The Influence of Alloy Composition and Interfacial Segregants on the Fracture and Fatigue of Metal/Ceramic Interfaces

by

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Submitted to the Department of Mechanical Engineering in partial fulfillment of the requirements for the degree of Doctor of Science in Mechanical Engineering at the MASSACHUSETTS INSTITUTE OF TECHNOLOGY

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Submitted to the Department of Mechanical Engineering on December 28, 1998, in partial fulfillment of the requirements for the degree of Doctor of Science in Mechanical Engineering

Abstract

The use of multi-layered composites in the aircraft, automotive, and electronics industries is becoming more common as performance requirements exceed the capabilities of homogeneous materials. As a result, the need to assess their failure is critical. Diffusion bonded joints, thermal-barrier and wear resistant coatings, and thin films in VLSI electronics are three examples. In each of these cases, elastic and plastic mismatch between layers, when combined with thermal and/or mechanical loading, results in geometry dependent failure modes.

Through a combination of experimental studies and analytical/numerical modeling, key parameters that affect the fracture and fatigue resistances of metal/ceramic interfaces have been captured. Specifically, results from fracture and fatigue experiments conducted on vacuum diffusion bonded interfaces between $\text{Al}_2\text{O}_3$ and (i) Ni, (ii) a $\gamma$-Ni alloy containing Cr and (iii) Al are presented along with numerical simulations of interface fracture in layered materials subjected to a monotonic variation in temperature. The influence of alloy composition, and the interdependence of impurity concentration and bonding state (liquid-phase/solid-state) on interface toughness and fatigue crack growth resistance are discussed, with important findings detailed as follows.

i) Experimental studies designed to characterize the fracture resistance of interfaces between $\text{Al}_2\text{O}_3$ and either pure Ni or a $\gamma$-Ni alloy containing Cr have revealed a profound influence of Cr on the debond toughness. The interface between pure Ni and $\text{Al}_2\text{O}_3$ is susceptible to stress corrosion caused by moisture, resulting in a fracture energy of order 10 Jm$^{-2}$. In contrast the interface between the alloy and the $\text{Al}_2\text{O}_3$ cannot be fractured, even at strain energy release rates in excess of 100 Jm$^{-2}$. An analysis of these interfaces has identified two influences of the alloy addition that govern its role in eliminating stress corrosion: (i) Cr "getters" the C near the interface by forming a Cr-carbide reaction product, and (ii) the alloy dissolves some of the alumina during bonding, exposing virgin material to the alloy at the interface. The factors leading to carbide formation and alumina dissolution are discussed.

ii) An investigation of the influence of bonding technique on the fatigue crack resistance of Ni(Cr) and $\text{Al}_2\text{O}_3$ interfaces has identified an important interdependence between sulfur impurity in the Ni(Cr) and bonding state. Solid-state diffusion bonded (SSDB) inter-
faces are tough and fatigue resistant. Liquid-phase bonded (LPB) interfaces suffer from stress corrosion because of sulfur segregation. Under nominally mode I loading, SSDB interfaces remain intact with cyclic crack growth occurring nearly exclusively in the adjacent Al$_2$O$_3$. In contrast, LPB interfaces fail by the propagation of edge cracks upon exposure to environmental moisture following removal from the bonding chamber.

iii) In order to better understand the origins of processing-related interface failure and to develop a basic understanding of the effect of plastic flow on the driving force for interface fracture, numerical simulations of interface edge-crack growth initiation in tri-layered material systems subjected to a monotonic variation in temperature have been examined. Elastic and incremental elasto-plastic analyses have been used to evaluate the interface energy release rate. A large-scale contact model, which predicts the shielding effect of contact in the wake of an interface crack, is also presented and the attendant reduction in the energy release rate is estimated. Closed-form solutions are derived, as functions of the thermo-mechanical properties and the geometry of the layers, for different critical temperatures at which distinct transitions occur in thermally induced deformation. Bounds are extracted for the three regimes of interface fracture; elastic, partially plastic and fully plastic. Finite element results, showing the influence of layer geometry and strain hardening on the energy release rate, are presented for a model system consisting of Al$_2$O$_3$/Ni(Cr)/Al$_2$O$_3$; these simulations confirm the bounds predicted by the analysis.

iv) Fracture and fatigue experiments have been conducted on liquid-phase and solid-state bonded Al$_2$O$_3$/Al interfaces. The LPB interfaces contain voids and dendritic FeAl$_3$ precipitates, whereas SSB interfaces are relatively defect-free. These precipitates result in local embrittlement, yet both interfaces are strong and tough overall. Upon cyclic loading, mode I cracks in both systems grow alternately along the interface and within the Al. The development of a tortuous crack path elevates the apparent fatigue threshold through crack closure. Under mixed mode loading, fatigue cracks approaching SSB interfaces propagate through the Al rather than along the interface. Conversely, for LPB interfaces, mixed mode cyclic crack growth along the interface occurs in preference to propagation in the Al. Experiments revealed for the first time, the development of fatigue striations in the thin Al layers. Correlation between the striation spacing and the crack tip opening displacement suggests a growth mechanism based on crack tip blunting.

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Chapter 1

Introduction

1.1 Background

Design requirements for the aircraft, automotive, and electronics industries are rapidly exceeding the capabilities of conventional homogeneous materials. To fulfill these requirements, it is necessary to join dissimilar materials to form layered composites. Typical techniques used to accomplish this include; diffusion bonding [1], plasma spraying, electron beam physical vapor deposition (EB/PVD) and adhesive bonding. Examples of metal/ceramic composites include thermal-barrier and wear resistant coatings [2] and layered films in VLSI electronics [3].

When materials are joined interfaces are inevitably created. As part of the performance enhancing objective these interfaces generally coincide with transitions in elastic, plastic, electrical and/or thermal properties. The composite, when subjected to thermal and/or mechanical loading, is susceptible to unique failure modes. Two of these modes, interface fracture and fatigue, occur when imperfections (cracks or flaws) within the transitional regions are loaded to a critical level. When this occurs adjoining layers separate and the composite fails.

As composites become more popular the need to assess their failure is becoming critical. The aim of this investigation is to determine how these interfaces fail under both monotonic and cyclic loading, and how alloy composition and the precipitation of interfacial segregants influence these failures. Two model metal/ceramic interfaces between Ni(Cr) and Al$_2$O$_3$, and Al and Al$_2$O$_3$ are considered. It is believed that the findings from these model systems can be used to rationalize behavior observed in more sophisticated
systems. A more detailed statement of the specific objectives of this thesis are given at the end of this chapter.

1.2 Overview of Relevant Fracture Mechanics

The singularity ahead of an interface crack differs from that for a crack in a homogeneous material subjected to the same far-field loading. This difference arises from the elastic mismatch between layers, Figure 1.1, characterized by the Dundurs’ parameters, $\alpha$ and $\beta$ and the bi-material constant, $\varepsilon$, which are defined as [4]:

$$
\beta = \frac{1}{2} \left( \frac{\mu_1(1-2\nu_2) - \mu_2(1-2\nu_1)}{\mu_1(1-\nu_2) + \mu_2(1-\nu_1)} \right), \quad \alpha = \frac{E_1-E_2}{E_1+E_1}, \quad \varepsilon = \frac{1}{2\pi} \ln \left( \frac{1-\beta}{1+\beta} \right)
$$

(1.1)

where $\nu$ is Poisson’s ratio, $\mu$ is the shear modulus and $\bar{E} = E/(1-\nu^2)$ is the plane strain modulus. These parameters influence the singular fields, $\sigma_{\alpha\beta}$, of the interface crack:

$$
\sigma_{\alpha\beta} = \frac{Re[\tilde{K}r^{i\alpha}]}{\sqrt{2\pi r}} \Sigma'_{\alpha\beta}(\theta, \varepsilon) + \frac{Im[\tilde{K}r^{i\alpha}]}{\sqrt{2\pi r}} \Sigma''_{\alpha\beta}(\theta, \varepsilon)
$$

(1.2)

where $r$ and $\theta$ are the coordinates shown in Figure 1.1, $\tilde{K}$ is the complex stress intensity for the interface crack and $\Sigma'_{\alpha\beta}(\theta, \varepsilon)$ and $\Sigma''_{\alpha\beta}(\theta, \varepsilon)$ are dimensionless constants [5]. Similar to the equivalent values for a crack in a homogeneous material $\Sigma'_{\alpha\beta}(0, \varepsilon) = \Sigma''_{\alpha\beta}(0, \varepsilon) = 1$, while $\Sigma'_{\alpha\beta}(0, \varepsilon) = \Sigma''_{\alpha\beta}(0, \varepsilon) = 0$. The oscillatory term, $r^{i\alpha}$, is also a direct result of elastic mismatch.

For a homogeneous material, tensile ($\sigma_{\theta\theta}$) and shear ($\sigma_{r\theta}$) stresses directly ahead of the crack scale with the mode I ($K_I$) and mode II ($K_{II}$) stress intensity factors from conventional fracture mechanics. For an interface crack subjected to the same far-field loading, the opening and shear modes are characterized by the complex stress intensity factor, $\tilde{K} = K_1 + iK_2$. 

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Figure 1.1 An interface crack situated between two elastic layers. The crack tip fields are characterized by the oscillatory singularity $\sigma_{\alpha\beta}$.

Due to elastic mismatch, the components of $\tilde{K}$ are not necessarily equal to $K_I$ and $K_{II}$. Furthermore, tensile or shear stress directly ahead of the crack tip can develop even in the absence of their respective far-field quantities. For example, a crack in an Al$_2$O$_3$ plate subjected to pure opening mode loading would experience only a tensile crack tip opening displacement. A crack along a Ni/Al$_2$O$_3$ interface subjected to the same far-field loading could experience both an opening and shear displacement at the crack tip.

As part of the present investigation, interfaces between metal foils (thickness $t$) bonded to ceramic substrates will be studied. To accomplish this, test specimens comprising two equal thickness Al$_2$O$_3$ substrates sandwiching thin Al or Ni(Cr) foils will be created by vacuum diffusion bonding and then tested. For the sandwich configuration the complex stress intensity factor for the interface crack is related to the nominal stress intensity factor, $K = K_I + iK_{II}$, by [6],[7]:

$$\tilde{K} = t^{-i\epsilon} \left( \frac{1 - \alpha}{1 - \beta^2} \right)^{1/3} (K_I + iK_{II}) e^{\alpha(\alpha, \beta)}$$

(1.3)
A plot of $\omega(\alpha, \beta)$, obtained from [7], is given in Figure 1.2. The energy release rates for both the sandwich and the equivalent homogenous specimen are considered to be the same [7]:

$$G = \frac{1}{E_1} (K_i^2 + K_{II}^2) = \frac{1}{E} \left| \tilde{K} \right|^2$$  \hspace{1cm} (1.4)

where $\frac{1}{E} = \frac{1}{2} \left( \frac{1}{E_1} + \frac{1}{E_2} \right)$.

Figure 1.2 The phase shift $\omega(\alpha, \beta)$ for thin foils sandwiched between two thick substrates.

The two sandwich-type test configurations used in this study include the double cleavage drilled compression (DCDC) specimen [8] and the 4pt-bend specimen [9][10], Figure 1.3. These two geometries were chosen because they provide information over the range of loading phase, $\Psi$, typically encountered in service:

$$\Psi = \tan \left( \frac{\sigma_{zz}^{\psi}}{\sigma_{zz}} \right)^{-1} = \tan \left( \frac{K_{II}}{K_I} \right)^{-1}.$$  \hspace{1cm} (1.5)
Figure 1.3 The sandwich test configurations used in this investigation a) the 4pt-bend specimen and b) the DCDC specimen.

The DCDC specimen is a nominally opening mode test ($\Psi \approx 0^\circ$) while the 4pt-bend configuration has nearly an equal proportion of opening and shear modes ($\Psi \approx 50^\circ$). The interface energy release rate for the DCDC specimen is given by:

$$G_{DCDC} = \frac{\sigma^2 \pi R}{E_1} \left( \frac{h}{R} + \left( \frac{0.235 h}{R} - 0.259 \right) \frac{a}{R} \right)^{-2}$$

(1.6)

where $h$ is half the specimen thickness, $b$ is the specimen width, $R$ is the radius of the drilled hole, $a$ is the crack length and $\sigma$ is the nominal compressive stress $Pl/(2hb)$. (1.6) is valid for $w/(2R) \leq a/R \leq 15$. The energy release rate for the 4pt-bend specimen is:

$$G_{4pt-bend} = \frac{21M^2}{4E_1h^3}$$

(1.7)

where $h$ is half the specimen thickness and $M = Pl/2b$.

Notice that $G$ for the DCDC specimen decreases as the crack length, $a$, increases. This feature makes the test stable, since under fixed load the interface energy release rate decreases with crack advance. The energy release rate for the 4pt-bend configuration is
independent of crack length as long as \( a \geq 2h \). When \( b > 3h \) plane strain conditions apply. The energy release rate can be decomposed into nominal stress intensity factors:

\[
K_I = (GE_1)^{\frac{1}{3}} \cos(\Psi), \quad K_{II} = (GE_1)^{\frac{1}{3}} \sin(\Psi).
\]

In the absence of bulk modulus mismatch, \( \beta = \varepsilon = 0 \), the loading phase for the interface crack can be determined by merely adding \( \omega(\alpha, \beta) \) and \( \Psi \) based on the homogeneous specimen.

### 1.3 Toughness and Interface Failure

#### 1.3.1 Characterization by \( \Gamma_{\text{int}} \)

In homogeneous materials with isotropic properties, cracks which are long in comparison to characteristic microstructural dimensions are free to grow in whatever direction maximizes the crack tip energy release rate [11]. Since this path, for the most part, coincides with a pure mode I path, crack growth begins when the applied driving force, \( G = (K_I^2 + K_{II}^2)/\bar{E} \), reaches a critical value of \( G_{ic} = K_{ic}^2/\bar{E} \) [7].

For an interface crack this single-parameter characterization is no longer valid since, in the absence of kinking, the crack is typically constrained to remain at the interface. Along this path the loading phase due to elastic mismatch and/or far-field loading defines the mixed-mode conditions at the crack tip. The shear and opening displacements in the wake of the crack that result from \( \Psi \), when combined with plasticity, crack path tortuosity and asperities, result in crack tip shielding [12][13]. These interactions lead to a pronounced increase in toughness and fatigue crack growth resistance with loading phase [7],[14].

On occasion, an interface crack can “kink” out of the interface into an adjoining layer. The likelihood that this will occur depends on \( \Psi \), the Dundurs’ parameters \( \alpha \) and \( \beta \), (1.1), and the relative ratio of the interface toughness to the toughness of the adjoining layer,
\( \Gamma_{int}/\Gamma_m \) as summarized for \( \beta = 0 \) in Figure 1.3 [8][15][16]. In the absence of plasticity, kinking occurs when \( \Gamma_{int}/\Gamma_m \) exceeds the transition toughness ratio for a particular \( \alpha \), as illustrated.

![Graph showing transition toughness ratio vs. loading phase](image)

**Figure 1.4** Kinking of an interface crack into an adjoining layer.

For the tests conducted in this investigation, layer 1 (labeled with \( E_1 \) and \( v_1 \)) represents the \( Al_2O_3 \) while layer 2 (labeled with \( E_2 \) and \( v_2 \)) represents the Al or Ni(Cr) in the sandwich-type test configurations. Since Al and Ni(Cr) are both tough (\( \Gamma_{Al} \) and \( \Gamma_{Ni(Cr)} > 1000 \) Jm\(^{-2} \) [17]) interface cracks which form as a result of quasi-static loading either grow along the interface, if \( \Gamma_{int} \) is small, or blunt and arrest if \( \Gamma_{int} \) is large. When the latter occurs a lower bound estimate of the interface toughness is \( \Gamma_{int} \approx \delta \sigma_o \), where \( \delta \) is the crack tip opening displacement measured by microscopy and \( \sigma_o \) is the yield strength of the Al or Ni(Cr).

Dundurs' parameters and loading phase for the Ni(Cr)/Al\(_2\)O\(_3\) and Al/Al\(_2\)O\(_3\) DCDC and 4pt-bend test configurations are summarized in Table 1.1.
<table>
<thead>
<tr>
<th>Bi-material system</th>
<th>DCDC, $\Psi$ (deg.)</th>
<th>4pt-bend, $\Psi$ (deg.)</th>
<th>$\alpha$</th>
<th>$\beta$</th>
<th>Phase Shift, $\omega$ (deg.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni(Cr)/Al$_2$O$_3$</td>
<td>~0</td>
<td>~50</td>
<td>0.27</td>
<td>0.05</td>
<td>~ -3</td>
</tr>
<tr>
<td>Al/Al$_2$O$_3$</td>
<td>~0</td>
<td>~50</td>
<td>0.71</td>
<td>0.17</td>
<td>~ -9</td>
</tr>
</tbody>
</table>

Table 1.1 Relevant Parameters for Crack Kinking.

1.3.2 Materials Issues

Experimental investigations have been conducted on numerous metal/ceramic interfaces, including those between Al$_2$O$_3$ (in single crystal form - sapphire) and Al [18]-[22], Au [23]-[27], Cu [28], Nb [29]-[33], Ni [34]-[36], Pt [37][38] and Ta(Ti) [39][40]. These studies have revealed that $\Gamma_{int}$ depends on a number of factors including the work of adhesion, plasticity in the metal, and the presence of interfacial reaction products and interfacial segregants. In general, reaction products are brittle and reduce interface toughness [39][40]. Similarly, interfacial segregants such as carbon [23][24][26][35] or sulfur [41]-[47] usually diminish toughness through a stress corrosion process whereby atmospheric moisture and segregants interact at the crack tip resulting in failure.

1.4 Organization

In the chapters that follow, results from experimental studies and analytical/numerical models are presented. As part of the organization each chapter is a self-contained work with its own introduction and conclusion. The introductory remarks regarding interface fracture mechanics that have been presented in this chapter provide a general background which is directly relevant to the approach and findings given in each subsequent chapter. A description of the specific objectives of each chapter is given below.
Interfaces between pure Ni and Al₂O₃ are susceptible to stress corrosion caused by moisture, resulting in a fracture energy, $\Gamma_{int} \sim 10$ Jm⁻² [35]. Chapter 2 considers the influence of Cr, as an alloy addition to Ni, on the toughness of Ni(x)/Al₂O₃ interfaces where x represents 20 at.% Cr. Experiments demonstrate that this addition results in a tenfold increase in interface toughness. As part of the objective, the fracture characteristics of solid-state bonded Ni(Cr)/Al₂O₃ interfaces are determined and differences in their behavior as compared to pure Ni/Al₂O₃ interfaces are rationalized in terms of interface attributes. This investigation, as well as those in succeeding chapters, makes use of numerous analytical and imaging techniques including Atomic Force Microscopy (AFM), Auger Electron Spectroscopy (AES), Bulk Chemical Analysis, Scanning Electron Microscopy (SEM), Secondary Ion Mass Spectroscopy (SIMS), Transmission Electron Microscopy (TEM), X-Ray Photoelectron Spectroscopy (XPS), and X-RAY diffraction.

Chapter 3 considers the effect that the type of bonding has on the toughness of Ni(Cr)/Al₂O₃ interfaces. In this chapter, liquid-phase and solid-state bonding techniques are used to create interfaces between the Ni(Cr) alloy used in Chapter 2 and Al₂O₃. Liquid-phase bonding was conducted at temperatures slightly below the melting temperature of the Ni(Cr) (1390°C) while solid-state bonding was conducted at 1275°C, consistent with the procedure adopted in Chapter 2. Fracture and fatigue experiments designed to characterize both interfaces are conducted, and observed differences in behavior are rationalized in terms of interface attributes. Results confirm that the toughness of these interfaces is strongly dependent on bonding technique, with liquid-phase bonding greatly facilitating the segregation of S to the interface. When the segregated interfaces are exposed to atmospheric moisture, they fail by stress corrosion. In contrast, solid-state bonded interfaces do not fail even after mechanical loading.
Chapter 4 considers the general problem of elasto-plastic fracture mechanics in a layered composite subjected to a monotonic variation in temperature. This analysis examines how the presence of a preexisting stationary edge defect, typically present as a result of processing, affects the tendency for subsequent interface failure. Emphasis is placed on a three-layered material system comprising two elastic layers sandwiching a thinner elastic-plastic layer. This analysis is intended to provide a basic understanding of the effect of plastic flow, such as that arising during cooling from the processing temperature, on the driving force for subsequent fracture. Results obtained from analytical modeling and numerical simulations are used to rationalize some of the experimental findings presented in chapter 3.

