \text{Im} \int_{c^+} \log \left[ \frac{Z_a + i\sqrt{L}}{Z_a - i\sqrt{L}} \right] \text{d}Y_o} {\pi} \quad \text{(A9)} \]

and
\[
\sigma_m^e = \frac{2K_c(1 + v_c)}{3} \Re \left( \frac{1}{\sqrt{2\pi Z}} \right) - \frac{2(1 + v_c)V_s}{3\pi} \left[ 2\Re \sqrt{\frac{L}{Z}} \right] + \Im \left( \log \frac{\sqrt{Z} - i\sqrt{L}}{\sqrt{Z} + i\sqrt{L}} \right) - \left( \frac{1 + v_c}{1 - v_c} \right) E_c V_t e_c^T \Re \left[ \frac{1}{\sqrt{Z}} \int_{c_l} \left( \frac{1}{Z^2 + Z_o^2} + \frac{1}{Z^2 + \overline{Z_o}^2} \right) \, dY \right]
\]

\text{(A10)}

Accounting for the combined effect of the layers and transforming particles within an energy balance framework gives:

\[
\frac{K_c^2(l - v_c^2)}{E_c} + \frac{K_m^2(l - v_m^2)(1 - V_t)}{E_m} + 2V_s u_f + 2H \sigma_m^e V_t e_c^T
\]

and

\[
K_m \sqrt{1 - V_t} = K_c - V_t \int_L Sdx - \frac{E_c V_t e_c^T}{3(i - v_c)} \sqrt{Z} \Re \int_{c_l} \frac{dY}{\sqrt{Z}}
\]

\text{(A12)}

To facilitate the presentation of the results, it is important to introduce the following non-dimensional variables:

\[
\Lambda = \frac{K_c}{K_m \sqrt{1 - V_l}}
\]

\[1 = \frac{L}{D}\]
\[
\begin{align*}
    w &= \frac{E_c v}{6(1-v_c)\sigma_m^c D} \quad h = \frac{H}{D} \\
    z &= x + iy = re^{i\phi} = \frac{Z}{D} \\
    \rho &= \frac{(1+v)\gamma S}{\sigma_m^c} \\

\end{align*}
\]

where \( D \) is a characteristic distance which is given by:

\[
    D = \frac{2(1-V_l)}{9\pi} \left[ \frac{(1+v_c)K_m}{\sigma_m^c} \right]^2 
\]  
(A13)

Substituting the above parameters into Equations A9-A12 gives:

\[
    w_f = A\sqrt{1} - \frac{2\rho}{3\pi} \frac{\omega}{9\pi} \text{Im} \int_{\infty}^{-1} \log \left[ \frac{1+i\sqrt{\frac{1}{z}}}{1-i\sqrt{\frac{1}{z}}} \right] dy 
\]  
(A14)

\[
    A \text{Re} \left( \frac{1}{\sqrt{z}} \right) - 2\rho \text{Re} \left( \sqrt{\frac{1}{z}} \right) + \text{Im} \log \left[ \frac{1-i\sqrt{\frac{1}{z}}}{1+i\sqrt{\frac{1}{z}}} \right] - \frac{\omega}{9\pi} \text{Re} \left[ \frac{1}{\sqrt{z}} \int_{-1}^{1} \left( \frac{1}{z^2 + z_0^2} + \frac{1}{z^2 + z_0^2} \right) dy_0 \right] = 1 
\]  
(A15)

In the case of \( E_m = E_c \) and \( \gamma_m = \gamma_c \):
The above equations may be used in two ways. First, they may be used to estimate the overall toughening ratio, $\Lambda$, when the bridging and transformation parameters are known from experiments. Alternatively, they may be used in parametric studies in which $\Lambda$ is determined for prescribed values of $\lambda_T$, $\Lambda_1$ and $\rho$ [14]. In such parametric studies, if $\omega$ is known as a function of $\lambda_T$, then $w_f$ may be obtained from:

$$\Lambda^2 = 1 + \frac{4}{3\pi} \left( 2\rho w_f + \frac{\omega h}{3} \right) \quad \text{(A16)}$$

or

$$\Lambda = 1 + \frac{4\rho \sqrt{l}}{3} + \frac{2\omega}{9\pi} \text{Re} \int_{k^*} \frac{dy}{\sqrt{z}} \quad \text{(A17)}$$

where $\Lambda_1$ may be obtained from Equation A17 when $\omega = 0$.

It is important to note here that the above formulation is similar to earlier derivations by Amazigo and Budiansky [14] and Cui [107]. However, the constants $v_f$, $w_f$ and $\rho$ employed in this study are different from those that were used in prior studies by
Amazigo and Budiansky [14] and Cui [107] for particulate and fiber bridging, respectively.