Interfacial segregants can have a profound effect on the fracture characteristics of interfaces. In chapter 5 an experimental study designed to determine how segregants affect fatigue crack growth characteristics are presented. In this study well bonded interfaces between commercially-pure and high-purity Al and Al₂O₃ are considered. As part of the investigation, liquid-phase and solid-state bonding techniques are used as a means of either facilitating or suppressing the precipitation of an interfacial segregant respectively.
Chapter 2

The Influence of Chromium Addition on the Toughness of γ-Ni/α-Al2O3 Interfaces

2.1 Introduction

Despite recent advances [24][39][48][49], the strength and fracture resistance of interfaces between metals and oxides are still not fundamentally understood. There are paradoxes, as well as conflicting information, that raise the following critical questions:

i) What are the roles of reaction products and segregants? Reaction products are predominantly "brittle" and diminish the interface toughness, as exemplified by intermetallic phases found between Ti and Al2O3 [39]. Segregants usually diminish the fracture toughness, particularly in conjunction with atmospheric moisture (stress corrosion). Such effects have been found in Al2O3/Au [24][26][50] and Al2O3/Ni [35] interfaces, wherein C segregation is the causal factor. There are also well-documented S segregation effects at interfaces between Al2O3 scales and Ni-based superalloys [44]-[47][51][52].

ii) Why are some interfaces so strong that failure occurs by ductile mechanisms within the metal? Interfaces between Al/Al2O3 [22][48], Al/SiC [54] and Cu/Al2O3 [55] behave in this manner.

iii) When do active metals such as Cr and Ti substantially enhance the fracture toughness? Most evidence indicates that interfaces formed at low temperature, by vapor deposition, benefit from a thin interlayer of active metal1. Examples include Cu on SiO2, polyamide and Si3N4 [49]. Two mechanisms could apply: (a) Cr or Ti act as a "getter" for contaminants, such as C or OH-, allowing for unexpurgated metal/ceramic bonding with

---

1. Loosely defined as a reactive element which readily forms carbides, oxides, or sulfides.
the "clean" oxide surface [56], and/or (b) Cr and Ti develop strong covalent bonds with the oxide. This type of bonding state provides a linkage to the predominant metal.

iv) Does dissolution of the oxide in the metal, during bonding, enhance the fracture toughness? Such dissolution has been identified in Nb/Al2O3 [31]-[33] and in Cu/SiO2 [57] and appears to result in reasonably tough interfaces.

With these questions as background, experiments have been performed that address these issues for interfaces between Al2O3 and γ-Ni(x) alloys, where x represents a solid solution addition to the Ni. In particular, comparisons are made between pure Ni and Ni with Cr, in order to address the role of an active metal. Furthermore, Ni(Cr) is a common alloy base used in heat-resistant alloys such as Nichrome, superalloys including Waspaloy and bond coats such as NiCrAlY. To motivate the dissolution and segregation mechanisms, the bonding temperature was chosen to be just below the eutectic temperature of the alloy.

Some previous studies have been performed on diffusion bonded interfaces between Al2O3 and Ni, Cr, as well as Nichrome [58][59]. In each case, after bonding, shear tests were conducted. These experiments illustrated that the Ni(Cr) interface, when appropriately bonded, could exhibit a greater shear resistance than either the Ni or Cr systems. The apparent benefit of Cr alloy additives, though neither explained nor quantified, provides a basis for the current exploration.

2.2 Materials and Bonding

2.2.1 Foil Preparation (vacuum annealing)

A cold-rolled 0.8 Ni-0.2 Cr alloy (Goodfellow Corp., Berwyn, PA) has been solid-state vacuum diffusion bonded to optically polished [\{1012\} R-PLANE] sapphire (Saphikon, Inc., Milford, NH). Prior to bonding the foil was ultrasonically cleaned in methyl alcohol and distilled water and then vacuum annealed inside high purity, 99.8% Al2O3, alumina
crucibles (Coors Ceramics Company, Golden, Colorado) at 1373 K and 10^{-7} torr for twelve hours. This process served to: (i) diminish hydroxides and organic residue present on the alloy surfaces, (ii) disassociate less stable disruptive surface oxides such as NiO and (iii) eliminate most of the O dissolved in the alloy [36]. As a result of the annealing process the alloy recrystallized, eliminating the initial rolling texture and producing equiaxed grains ~200 μm in diameter.

The annealing furnace (Vacuum Industries, Model 1822) and the time vs. temperature profile used for the annealing process are shown in Figure 2.1. Each crucible shown contains a single Ni(Cr) foil. Beforehand the crucibles had been baked-out at 1773K and 10^{-7} torr for > 100 hrs, in order to deplete them of volatile impurities which would otherwise coat the foils during the annealing process.

Figure 2.2 contains a graph of the temperature vs. oxygen partial pressure required for the disassociation of various oxides, \( oxide \rightarrow \text{metal} + O_2 \), expected to grow either on the Ni(Cr) surface [60] or on other components within the bonding environment. Here it has been assumed that the furnace maintains a molar O_2 concentration of ~ 20%. Temperature-dependent energy of formation formulas for each of the respective reactions were obtained from [61].

Notice that the figure suggests NiO can be readily disassociated at both the annealing and bonding temperatures. This is supported by the noticeable absence of NiO scales on the surface of the foil following the annealing process. Cr_2O_3, on the other hand, cannot be disassociated. A dendritic Cr, C, and O phase believed to have formed during processing is sparsely distributed on the alloy surface Figure 2.3.
**Figure 2.1** The vacuum chamber used to degas the metal foils. Each crucible contains one foil. Crucibles are needed to prevent contamination of the foils by other metals within the chamber.

**Figure 2.2** Dissociation temperature vs. vacuum for various oxides present on the surface of the Ni(Cr) alloy or in the furnace environment. Ranges for the furnace vacuum and temperature experienced during diffusion bonding of Ni(Cr) and Al₂O₃ are shown.
The decomposition reaction $Al_2O_3 \rightarrow 2Al + (3/2)O_2$ could not be obtained within the vacuum and temperature ranges shown. Thus the single crystal $Al_2O_3$ substrates were not affected by the temperatures and vacuum levels encountered during diffusion bonding.

![Image](image.jpg)

**Figure 2.3** The Ni(Cr) surface after being vacuum annealed at 1100°C. Labeled regions are; a) Ni(Cr) solid solution grains and b) a sparse Cr, C, and O phase.

### 2.2.2 Sapphire Preparation

The sapphire substrates were cleaned using a multi-step process involving numerous solvents, oxidizers and acids, namely; 1) trichloroethylene, 2) acetone, 3) methanol, 4) isopropanol, 5) solutions containing distilled water and concentrated hydrogen peroxide (30%) and 6) ammonium hydroxide (30%) or 7) hydrochloric acid (30%) with distilled water. The oxidizer/acid/distilled water solutions were comprised of 1 part concentrated hydrogen peroxide, 1 part either hydrochloric acid or ammonium hydroxide and 5 parts distilled water. Lastly, substrates were ultrasonically cleaned in distilled water. All chemicals were high purity/HPLC grade with typical impurity analysis given in the ppm range. The general cleaning procedure is summarized as follows:

i) Substrates were first washed with soap, rinsed with distilled water and blown dry with compressed air.
ii) Next, the substrates were placed in a beaker containing trichloroethene (TCE) and ultrasonically cleaned for either 5 min. (for solvents) or 15 min. (for acid/oxidizer).

iii) Substrates were removed from the beaker, rinsed with fresh chemicals from the following step, blown dry with compressed air and placed in another beaker containing the next chemical.

iv) Steps ii and iii were repeated until completion of the cleaning process.

Following the last cleaning, each substrate was blown dry with compressed air and retained in an oven at 450 K until bonding.

2.2.3 Solid-State Diffusion Bonding

The materials were bonded in the form of 50 mm square plates with two 0.125 μm thick foils sandwiched between two 1 mm thick sapphire substrates. While the materials were being assembled care was taken to avoid contacting the faces of either the sapphire or the foils. Bonding was done in a high-vacuum furnace (Centorr Associates Inc.) mounted within a servo-hydraulic mechanical test frame (MTS Industries), where each sample was vacuum-hhot-pressed at 1550 K for 4 hours. A compressive load of 12.5 kN (5MPa) was used to bring the alloy and sapphire surfaces into close physical contact during bonding.

Figure 2.4 contains a photograph of the assemblage within the hot press. The Al₂O₃/Ni(Cr)/Al₂O₃ tri-layer is in the middle of the four circular graphite dies located between the lower stator and upper servo-hydraulic push-rod. Multiple sheets of flexible graphite foil (0.125 μm thick) were used to compensate for any misalignment in the load train. Included in the figure is the temperature profile used during bonding. A three-tier heating process allowed sufficient time for the vacuum system to maintain a high vacuum environment within the chamber.
Figure 2.4 The diffusion bonding chamber shown with sample. Temperature control during bonding is regulated through the thermocouple on the left.

2.3 Measurement Procedures

After bonding, a portion of the perimeter measuring about 4 mm in width was removed from each plate using a high speed diamond saw. The remainder was cut into beams approximately 5 mm wide and 40 mm long. The edges of each beam were ground and polished using a diamond grinding disk and a succession of diamond polishing suspensions ranging in size from 9 to 1 μm. Lastly, in order to obtain a virtually scratch-free alloy surface, the edges were polished with a suspension of 0.05 μm Al₂O₃.
The beams were pre-cracked along the mid-section by first applying Knoop indentations using a 50 N load (0.5 mm apart), across one side of the mid-span (Figure 2.5). Displacing each beam in 3 point bending at a rate of 0.1 μm/s, with the Knoop indentations in tension, induced a crack that originated at the indentations and extended to the interface, where it arrested. Subsequently, for crack growth studies, the pre-cracked beams were displaced in 4 point bending at a rate of 0.1 μm/s.

Figure 2.5 A schematic illustration of the specimen prep. process, including: cutting with a diamond saw, applying Knoop indentations and pre-cracking in three point bending.

The flow strengths of the alloy and the pure Ni were determined by using two complementary methods. 1) Tensile stress/strain curves were obtained from tension tests conducted on reduced section samples having the same thermal treatment used for bonding. This method characterizes the behavior of the alloy, but does not account for the possible influence the sapphire may have on the microstructure development or the chemistry of the alloy. 2) Microhardness measurements, using a diamond pyramid indenter with 50
gram load, were made on the polished metal surface while in the bonded configuration. These measurements provided an estimate of possible changes induced by bonding.

A TENCOR FLX 2908 (Tencor Instruments, Mountain View, Ca) was used to obtain in-situ curvature measurements on an asymmetric Al₂O₃/Ni(x)/Al₂O₃ tri-layer subjected to a monotonic temperature increase. This technique explored effects related to the stresses in the Ni alloy. The asymmetry was introduced by grinding and polishing the sapphire layers until the layers had thicknesses of 175/250/720 μm (Al₂O₃/Ni(x)/Al₂O₃). Because of the residual stress in the Ni, some bending occurred during the grinding process causing the Ni layer at the center of the tri-layer to be curved.

2.4 Characterization Methods

Analytical spectroscopies and microscopies have been used to characterize the Ni(x) and Al₂O₃ surfaces prior to bonding, as well as the Ni(x)/Al₂O₃ interface after bonding. The methods used comprise: Auger Emission Spectroscopy (AES), Energy Dispersive Spectroscopy (EDS), X-ray Photoelectron Spectroscopy (XPS), X-Ray Diffraction (XRD), Atomic Force Microscopy (AFM), Secondary Ion Mass Spectrometry (SIMS) and Transmission Electron Microscopy (TEM). For some of the measurements, the interface was exposed either by chemical dissolution of the alloy, or by mechanical milling followed by sputtering. A three part HCl and one part HNO₃ acid solution (aqua regia) was used for the former. Benchmark tests conducted on the unbonded Al₂O₃ confirmed that the aqua regia did not alter the sapphire morphology. When charging-related complications were encountered, exposed interfaces were coated with 40 nm of Au/Pd. Cross sections for TEM analyses were prepared by mechanical dimpling and ion-beam thinning.

The XPS and SIMS analyses were performed by sputtering through the Ni(x) towards the Ni(x)/Al₂O₃ interface. This allowed for the measurement of elemental concentration.
gradients on both the alloy and oxide sides of the interface. The XPS analysis was also used to determine the bonding state of the elements, in particular that of C. Carbon, when in the form of a carbide, has a characteristically lower binding energy than in other bonding states.

The bulk elemental composition was determined using standard analytical methods, by dissolving the alloy in aqua regia, filtering to separate the undissolved particles and separately analyzing the elements in the solution and the residue. Such analyses were conducted both before and after diffusion bonding.

2.5 Mechanical Measurements

2.5.1 Yield Strength

The tensile stress/strain curve of the annealed Ni(Cr) foil is summarized in Figure 2.6a. The yield strength, \( \sigma_0 \), is approximately 330 MPa and the strain hardening is nearly linear with a slope \( H \approx 0.01E \), where E is Young's modulus. Analogous tests conducted on the pure Ni show a yield strength of about 150 MPa. Microhardness tests conducted on the bonded Ni(Cr) (Figure 2.6b) indicate a flow strength of \( \sigma_0 = 630 \pm 90 \) MPa. This test provides information about the strength at \( \sim 7\% \) plastic strain [62]. Consistency with the tensile flow strength at this strain level (Figure 2.6a) indicates that the bonding had minimal effect on the stress-strain behavior of the alloy.

The curvature of the asymmetric tri-layer (Figure 2.6c) was linear and reversible up to 265°C. However, at this temperature one of the sapphire layers developed multiple cracks as the residual stress in the alloy relaxed. Consequently, the stresses in the alloy did not reach its yield strength before the tensile stresses in the sapphire exceeded its fracture strength. The latter arise because of the initial curvature of the Ni layer after grinding. Nevertheless, even with the development of multiple cracks in the sapphire, the interfaces
remained completely intact, reaffirming the exceptional strength of the Ni(Cr)/Al₂O₃ bond.

**Figure 2.6** a) The tensile stress-strain curve for annealed Ni(Cr) foil. b) Flow strengths σₚ for the Ni(Cr) alloy after diffusion bonding, estimated from the micro-vickers hardness σₚ ≈ Hᵥ/3. c) The curvature as a function of temperature for an asymmetric tri-layer. Note the incidence of sapphire cracking at 265° C.
2.5.2 Fracture Resistance

Vastly different mechanical responses are evident for the interfaces made with the Ni(Cr) alloy and those made with pure Ni, particularly when tested in ambient air. In the Ni(Cr)/Al₂O₃ system, cracks extending into the sapphire always arrest at the interface, followed by blunting, Figure 2.7. In some cases, the crack attempts to reorient along the interface and then arrests (Figure 2.8). As the load is raised, blunting continues until the crack re-initiates in the intact sapphire. Since there is no crack growth, only a lower bound on the initiation toughness can be ascertained, by assessing the energy release rate at the tip, $J_{\text{tip}}$. The maximum residual blunting displacement is typically 0.3 μm. With the alloy yield strength of $\sigma_y \approx 330$ MPa, this blunting is indicative of an energy release rate, $J_{\text{tip}} \equiv \sigma_y \delta \approx 100$ Jm$^{-2}$.

![Image](image.png)

**Figure 2.7** A crack arrested at the interface. Differences in atomic number contrast in backscatter mode emphasize a Cr, C, and O phase at the interface.

The high toughness of the interface is reaffirmed upon continued flexural loading. Cracks re-initiate and propagate in the sapphire, rather than at the interface, and exhibit a tortuous crack path. Such cracks are attracted to the interface, but then kink back into the sapphire. *They never extend along the interface*. During this process, slip in the alloy is
extensive and inhomogeneous (Figure 2.9), indicating the development of stresses in the alloy exceeding the yield strength. Yet the interfaces remain intact and cannot be separated, even upon subsequent fragmentation of the sapphire.

![Image](image.png)

**Figure 2.8** A crack deflected along the interface exhibits blunting with an opening displacement of 0.3 μm.

In contrast with this behavior, the pure Ni/Al₂O₃ interface debonds readily with a fracture energy as low as $\Gamma_i = 10 \text{ Jm}^{-2}$ (Figure 2.10) [54]. However, upon reducing the relative humidity (by using a dry N₂ atmosphere), the pre-crack blunts and does not propagate, even at energy release rates exceeding 100 Jm$^{-2}$ [35]. The blunting displacements reach $\sim$1 μm. Similar effects of moisture have been found for other interfaces [24][26] and are attributed to moisture-induced stress corrosion. Moreover, these corrosion effects have also been found to depend on the presence of segregants, such as C, that affect the work of adhesion [23]. Moisture induced stress corrosion is a common feature in oxides, such as glasses and Al₂O₃ [63][64][65], and is attributed to a stress dominated reaction with the OH$^-$ ions. The corresponding mechanism that operates at certain metal/oxide interfaces has yet to be ascertained.
Figure 2.9 An optical micrograph showing extensive inhomogeneous slip in the alloy.

Figure 2.10 The crack growth resistance of the pure Ni/Al₂O₃ interface tested in ambient air. Upon using dry N₂, the crack does not propagate, even at an energy release rate exceeding 100 Jm⁻².
2.6 Characterization

2.6.1 Bulk Chemistry

Bulk chemical analysis was performed on the soluble and insoluble parts of the alloy, with analysis being done both before and after bonding. The results are summarized in Table 2.1. This analysis reveals that the alloy contains some Si, Al, and Mg. Within the accuracy of such analysis, the implications are that the Al concentration in solution in the alloy increases upon diffusion bonding. The Cr content appears to decrease slightly. The analysis of insoluble particles indicates that there may be a small increase in the Al₂O₃ content upon diffusion bonding. Cr-containing particles are not evident at this level of analysis.

<table>
<thead>
<tr>
<th>a) Element</th>
<th>Before Bonding (atomic concentration)</th>
<th>After Bonding (atomic concentration)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chromium</td>
<td>19.2%</td>
<td>18.3%</td>
</tr>
<tr>
<td>Nickel</td>
<td>80.7%</td>
<td>81.5%</td>
</tr>
<tr>
<td>Silicon</td>
<td>0.05%</td>
<td>0.05%</td>
</tr>
<tr>
<td>Aluminum</td>
<td>0.07%</td>
<td>0.09%</td>
</tr>
<tr>
<td>Magnesium</td>
<td>160 PPM</td>
<td>-</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>b) Element</th>
<th>Before Bonding (atomic concentration)</th>
<th>After bonding (atomic concentration)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chromium</td>
<td>2.11%</td>
<td>2.40%</td>
</tr>
<tr>
<td>Nickel</td>
<td>2.11%</td>
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<td>Silicon</td>
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<td>85.1%</td>
</tr>
<tr>
<td>Aluminum</td>
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</tr>
</tbody>
</table>

Table 2.1 Bulk Chemical Analysis of the Ni(Cr) alloy a) constituents soluble in aqua regia and b) constituents insoluble in aqua regia.
2.6.2 Interface Morphology

Characterization of the sapphire side of the interface after dissolving the alloy reveals some of the thermo-chemical phenomena that accompany diffusion bonding. An AFM image of the alloy interface (Figure 2.11) indicates that two product phases have formed. One is continuously distributed with an area fraction of about 0.3. It has a thickness of 0.2-0.4 μm and a width of about 1 μm. The other phase is preferentially coincident with the grain boundaries in the alloy. The regions between both phases are finely faceted, with ~10 nm spacing and amplitude. These features contrast with those found on the unbonded sapphire surface which comprises relatively large facets characteristic of annealed Al₂O₃ surfaces.

![AFM Image](image)

*Figure 2.11* An AFM image of the Al₂O₃ side of the interface after the Ni(Cr) has been dissolved with aqua regia. The spinel and Cr carbide interphases are identified, as well as the intervening sapphire.

The interface with the pure Ni is essentially the same as the unbonded surface. There is no evidence of a reaction product.
Figure 2.12 X-ray Photoelectron Spectrographs of the Ni(Cr) alloy surface a) before b) and after sputtering for several seconds to remove the C contamination.

2.6.3 Interface Chemistry

XPS analysis of the alloy surface before bonding indicates the presence of C and other contaminants (Figure 2.12a). Following several seconds of argon ion sputtering, contaminant-free alloy surfaces are exposed with some residual oxygen (Figure 2.12b). Characterization of the interface exposed by acid dissolution of the alloy using EDS (Figure 2.13) indicates that the product phases at the alloy interface contain Mg, Cr and C. Further
analysis of the interface using AES has revealed that the product phase that occurs preferentially at the alloy grain boundaries is Cr and C rich, probably a Cr carbide (Figure 2.14). The finely faceted regions between the product phases are composed of only Al and O. X-ray diffraction (Figure 2.15) confirms that the other uniformly distributed product phase is epitaxial (111) MgAl$_2$O$_4$. There are also x-ray peaks arising from the sapphire and an unidentified peak at 81.24°. The x-ray pattern does not have recognizable Cr carbide peaks because it is present as non-epitaxial, small particles, which yield broad, low intensity peaks.

![EDS spectrum of the Al$_2$O$_3$ side of the interface.](image)

**Figure 2.13** EDS spectrum of the Al$_2$O$_3$ side of the interface.

The SIMS measurements (Figure 2.16) provide additional insight. i) There is a Mg zone concentrated primarily in the alloy near the interface. Moreover, Mg is also present on the Al$_2$O$_3$ side of the interface, having a concentration that diminishes with distance from the interface. This suggests that the alloy contains Mg that diffuses to the interface and concentrates there, but also diffuses into the Al$_2$O$_3$. Oxygen is present within the concentrated Mg region, suggestive of a mixed Al, Mg oxide. ii) The Al and O profiles are consistently displaced from each other by ~ 0.2 μm, with the Al being retained further into

2. Since the electron beam used during EDS excites the sample to a depth of 1-5 μm, x-rays emitted from the Al$_2$O$_3$ also make up a large percentage of the spectrum.
the alloy side of the interfacial zone. This suggests some alumina dissolution in the alloy, with the excess Al concentrated near the interface. iii) Cr and Ni levels appear to exceed background over a distance of up to ~ 0.2 µm into the oxide, whereas the Si concentration reverts to background levels coincident with the O level attaining equilibrium. This suggests a thin region of "mixed" oxides comprising cations of Al, Cr, Ni, as well as the Mg noted above. iv) There is a clear increase in the C concentration at the interface.

**Figure 2.14** Auger Emission Spectra of the Cr rich product phase on the Al₂O₃ side of the interface identified on Fig. 2.11.

**Figure 2.15** The X-ray diffraction spectrum of the Al₂O₃ side of the interface.
Figure 2.16 SIMS depth profiles (wedge sample used for analysis pictured above); a) Al, O, Ni, Cr, and Si. b) highlighting the C distribution near the interface relative to Al and O. c) highlighting the Mg distribution near the interface relative to Al.

The XPS measurements (Figure 2.17b) highlight C levels and its bonding state in the alloy. There is a high C concentration at the original alloy surface, in bonding states indicative of C-C, C-H, and C-O bonds (Figure 2.17a). This C is regarded as surface contamination formed on the Ni(Cr). Beyond this surface layer, C is present with a relatively uniform concentration of about ~ 0.5% (Figure 2.17b). The bonding state for this C (a peak at 283 eV) is indicative of a carbide (Figure 2.17a). The absence of C-C bonds remote from the surface suggests minimal C segregation.
Figure 2.17 a) Binding energy levels associated with the state of C. b) The XPS depth profile for C in the alloy.

2.6.4 Cross-Sections

Cross-sections of the interface have been characterized by TEM. Although the area sampled is minimal three major findings do emerge from these studies. i) The interphase noted by AFM in Figure 2.11 is evident, Figure 2.18a. Diffraction patterns, combined with elemental analysis by EDS, establish that this phase is spinel, MgAl$_2$O$_4$. The presence of this phase accounts for the Mg concentration near the interface found by SIMS (Figure
2.16c). ii) In the alloy near the interface, Cr-containing precipitates are evident in a few instances (Figure 2.18b). While elemental analysis for C in these precipitates has not been possible (because of the C deposited on the foil to avoid charging), the presence of Cr carbides would be in accord with the XPS bonding state found for the C present in the alloy (Figure 2.17) as well as the EDS and AES spectra from the interface (Figure 2.13 and Figure 2.14). Otherwise, the alloy comprises a single phase Ni(Cr), solid solution γ-alloy [66].

iii) The alloy contains a high density of dislocations, including pile-ups inferred from intense strain fringes in the Al₂O₃ at the interface. The large strains sustained at the interface reaffirm the high strength of the metal/oxide bond in this material system.
Figure 2.18 a) TEM micrographs showing the MgAl$_2$O$_4$ interphase attached to the Al$_2$O$_3$ at the Ni(Cr)/Al$_2$O$_3$ interface. The arrows highlight the strain fringes in the sapphire near the interface caused by dislocation pile ups. Note the high density of dislocations in the alloy. b) a Cr (carbide) precipitate in the alloy.

2.7 Discussion

2.7.1 Interface Microstructure

Binary and ternary phase diagrams within the system Ni, Cr, Al, O, C [36][60][67]-[69] provide further insights into the above findings. The Ni, Cr, C diagram (Figure 2.19) [67] indicates equilibrium between γ-Ni and Cr$_7$C$_3$ at the approximate concentrations of the elements in the alloy (20% Cr and ~ 0.5% C). The Ni, Al, O ternary diagram [36] together with that for Ni, Cr, O [60] indicate that for small levels of O, Cr$_2$O$_3$ should not form. Moreover, at the Al levels in the alloy (1000 ppm), γ-Ni is in equilibrium with α-Al$_2$O$_3$ at an oxygen concentration < 0.025 at. % [36]. That is, Ni spinel should not form.

The Al$_2$O$_3$/MgO binary diagram [68] is consistent with the formation of the spinel interphase but does not indicate the solubility of MgO in Al$_2$O$_3$. The Al$_2$O$_3$/Cr$_2$O$_3$ binary diagram [69] reveals complete solid solubility, consistent with Cr diffusion into the Al$_2$O$_3$.
to form a solid solution zone, with the Al diffusing into the alloy. This might explain the displacements of the Al and Cr levels relative to O (see the discussion in conjunction with the SIMS measurements, Section 2.6.3, Figure 2.16).

![Phase Diagram](image)

**Figure 2.19** The Ni rich corner of the Ni, Cr, and C ternary phase diagram.

The phenomena involved in the diffusion bonding of Ni(Cr) to Al₂O₃ suggested by this characterization and by the phase equilibrium are depicted in Figure 2.20. Mg in the alloy diffuses to the interface. It is also proposed that Al₂O₃ dissolves in the alloy and that the O in solution combines with the Mg, which reacts with the Al₂O₃ to form the spinel interphase [70]. The faceted nature of the Al₂O₃/alloy interface found by AFM is consistent with some dissolution. The C contaminant on the Ni(Cr) surfaces, upon bonding, diffuses into the alloy and combines with some of the Cr to form carbide precipitates. The phase diagram (Figure 2.19) suggests Cr₇C₃. A determination of the C activity in equilibrium with Cr₇C₃ in a γ-Ni(Cr) alloy indicates that low activities ($a_c < 10^{-5}$) arise at temperatures below ~500 K. Hence, if C is still able to diffuse in the alloy at this temperature, its
concentration in the alloy (and by inference the interface) would diminish to very low levels that prevent interface weakening.

![Diagram of interface bonding](image)

**Figure 2.20** A schematic illustrating the proposed phenomena responsible for the strong bond found in the Ni(Cr)/Al₂O₃ system.

### 2.7.2 Interface Bonding

The high strength of the γ-Ni(Cr)/Al₂O₃ interface relative to the pure Ni/Al₂O₃ interface appears to be a major new finding that requires explanation. Taken together with the documented effects of C segregation weakening of other metal/oxide interfaces, particularly Au/Al₂O₃ [24][50], it is tempting to attribute the behavior of the Ni alloy/Al₂O₃ interface to the presence or absence of C segregation. In the γ-Ni(Cr) alloy, it is clear that the Cr has the ability to "getter" much of the C contamination to form carbide precipitates. This would allow the full strength of the Ni/Al₂O₃ bond to develop. Such a behavior would be consistent with the strong bonding at clean metal/oxide interfaces predicted by quantum mechanical calculations [71][72]. Moreover, it is likely that the Al₂O₃ at the
interface has some Cr and Ni in solution (on the Al sites). Their role in forming a strong bond could be significant, but is beyond the scope of the present study.

A further implication is that the nominally pure Ni/Al<sub>2</sub>O<sub>3</sub> interface has C segregant caused by contamination either on the surface prior to bonding, from within as a bulk impurity or from C present in the bonding environment. There is an adjunct implication that C segregant reduces the bond strength in the manner found for Au/Al<sub>2</sub>O<sub>3</sub> [50]. The presence of C on the alloy surfaces found by XPS (Figure 2.12 and Figure 2.17) demonstrates how susceptible surfaces are to such contaminants. Furthermore, surface contamination may also arise as carbon impurity in the bulk segregates to the free surface during annealing [73]. Experiments conducted in ultra high vacuum have found this to be true even at C impurity levels as low as 100 ppm. Moreover, small amounts of C in the bonding environment, when O is also present as a mobile "carrier" (by forming CO), can result in rapid C infusion by migration along the interface [23].

The possibility of some Al<sub>2</sub>O<sub>3</sub> dissolution in the alloy may be relevant. Such dissolution would tend to remove a contaminated surface layer and disperse the contaminant in solution in the alloy. This could be as important as carbide formation. It is speculated that the Al and O needed to form the spinel by reaction with the Mg in the alloy may originate from the interfacial region between the spinel interphase. Should this be the case, spinel formation would effectively dissolve and displace the original alloy/Al<sub>2</sub>O<sub>3</sub> interface.

2.7.3 Dissolution of the Alumina

The AFM evidence that there may be some dissolution of the Al<sub>2</sub>O<sub>3</sub> deserves some additional consideration. Equilibrium at the α-Al<sub>2</sub>O<sub>3</sub>/Ni interface has indicated that relatively low Al concentrations in the alloy suppress dissolution at least when the O concentration is greater than or equal to 10<sup>-3</sup> at.%. Moreover, the low diffusivity of Al in Ni
allows the equilibrium Al concentration to be sustained near the interface. This argument, which has been given for the absence of dissolution at pure Ni/Al₂O₃ interfaces [36], does not change by having Cr in solution in the alloy: especially since a low oxygen activity has been affirmed by the absence of Cr₂O₃ precipitates. But, there are two possible causes of dissolution that require further exploration. One of these has been discussed above, i.e. that the Mg in the alloy getters some Al and O to form the spinel interphase leaving the excess Al in solution in the alloy. The other possibility is that Cr in solution in the Al₂O₃ changes the equilibrium and allows higher Al concentrations in the alloy.

2.8 Concluding Remarks

Cr in solution exerts a major influence on the fracture resistance of the γ-Ni/α-Al₂O₃ interface in a moist environment. The Cr seems to eliminate the sensitivity of the Ni interface to stress corrosion. (In the absence of moisture, the interfaces are tough with and without Cr) [35]. Two factors seem to be important in the realization of high ambient toughness. i) The Cr getters C from the interfacial zone through the formation of a carbide. This negates the role of C segregation in stress corrosion cracking of the interface. ii) Dissolution of Al₂O₃ in the alloy disperses the interface contaminants into solution in the alloy and enables strong bonding. Future studies are needed to unequivocally identify the more dominant of these possibilities, although it is believed from the present work that the evidence is primarily supportive of C gettering by Cr.
Chapter 3

Effects of Sulfur on the Toughness and Fatigue Resistance of Interfaces between \(\gamma\)-Ni(Cr) and \(\alpha\)-Al\(_2\)O\(_3\)

3.1 Introduction

Interfaces between Ni alloys and Al\(_2\)O\(_3\) exhibit a wide spectrum of behaviors [34],[35],[58],[59]. That for a \(\gamma\)-Ni(Cr) alloy solid-state diffusion bonded to \(\alpha\)-Al\(_2\)O\(_3\) has remarkable strength and toughness, Chapter 2. Crack blunting occurs in preference to crack growth, Figure 2.8, with extensive plastic deformation in the alloy, Figure 2.9. Eventual interface failure proceeds by a ductile mechanism, with a toughness in excess of 300 Jm\(^{-2}\). The Cr in the alloy appears to contribute to the strength and toughness by gettering C (to form Cr\(_7\)C\(_3\)), which would otherwise segregate to the interface and cause weakening. Such weakening is apparent at interfaces between high purity Ni and Al\(_2\)O\(_3\) [35]. These interfaces are susceptible to stress corrosion and have relatively low toughness (10 Jm\(^{-2}\)) when tested in moist air, Figure 2.10. Absent moisture, the interfaces are again strong and tough (>100 Jm\(^{-2}\)). It has been surmised that the weakness in moisture arises because of the combined effect of C segregation and reaction with water in the environment.

Other important interface phenomena have been identified for thermally grown \(\alpha\)-Al\(_2\)O\(_3\) (referred to as TGO) on Fe and Ni-based alloys containing Al [42],[44]-[47],[51]-[53]. The resultant interface is between the Al\(_2\)O\(_3\) and an Al depleted layer comprising Fe or \(\gamma\)-Ni. These interfaces are profoundly affected by S segregation. When S levels in the alloy are reduced below 2 ppm by hydrogen annealing, the TGO is adherent [44]-[46]. Otherwise, it detaches by buckling and spalling, motivated by a large residual compression in the TGO (about 3 GPa, caused by thermal expansion misfit). Addition of Y (and other rare earth elements) to the alloy getters much of the S, limiting interface segregation and
restoring the TGO durability [47][51][74]. A remaining paradox is that even durable TGOs formed on alloys containing Y fail at the interface with a brittle appearance (no evidence of plastic deformation in the alloy) and exhibit low toughness (5-10 Jm^{-2}). The present study augments this previous work by addressing explicit effects of S on adhesion.

A previous investigation of solid-state diffusion bonded interfaces between Ni and \(\alpha\)-Al\(_2\)O\(_3\) revealed some effects of S, manifest as differences in toughness between interfaces formed with and without hydrogen annealing [35]. There were accompanying trends in the intensity of plasticity in the Ni, induced by interface crack extension. Here, more dramatic effects of S are demonstrated by using disparate bonding conditions that release vastly different S levels to the interface. This is made possible because S in \(\gamma\)-Ni(Cr) is largely present as CrS precipitates [81]. Moreover in the Ni-Cr-S ternary, there is a eutectic reaction at about 1625K that results in a S-rich liquid [82][83]. Accordingly, if bonding is conducted below this temperature, the S should remain as CrS and should not segregate, resulting in the strong/tough interface reported previously. Conversely, interfaces made at higher temperature should release appreciable levels of S that concentrate in the liquid phase near the interface. A comparison of interfaces made above and below 1625K should thus reveal dramatic differences, if S has a major influence on adhesion. This hypothesis is tested in the present study. Interfaces formed below 1625K are referred to as solid-state diffusion bonded (SSDB), while those created above 1625K are designated liquid-phase bonded (LPB).

3.2 Materials and Bonding

Ni-20 at.% Cr foil has been both solid-state and liquid-phase vacuum bonded to optically polished \(\{0001\}\) sapphire (Crystal Systems, Inc., Salem, MA). Bulk chemical analysis of the Ni(Cr) accomplished using the inductively coupled plasma (ICP) method revealed the
presence of S and Ti (Table 3.1), in addition to Ni and Cr. Secondary ion mass spectroscopy (SIMS) measurements made in the γ-Ni(Cr) foil after annealing at 1100° C, but before bonding, indicate a uniform S concentration (at about 10^19 atoms/cm^3) with no obvious segregation to the surface. Auger emission spectroscopy (AES) affirms that there is no significant segregation of S to the surface.

<table>
<thead>
<tr>
<th>Element</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>S (as received)</td>
<td>165 ppm wt.%</td>
</tr>
<tr>
<td>S (post vac. anneal)</td>
<td>200 ppm wt.%</td>
</tr>
<tr>
<td>Ti</td>
<td>980 ppm at.%</td>
</tr>
</tbody>
</table>

Table 3.1 Concentration of Sulfur and Titanium in the Ni(Cr).

Prior to bonding, the foils and substrates were prepared as described in Section 2.2. Following these procedures, a three layered arrangement was assembled consisting of two sapphire substrates sandwiching Ni(Cr) foil. Each assembly was placed inside a vacuum furnace (Oxygon Industries, Inc., Epsom, NH) mounted inside a pneumatic mechanical test frame. In an effort to minimize all external sources of carbon, the furnace fixtures comprised exclusively of TZM (Titanium-Zirconium-Molybdenum alloy) and boron nitride, with a lubricant-free turbomolecular pumping system. Pressure bonding was performed at either 1550K or 1650K.

Specimens produced by SSDB consisted of two 58 x 32 x 2.5 mm plates sandwiching two 125 mm Ni(Cr) foils. Three different LPB plates were produced. The first two consisted, respectively, of single and double 125 μm thick Ni(Cr) foils sandwiched between 25 x 25 x 1 mm sapphire substrates. The third contained one foil sandwiched between 25 x 25 x 2.5 mm substrates.
After bonding, the SSDB plates remained intact and were sufficiently robust to allow cutting and machining into test specimens suitable for measuring the interface properties, described below. Conversely, all LPB plates exhibited some amount of delamination or debonding, dependent on the relative thickness of the Al₂O₃ and Ni layers, \( \eta = h/t \) where \( h \) and \( t \) are the thickness of the Al₂O₃ and Ni(Cr) respectively. Plates having the smallest \( \eta \) completely delaminated upon removal from the bonding furnace. Those with intermediate \( \eta \) delaminate from the edges, Figure 3.1, but remain connected by an attached region at the center, with an attachment diameter that diminished with time because of stress corrosion. The stress corrosion accelerated with the addition of water to the interface accomplished by placing a drop of H₂O at the sample edge. These plates were too fragile to be cut into test specimens. The plates with the greatest \( \eta \) contained a multiplicity of small unbonded patches. These were revealed by using differential interference contrast (DIC) optical microscopy, upon imaging through the sapphire, Figure 3.2.

**Figure 3.1** The liquid phase bonded interface, \( \eta = 8 \), as viewed through the sapphire. The optical interference fringes near the edge indicate the interface has delaminated following exposure to water.
Figure 3.2 An optical image of a LPB interface in a sample with a relative thickness $\eta = 20$ (viewed through the sapphire). The lighter regions are local debonds revealed using differential interference contrast. Debonds always encompass grain boundaries.

These observations provide an immediate, though qualitative, demonstration of the dominant role of S on the adhesion of the $\gamma$-Ni(Cr)/$\alpha$-Al$_2$O$_3$ interface.

3.3 Mechanical Measurements

3.3.1 Procedures

After bonding, the perimeter of each SSDB plate was reduced by 4 mm using a high speed diamond saw. The remainder was cut into beams 5 mm wide and 50 mm long. These were converted into double cantilever drilled compression (DCDC) specimens (Figure 1.3) for mode I testing by drilling a 2.25 mm diameter hole through the width, along the interface, at mid-span. The edges of each specimen were polished.

Interface mechanical measurements have emphasized the fatigue threshold. Each measurement was conducted in a laboratory air environment (~50% relative humidity and 20°C) using a servo-hydraulic testing frame with constant load amplitude, at a frequency
of 30 Hz, and a load ratio \( R = 0.1 \). Eccentricities in the load train were compensated for by using a high-pressure grease lubricated stainless steel ball and socket. The threshold determination was facilitated by the inverse dependence of the energy release rate range, \( \Delta G \), on crack length, \( a \), for the DCDC configuration, (1.6). Accordingly, by fixing the loading amplitude, an interface crack could be grown above the threshold and the behavior monitored by optical microscopy as the crack decelerated. For present purposes, the threshold, \( \Delta G_{th} \), is defined as the strain energy release rate range at which the average crack growth rate diminishes to \( \sim 0.5 \) nm per cycle.

3.3.2 Results

Fatigue crack growth measurements conducted on the SSDB interfaces have reaffirmed the strength and toughness of the \( \gamma \)-Ni(Cr)/Al\(_2\)O\(_3\) bond, Chapter 2. Under mode I cyclic loading, failure of the interface could rarely be induced. Instead, fatigue cracks traveled almost exclusively in the Al\(_2\)O\(_3\) adjacent to the interface. This behavior is exemplified by an optical micrograph, taken in cross-section, revealing a fatigue crack traveling over 10 mm within the Al\(_2\)O\(_3\), Figure 3.3. Note that, when the crack is short \((a < 8 \text{mm})\) it is serrated, but becomes planar as it elongates. These observations made in mode I differs from those reported previously for mixed mode loading, Section 2.5.2. In the present case, the absence of mode II allows cracks to deflect away from the interface and extend in the lower toughness Al\(_2\)O\(_3\). In mixed mode situations, with clockwise mode II, deflection of the crack into the Al\(_2\)O\(_3\) from the interface is prohibited, causing it to blunt and eventually extend at the interface, by a ductile mechanism, with exceptional toughness \((>300 \text{ Jm}^{-2})\).

In some SSDB specimens, the crack was attracted to the interface. When this occurred, it typically remained at the interface for distances of order the grain size \((\sim 200 \ \mu\text{m})\). Thereafter, it re-entered the Al\(_2\)O\(_3\). A pair of SEM micrographs illustrates this behavior, Figure 3.4. The serrated sapphire visible in both figures indicates the local crack growth
direction. On the Al₂O₃ side of the interface, Figure 3.4a, MgAl₂O₄ asperities are visible, consistent with earlier studies. The asperities are mirrored by pullouts on the Ni(Cr) side of the interface (Figure 3.4b).

**Figure 3.3** An optical micrograph, taken in cross-section, of a fatigue crack traveling exclusively in the Al₂O₃.

**Figure 3.4** A pair of SEM images showing interface failure in the SSDB material (between 70 and 90% of the exposed surface is comprised of Al₂O₃): a) Serrated cleavage in the sapphire surrounding a region where the interface failed. The asperities on the sapphire surface are MgAl₂O₄ precipitates and b) A region showing pullouts on the exposed Ni(Cr) surface. AES indicated a S peak on the surface of the Ni(Cr) at locations where the interface failed.
The threshold measurements indicate that, for long cracks \((a > 8 \text{ mm})\) the threshold is approximately equal to the sapphire toughness (20 Jm\(^{-2}\)), Figure 3.5. For small cracks \((a < 8 \text{ mm})\) the threshold is higher. The measurements in this region can be compared with those in the planar regions by adjusting for the crack deflection, using the measured serration angle \((\theta = 50^\circ)\). These are the triangular symbols on the figure. Adjustment was made using the approximate relation \(\Delta G_{\text{tip}} = \Delta G_{\text{nom}} \cos(\theta/2)^4\) [14] which is valid when \(K_{\text{max}} \gg K_{\text{min}}\).

![Diagram](image.png)

**Figure 3.5** Fatigue threshold data for the SSDB interface. The crack extends exclusively in the sapphire, taking a serrated path. The measurements, after adjusting for serrated growth by using a deflection factor of \(\cos^4(\theta/2)\), show that the threshold energy release rate is equal to the toughness of sapphire.