Finally in this section, it is important to note that the coupling parameters $\eta$ and $\rho$ are inter-related via the following expression [14]:

$$\eta = \frac{4\rho\left(\lambda^2 - 1\right)}{\pi\omega\left(\Lambda^2_i - 1\right)}$$  (A19)
APPENDIX B

Limiting Values of Synergistic Toughening Ratio

The bounds in the overall synergistic toughening are considered in this appendix. The upper bound in the toughening may be estimated by considering the condition for which $\rho \to \infty$ for a fixed $\Lambda_p$. In this case, $S \to \infty$, $L \to 0$, with $S\sqrt{L}$ and $S\nu_\tau$ remain bounded. Also, $\phi_i = 0$ for $Z \neq 0$, but the crack faces continue to affect $K_{tip}$ which is given by $K_m \sqrt{1-V_1}$. If we assume that the zone height, $H$, does not change in the presence of layers since the crack-tip stress do not change for $Z \neq 0$, then, from energy balance (Equation A11), we can write:

$$\frac{K^2_e(1-v_i^2)}{E_c} = \frac{K^2_m(1-v_m^2)\Lambda_i^2}{E_m}(1-V_i) + 2\nu V_1 + 2H\sigma_v e_{1}$$

(B1)

and

$$\frac{K^2_e}{E_c} = \frac{K^2_m\Lambda_i^2}{E_m}(1-V_i) + \frac{K^2_e}{E_c} 2\omega f(\omega)$$

(B2)
Rearranging Equation B2 now gives:

\[
\frac{1}{\lambda_T^2} \frac{K_c^2}{K_m^2} = \frac{E_c}{E_m} \Lambda_i^2 (1 - V_i) \frac{1 - V_m^2}{1 - V_c^2}
\]

(B3)

where

\[
\lambda_T = [1 + 2\omega g(\omega)]^{\frac{1}{2}}
\]

(B4)

or

\[
\lambda_T = [1 - 2\omega f(\omega)]^{\frac{1}{2}}
\]

(B5)

Substituting \( \Lambda = \frac{K_c}{K_m \sqrt{1 - V_i}} \) into Equation B3 gives:

\[
\frac{\Lambda^2}{\lambda_T^2} = \frac{E_c}{E_m} \Lambda_i^2 \frac{1 - V_m^2}{1 - V_c^2}
\]

(B6)

or
\[ \Lambda = \Lambda_1 \lambda_T \left[ \frac{E_p}{E_m} \frac{1 - v_m^2}{1 - v_e^2} \right]^{\frac{1}{2}} \]  

(B7)

Equation B7 is similar to the limiting expression obtained by Amazigo and Budiansky [14] for the case in which \( E_m = E_p = E_c \) and \( v_m = v_p = v_e \) (p stands for particulate reinforcement). Under such conditions, Equation B7 reduces to [14]:

\[ \Lambda = \Lambda_1 \lambda_T \]  

(B8)

Similarly, we may derive a condition for the lower toughening by considering the limiting conditions for which \( \rho \to 0 \) and \( S \to 0 \), \( L \to \infty \) with \( S \sqrt{L} \) remains bounded. Under such conditions, the potential \( \phi_i \) becomes indistinguishable from the potential due to the K-field. Considering only the transforming particles and applying K to give \( K_{sp} = K_m \sqrt{1 - V_i} \), we obtain the following relationship for the transformation zone size, \( H \):

\[ H = g(\omega) \left[ \frac{(1 + \nu)K_m}{\sigma_m^c} \right]^2 (1 - V_i) \]  

(B9)

Now introducing the bridging layers and adding an equivalent K to keep \( H \) unchanged, then K must satisfy the following energy balance:
Substituting $\Lambda = \frac{K_c}{K_m \sqrt{1 - V_i}}$ into Equation B10 gives

$\Lambda^2 = \frac{E_c}{E_m} \frac{1 - V_m^2}{1 - V_c^2} \left[ \Lambda_i^2 + 2\omega g(\omega) \right]$  \hspace{1cm} (B11)

Recalling from Equation B4, Equation B11 may be simplified to give:

$\Lambda^2 = \frac{E_c}{E_m} \frac{1 - V_m^2}{1 - V_c^2} \left[ \Lambda_i^2 + \lambda_\tau^2 - 1 \right]$  \hspace{1cm} (B12)

or

$\Lambda = \left[ \frac{E_c}{E_m} \frac{1 - V_m^2}{1 - V_c^2} \right]^{1/2} \left[ \Lambda_i^2 + \lambda_\tau^2 - 1 \right]^{1/2}$  \hspace{1cm} (B13)

Equation B13 is equivalent to the expression derived by Amazigo and Budiansky [14] for $E_m = E_p = E_c$ and $V_m = V_p = V_c$. Under such conditions, Equation B13 reduces to [14]:

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\[ \Lambda = [\Lambda_1^2 + \lambda_T^2 - 1] \]  \hspace{1cm} (B14)

The upper and lower bound expressions are, therefore, equivalent to those derived earlier by Amazigo and Budiansky [14] for interacting bridging particles and transforming particles. However, the spring constants will be different for the different types of bridging reinforcements (particles, fibers, layers etc.). The expressions presented in this appendix may therefore be applied generally to the assessment of synergistic toughening in dilute brittle matrix composites reinforced with ductile reinforcements with different geometries. The results are also applicable to brittle matrix composites for which the matrix is not necessarily a polymorph of transforming phase.
Figure A.1 Schematic illustration of bridged length and transformed zone during steady crack growth (after Amazigo and Budiansky [14]).