An estimate of the toughness of the LPB interfaces can be made upon realizing that the residual stresses are sufficient to cause delamination. Residual stresses induce steady-state energy release rates, \(J_{ss}\), at edge delaminations. These \(J_{ss}\) are governed by the relative thickness \(\eta\) of the \(\text{Al}_2\text{O}_3\) and Ni(Cr) layers, the thermal expansion misfit and the yield
strength of the alloy. The results, derived in Chapter 4, are summarized in Figure 3.6. With the assumption that an edge delamination large enough to be in steady-state pre-exists at the interface upon bonding (about equal to the γ-Ni(Cr) layer thickness) the occurrence of edge delamination upon cooling for intermediate η but not for large η indicates that Figure 3.6 may be used to obtain bounds on the interface toughness\(^3\). Specifically, delamination at η = 8 (Figure 3.1) implies that, \(G_{int} < 7.5 \text{ Jm}^{-2}\); whereas, the absence of such delamination for η = 20 (Figure 3.2) implies that, \(G_{int} > 2 \text{ Jm}^{-2}\). These bounds encompass a range found for other metal/oxide interfaces embrittled by segregation, including measurements for \(\alpha\)-Al\(_2\)O\(_3\) TGO films on γ-Ni.

![Figure 3.6](image)

**Figure 3.6** Steady-State energy release rate for γ-Ni(Cr)/α-Al\(_2\)O\(_3\) sandwich specimens with edge delamination, as a function of the relative thickness, \(\eta\), of the layers. Specimen A delaminates, the associated \(J_{ss}\) represents an upper bond. Specimen B remains intact, the associated \(J_{ss}\) is a lower bound.

### 3.4 Characterization

Interfaces exposed by decohesion were analyzed using a number of characterization meth-

\(3.\) Note that the associated loading phase angle is \(\sim 40^\circ\).
ods including: Auger Emission Spectroscopy (AES), Energy Dispersive Spectroscopy (EDS), and Secondary Ion Mass Spectroscopy (SIMS).

Inspection of the Ni(Cr) surface of LPB specimens could be made by removing the top sapphire layer, Figure 3.7. The pull-outs are the result of the MgAl₂O₄ interphase. Examination by AES, Figure 3.8a, revealed that the average sulfur concentration on the Ni(Cr) surface was ~3 at.%. Some locations rich in Cr had slightly higher S levels, Figure 3.8b. Sputtering by Ar ions for approximately ten minutes completely removed the S containing layer, Figure 3.8c, revealing that it is an interface segregant. SIMS measurements also indicate that the S concentration is substantially greater than that prior to bonding, especially near the grain boundaries in the alloy, Figure 3.9. At about 2 µm beneath the surface, the concentration of S reverts back to that found before bonding, consistent with the AES: while near the grain boundaries, the concentration remains approximately two orders of magnitude higher than its original level.

SEM images, Figure 3.10, in combination with EDS has revealed four different phases in the exposed alloy surface, Figure 3.11. The predominant phase consists of a γ-Ni(Cr) solid solution, Figure 3.11a. The three other phases present contain Ti-O, Al-Mg-O, Cr-O-C-S, Figure 3.11 b, c and d respectively. The Mg-Al-O phase appears with an area coverage comparable to that for the MgAl₂O₄ precipitates found on the exposed surface of the alumina. Only the phase (Cr-C-O-S) has a detectable sulfur peak. These observations, taken together with the AES and SIMS results, indicate that this phase comprises a thin, plate-like, interfacial layer. This S containing phase is regarded as the major cause of embrittlement.
Figure 3.7 The exposed γ-Ni(Cr) surface of the LPB material following delamination. An SEM image showing a large area fraction of pull-outs. These are mirrored as asperities attached to the sapphire.

Figure 3.8 Elemental analysis of the Ni(Cr) surface after interface failure: a) a ~80x60 μm scan showing average C, Cr, O, Ni and S peaks, b) a Cr-rich region with a more pronounced S peak, and c) a montage plot showing the near surface distribution of S revealed upon Ar ion sputtering. Here Cr was chosen as a baseline element. Note that as Cr attains a plateau level, the S diminishes below detectable levels.
Figure 3.9 Sulfur depth-profiles conducted on the surface of the alloy of LPB material exposed by delamination (SIMS). Two different locations are shown: within the grains and the other encompassing grain boundaries/triple points. The comparison suggests that S is concentrated in the grain boundaries. The count statistics are relative since a calibration was not available.

Figure 3.10 SEM backscatter image of the γ-Ni(Cr) surface of LPB material exposed by delamination. AES conducted on this sample indicated S was present with a surface concentration of ~3 at.%. 
Figure 3.11 Four different phases present on the alloy surface: a) a Ni(Cr) solid solution phase, b) Ti-O rich phase, c) Al-Mg-O rich phase, and d) C-Cr-O-S phase. The in-plane cracking is believed to be a result of large tensile stresses that develop in the Ni(Cr) as a result of bonding to the Al$_2$O$_3$.

3.5 Discussion

The fatigue measurements on SSDB specimens affirm the high intrinsic toughness of the Ni(Cr)/Al$_2$O$_3$ interface. Because of this toughness, fatigue cracks divert into the sapphire, instead of remaining at the interface. Occasionally, the interface fails in small areas. When this happens, sulfur is found on the exposed alloy. This finding implies that the interface is locally embrittled where S is able to segregate.

Upon using LPB bonding conditions that release a S-rich liquid from a CrS phase present in the alloy, a dramatic embrittlement has been demonstrated. In such material, the
residual stresses associated with the thermal expansion misfit are sufficient to induce edge delamination along the interfaces. An analysis based on delamination mechanics bounds the toughness between 2 and 7 Jm$^{-2}$ at a mixity angle $\sim 40^\circ$. In this condition, a relatively high S concentration exists near the interface within a layer about 2 $\mu$m in thickness. Much of this S appears to be within a plate-like interphase containing Cr-C-O-S, which appears to be the cause of the embrittlement.

In both SSDB and LPB materials MgAl$_2$O$_4$ precipitates grow epitaxially on the sapphire. That LPB interfaces have this interphase, yet still fail by stress corrosion, affirms a previous assertion that the O and Al gettering accompanying MgAl$_2$O$_4$ formation can not be responsible for the high intrinsic toughness. Moreover, mechanical keying associated with their presence is insufficient to enhance the toughness of LPB interfaces, even under the mixed mode loading conditions associated with edge delamination.

The occurrence of internal, debonded patches in the LPB plates having the greatest relative thickness ($\eta = 20$) requires explanation. On a planar interface subject to misfit strains, internal separations do not experience an energy release rate. Either morphological imperfections on the interface or an internal gas pressure are required. In this case, gas pressures related to either SO$_2$ or CO formation seem likely, with the oxygen produced by dissolution and reduction of Al$_2$O$_3$ near the interface during MgAl$_2$O$_4$ formation.

### 3.6 Conclusions

An investigation of the fracture and fatigue of $\gamma$-Ni(Cr) /Al$_2$O$_3$ interfaces has affirmed a major effect of S segregation. Solid-state diffusion bonded interfaces are sufficiently tough and fatigue resistant that cracks divert into the Al$_2$O$_3$ rather than remain at the interface. The associated system toughness is that for Al$_2$O$_3$. At sites where the interface fails in preference to sapphire, trace quantities of S are found on the exposed surface of the
Ni(Cr). The implication is that local embrittlement occurs where S segregates. Conversely, liquid phase bonding that releases S to the interface results in low adhesion (2-7 Jm\(^{-2}\)), such that delamination is induced solely by the residual stresses in the system.

These findings suggest that tough Ni(Cr)/Al\(_2\)O\(_3\) interfaces can only be achieved when the interface is free of segregants present as a result of diffusion of impurities during bonding, and/or surface contamination of the starting materials prior to bonding. For the solid-state bonded interfaces, Cr was found to getter C by forming carbides. This effectively eliminated the stress corrosion mechanism observed in the pure Ni/Al\(_2\)O\(_3\) interfaces. Moreover, the bonding temperature was below the Ni-Cr-S eutectic, such that S within the Ni(Cr) remained as Cr sulfides. Liquid-phase bonding, on the other hand, utilized temperatures above the eutectic. As a result, a sulfur-rich liquid originating at grain boundaries spread across the interface. This produced a plate-like S-containing phase that embrittled the interface.
Chapter 4

Interface Fracture in Layered Materials SubJECTED to Thermal Loading

4.1 Introduction

When layers of dissimilar materials are bonded, differences in the thermal expansion coefficients, combined with a change in temperature $|\Delta T|$ relative to the stress-free state, result in thermal stresses [84][85]. These stresses, along with the singular nature of free edges [86]-[89] or manufacturing-related edge flaws, can result in the development of interface cracks.

When these cracks form, the driving force for crack growth initiation depends on the magnitude of stress in each layer. For small $|\Delta T|$ all the layers in the composite are nominally elastic. Under these circumstances stress is quantified by elastic mismatch and $|\Delta T|$, and the driving force for interface fracture is the energy release rate $G$ [90]-[92]. As $|\Delta T|$ increases, a point is reached at which nominal thermal stresses in the layers exceed the elastic limits of the materials. At this point an elasto-plastic analysis is needed. Interface fracture then has to be predicated upon a different measure of crack driving force, such as the $J$-integral [93].

The analytical and numerical study presented below is intended to elucidate the fracture mechanics of edge-cracks in a three-layered material system (tri-layer) having sharp interfaces and subjected to a monotonic temperature change. This type of loading and geometry is typical of diffusion-bonded solids (Chapter 2) or of thermal-barrier/wear-resistant coatings. For both of these examples the tri-layer is stress free at an elevated processing temperature, but, develops thermal stresses upon cooling.
The purpose of the following analysis is to provide a theoretical basis for estimating the bounds for the crack driving force in layered specimens that are bonded and then cooled to room temperature.

Specific objectives of the present work include:

i) The derivation of analytical expressions for the plane-stress-steady-state elastic energy release rate for an interface crack in a general tri-layer having sharp interfaces (Figure 4.1) and in particular to obtain explicit results for two important geometries; Case A and Case B, Figure 4.2a and Figure 4.2b. These cases are typical of the diffusion bonded tri-layer and thermal barrier/wear resistant coatings respectively. A presentation of results for other stress states including generalized plane strain and plane strain will be given at the end.

![Layered structure diagram](image)

**Figure 4.1** The tri-layer geometry. An interface crack, length $a$, exists between layers 2 and 3. CTE mismatch, $\Delta \alpha$, and a uniform temperature change, $|\Delta T|$, are the driving force for interface fracture.

ii) The creation of a model to estimate the effect of large-scale contact in the wake of an interface crack on the crack driving force.

iii) The development of analytical expressions for the critical transition temperatures corresponding to the onset of nominal yielding and the development of full plasticity both far ahead and far behind the interface crack tip.
iv) The identification of global transition temperatures which bound the three regimes of interface fracture (elastic, partially plastic, and fully plastic) by comparing critical transition temperatures in the tri-layer and bi-layer ahead of and behind the crack tip respectively.

v) The determination of the elasto-plastic and fully plastic driving force, $J$, of a stationary interface crack using finite element analysis. Compare these numerical results with the analytical solutions.

![Diagram](image)

Figure 4.2 Configurations considered for analysis: Case A, a diffusion-bonded tri-layer, and Case B, a thermal-barrier/wear-resistant coating.

4.2 Problem Formulation and Material Model

For the present work, only metal-ceramic layered systems are studied. This restriction has been imposed to limit the scope. However, the methodology presented is equally applicable to metal-metal and ceramic-ceramic systems. The materials are modeled as isotropic,
elastic, or elasto-perfectly plastic and their plastic response is described by the rate-independent $J_2$-flow theory. All inelastic deformation is attributed to conventional metal plasticity: creep is not considered. Except for the crack, the materials are assumed to be perfectly bonded, and the crack is assumed to be stationary. Because the problem is formulated as quasi-static, inertia and body forces are ignored. The instantaneous temperature is considered uniform throughout. Transient thermal response, e.g. thermal shock, is not accounted for.

The thickness of each layer ($H, h, \text{and } t$ from Figure 4.1) is assumed to be significantly larger than the dimensions of microstructural features such as grain size. The crack length, $a$, and the ligament ahead of the crack tip, $w$, must satisfy $a, w > (H + t + h)$, in order to neglect edge effects. Under these circumstances a steady state solution is valid and any dependence of the energy release rate on the crack length is eliminated.

A state of plane stress is considered. The actual three-dimensional thermal stresses will affect the plane stress solutions near the interface over a distance comparable to the layer thickness, as has been shown from three-dimensional elastic calculations [94]. Nevertheless, a plane stress model captures the essential features of the elasto-plastic deformation. Under elastic conditions, plane stress results can be carried over for the plane strain state by replacing the elastic modulus, $E$, and the coefficient of thermal expansion, $\alpha$, of each layer with $E/(1-v^2)$ and $\alpha(1+v)$ respectively [84].

Small strain kinematics are assumed, with the total strain being decomposed into the elastic, plastic, and thermal parts, $\varepsilon_{ij} = \varepsilon_{ij}^{\text{elastic}} + \varepsilon_{ij}^{\text{plastic}} + \varepsilon_{ij}^{\text{thermal}}$, respectively.

The properties and field quantities for the metal layer are denoted by the subscript 2. All materials are assumed to be stress free at the initial temperature $|\Delta T| = 0$. It is sufficiently general to model layers 1 and 3 as isotropic and linear elastic with Young's moduli
E₁ and E₃ respectively. This assumption is consistent with the diffusion bonded Al₂O₃/ Ni(Cr)/Al₂O₃ tri-layer (Chapter 2). It is also consistent with a thermal barrier coating being deposited on a high yield strength substrate, i.e. a Waspaloy substrate with a deposited NiCrAlY bond coat and protective ceramic coating. For the purposes of obtaining closed-form solutions, the properties of all layers are assumed to be independent of temperature.

In sections 4.3-4.5 elastic stress analysis is used along with the J-integral to derive an expression for the elastic interface energy release rate. This result is then tailored for cases A and B. In section 4.5 an interface contact model is presented. The model predicts the shielding effect associated with large scale elastic contact in the wake of an interface crack.

Section 4.6 contains analytical plasticity derivations, including those for characteristic temperature changes required for layer 2 to begin yielding and for it to fully plastify. Expressions for the limiting elastic energy release rate, related to the former temperature change, are also given. Since the analysis for a three layered material requires an understanding of the happenings in the bi-layer comprising the crack wake and the tri-layer ahead of the crack tip, a discussion of the plastic yielding sequence is presented. The results establish important bounds on the elasto-plastic crack driving force, J, for tri-layers.

Sections 4.9 through 4.10 present and discuss finite element results for the Al₂O₃/ Ni(Cr)/Al₂O₃ tri-layer.

4.3 Elastic Analytical Results

4.3.1 Elastic Interface Energy Release Rate G
The elastic interface energy release rate, $G$, for a general three-layered material will be presented first. The method for obtaining the solution is analogous to evaluating the $J$-integral (4.1) along the contour $\Gamma$, depicted in Figure 4.3 [90]. Here, $\Gamma$ could be chosen as a far-field path since $J$ is path-independent for the elastic case. In making this choice $J = G$ can be evaluated without specific knowledge of the singular field around the crack tip. The near-tip contour $\Gamma^*$, also shown in the figure, will be discussed in conjunction with finite element results presented at the end.

![Diagram of three layers with contours](image)

**Figure 4.3** The far-field and near-tip contours $\Gamma$ and $\Gamma^*$, respectively.

\[
J = \int_{\Gamma} \left( \sigma_{ij} d\varepsilon_{ij} \right) dz - \sigma_{ij} n_j \frac{\partial u_i}{\partial y} d\Gamma \right) + \int_{A} \sigma_{ij} \frac{\partial \varepsilon_{ij}^T}{\partial y} dA \tag{4.1}
\]

In (4.1) $\varepsilon_{ij}^T$, $\sigma_{ij}$, $n_j$, and $u_i$ are the thermal strain tensor, the stress tensor, the vector normal to the contour $\Gamma$, and the displacement vector, respectively. $A$ is the area enclosed by $\Gamma$.

The coordinate system for stress analysis is located such that the $y$-direction is parallel to and on the layer 1/layer 2 interface (henceforth referred to as the 1-2 interface). The $z$-direction is normal to the 1-2 interface at a position such that $y = 0$ corresponds to the location of the crack tip as indicated in Figure 4.3.
4.3.2 Stress Analysis and Elastic Strain Energy

Far ahead of the crack the three layered system behaves elastically for small $\Delta T$. For plane stress the stress-strain relationship for each layer is given by:

$$
\sigma_{y y_1, y_2, y_3, l a y e r} (z) = E_{1, 2, 3}(\varepsilon_{o (l a y e r)} + \kappa_{(l a y e r)} z - \alpha_{1, 2, 3} \Delta T)
$$

(4.2)

where $E$, $\alpha$, $\Delta T$, $\varepsilon_o$, and $\kappa$ are the Young’s modulus, the coefficient of thermal expansion, the temperature change relative to a stress free state, the strain at the 1-2 interface and the curvature, respectively. The subscripts 1, 2, or 3 refer to the layer number.

By substituting (4.2) into the force and moment equilibrium equations, (4.3) and (4.4), equations for the strain, $\varepsilon_o$ and the curvature, $\kappa$, far ahead of the crack tip can be obtained, (4.5).

$$
\int_{-H}^{0} \sigma_{y y_1} (z) dz + \int_{0}^{t} \sigma_{y y_2} (z) dz + \int_{t}^{h+t} \sigma_{y y_3} (z) dz = 0
$$
$$
\int_{-H}^{0} \sigma_{y y_1} (z) dz + \int_{0}^{t} \sigma_{y y_2} (z) dz + \int_{t}^{h+t} \sigma_{y y_3} (z) dz = 0
$$

(4.3)

(4.4)

$$
\varepsilon_{o (l a y e r)} = \alpha_2 \Delta T \left( \frac{4 \lambda_3 \lambda_4 - 3 \lambda_2 \lambda_5}{4 \lambda_1 \lambda_3 - 3 \lambda_2^2} \right), \quad \kappa_{(l a y e r)} = \frac{6 \alpha_2 \Delta T}{t} \left( \frac{\lambda_1 \lambda_5 - \lambda_2 \lambda_4}{4 \lambda_1 \lambda_3 - 3 \lambda_2^2} \right)
$$

(4.5)

The dimensionless variables used in these equations are defined as:

$$
\lambda_1 = X \zeta + Z \eta + 1, \quad \lambda_2 = -X \zeta^2 + Z[(\eta + 1)^2 - 1] + 1
$$
$$
\lambda_3 = X \zeta^3 + Z[(\eta + 1)^3 - 1] + 1, \quad \lambda_4 = X Y \zeta + Z W \eta + 1
$$
$$
\lambda_5 = -X Y \zeta^2 + Z W[(\eta + 1)^2 - 1] + 1
$$

(4.6)

where $\eta = \frac{h}{t}$, $\zeta = \frac{H}{t}$, $\theta = \frac{\zeta + 1}{\eta}$, $X = \frac{E_1}{E_2}$, $Z = \frac{E_3}{E_2}$, $Y = \frac{\alpha_1}{\alpha_2}$, $W = \frac{\alpha_3}{\alpha_2}$. 

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By substituting (4.5) into (4.2) the stress distribution in each layer can be obtained. These distributions, along with (4.7), give the total elastic strain energy stored in the tri-layer far ahead of the crack tip. Here, the stress distribution is assumed to be independent of the \( x \) and \( y \) directions. (4.7) is given as the elastic strain energy normalized by an in-plane area \((ab)\); equal to the crack area, \( b \) (specimen width) \( \times a \) (crack length), for reasons that will become obvious later.

\[
\overline{U}_{\text{(tri-layer)}} = \frac{U_{\text{(tri-layer)}}}{ab} = \frac{1}{2} \sum_{i=1}^{3} \int_{z_{i-1}}^{z_{i}} \frac{(\sigma_{yy,\text{layer}_{i}}(z))^2}{E_i} \, dz
\]  

(4.7)

When an interface crack is located between layers 2 and 3, the tri-layer (for \( y < 0 \)) behaves as a perfectly bonded bi-layer \((z < t)\) and a homogeneous layer (layer 3) \((z > t)\). Since both parts of the tri-layer experience the same \( \Delta T \), the bi-layer has its own strain, \( \varepsilon_o \), and curvature, \( \kappa \). In the absence of contact for \( y < 0 \), \( \varepsilon_o \) and \( \kappa \) for the bi-layer can be obtained from (4.5) by setting \( \eta = h/t = 0 \). The results are:

\[
\frac{\varepsilon_{o\text{(bi-layer)}} - \alpha_2 \Delta T}{\Delta T(\alpha_2 - \alpha_1)} = -\frac{X\zeta(X\zeta^3 + 3\zeta + 4)}{\xi} 
\]  

(4.8)

\[
\frac{\kappa_{\text{(bi-layer)}}}{\Delta T(\alpha_2 - \alpha_1)} = \frac{6X\zeta(\zeta + 1)}{\xi} 
\]  

(4.9)

where \( \xi = X\zeta(X\zeta^3 + 4\zeta^2 + 6\zeta + 4) + 1 \). Layer 3 is stress free behind the crack tip so that \( \varepsilon_o = \alpha_3 \Delta T \), \( \kappa = 0 \). When (4.8) and (4.9) are substituted into (4.2) the equilibrium stress state in the bi-layer is obtained. Further substitution into (4.7) gives the elastic strain energy, \( U_{\text{(bi-layer)}} \), stored in the wake of the interface crack.

In the absence of external work, \( W \), the elastic interface energy release rate is a result of two processes; i) the release of all elastic strain energy in layer 3 and ii) a redistribution
of stress resulting from the transition from a tri-layer for \( y > 0 \) to a bi-layer for \( y < 0 \). The elastic interface energy release rate is given by:

\[
J = G = \frac{\partial}{\partial A}(W - U) = \bar{U}_{\text{tri-layer}} - \bar{U}_{\text{bi-layer}}.
\] (4.10)

### 4.4 The Energy Release Rate \( G \) for Particular Cases

If additional assumptions regarding the material make-up of layers 1-3 are made then (4.5)-(4.9) can be simplified to yield compact expressions for \( G \). Cases A and B are based on two sets of assumptions. For Case A, layers 1 and 3 are elastic and have the same material properties while layer 2 is elastic-perfectly plastic. The diffusion bonded tri-layers in Chapter 2 and Chapter 3 are examples of this configuration. For Case B layers 1 and 3 are elastic and layers 1 and 2 have the same elastic properties; yet layer 2 is elastic-perfectly plastic (typical of a thermal barrier coating with low yield strength bond coat). We will first examine the purely elastic response for each case.

For Case A, \( Z = X \) and \( W = Y \) thus \( \lambda_1, \lambda_2, \) and \( \lambda_3 \) simplify from their previous form given in (4.6) to, \( \lambda_1^A = X(\eta + \zeta) + 1 \), \( \lambda_2^A = X(\eta^2 - \zeta^2 + 2\eta) + 1 \) and \( \lambda_3^A = X((\eta + 1)^3 + \zeta^3 - 1) + 1 \). Making these substitutions along with those for \( \lambda_4 \) and \( \lambda_5 \) into (4.5) we obtain expressions for \( \varepsilon_{\alpha}, \) and \( \kappa: \)

\[
\frac{\varepsilon_{\alpha}^{(\text{tri-layer})} - \alpha_3 \Delta T}{\Delta T(\alpha_1 - \alpha_2)} = \frac{2X^2\zeta\eta[2(\eta + \zeta)^2 + 6(\eta + \zeta + 1) - \zeta\eta] + X^2(\eta^4 + \zeta^4)}{4\lambda_1^A\lambda_2^A - 3(\lambda_2^A)^2} + \frac{3X(\zeta^2 - \eta^2) + 2X(2\zeta - \eta)}{4\lambda_1^A\lambda_3^A - 3(\lambda_2^A)^2} = C_1
\]

\[
\frac{\kappa^{(\text{tri-layer})}}{\Delta T(\alpha_1 - \alpha_2)} = \frac{6X(\eta^2 + \eta - (\zeta^2 + \zeta))}{4\lambda_1^A\lambda_3^A - 3(\lambda_2^A)^2} = C_2
\]

These equations have been non-dimensionalized to yield functions of material properties and loading (left hand side), and moduli and geometric ratios (right hand side). \( \eta = h/t, \zeta = \)
$Hl_t$, and $X$ is the elastic modulus ratio $E_1/E_2$. The superscript $A$ is used to indicate that the solution is for Case A.

Substituting (4.11) into (4.2) and (4.7) provides the normalized elastic strain energy, $\bar{U}_{(tri-layer)}^A$, ahead of the crack:

$$\frac{\bar{u}_{1(tri-layer)}^A}{E_2t(\Delta T(\alpha_2 - \alpha_1))^2} = \frac{X\xi}{6}[3(C_1 - 1)^2 - 3C_2\zeta(C_1 - 1) + (C_2\zeta)^2]$$

$$\frac{\bar{u}_{2(tri-layer)}^A}{E_2t(\Delta T(\alpha_2 - \alpha_1))^2} = \frac{1}{6}[3C_1^2 + 3C_1C_2 + C_2^2]$$

$$\frac{\bar{u}_{3(tri-layer)}^A}{E_2t(\Delta T(\alpha_2 - \alpha_1))^2} = \frac{X\eta}{6}[3(C_1 - 1 + C_2)^2 + 3C_2\eta(C_1 - 1 + C_2) + (C_2\eta)^3]$$

$$\bar{U}_{(tri-layer)}^A = \sum_{i=1}^{3}\bar{u}_{i(tri-layer)}^A$$ \hspace{1cm} (4.12)

Setting $\eta = h/t = 0$ in (4.11) and (4.12) gives the normalized elastic strain energy, $\bar{U}_{(bi-layer)}^A$, in the crack wake:

$$\frac{\bar{U}_{(bi-layer)}^A}{E_2t(\Delta T(\alpha_2 - \alpha_1))^2} = \frac{X\zeta(X\zeta^3 + 1)}{2\xi^2}$$ \hspace{1cm} (4.13)

Note that this is equal to the interface energy release rate for the two layered problem [90][93]. They are the same because following interface fracture in a bi-layer the two layers become stress free.

When $h = H$ there is both material and geometric symmetry. As a result $\zeta = \eta$ and the equation for the interface energy release rate reduces to:

$$\frac{G^A}{E_2t(\Delta T(\alpha_2 - \alpha_1))^2} = \frac{X\eta}{2(2X\eta + 1)}\frac{(X\eta^2(7\eta + 12) + 6X\eta + 1)}{\xi'}$$ \hspace{1cm} (4.14)

where $\xi' = \xi(\zeta \to \eta)$.
For Case B, \( X = 1 \) and \( Y = 1 \). Thus, when layers 1 and 2 have the same elastic properties, the tri-layer problem converges to the bi-layer problem (for \( G \); differences will be apparent for \( J \)). By making the substitutions \( X = (1/Z) \), \( \zeta \to \theta = (\zeta + 1)/\eta \), \( E_2 \to E_3 \), \( E_1 \to E_2 \), \( \alpha_2 \to \alpha_3 \), \( \alpha_1 \to \alpha_2 \), and \( t \to h \) into (4.8), (4.9), and (4.13) we get the complete solution for Case B:

\[
\frac{\varepsilon_{\theta(tri-layer)} - \alpha_1 \Delta T}{\Delta T(\alpha_1 - \alpha_2)} = \frac{-\theta[(\theta^3/Z) + 3\theta + 4]}{\theta^2[(\theta^3/Z) + 4\theta + 6] + 4\theta + Z}.
\]

\[
\frac{\kappa_{\theta(tri-layer)}h}{\Delta T(\alpha_1 - \alpha_2)} = \frac{\theta^2[(\theta^3/Z) + 4\theta + 6] + 4\theta + Z}{6\theta(\theta + 1)}.
\]

(4.15)

The resulting equation for the interface energy release rate is then:

\[
\frac{G^B}{E_3h(\Delta T(\alpha_1 - \alpha_2))^2} = \frac{1}{2(\theta^4/Z) + \theta(4\theta^2 + 6\theta + 4) + Z}.
\]

(4.16)

### 4.5 Interfacial Contact

Equations (4.10), (4.14) and (4.16) assume there is no contact in the wake of the crack. For the general three layered system there are four possible modes of deformation. These modes are shown in Figure 4.4. Figure 4.4a and Figure 4.4c represent the two possible scenarios for contact. In both instances the unconstrained curvature of the wake bi-layer is negative. This leads to the criterion \( \Delta T(\alpha_2 - \alpha_1) < 0 \) for contact.

For Case B layers 1 and 2 are elastically matched (\( E_1 = E_2 \), and \( \alpha_1 = \alpha_2 \)). As a result the curvature in the wake of the crack is zero. Furthermore the substrate, layer 1, for thermal-barrier/wear-resistant coatings would be substantially thicker than the other dimensions thus there would be negligible curvature ahead of the crack tip. Considering both of these conditions Case B would never experience large-scale contact in the crack wake. However, this is not true for Case A.
When contact occurs, the bi-layer is subjected to a superimposed mechanical stress distribution and layer 3 is no longer stress free. This results in more elastic strain energy being preserved in the wake causing (4.14) to overestimate $G$. If we assume the contact is frictionless and that the stress distributions in layers 1-3 under these circumstances vary only in the $y$ and $z$ directions, then an estimate of the "shielding effect" can be obtained. By virtual work, the difference between the actual energy release rate, $G_{(contact)}$, and the energy release rate without contact, $G_{(no\ contact)}$, is given by: 4

![Diagram of modes of deformation during interface fracture in the three layered system.](image)

**Figure 4.4** Modes of deformation during interface fracture in the three layered system. a) and c) illustrate the conditions when large-scale contact must be accounted for. For b) and d) there is no contact.

---

4. This assumption is appropriate as long as $a > 3(H + t)$ and the specimen width $b < 3(H + t)$.
\[ \Delta G = G_{(no\,-\,contact)} - G_{(contact)} = \sum_{i = 1}^{3} \frac{E_i}{a} \int_{-a}^{a} \int_{0}^{Z_i} \Delta \varepsilon_{yy}^{(mech)}(y, z) \, dz \, dy \]  

(4.17)

where \( \Delta \varepsilon_{yy}^{(mech)} \) is the change in strain distribution for layer \( i \) due to the superimposed mechanical loads associated with contact. Here the relation \( W \), the work of contact, equals \( 2U \) has been used.

In order to estimate (4.17) a simple contact model has been created, Figure 4.5. The model is based on the assumption that frictionless contact takes place at the end of the crack at \( y = -a \) and that the contact force per unit width, \( P \), results in curvature compatibility between layers 1-3 at \( y = 0 \). Since equilibrium requires the contact force on the bi-layer and layer 3 to be equal and opposite the net effect of \( P \) is to decrease the negative curvature of the bi-layer while creating the same curvature in layer 3:

\[ \kappa_{(bi-layer)} + \frac{Pa}{EI} = \frac{-12Pa}{E_3h^3} \]  

(4.18)

where \( EI \) is the mechanical flexural stiffness of the bi-layer, (4.19). It relates curvature to the mechanical moment per unit width.

\[ EI = \frac{E_3t^3}{12(X\xi + 1)\xi} \]  

(4.19)

When (4.9) and (4.19) are substituted into (4.18) an expression for the contact force is obtained:

\[ P = \frac{\Delta T(\alpha_1 - \alpha_2)E_3t^2}{2a} \frac{X\eta^3\xi(\xi + 1)}{[Z\eta^3(X\xi + 1) + \xi]} \]  

(4.20)
Figure 4.5 The elastic contact model based on single point contact in the wake of an interface crack.

The mechanical bending moment $M$, associated with $P$, is a linear function of $y$ varying from 0 at $y = -a$ to $Pa$ ($-Pa$ for layer 3) at $y = 0$. At any given position along the crack length $M(y) = P(a + y)$. By substituting $M(y)$ into (A.9) and (A.10) the raid-plane strain and curvature resulting from mechanical loading can be determined. By adding these two strain components to those given by (4.8) and (4.9) an expression for the total strain in both layer 1 and 2 can be determined:

$$\varepsilon_{i, 1, 2} = \varepsilon_{\text{mech}} + \varepsilon_{\text{thermal}} + \kappa_{\text{mech}}z + \kappa_{\text{thermal}}z - \alpha_i \Delta T$$  \hspace{1cm} (4.21)

Note that the sign convention for the strain components is completely specified by (A.9), (A.10), (4.8) and (4.9).

Substituting (4.21) into (4.17) yields an expression for the shielding effect,
\[
\Delta G = \sum_{i=1}^{2} \int_{-a_{z_i}}^{0} \int_{-a_{z_i}}^{0} \varepsilon_{1} dz_{1} dy + \frac{E_{3}}{\varepsilon_{3}} \int_{-a_{z_i}}^{0} \left( \frac{12M(y)z}{E_{3}h^{3}} \right)^{2} dz_{1} dy - 2U_{(bi-layer)}^{A} \tag{4.22}
\]

Figure 4.6 contains a plot of (4.22) normalized by \( G^{A} \) for \( H = h \), (4.14). The contours show the shielding effect as a percentage of the no-contact energy release rate. As defined this percentage represents the reduction in energy release rate resulting from contact. It is interesting to note that this ratio does not depend on \( \Delta T \), \( \alpha \)'s, or any individual thickness parameters. \( \Delta G / G^{A} \) for the \( \text{Al}_{2}\text{O}_{3}/\text{Ni(Cr)}/\text{Al}_{2}\text{O}_{3} \) tri-layer has been identified in the figure.

For the range of \( E_{1}/E_{2} \) and \( \eta \) shown in this figure \( \Delta G / G^{A} \) can be approximated by:

\[
\frac{\Delta G}{G^{A}} = \frac{2X^{2}\eta^{4}(\eta + 1)^{2}(2X\eta + 1)}{(7X\eta^{3} + 12X\eta^{2} + 6X\eta + 1) + (2X^{2}\eta^{4} + 5X\eta^{3} + 6X\eta^{2} + 4X\eta + 1)}.
\tag{4.23}
\]

---

**Figure 4.6** The shielding effect of large-scale contact between the wake bi-layer and layer 3 for Case A with \( H = h \).
4.6 Analytical Results for Plasticity

4.6.1 Characteristic Temperature Changes: the onset of yielding

The preceding derivations assume nominally elastic conditions. Since most materials have a well-defined elastic limit, this assumption breaks down once a critical temperature change is reached. For metals with yield strength, \( \sigma_0 \), the limits of elasticity are reached when nominal yielding within any of the three layers begins for the first time (here far-field yielding is the criterion used for judging the limits of elasticity). Beyond this point fracture must be characterized by \( J \) rather than the elastic interface energy release rate, \( G \).

Determining the critical temperature change, referred to as \( |\Delta T_{\text{onset}}| \), requires that the absolute value of the maximum stress in each layer be compared with its yield strength, \( |\sigma_{3i}| \leftrightarrow |\sigma_{n}|, i=1-3 \). Since this will always occur at the end of the layer, i.e. at positions \( z_i \) (Figure 4.3), \( |\Delta T_{\text{onset}}| \) is equal to the minimum of all \( |\Delta T| \) required to yield either layer 1, 2, or 3 at the positions \( z_i \) in either the tri-layer far ahead of the crack tip or the bi-layer in the crack wake.

Using equations (4.2) and (4.5) the six temperature changes corresponding to
\[
|\sigma_{3i,13,1}(z_i)| = |\sigma_{n,13,1}|
\]
in the tri-layer can be obtained:

\[
\frac{E_2 |\Delta T_{\text{tri-layer}}^{13,1}|}{\sigma_{n3}} = \frac{|\psi_1|}{Z\alpha_2 (\eta+1) \psi_1 - W\psi_1} \quad (a)
\]

\[
\frac{E_2 |\Delta T_{\text{tri-layer}}^{13,1}|}{\sigma_{n3}} = \frac{|\psi_1|}{Z\alpha_2 \psi_1 - W\psi_1} \quad (b)
\]

\[
\frac{E_2 |\Delta T_{\text{tri-layer}}^{13,1}|}{\sigma_{n2}} = \frac{|\psi_1|}{\alpha_2 \psi_1 - \psi_1 - \psi_1} \quad (c)
\]

\[
\frac{E_2 |\Delta T_{\text{tri-layer}}^{13,1}|}{\sigma_{n2}} = \frac{|\psi_1|}{\alpha_2 (\psi_2 - \psi_1)} \quad (d)
\]

\[
\frac{E_2 |\Delta T_{\text{tri-layer}}^{13,1}|}{\sigma_{n1}} = \frac{|\psi_1|}{X\alpha_2 (\psi_2 - Y\psi_1)} \quad (e)
\]
\[ \frac{E_2}{\sigma_{o2}} \left| \Delta T^{x_{i-1}-layer}_{1,2} \right| = \frac{\left| \psi_1 \right|}{X\alpha_2 \left| \psi_2 + \psi_3 - Y \psi_1 \right|} \] (f)

The new symbols used in are defined as \( \psi_1 = 4\lambda_1\lambda_3 - 3\lambda_2^2, \psi_2 = 4\lambda_3\lambda_4 - 3\lambda_2\lambda_5, \) and \( \psi_3 = 6(\lambda_2\lambda_4 - \lambda_1\lambda_5) ; \) where all \( \lambda \)'s have been defined in (4.6). The number in the subscript refers to the layer and the second term refers to the position \( z \) within the layer.

Equations (4.2), (4.8), and (4.9) can be used to obtain the corresponding four temperatures for the bi-layer in the wake of the interface crack. These temperatures are given by:

\[ \frac{E_3}{\sigma_{o2}} \left| \Delta T^{h_i-layer}_{2,0} (\alpha_1 - \alpha_2) \right| = \frac{\xi}{X\zeta(X\zeta^3 - 3\zeta - 2)} \] (a)

\[ \frac{E_3}{\sigma_{o2}} \left| \Delta T^{h_i-layer}_{2,0} (\alpha_1 - \alpha_2) \right| = \frac{\xi}{X\zeta(X\zeta^3 + 3\zeta + 4)} \] (b)

\[ \frac{E_1}{\sigma_{o1}} \left| \Delta T^{h_i-layer}_{1,0} (\alpha_1 - \alpha_2) \right| = \frac{\xi}{3X\zeta^2 + 4X\zeta^3 + 1} \] (c)

\[ \frac{E_1}{\sigma_{o1}} \left| \Delta T^{h_i-layer}_{1,0} (\alpha_1 - \alpha_2) \right| = \frac{\xi}{3X\zeta^2 + 2X\zeta^3 - 1} \] (d)

The overall minimum, \( |\Delta T_{onset}| \), is given by:

\[ |\Delta T_{onset}| = \min \left\{ |\Delta T^{h_i-layer}_{i, z, or z_{-1}} |, |\Delta T^{h_i-layer}_{i, z, or z_{-1}} | \right\} \] (4.26)

(4.24) and (4.25) were derived for a general three layered material. If the equations are specialized for Cases A and B, the results simplify substantially.

For Case A with \( E_f = E_3 \) and layers 1 and 3 elastic, yielding always begin in layer 2 at either the 2-3 interface or the 1-2 interface. Making the appropriate substitutions, \( Z = X \) and \( W = Y \) into (4.6), the temperature changes at which yielding begins at these locations are given by:

\[ \frac{E_2}{\sigma_{o2}} \left| \Delta T^{eff-A}_{1/2} (\alpha_1 - \alpha_2) \right| = \frac{1}{C_1 + C_2} \] (4.27)
and

\[ \frac{E_2 \Delta T_{1/2}^{elli-A}(\alpha_1 - \alpha_2)}{\sigma_{o2}} = \frac{1}{C_1} \]  

(4.28)

respectively. \((C_1 \text{ and } C_2 \text{ were defined in (4.11) and } \sigma_{o2} \text{ is the yield strength of the second layer.})\)

When the thickness of layer 1 and 3 are the same, \(H = h\), (4.27) and (4.28) give the same value indicating that yielding occurs uniformly through the entire thickness of layer 2:

\[ \frac{E_2 \Delta T_{unif}^{elli-A}(\alpha_1 - \alpha_2)}{\sigma_{o2}} = \frac{1}{2X\eta} + 1 \]  

(4.29)

Nominal yielding in the bi-layer will always begin at the 1-2 interface and is given by (4.25b). This fact can be seen by comparing (4.25a) and (4.25b). Both share the same numerator, yet (4.25a) has a smaller denominator \((X \text{ and } \zeta \text{ are always positive})\).

For Case B, layer 1 and 2 are elastically matched. Under these circumstances yielding will always begin at the interface between layers 2 and 3 in the tri-layer ahead of the crack tip. The temperature at which this occurs can be found from the bi-layer solution (4.25c) by substituting \(E_1 \rightarrow E_2\), \(\alpha_1 \rightarrow \alpha_2\), \(\alpha_2 \rightarrow \alpha_3\), \(\sigma_{o1} \rightarrow \sigma_{o2}\), \(X = E_1/E_2 \rightarrow 1/Z \rightarrow E_2/E_3\) and \(\zeta \rightarrow \theta = (\zeta + 1)/\eta\):

\[ \frac{E_2 \Delta T_{1/3}^{elli-B}(\alpha_3 - \alpha_2)}{\sigma_{o2}} = \frac{\theta^2(\theta^2/Z + 4\theta + 6) + 4\theta + Z}{3\theta^2 + 4\theta^3 + Z} \]  

(4.30)

4.6.2 The Yielding Sequence: Cases A and B

Equations (4.27)-(4.30) define temperatures at which the local stress in layer 2 equals the yield strength. Since yielding will begin at the lowest of all these values, \(|\Delta T_{unif}|\), a comparison of the temperatures must be made. For Case B this comparison is trivial. In the
crack wake the bi-layer is elastically homogeneous and, therefore, it does not yield. Under these circumstances the critical temperature change must occur in the tri-layer ahead of the crack tip. It is given in (4.30), \( \Delta T_{\text{onset}} = |\Delta T^{\text{tri-}\ell}_{2/3}| \).

Case A has two important temperature changes which must be compared in order to establish \( |\Delta T_{\text{onset}}| \). They are the minimum temperature change required to start nominal yielding in the tri-layer and in the bi-layer. Comparing (4.25a) and (4.25b) demonstrated that nominal yielding in the bi-layer will always begin at the 1-2 interface. By comparing (4.27) and (4.28) it can be shown that yielding in the tri-layer will always begin at the interface adjacent to the thicker of layers 1 and 2. For example, if \( H > h \) yielding will begin at the 1-2 interface. Furthermore, if (4.28) and (4.25b) are compared for \( h < H \), it can be seen that \( |\Delta T^{\text{tri-}\ell}_{1/2}| < |\Delta T^{\text{bi-layer}}_{1/2}| \) whenever the following is satisfied:

\[
\frac{(\psi_2^A - \psi_1^A)(X\zeta^2(X\zeta + 4) + 6\zeta + 4) + 1)}{\psi_1^A(Y - 1)(X\zeta(X\zeta^3 + 3\zeta + 4))} > 1
\]

(4.31)

Thus, nominal yielding starts ahead of the crack tip and \( |\Delta T_{\text{onset}}| = |\Delta T^{\text{tri-}\ell}_{1/2}| \) whenever the conditions described by (4.31) are satisfied.

If \( h = H \) layer 2 yields uniformly ahead of the crack. Under these circumstances yielding in the tri-layer will always occur before yielding in the bi-layer whenever the following condition is satisfied:

\[
7X\zeta^4 + 6X\zeta^3 - 3\zeta^2 - 2\zeta > 0.
\]

(4.32)

For most metal/ceramic interfaces with \( X > 1 \) and \( \zeta > 1 \) (4.31) and (4.32) are generally satisfied, therefore, \( |\Delta T_{\text{onset}}| = |\Delta T^{\text{tri-}\ell}_{1/2}| \) and \( |\Delta T_{\text{onset}}| = |\Delta T^{\text{tri-}\ell}_{\text{uniform}}| \), for the unsymmetric and symmetric configurations respectively. Problems do however arise when \( \zeta = h/l << 1 \). Under these circumstances it is possible that (4.32) is not satisfied and nominal yielding starts in the bi-layer.
4.7 The Limiting Elastic Energy Release Rate: Cases A and B

By combining $|\Delta T_{inter}|$ with (4.10), (4.14) and (4.16), limits bounds for the elastic interface energy release rate can be obtained. For Case A with $H = h$, this limit is given by equation (4.33). This equation is plotted in Figure 4.7a for a range of $\zeta = h/t = H/t = \eta$ and $X = E_1/E_2 = 1, 3, 5, \text{ and } 10$ (typical of metal/ceramic diffusion bonded interfaces including Ni/Al$_2$O$_3$ and Al/Al$_2$O$_3$ with $E_1/E_2 = 2$ and 6 respectively). Since all $\zeta$ and $X$ shown in the figure satisfy (4.32), the maximum elastic driving force, $G_{max}^A$, is achieved when layer 2 ahead of the crack tip yields uniformly. For further increases in $|\Delta T|$, $J$ diverges from $G$.

A similar, yet significantly more cumbersome expression, exists for the case when geometric symmetry does not exist.

$$\frac{G_{max}^A E_2}{h(\sigma_{n2})^2} = \frac{2X\eta + 1}{8XE} \frac{X\eta^2(7\eta + 12) + 6X\eta + 1}{X\eta[4(\eta + 1)^3 + \eta(\eta^3 - 2)] + 1} \quad (4.33)$$

For case B, yielding always starts at the 2-3 interface in the tri-layer. When this occurs the upper bound on $G$ can be found by substituting (4.30) into (4.16) which gives:

$$\frac{G_{max}^B E_2}{h(\sigma_{n2})^2} = \frac{(\theta^4 + \theta Z)[(\theta^4 + \theta (4\theta^2 + 6\theta + 4) + Z]}{2(4\theta^3 + 3\theta^2 + Z)^2} \quad (4.34)$$

where $\theta = (H+t)/h$ and $Z = E_3/E_2$. Figure 4.7b is a plot of (4.34) for $H = 100t$ typical of thin layers deposited on a thick substrate.
Figure 4.7 The limit for the elastic interface energy release rate, $G_{\text{max}}$: a) Case A, with geometric symmetry and b) Case B, with $H/t = 100$ (typical of thin coatings on a thick substrate).
4.8 Fully Plastic Temperatures: Case A and B

Further monotonic temperature change beyond $|\Delta T_{\text{net}}|$ will result in the following:\n: i) a plastic front will propagate through the thickness of layer 2 ahead of the crack (Case A and B), ii) plasticity will begin in layer 2 at the 1-2 interface in the wake of the crack (Case A), and iii) a plastic front will propagate through the thickness of layer 2 in the wake of the crack (Case A). For both i) and iii) transitional temperature changes will be reached at which layer 2 will become fully plastic at these respective locations.

When layer 2 is elastic-perfectly plastic, analytical expressions for the fully plastic temperatures associated with i) and iii) can be obtained. For clarity these $|\Delta T|$ will be labeled $|\Delta T_{FP}|$ with a superscript defining the region where layer 2 plastifies completely for the first time.

For Case A the condition $|\Delta T_{FP}| = |\Delta T_{FP}^{\alpha - \alpha}|$ leads to the following [85]:

$$
\frac{|\Delta T_{FP}^{\alpha - \alpha}|(\alpha_1 - \alpha_2)}{\sigma_{\alpha 2}} E_2 = \frac{1}{X\eta} \left( \frac{D_1^4 + D_2^4}{D_3^4 + D_4^4 + D_5^4} \right)
$$

\begin{align*}
D_1^4 &= \frac{1}{3}(X\eta(\phi + 1) + 1)|\eta^2(\phi^4 + 1) + 3\phi(\eta\phi + 1)| \\
D_2^4 &= -\frac{1}{4}(\eta(\phi^2 - 1) + 2\phi)|X\eta\phi(\eta(\phi + 2) - X\eta^2 + 1)| \\
D_3^4 &= \frac{1}{12}\eta^2(\phi^4 + 1), D_4^4 = \frac{1}{6}\eta^2(2\phi^2 + 3\phi + 2), D_5^4 = \phi(|\eta\phi + \eta + 1|)
\end{align*}

In deriving (4.35), it is assumed that $H > h$, which asserts, that yielding begins at the 1-2 interface and propagates toward the 2-3 interface. Here $\phi = H/h$. When $\phi = 1$, we obtain (4.29). If we define $\phi$ in terms of $\zeta$ and $\eta$ ($\phi = \zeta/\eta$) and then let $\eta$ approach zero (4.35) also yields the fully plastic solution for the bi-layer, $\Delta T_{FP}^{\alpha - \alpha}$.

---

5. For Case A, i) - iii) occur when $H > h$. When $H = h$ yielding occurs uniformly ahead of the crack tip and only ii) and iii) apply.
Figure 4.8a contains a plot of $\Delta T^{tri-A}_{uniform}$, $\Delta T^{bi-layer}_{1/3}$ and $\Delta T^{tri-A}_{FP}$ ((4.29), (4.35), respectively) as a function of $h/t = H/t$ for $E_1/E_2 = 3$. By plotting these three temperature changes together their relative magnitudes can be compared. In this case, a three layered material with complete symmetry, yielding always begins ahead of the crack tip. Next comes the development of plasticity in the wake of the crack at the 1-2 interface. Lastly, the plasticity propagates from the 1-2 interface in the wake of the crack to the free surface of layer 2.

Figure 4.8 The yielding sequence: a) Case A with geometric symmetry and b) Case B with $H/t = 100$ (no yielding in the wake bi-layer).
For Case B, $|\Delta T_{unif}| = |\Delta T_{2/3}^{\text{fit}-B}|$ and further temperature change will result in the spread of plasticity from the 2-3 interface to the 1-2 interface ahead of the crack. $|\Delta T_{FP}| = |\Delta T_{FP}^{\text{fit}-B}|$ is given by:

$$\frac{|\Delta T_{FP}^{\text{fit}-B}(\alpha_1 - \alpha_2)|E_2}{\sigma_{u2}} = \frac{1}{Z}\left(\frac{D_1^\theta + D_2^\theta}{D_3^\theta + D_4^\theta + D_5^\theta}\right)$$

$$D_1^\theta = \frac{1}{3}(Z\eta + \zeta + 1)[Z\eta^3 + 3Z\eta^2 + 3Z\eta + \zeta^3]$$

$$D_2^\theta = \frac{1}{4}(-Z\eta(\eta + 2) + \zeta^2)(Z\eta^3 + 2Z\eta - \zeta^2 + 1)$$

$$D_3^\theta = \frac{Z\eta}{12}, D_4^\theta = \eta \zeta^2 \left(\frac{\zeta}{3\eta} + \frac{1}{4}\right), D_5^\theta = \frac{\zeta^2}{2}$$

(4.36)

Figure 4.8b contains a plot of these two temperatures as a function of $h/t$ for $H = 100 t$ and $E_2/E_2 = 3$. The close proximity of the two lines indicates that the temperature change required to go from an elastic solution to a fully plastic solution is very small due to the high thickness of the substrate ($100 t$).

In summary, nominal yielding for Case A always starts in the tri-layer ahead of the crack tip at $|\Delta T_{unif}| = |\Delta T_{unif}^{\text{fit}-A}|$ or $|\Delta T_{1/2}^{\text{fit}-A}|$ (assuming $X > 1$, $\zeta > 1$, and $H > h$). Once this temperature is reached elastic stress analysis and therefore $G$ are no longer valid. Further monotonic temperature change causes plasticity to spread ahead of the crack tip and begin at the 1-2 interface in the wake of the crack.

By the time $|\Delta T_{FP}^{\text{fit}-A}|$ is reached layer 2 is fully plastic throughout. Beyond this point a fully plastic solution for both stress analysis and the energy release rate is required. Figure 4.9 illustrates the three regimes of interface fracture for the Al$_2$O$_3$/Ni(Cr)/Al$_2$O$_3$ tri-layer with $H = h$ (Chapter 2): elastic, partially plastic, and fully plastic. The curve separating the elastic and elasto-plastic solutions is $|\Delta T_{unif}^{\text{fit}-A}|$ and the curve separating the elasto-plastic and fully plastic solutions is $|\Delta T_{FP}^{\text{fit}-A}|$. The symbols represent finite element results for $\eta =$
\( h/t = 5,8,12,15, \text{ and } 18. \) Figure B.1 contains contour plots showing the evolution of \( \sigma_{yy} \) with \( |\Delta T| \) for this tri-layer when \( h/t = 4. \)

![Graph showing the evolution of stress with temperature difference](image)

**Figure 4.9** Nominal yielding characteristics of a symmetric tri-layer with elastic-perfectly plastic sandwich layer. Finite element results validate the analytical expressions.

In the fully plastic regime, \( |\Delta T| > |\Delta T_{\text{f,p}}^{h-A} | \) or \( |\Delta T| > |\Delta T_{\text{f,p}}^{h-B} | \) for Cases A and B respectively, \( J \) has an approximate analytical solution when layer 2 is elastic-perfectly plastic, \( \Delta T \) is uniform, and there is no contact in the wake of the crack. Under these conditions (4.1) can be approximated as [93]:

\[
|J| = \left( \int_{-H}^{0} u_{e} \, dz + \int_{0}^{H+t} u_{e} \, dz + \int_{0}^{t} \left( u_{e} + \sigma_{yy} \varepsilon_{yy}^{p} \right) dz \right)_{\text{tri-layer}}
+ \left( \int_{-H}^{0} u_{e} \, dz + \int_{0}^{t} \left( u_{e} + \sigma_{yy} \varepsilon_{yy}^{p} \right) dz \right)_{\text{bi-layer}}
\]

(4.37)

where \( u_{e} \) is the elastic strain energy density stored in the layer identified by the limits of the integral. \( \sigma_{yy} \) and \( \varepsilon_{yy}^{p} \) are the far-field stress and plastic strain respectively (distant from the crack tip). For Case A with \( H = h \), (4.37) is equal to:

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\[ J_{FP}^{tri-sym} = \frac{(\sigma_{\alpha 2})^2 t}{4E_2 \eta^3} \left( 7\eta^2 + 12\eta + 6 \right). \]  

(4.38)

This equation was derived from (4.13), (4.29), (4.33). For the fully plastic bi-layer [93]:

\[ J_{FP}^{pl-layer} = \sigma_{\alpha 2} \Delta T (\alpha_2 - \alpha_1) t - \frac{t(\sigma_{\alpha 2})^2}{2E_2} \left[ 1 + \frac{1}{X\eta} \left( \frac{3}{\eta^2} + \frac{6}{\eta} + 4 \right) \right] \]  

(4.39)

Note that unlike (4.39), equation (4.38) is not influenced by further temperature change, \( \Delta T \), once in the fully plastic regime. This "plateau" in the driving force, \( J \), means that the symmetric tri-layer is capable of obtaining a \( J \) which is an absolute limit.

### 4.9 Finite Element Results

Equation (4.10) along with conventional elastic stress analysis have provided analytical expressions for \( G \), (4.12)-(4.16). Equation (4.37) has been used to obtain an analytical expression for the fully plastic \( J_{FP} \), (4.38) and (4.39). Combined, (4.10) and (4.37) are bounds for the interface energy release rate. The region between these bounds, marked by \( |\Delta T_{unsol}| \leq |\Delta T| \leq |\Delta T_{unsol}^{l-layer}| \) and \( |\Delta T_{unsol}| \leq |\Delta T| \leq |\Delta T_{unsol}^{tri-layer}| \) for cases A and B respectively, is described by an elasto-plastic regime. Since there is no analytical solution for this regime, representative results have been obtained using finite element analysis.

Two finite element models have been used in this investigation. The first model consisted of 600 eight node quadratic plane stress elements (ABAQUS: CPS8) arranged in four columns [93]. This model was used to evaluate the \( J \)-integral along two far-field contours consistent with \( \Gamma \) illustrated in Figure 4.3. The second model consisted of approximately 4500 CPS8 elements with an overall geometry illustrated in Figure 4.10. The
refined mesh in the vicinity of the crack tip for this model allowed for the evaluation of $J$ along several contours $\Gamma'$.  

The $J$-integral was evaluated using the intrinsic Contour Integral (type = $J$) routine in ABAQUS Version 5.7 [95]. Periodic boundary conditions were imposed in front of and behind the crack tip such that infinite strip kinematics hold throughout the deformation.

**Figure 4.10** The refined finite element mesh used to calculate $J$ along $\Gamma'$. 

4.9.1 Far-Field J-Integral Evaluation - no contact 

This section contains results obtained from the first finite element model with the $J$-integral evaluated along the far-field contour $\Gamma$. Of the two contours over which $J$ was evaluated, both lead to the same result. Contact is not considered in this section. Material properties used in the model are given Table 4.1. In this case the thermo-mechanical properties were kept constant with temperature; however, the finite element code allows for temperature dependence. If the material properties vary only moderately over the temperature range of interest, then temperature-averaged properties could also be used to provide
more accurate results [93]. Similarly, plane strain and generalized plane strain can also be modeled within this code.

**Figure 4.11** $J$ vs. Temperature curves for an $\text{Al}_2\text{O}_3$/Ni(Cr)/$\text{Al}_2\text{O}_3$ tri-layer: a) with $t = 500 \ \mu\text{m}$ and b) with $t = 250 \ \mu\text{m}$. $H = h = 1000 \ \mu\text{m}$ for both.

Figure 4.11 and Figure 4.12 contain numerical results for a symmetric $\text{Al}_2\text{O}_3$/Ni(Cr)/$\text{Al}_2\text{O}_3$ tri-layer (Case A: $H = h$) subjected to monotonic cooling. Here the figures have been truncated at $|\Delta T| > 600$ since creep would allow stresses in the Ni(Cr) to relax for $T >$
$0.5T_M$ (the melting point, $T_M(Ni(Cr)) = 1390^\circ C$). In each figure, $J$ vs. temperature is plotted and the regime of interface fracture is labeled.

![Diagram](image)

**Figure 4.12** a) The influence of strain hardening on $J$ and b) $J$ for a geometrically equivalent bi-layer with no strain hardening.

The results presented in Figure 4.11a and b are for the same tri-layer with two different values of $t$, 500 and 250 μm respectively. When $t = 500$ μm cooling in the range $0 < |\Delta T| < 600$ is not enough to fully yield the bi-layer in the wake of the crack. As a result, $J_{FP}$ is not reached and therefore only the elastic and elasto-plastic regimes are
present. The deviation from a linear elastic solution occurs at $|\Delta T| = 255^\circ C$ consistent with the onset of uniform yielding far ahead of the crack tip, (4.29). The limiting elastic energy release rate at which this occurs is given by equation (4.33).

<table>
<thead>
<tr>
<th>Material</th>
<th>Elastic Modulus (GPa)</th>
<th>$\sigma_0$ (MPa)</th>
<th>CTE ($10^{-6}/^\circ C$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Al}_2\text{O}_3$</td>
<td>378</td>
<td>-</td>
<td>6.2</td>
</tr>
<tr>
<td>Ni(Cr)</td>
<td>208</td>
<td>330</td>
<td>13.3</td>
</tr>
</tbody>
</table>

**Table 4.1 Material Properties used in Finite Element Model**

When the thickness of layer 2 is reduced to 250 $\mu$m, both $t$ and $\eta = hlt = H/t$ change. The net effect is a reduction in the yielding temperatures and a reduction in the plateau value of $J$ (4.38). For this geometry, the elastic solution, $J = G$, is valid up to $|\Delta T| = 247^\circ C$. The fully plastic plateau is reached at $|\Delta T| = 427^\circ C$ with a plateau value equal to 48 $\text{Jm}^{-2}$. Thus the finite element model captures the trends given in (4.38).

Comparing these two configurations, four important findings are apparent. First, the elastic energy release rate significantly overestimates the elasto-plastic $J$ for $|\Delta T| > |\Delta T_{unsel}|$. Secondly, by reducing the thickness of layer 2 the fracture regimes have been modified and the energy release rate has been dramatically reduced $|\Delta T| = 600^\circ C$. This attests for the strong dependence of $J$ on geometry. Third, the interlayer yield strength, $\sigma_{n_z}$, plays an important role in determining $J$ through both the scaling of the temperature bounds and $J_{FP}$. Lastly, these finding confirm that the regimes depicted in Figure 4.9, based on far-field nominal yielding, also capture the transition temperatures observed for the $J$-integral.

Figure 4.11a and Figure 4.11b have shown results for the case when layer 2 is elastic-perfectly plastic. If layer 2 is capable of strain hardening the plateau in $J$ can be removed. Figure 4.12a shows how $J$ changes as a result of moderate linear strain hardening defined
by a tangent modulus equal to <1%, 5%, and 20% of the elastic modulus $E_2$. The small change in $J$ for $H = < 1\% E_2$ and $5\% E_2$ suggests the elastic-perfectly plastic solution can still modestly predict the response of materials which exhibit little strain hardening, e.g. pure annealed FCC metals.

Figure 4.12b shows the evolution of $J$ with temperature for an Al$_2$O$_3$/Ni(Cr) bi-layer obtained by setting $H = 0$. The shaded region in the bottom of the figure marks the area which would completely enclose the equivalent tri-layer solution. Note that the bi-layer and the tri-layer in Figure 4.11b have the same $|\Delta T_F|$. A comparison of Figure 4.11b and Figure 4.12b shows the two central differences between these solutions. First, the driving force, $J$, for interface fracture is higher in the bi-layer than it is for the equivalent symmetric tri-layer. Second, the difference between the elastic, $G$, and elastic-plastic, $J$, is much more pronounced for the tri-layer. The latter indicates the advantage of having plasticity develop and spread both in the wake and ahead of the crack tip.

![Figure 4.12b](image)

**Figure 4.13** $J$ vs. Temperature curves for Case B using Ni(Cr) and Al$_2$O$_3$ properties.

Finite element results representative of Case B are shown in Figure 4.13. In this example layers 1 and 2 have the elastic properties of Ni(Cr) and layer 3 has the properties of
Al₂O₃. The interlayer (layer 2) has been given a very small yield strength, \( \sigma_{02} = 20 \text{ MPa} \), in order to accentuate results in the fully plastic regime. Since layers 1 and 3 remain elastic, plastic deformation remains confined within layer 2.

Equations (4.16), (4.39), and (4.38) have shown that the energy release rate under thermal loading has either second, first, or zeroth order dependence on \( \Delta T \) \( (G \propto \Delta T^2, \ J_{FF}^{h} - \text{layer} \propto \Delta T \) and \( J_{FF}^{r} - \text{sym} \propto \Delta T^0 \). In Figure 4.13 the two \( J \) curves, each representing a different amount of confinement \( (H + t = 1100 \mu \text{m}) \), have neither linear nor second order dependence on \( \Delta T \). By plotting \( \ln (J) \) vs. \( \ln (\Delta T) \) we find that \( J_1 \sim \Delta T^{1.96} \) and \( J_2 \sim \Delta T^{1.90} \). This suggests that unlike the fully plastic bi-layer solution the fully plastic \( J \) for confined plasticity can still maintain a strong temperature dependence.

If we consider the configuration limits of Case B we can establish bounds on the temperature dependence of \( J \). In the limit as \( H \to 0 \), Case B approaches the fully plastic bi-layer solution; provided \( |\Delta T| > |\Delta T_{FF}^{h} - A| \). Likewise, as \( t \to 0 \), Case B approaches the elasticity solution. In light of these two bounds, we can deduce that for Case B the dependence of \( J \) on temperature will always lie somewhere between linear and parabolic.

### 4.9.2 J-Integral Path-Dependence and Alternative Stress States - no contact

The analytical derivations and finite element results up to this point are valid for plane stress. This section will consider alternative stress states and the path dependence of the J-integral in the elasto-plastic and fully plastic regimes. In order to do this, the second finite element model, having a refined mesh in the vicinity of the crack, was used. As a means of comparing near-tip and far-field values the J-integral was evaluated along fifty concentric contours having origins centered at the crack tip and radii ranging from \( y/t = 0.0025 \) to \( y/t = 1 \) (Figure 4.3). For plane stress, results from the latter were in exact agreement with those obtained along the far-field contour \( \Gamma \) discussed in section 4.9.1.
In order to limit the scope only representative solutions for the Al₂O₃/Ni(Cr)/Al₂O₃ tri-layer (Case A/Chapter 2) with \( t = 250 \, \mu \text{m} \) will be discussed.

![Graph](image)

**Figure 4.14** The near-tip (\( y/t = 0.0025 \)) and far-field (\( y/t = 1 \)) \( J \) for plane stress, plane strain and generalized plane strain.

Figure 4.14 contains plots of \( J \) vs. \( \Delta T \) evaluated along a far-field path (\( y/t = 1 \)) and near tip path (\( y/t = 0.0025 \)). Results for plane stress, plane strain and generalized plane strain are presented. In each case a small amount of strain hardening, defined by a linear tangent modulus, \( H \), was added to facilitate numerical convergence. \( J_{FP} \) based on plane stress has
been plotted in each figure for comparison. When modeling the generalized plane strain state the mesh length \( w \) (Figure 4.1) was varied from 4 to 8 times the crack length \( a \) in order to determine the dependence of \( J \) on model length\(^6\). This procedure indicated that beyond \( w = 5a \) there was negligible effect of length, \( w \), on \( J \). The results provided are for \( w = 5a \).

Figure 4.14a and b illustrate two points. First, when \((y/t = 1)\) the generalized plane strain and plane stress solutions have similar values with both being approximately equal to \( J_{FP} \) in the fully yielded regime. The plane strain solution lies significantly below these two because the additional out-of-plane constraint reduces \(|\Delta T|\) for both yield initiation and fully plasticity. Second, the near-tip \( J \) \((y/t = 0.0025)\) for all stress states deviates from the far-field \( J \).

The plane strain state, though modeled here, is not appropriate for the thermal problem since it over-constrains the tri-layer; Appendix B, Section B.2. Thus the deviation from \( J_{FP} \) for this stress state is not a significant source for concern. The noted difference between \( J_{Near-Tip} \) and \( J_{Far-Field} \) for \(|\Delta T| > 400^\circ C\), however, does warrant further consideration.

Figure 4.15a-c contain plots of the stress fields ahead of the crack tip for the generalized plane strain and plane stress states. The evolution of these fields particularly \( \sigma_{yz} \) and \( \sigma_{zz} \) in plane stress and generalized plane strain respectively, for \(|\Delta T| > |\Delta T_{FP}^{n-\lambda}| = 427^\circ C\), suggests that the single parameter characterization is breaking down. Note the normalization used for both the ordinate and abscissa in Figure 4.15a and b is such that the stress fields would be invariant with temperature if a single parameter characterization existed.

---

\(^6\) The overall model length \((a + w)\) must resemble an edge crack in a semi-infinite slab. For generalized plane strain the length \( w \) influences the out-of-plane constraint for \( y < 0 \); Appendix B section B.2.
Figure 4.15 Near-tip stress fields: opening and shear mode stress for a) plane stress and b) generalized plane strain and c) loading phase.

Furthermore, Figure 4.15c suggests that stress-state may influence the fracture characteristics of these interfaces through its effect on loading phase. This figure demonstrates that $\Psi$ for generalized plane strain is significantly lower than it is for plane stress.

The findings shown in these figures are typical of the large scale yielding conditions that develop in the fully plastic regime. One consequence is that $J$ may develop further configuration dependence (other than that given in (4.38)) as plasticity propagates through the layers [96]:
\[ \frac{\sigma_{ij}}{\sigma_u} = F_{ij}^{LSY} \begin{pmatrix} \bar{E}J, \theta, \frac{w\sigma_u}{J}, a, b, \Delta a, w, n \end{pmatrix} \]  

where \( F_{ij}^{LSY} \) is a function defining the stress fields under large scale yielding and \( n \) is the strain hardening exponent. Likewise, a failure or growth criterion may also have to take into account this new dependency [97]. Despite these findings, it is believed that \( J_{FP} \) still remains a better approximation of the near-tip \( J \) than the elasticity solution \( G \). Note that \( G = 177, 334, \) and \( 371 \) Jm\(^{-2}\) for plane stress, generalized plane strain and plane strain respectively. The latter value, though obtained from the finite element model, could be calculated by substituting \( E_i \to E_i/(1 - \nu_i^2) \) and \( \alpha_i \to \alpha_i(1 + \nu_i) \) into (4.14) as suggested in [84]. Furthermore, the analytical solution \( J_{FP} \) provides a convenient and quick starting place for more detailed analysis.

4.9.3 Interfacial Contact

The contact model presented in Section 4.5 predicted that contact in the wake of the interface crack would reduce the driving force for interface fracture. In this section results from finite element simulations of contact are presented. The finite element model used the refined mesh (Figure 4.10) with slideline contact elements (AB AQUS: ISL22) added along the interface between layer 3 and 2 over the entire length (-\( a < y < 0 \)). Figure 4.16a and b contain results for plane stress. In Figure 4.16a elastic conditions are assumed for direct comparison with the results from the contact model, Figure 4.6. Plotted in this figure are the: \( i) \) no contact solution, \( ii) \) the contact solution using slideline elements, and \( iii) \) the solution predicted by (4.22). Figure 4.16b contains elastic-plastic results for Ni(Cr) trilayer with \( H = 1\% E_2 \).

Under elastic conditions the finite element model predicts a shielding effect of \( \sim 26\% \). This value agrees quite well with 22\% predicted from (4.22). Additional model results fur-
ther confirm two other points; i) the shielding affect as a percent of $G$ is nearly constant and ii) the assumption of single point contact in the crack wake is reasonable, Figure 4.17. This figure contains a picture of the deformed mesh following contact. The crack length has been extended to accentuate the contact region. The localization of contact in the vicinity of $y = -\alpha$ is consistent with the single point assumption used in the analytical contact model.

During cooling yielding in the Ni(Cr) causes $J$ to deviate from $G$. With contact the deviation is further enhanced as additional strain energy builds up in the crack wake. These trends are demonstrated in Figure 4.16b. The “predicted $J$” shown in the figure was obtained by applying uniformly the elastic analysis correction obtained from (4.22) to $J_{FP}$ (4.38). It represents an approximate analytical expression for the far-field $J$ in the presence of contact.
Figure 4.16 Finite element simulations of large-scale interfacial contact in the wake of an interface crack: a) elastic conditions for comparison with the contact model and b) elastic-plastic conditions for the Ni(Cr) tri-layer.

Figure 4.17 The deformed mesh illustrating highly localized contact in the crack wake.

4.10 Discussion of Results

The present work has examined the evolution of the energy release rate, $J$, for a stationary crack in a three layered metal/ceramic system subject to monotonic thermal loading. For a plane stress state with incremental thermo-elasto-plasticity, analytical expressions for the deformation and the energy release rate were derived. In addition, finite element calculations confirming the analytical expressions were carried out.
The overall behavior of the composite was found to depend on characteristic temperatures which mark the bounds between the three regimes of interface fracture; elastic, elasto-plastic, and fully plastic. For interfaces that debond at a critical value of $J$, the results of this paper may be used to define a new characteristic temperature at which growth of an edge-crack might initiate.

This work has been concerned with three layered material systems. In some instances assumptions regarding the material behavior of the layers have been made for purposes of simplification. In spite of this, the adopted solution procedure is general in the sense that it can be applied to $n$-layered material systems with each layer having unique thermal, elastic and plastic properties. Besides thermal strains, other eigenstrains, such as sintering and moisture swelling, can be dealt with in a similar way.

The most important features identified in this work relate to the interacting roles of plasticity, geometry, and large scale contact. It has been shown that each of these features plays a role in determining $J$. If a layered material can be designed with low characteristic temperatures, $|\Delta T_{onset}|$ and $|\Delta T_{FP}|$, it can benefit substantially from the shielding effects of plasticity. Furthermore, if that system also utilizes an optimized geometry, additional benefits can be realized. Case A with $H = h$ is an example. By reducing the thickness of layer 2 we reduced $|\Delta T_{onset}|$ and $|\Delta T_{FP}|$. At the same time, by making the geometry symmetric we also received the added benefit of a $J$ that plateaus.

The development of plasticity across the entire interface, ahead of the interface crack-tip, for $|\Delta T| > |\Delta T_{onset}|$, leads to large scale plasticity. This branch of fracture mechanics is notorious for the scarcity of analytical results as well as the break-down of the path-independence of line integrals used to characterize non-linear elastic fracture [93]. If the
energy release rate, $J$, were to be used against thermal interface fracture initiation in layered materials the following points have to be considered:

i) The crack driving force, $J$, does not depend on crack length provided that the crack is longer than the smallest layer thickness.

ii) $J$ can be calculated either by full FEM, or be approximated by a far-field line integral in the elastic and elasto-plastic regime.

iii) $J$ can take into account the effects of macroscopic contact in the elastic regime. An elastic contact model has shown that contact reduces the energy release rate < 25% for Case A with $H = h$.

iv) $J$ is strongly dependent on material properties, layer thickness, and configuration.

v) $J$ alone can not predict the stability of the crack path, e.g. kinking of the crack out of the interface into the most brittle layer.
Chapter 5

The Influence of Solid-State and Liquid-Phase Bonding on Fatigue at Al/Al₂O₃ Interfaces

5.1 Introduction

Factors that influence the adhesion of metal/oxide interfaces have been established by means of measurements, first principles calculations and interface crack growth simulations. Adhesion measurements have been made on well-characterized interfaces between Al₂O₃ (typically sapphire) and the metals: Al [19]-[22][48], Ni [34][98], Cu [28], Au [24][26], Nb [29]-[33], and Pt [37]. First principles calculations of atomic decohesion demonstrate aspects of bonding attributed to the work of bond rupture and bond strength [99]-[102]. Simulations that couple atomic-level bond rupture phenomena with plasticity occurring in the metal reveal interconnections between these factors and their role in interface adhesion, Γ_{int} [103]-[105]. Based on these measurements, simulations, and calculations, the following two generalizations apply:

i) Clean metal/oxide interfaces devoid of segregants are strong and tough. Adhesion energies exceed 200 Jm⁻².

ii) Segregants and contaminants embrittle and weaken the interface: C and S may reduce the adhesion energy to 1-5 Jm⁻². Gettering of these contaminants by alloy additives such as Cr again results in high adhesion energies, exceeding 100 Jm⁻² [34].

When the interfaces are strong, cracks blunt and activate interface failure by initiating and coalescing debonds ahead of the crack front. This occurs at weak sites along the interface. Such behavior has been demonstrated on interfaces involving Al₂O₃ bonded to Al, Cu, Ni, γ-Ni, or Nb [19][22][24][26][28]-[34][48][98]. At embrittled interfaces, cracks
remain sharp and subject to atomic scale opening displacements. Brittle behavior has been demonstrated by injecting C and S into interfaces with Au [23] and Ni [106], respectively. Similar effects have been shown upon introducing Ag at interfaces with Nb [29][30]. The interface between Al alloys and Al₂O₃ is generally tough, virtually regardless of the presence of segreagants. Accordingly, cracks extend by the growth and coalescence of voids in the alloy, near the interface, by means of plasticity mechanisms similar to those that cause ductile fracture [107].

Strong, tough metal/oxide interfaces are susceptible to fatigue crack growth, at rates somewhat higher than those found in the monolithic alloy [19][20]. This trend is also expected to influence the thermomechanical fatigue characteristics of interfaces in multi-component devices and systems. The intent of the present study was to explore those features of Al/Al₂O₃ interfaces that affect fatigue crack growth, with an emphasis on the crack growth threshold. The objective was to devise a threshold-based design criterion. For this purpose, interfaces made by solid state and liquid phase bonding have been studied. In the latter, the importance of impurities that segregate to the interface and form intermetallic reaction products are examined.

Previous studies of fatigue crack growth at metal/oxide interfaces, especially Al/Al₂O₃, have revealed three predominant features [19][20]:

i) Striations are evident on the Al side of the fatigued interface, indicative of a classical mechanism of crack growth based on the extent of crack tip blunting per cycle.

ii) There is a fatigue threshold at an energy release rate range, ΔGₘₘ, comparable to that for the alloy itself.

iii) Cyclic crack growth rates at energy release rates above the threshold exceed those for the alloy by about an order of magnitude.
The present study is largely consistent with these findings, but also identifies several new factors that benefit the design of fatigue resistant interfaces.

5.2 Materials and Bonding

The mechanical measurements duplicate the range of mode mixities expected in application. These measurements have been made in both mode I (opening) and mixed mode using the DCDC and 4pt-bend configurations described in Chapter 1.

Aluminum has been both liquid-phase and solid-state vacuum diffusion bonded to \{0001\} sapphire substrates. Prior to bonding, the aluminum foils were degreased by sonicing in trichloroethylene, acetone, isopropanol and distilled water (for 5 minutes each). Following degreasing, the foils were immersed in 0.1 molar NaOH at 60°C for 5 minutes in order to dissolve disruptive oxides present on the surface [1]. Thereafter, they were dried by blowing compressed N₂ over the surface. The sapphire substrates were prepared using a three step process comprising: i) washing with a detergent, ii) rinsing with distilled water and iii) preconditioning by annealing in an air furnace at 1000°C for 24 hours. After these initial preparations, the materials were assembled into a tri-layered arrangement of Al₂O₃/Al/Al₂O₃ as either 50 mm square or 58 mm x 32 mm rectangular plates. Table 5.2 lists the aluminum foil thicknesses used. The table contains both the initial (prior to bonding) and final (after bonding) thicknesses, as well as the sapphire thicknesses.

<table>
<thead>
<tr>
<th>Aluminum</th>
<th>Iron</th>
<th>Silicon</th>
<th>Zn, Cu, Mn</th>
</tr>
</thead>
<tbody>
<tr>
<td>98.7%</td>
<td>0.71%</td>
<td>0.12%</td>
<td>balance</td>
</tr>
</tbody>
</table>

Table 5.1 Composition of the Commercially Pure Aluminum (at.%)
<table>
<thead>
<tr>
<th>Specimen Configuration</th>
<th>Sapphire (mm)</th>
<th>Aluminum Thickness (µm) Liquid Phase</th>
<th>Solid-State</th>
</tr>
</thead>
<tbody>
<tr>
<td>DCDC</td>
<td>2.5</td>
<td>75 (28)a</td>
<td>125 (90)</td>
</tr>
<tr>
<td>Flexural</td>
<td>1.0</td>
<td>75 (45)</td>
<td>460 (350)</td>
</tr>
</tbody>
</table>

**Table 5.2 Dimensions of the Sandwich Test Configurations**

a. The quantity in parenthesis is that measured after bonding.

Solid-state bonding (SSB) was conducted at 645°C for 15 hours under an interface pressure of 1.5 MPa. Liquid-phase bonding (LPB) was conducted at 665°C with a 50 g TZM platen placed on the assemblage to apply a slight interface pressure. Both were conducted subject to an environment created by purging with ultra-high purity N₂, followed by evacuating to <2×10⁻⁶ torr.

After bonding, the perimeter of each plate was reduced by 4 mm, by removing material using a high speed diamond saw. The remainder was cut into beams approximately 5 mm wide. The DCDC specimens were prepared from the beams by drilling a 2.25 mm diameter hole through the width, along the interface at mid-span. The flexural specimens were pre-cracked along the mid-section by first applying 50 N Knoop indentations (0.5 mm apart), across one side. Thereafter, upon displacing each beam in 3 point bending (at 0.1 µm/s), with the Knoop indentations in tension, a crack was induced that extended to the interface, where it arrested.

The edges of each beam were ground and polished using a diamond grinding disk and several diamond polishing suspensions ranging in size from 9 to 1 µm. Lastly, in order to obtain a virtually scratch-free aluminum surface, the edges were polished with a 0.05 µm Al₂O₃ suspension.

Three basic configurations have been produced for the fatigue investigations. Two of these comprise relatively thick (100 - 400 µm) Al layers: one being SSB and the other
LPB. The third was high purity Al (99.999%) as a very thin (~2 μm) layer. It was bonded using the liquid phase method.

5.3 Characterization

Optical imaging of the interfacial region, made possible by the transparency of the sapphire (Figure 5.1), revealed a major difference between SSB and LPB interfaces, even though they were made with identical materials. The former were featureless (Figure 5.1a) while the latter resulted in interface precipitates with a dendritic morphology (Figure 5.1b), as well as occasional voids. The consequences for interface fracture and fatigue are addressed below.

![Diagram](image)

**Figure 5.1** The Al/Al₂O₃ interface as viewed through the transparent sapphire: a) solid phase bonded and b) liquid phase bonded.

Cross sections of the LPB interfaces examined using the Scanning Electron Microscope (SEM) with Energy Dispersive Spectroscopy (EDS) as well as by Auger Electron Spectroscopy (AES), indicate two product phases (Figure 5.2). One phase, coincident with
the dendritic features observed optically, contains Fe and Al, revealed by EDS (Figure 5.2a). It is believed to comprise the intermetallic, FeAl₃ [108]-[112]. Further information has been obtained by dissolving the Al using a solution comprising three parts HCl to one part HNO₃ and then examining the unaffected sapphire by Atomic Force Microscopy (AFM). Dissolution removed both the Al and Fe intermetallic, resulting in the features illustrated in Figure 5.3. At sites previously occupied by the intermetallic, the original sapphire surface was apparent, inclusive of the polishing scratches, suggesting that the intermetallic precipitated directly onto the original sapphire surface. The second product phase, which covers the remainder of the interface, is located ~ 50 nm from the original surface (Figure 5.3). It contains only Al and O (Figure 5.2b).

Figure 5.2 Elemental analysis of the product phases found at the interface: a) an EDS spectrum of the cross section showing both Fe and Al present near the interface and b) AES spectrum indicating only the presence of Al and O following chemical dissolution of the metal.
Figure 5.3 An AFM image of the interface following chemical dissolution of the metal using aqua regia. The topographical profile indicates a product phase with thickness \( \sim 50 \text{nm} \).

These observations may be understood as follows. In the liquid state, the Fe impurity in the Al preferentially migrated to the interface. On cooling, FeAl\(_3\) precipitates with dendritic appearance [108]-[111] form in regions having a Fe concentration in the liquid which is in excess of 0.03\% [112]. The absence of interface precipitates in the solid state bonded system reflects the much longer times needed for Fe to diffuse to the interface. Accordingly, Fe remains in solution in the Al, as well as in small equiaxed FeAl\(_3\) precipitates.

The second product phase is thought to be Al\(_2\)O\(_3\) that dissolved during bonding (either from the sapphire or as an oxide layer on the Al) and reprecipitated upon solidification. Analogous reprecipitation effects have been noted in the Al\(_2\)O\(_3\)/Nb system [32][33].
5.4 Experimental Procedures

Fatigue experiments have been conducted in a laboratory air environment (~50% relative humidity and 20°C) using a servo-hydraulic testing frame with constant load amplitude, at a frequency of 30 Hz, and a load ratio \( R = 0.1 \). The flexural fixture had a major span of 40 mm and a minor span of 20 mm. The DCDC specimens were 50 mm in length. Mode I fatigue crack growth thresholds were readily determined upon using the DCDC specimen because, at fixed load amplitude, the energy release rate range \( \Delta G \) (1.6) decreases as the crack (length \( a \)) extends. Accordingly, by fixing the loading amplitude, the interface crack was grown above the threshold and the behavior was monitored by optical microscopy as the crack decelerated.

For present purposes, the threshold, \( \Delta G_{th} \), is defined as the strain energy release rate range at which the crack growth rate diminishes to 0.5 nm per cycle.

The flow strength of the pure Al was estimated by micro-hardness measurements using a diamond pyramid indentor at 0.5 N. These measurements were made on the polished aluminum surface in the bonded configuration. The measured hardness implies a yield strength \( \sigma_y \approx 100 \) MPa.

5.5 Observation of Fatigue Crack Growth Characteristics

At SSB interfaces, mode I cracks grow alternately along the interface and within the Al at 5 to 20 \( \mu \)m beneath the interface (Figure 5.4). Interface crack growth predominates at large energy release rates (\( \Delta G > 75 \) Jm\(^{-2} \)) and small crack lengths \( (a < 3 \) mm). Growth within the Al is non-planar (Figure 5.5). The oscillations in the crack path create a surface subject to regions of contact. Observations made through the sapphire reveal that crack growth is strongly crystallographic (Figure 5.4b) with the crack locally deflecting away from the interface and into the Al at specific grain boundaries. When the crack advances along the
interface, striations well-correlated with the applied $CTOD = \Delta G / 2 \sigma_a$, have orientations unique to each grain. These are apparent on the Al in the crack wake (Figure 5.6).

---

**Figure 5.4** a) A schematic of crack growth characteristics found for the solid-state bonded interface: FeAl$_3$ is distributed as small precipitates throughout the aluminum. Crack growth always occurs near the same interface. Tunneling into the Al occurs at grain boundaries and appears to be crystallographic. b) The interface after fatigue loading as viewed through the sapphire. Fatigue striations are visible on the interface in regions labeled fatigued. When the crack tunnels the interface appears bonded with no evidence of failure. These regions are labeled bonded.

---

7. The crack tip opening displacement is approximately equal to the crack advance per cycle ($CTOD = da/dN = \Delta G / 2 \sigma_a$).
Figure 5.5 A crack traveling in the Al in a solid-state bonded DCDC specimen.

Figure 5.6 An AFM image of a single grain on the aluminum surface following nominally mode I fatigue in the solid-state bonded interface. Striations are crystallographic. At this location, $\Delta G = 100 \text{ Jm}^{-2}$, $a = 2 \text{ mm}$, and the striation spacing is $\sim 2.25 \text{ } \mu\text{m}$. 
Inspection of the mode I fatigued interface in LPB specimens was achieved by cutting near the crack tip and removing one sapphire layer, Figure C.1. Such observations have revealed (Figure 5.7)\(^8\) that interface crack growth resulted from a) local brittle failures at intermetallic/Al\(_2\)O\(_3\) sites and b) fatigue within the adjacent Al. Further examination (Figure 5.8) revealed striation spacings in the Al ranging from 35 to 250 nm, as the energy release rate \(\Delta G\) varied from 40 to 65 Jm\(^{-2}\). Optical observations with differential interference contrast demonstrate that the FeAl\(_3\) decoheres from the Al\(_2\)O\(_3\) at loads far below those required to initiate fatigue.

![Image of fatigued interface](image)

**Figure 5.7** SEM image of the fatigued interface following the removal of one of the sapphire layers. Atomic number contrast differences present in backscatter mode highlight the intermetallic precipitate responsible for initial interface failure.

These behaviors are summarized on Figure 5.9. In regions devoid of FeAl\(_3\), the crack advances along the interface when \(\Delta G\) is high and \(\alpha\) is small, consistent with the SSB interfaces. Between the intermetallic, it periodically tunnels into the Al, with a typical depth of 10 \(\mu\)m. Occasionally, it grows completely through the Al layer, emerging on the other interface.

---

8. Figure 8 was taken in backscatter mode to highlight the distinct differences in atomic number contrast associated with the two phases.
Figure 5.8 Fatigue striations found on the liquid-phase bonded Al/Al₂O₃ interface: a) region where $\Delta G = 40$ Jm⁻² and b) region where $\Delta G = 65$ Jm⁻². Note the order of magnitude difference in scaling between a) and b).

Upon mixed mode loading, the two interfaces behaved differently. The SSB interfaces remained intact. Fatigue cracks that initiated at the specimen pre-crack grew into the aluminum layer (Figure 5.10). Conversely, in LPB specimens, the crack deflected and subsequently grew by fatigue along the interface, Appendix A. The fatigue appearance was similar to that in mode I.
Figure 5.9 A schematic of crack growth characteristics found for the liquid-phase bonded specimens: FeAl$_3$ precipitates are located at the Al/Al$_2$O$_3$ interface. Crack growth alternates between the two Al/Al$_2$O$_3$ interfaces, deflecting at some of the FeAl$_3$ precipitates. The ease whereby the Al$_2$O$_3$/FeAl$_3$ interface fails suggests little or no bonding between these phases.

These observations provide comparisons between the mechanical response of the SSB and LPB systems:

i) The intermetallic precipitates are weakly adhered to the Al$_2$O$_3$, consistent with previous findings for CuAl$_2$ precipitates [113]. A rationale for the weak bonding between Al intermetallics and Al$_2$O$_3$ has yet to be made.

ii) The intervening Al$_2$O$_3$/Al regions are strongly bonded and only fail upon cyclic loading, despite the presence of voids. Interface cracks blunt under monotonic loading.

iii) The area fraction of interface covered by FeAl$_3$ appears to be large enough to bias the trajectory taken by mixed mode pre-cracks introduced through the Al$_2$O$_3$. That is, absent this precipitate, the interface remains intact such that cracks in the Al$_2$O$_3$, after arresting at the interface, extend in the Al. Conversely, the precipitates present at LPB interfaces allow cracks originating in the alumina to deflect along the interface, causing the interface to be susceptible to crack growth upon subsequent mixed mode cyclic loading.
Figure 5.10 An SEM image showing a fatigue crack growing into the aluminum in the solid-state bonded Al$_2$O$_3$/Al/Al$_2$O$_3$ tri-layer subject to flexural loading. There is no interface failure. The crack has extended from top to bottom.

Despite these differences in mechanical response, the fatigue crack growth resistance of the interfaces must be sufficiently similar that, in both cases, the cracks deviate from the interface into the Al (Figure 5.4 and Figure 5.9). In the SSB system, the deviations appear
to be crystallographic. That is, the crack extends along the interface with well-delineated striations, but diverts into the Al at grain boundaries, when specific grain orientations are encountered. Such effects are consistent with the crystallographic nature of fatigue [14]. In the LPB system, deviations into the Al occur preferentially after the crack has encountered FeAl₃ precipitates. Local loading phase changes caused by the interaction of the crack tip with the precipitates may be responsible.

5.6 Thin Ultra-High Purity (99.999% Al) Al/Al₂O₃ Interfaces

Both LPB and SSB interfaces experience highly tortuous fatigue crack growth. By reducing the foil thickness and removing the Fe impurity tortuosity is suppressed and an interface crack is forced to take a planar path. Specimens made with the thin, high-purity Al behaved in this manner, Figure C.2 and Figure C.3. In all cases, Mode I cracks remained at the interface and extended in a planar manner.

5.7 Fatigue Threshold Behavior

Threshold experiments were conducted by incrementally growing mode I fatigue cracks using the DCDC configuration. Testing consisted of initial fatigue pre-cracking followed by constant amplitude loading at 30 Hz and $R = 0.1$. Threshold behavior was achieved by growing an interface crack until the observed growth rate declined to 0.5 nm per cycle. The corresponding load amplitude and overall crack length were used to calculate $\Delta G_{th}$ [83]. Following each arrest, the load amplitude was systematically increased and the monitoring procedure repeated such that the evolution of $\Delta G_{th}$ with crack length was determined.

These threshold measurements are summarized on Figure 5.11. Some general findings follow:
i) The specimens comprising the high purity, very thin Al had a constant threshold ($\Delta G_{th} = 10$ Jm$^{-2}$) independent of crack length.

ii) The SSB interfaces had a short crack threshold, ($\Delta G_{th} = 10$ Jm$^{-2}$), similar to that for the thin, high purity Al. Thereafter, it significantly increased and reached $\sim$60 Jm$^{-2}$ for cracks $\sim$6 mm in length. At larger crack lengths, the sapphire fractured.

iii) The LPB interfaces could only be tested at crack lengths in the range 5-8 mm. In this range, the threshold occurred at $\Delta G_{th} = 50$ Jm$^{-2}$.

![Graph showing crack length vs energy release rate]

**Figure 5.11** Effect of crack length on the fatigue crack growth threshold.

The constancy of the threshold for the thin layers is consistent with the planarity of the crack growth. That is, there are no crack wake effects and, accordingly, the threshold is unaffected by apparent changes to the crack driving force arising from crack wake contact and crack path tortuosity. The similarity in the threshold found for short cracks in the SSB system (before deviation into the Al) affirms this assertion. This threshold is regarded as the benchmark against which other phenomena can be assessed.
Larger values of the threshold develop only after crack deviation away from the interface. The consequent tortuosity of the crack path results in crack wake closure effects, exactly analogous to those reported for monolithic alloys [14]. Evidence for closure is apparent in Figure 5.5. These effects systematically elevate the threshold. Fundamentally, the phenomenon is governed by features that deflect the crack into the Al (especially grain boundaries and precipitates) and promote a tortuous crack path. Closure is facilitated by loading phase resulting from elastic mismatch (present even in the DCDC configuration - Chapter 1). That is, shear displacements that arise as the crack extends induce contact between the crack surfaces during unloading [20].

Crack wake closure also rationalizes the striation spacing measurements exhibited in Figure 5.8. For conventional cyclic crack growth, the striation spacing should be: \( \frac{da}{dN} = \frac{\Delta G}{2\sigma_u} \). At the imposed \( \Delta G \) (40 to 65 Jm\(^{-2}\)), upon using the yield strength estimated by microhardness measurements (Section 5.4), the striation spacings (200 to 325 nm) are found to be somewhat higher than the measured spacings (35 to 250 nm). Tip energy release rates smaller than the applied values, caused by tortuosity-related crack closure would account for this difference.

The tendency for the crack to deflect away from the interface into the Al, thereby causing closure, suggests close similarity in the fatigue crack growth rates for the interface and the alloy itself. In some grain orientations, interface crack growth is preferred. In others, crack growth in the Al predominates. This cross-over behavior enables deflection which, in turn, allows closure and thereby elevates the threshold. These effects would be absent if the crack growth rate were systematically smaller on the interface.

### 5.8 Concluding Remarks

The purity level of the constituent materials, formation of intermetallic precipitates, and
crystallographic fatigue crack growth processes all play a significant role in determining the overall fatigue response of these interfaces in nominally mode I and mixed mode loading. Whether SSB or LPB is beneficial for interface fatigue is strongly influenced by the relative dominance of these factors:

i) Al/Al₂O₃ interfaces which are inherently tough under monotonic loading are prone to fatigue crack growth either exclusively along the interface or alternately within the metal and along the interface.

ii) The development of a tortuous crack path, facilitated by the presence of either FeAl₃ precipitates (LPB) or crystallographic fatigue (SSB) elevates the fatigue threshold. This effect is attributed to tortuosity-related crack closure.

iii) Crack closure effects cause the striation spacing to be lower than that expected from the applied energy release rate. However, in the absence of such effects (small crack lengths in Figure 5.11), observed crack growth rates are well correlated with the applied energy release rate and are largely consistent with previously published results [19].

iv) The loading phase affects the likelihood of creating an interface fatigue crack. High mixity angle loading imposed on SSB interfaces causes fatigue through the Al rather than at the interface. Conversely, such loading imposed on LPB interfaces causes interface cracking, resulting in subsequent mixed mode cyclic crack growth.
Chapter 6

Conclusions and Future Work

6.1 Overview
Mechanical characterization of vacuum diffusion bonded Al/Al₂O₃ and Ni(Cr)/Al₂O₃ interfaces has revealed an important interconnection between alloy addition, material purity and processing. Findings suggest that solid-state and liquid-phase bonding techniques result in significantly different interface attributes. The enhanced mobility of impurities in solution (Al/Al₂O₃) or eutectic-type reactions (Ni(Cr)/Al₂O₃) encountered during the latter are believed to be responsible. Furthermore, in the absence of differences in bonding technique, the addition of an active element such as Cr in Ni was found to be responsible for a significant improvement in interface toughness. Similar beneficial effects from sulfur-gettering elements have been well documented in native oxide/alloy adherence studies. The results from individual chapters supporting these conclusions have been summarized below.

6.2 Solid-State Bonded Ni(Cr)/Al₂O₃ Interfaces
Cr in solution exerts a major influence on the fracture resistance of the γ-Ni/α-Al₂O₃ interface in a moist environment. The Cr seems to eliminate the sensitivity of the Ni interface to stress corrosion. (In the absence of moisture, the interfaces are tough with and without Cr) [35]. Two factors seem to be important in the realization of high ambient toughness: i) The Cr getters C from the interfacial zone through the formation of a carbide, thus negating the role of C segregation in stress corrosion cracking of the interface. ii) Dissolution of Al₂O₃ in the alloy disperses the interface contaminants into solution in the alloy, enabling strong bonding. Future studies are needed to unequivocally indentify which possibility is
dominant. However, in the present work the evidence is primarily supportive of C gettering by the Cr.

6.3 Liquid-Phase Bonded Ni(Cr)/Al₂O₃ Interfaces

An investigation of the fracture and fatigue of γ-Ni(Cr) /Al₂O₃ interfaces has affirmed a major effect of S segregation. Solid-state diffusion bonded interfaces are sufficiently tough and fatigue resistant that cracks divert into the Al₂O₃ rather than remain at the interface. The associated system toughness is that for Al₂O₃. At sites where the interface fails in preference to sapphire, trace quantities of S are found on the exposed surface of the Ni(Cr). The implication is that local embrittlement occurs where S segregates. Conversely, liquid phase bonding that releases S to the interface results in low adhesion (2-7 Jm⁻²), such that delamination is induced solely by the residual stresses in the system.

These findings suggest that tough Ni(Cr)/Al₂O₃ interfaces can only be achieved when the interface is free of segregants present as a result of diffusion of impurities during bonding, and/or surface contamination of the starting materials prior to bonding. For the solid-state bonded interfaces, Cr was found to getter C by forming carbides. This effectively eliminated the stress corrosion mechanism observed in the pure Ni/Al₂O₃ interfaces. Moreover, the bonding temperature was below the Cr-S eutectic such that S within the Ni(Cr) remained as Cr sulfides. Liquid-phase bonding, on the other hand, utilized temperatures above the eutectic. As a result, a sulfur-rich liquid originating at grain boundaries spread across the interface.

6.4 Interface Fracture Under Thermal Loading

The overall behavior of a tri-layered composite subjected to a monotonic temperature change depends on characteristic temperatures which mark the bounds between the three
regimes of interface fracture: elastic, elasto-plastic, and fully plastic. The most important features identified in this work relate to the interacting roles of plasticity, geometry, and large-scale contact. It has been shown that each of these features plays a role in determining \( J \). If a layered material can be designed with low characteristic temperatures, \( |\Delta T_{unsel}| \) and \( |\Delta T_{rel}| \), it can benefit substantially from the shielding effects of plasticity. Furthermore, if that system also utilizes an optimized geometry, additional benefits can be realized. Case A with \( H = h \) is an example. In this case reducing the thickness of layer 2 reduced \( |\Delta T_{unsel}| \) and \( |\Delta T_{rel}| \). At the same time, making the geometry symmetric also produced the added benefit of a \( J \) that plateaus.

The development of plasticity across the entire interface, ahead of the interface crack-tip, for \(|\Delta T| > |\Delta T_{unsel}|\), puts the present problem in the category of large-scale plasticity fracture mechanics. This branch of fracture mechanics is notorious for the scarcity of analytical results as well as the break-down of the path-independence of ordinary line integrals used to characterize non-linear elastic fracture [93]. If the energy release rate, \( J \), were to be used against thermal interface fracture in layered materials, the following points would have to be considered:

i) The crack driving force, \( J \), does not depend on crack length provided that the crack is longer than the smallest layer thickness.

ii) \( J \) can either be calculated by full FEM or approximated by a far-field line integral.

iii) \( J \) can take into account the effects of macroscopic contact. An elastic contact model has shown that contact reduces the energy release rate by \(< 25\%\) for Case A with \( H = h \).

iv) \( J \) is strongly dependent on material properties, layer thickness, and configuration.
v) $J$ alone can not predict the stability of the crack path, e.g. kinking of the crack out of the interface into the most brittle layer.

6.5 Fatigue along Al/Al$_2$O$_3$ Interfaces

It has been shown for the first time that thin Al films are capable of fatigue crack growth by a striation mechanism. Under nominally mode I and mixed mode loading the overall fatigue response of these interfaces is influenced by several factors: the purity level of the constituent materials, the formation of intermetallic precipitates, and the crystallographic fatigue crack growth processes. Whether SSB or LPB is beneficial for interface fatigue is strongly influenced by the relative dominance of the following:

i) Al/Al$_2$O$_3$ interfaces, which are inherently tough under monotonic loading, are prone to fatigue crack growth either exclusively along the interface, or alternately within the metal and along the interface.

ii) The development of a tortuous crack path, facilitated by the presence of either FeAl$_3$ precipitates (LPB) or crystallographic fatigue (SSB) elevates the fatigue threshold. This effect is attributed to tortuosity-related crack closure.

iii) Crack closure effects cause the striation spacing to be lower than that expected from the applied energy release rate. However, in the absence of such effects (small crack lengths, in Figure 5.11), observed crack growth rates are well correlated with the applied energy release rate and are largely consistent with previously published results [19].

iv) The loading phase affects the likelihood of creating an interface fatigue crack. High mixity angle loading imposed on SSB interfaces causes fatigue through the Al rather than at the interface. Conversely, such loading imposed on LPB interfaces causes interface cracking, resulting in subsequent mixed mode cyclic crack growth.
6.6 A Note about Bonding

In general, these findings suggest that liquid-phase bonding facilitates interfacial segregation. This was seen for both Ni(Cr) and commercially pure Al. For the Ni(Cr), bulk sulfur impurity at a level of ~150 ppm accumulated at the Ni/Al₂O₃ interface, causing interfaces levels as high as ~4 at.%. This resulted in interface failure by a stress-corrosion-type mechanism. The same material bonded using the solid-state technique, having a temperature below the CrS eutectic, did not fail after cooldown or as a result of post-bond mechanical testing.

Similar effects were observed for commercially pure Al with ~0.7 at.% Fe. For this material, interfaces formed by the solid-state bonding technique were free of segregant. The liquid-phase bonded interfaces, on the other hand, contained a FeAl₃ intermetallic segregant that is believed to have precipitated during solidification. Only for the case of extreme purity (99.999% Al) did the liquid phase technique produce apparently segregant-free interfaces.
Appendix A

The Interface Energy Release Rate under 4pt-Bend Loading

A.1 Introduction

The elastic interface energy release rate for the symmetric diffusion bonded/three-layered beam can be determined by using the J-integral, (A.1). Since J is path-independent for elasticity its evaluation can be made using far-field stress analysis and a contour, \( \Gamma \), located far away from the singular field of the crack tip, Figure A.1.

\[
J = \int_{\Gamma} \left( (\int \sigma_{ij} d\varepsilon_{ij}) dz - \sigma_{ij} \eta \frac{\partial u_i}{\partial y} d\Gamma \right)
\]  
(A.1)

Figure A.1 The 4pt-bend test configuration with far-field contour, \( \Gamma \). Here the geometry is symmetric with top and bottom layer having the same thickness and material properties.

A.2 Equilibrium and Elastic Stress-Strain Relation

Force and moment equilibrium for the tri-layer ahead of the crack tip is described by (A.1) and (A.2) respectively. The corresponding values for the bi-layer in the crack wake are given by (A.3) and (A.4). M, the applied moment, is the same for both the bi-layer and tri-

135
layer and is equal to PL/2b, where P/2 is the applied load as depicted in Figure A.1, b is the specimen width and L is the span for 4pt-bending.

\[
\begin{align*}
\int_{-h}^{t} \sigma_{33\text{tr-st-layers}}(z)\,dz + \int_{0}^{t} \sigma_{33\text{tr-st-layers}}(z)\,dz + \int_{0}^{t} \sigma_{33\text{tr-st-layers}}(z)\,dz &= 0 \quad (A.1) \\
\int_{-h}^{t} \sigma_{33\text{tr-st-layers}}(z)z\,dz + \int_{0}^{t} \sigma_{33\text{tr-st-layers}}(z)z\,dz + \int_{0}^{t} \sigma_{33\text{tr-st-layers}}(z)z\,dz &= M \quad (A.2)
\end{align*}
\]

\[
\begin{align*}
\int_{-h}^{t} \sigma_{33\text{tr-bi-layers}}(z)\,dz + \int_{0}^{t} \sigma_{33\text{tr-bi-layers}}(z)\,dz &= 0 \quad (A.3) \\
\int_{-h}^{t} \sigma_{33\text{tr-bi-layers}}(z)z\,dz + \int_{0}^{t} \sigma_{33\text{tr-bi-layers}}(z)z\,dz &= M \quad (A.4)
\end{align*}
\]

When all layers are elastic the stress and strain distributions in each layer ahead of and behind the crack tip are related by (A.5) and (A.6), respectively:

\[
\begin{align*}
\sigma_{33,2\text{-tr-layers}}(z) &= E_{1,2,1} \epsilon_{\sigma\text{(tr-layer)}} + \kappa_{\sigma\text{(tr-layer)}}z \quad (A.5) \\
\sigma_{33,2\text{-bi-layers}}(z) &= E_{1,2} \epsilon_{\sigma\text{(bi-layer)}} + \kappa_{\sigma\text{(bi-layer)}}z \quad (A.6)
\end{align*}
\]

Where: E, \( \epsilon_{\sigma} \), and \( \kappa \) are the Young’s modulus, the strain at \( z = 0 \) (Figure A.1) and the curvature, respectively. The subscripts 1, 2, or 3 refer to the layer number. Since \( E_3 = E_1 \) an appropriate substitution was made.

Substituting (A.5) into both (A.1) and (A.2) yields (A.7) and (A.8), \( \epsilon_{\sigma} \), and \( \kappa \) for the tri-layer ahead of the crack tip. (A.9) and (A.10) are the equivalent values for the bi-layer obtained by substituting (A.6) into (A.3) and (A.4) respectively.
\[
\varepsilon_{u(\text{tri-layer})} = -\frac{6M}{E_2\gamma t^2} \\
\kappa_{(\text{tri-layer})} = \frac{12M}{E_2\gamma t^3} \\
\varepsilon_{u(\text{bi-layer})} = \frac{6M(\eta^2X - 1)}{E_2\xi t^3} \\
\kappa_{(\text{bi-layer})} = \frac{12M(\eta X + 1)}{E_2\xi t^3}
\]

Where: \( \eta = h/t, \quad X = E_1/E_2, \quad \gamma = 8\eta^3X + 12\eta^2X + 6\eta X + 1 \) and \( \xi = \eta^4X^2 + 4\eta^3X + 6\eta^2X + 4\eta X + 1 \).

Substituting (A.7) - (A.10) back into (A.5) and (A.6) gives the necessary stress distribution. Substituting these into the J-integral yields the interface energy release rate (A.11).

\[
J = \frac{E_1}{2} \int_{-h}^{0} (\varepsilon_{u(\text{bi-layer})} + \kappa_{(\text{bi-layer})}z)^2dz + \frac{E_2}{2} \int_{-h}^{0} (\varepsilon_{u(\text{bi-layer})} + \kappa_{(\text{bi-layer})}z)^2dz \\
- E_1 \int_{-h}^{0} (\varepsilon_{u(\text{tri-layer})} + \kappa_{(\text{tri-layer})}z)^2dz - \frac{E_2}{2} \int_{-h}^{0} (\varepsilon_{u(\text{tri-layer})} + \kappa_{(\text{tri-layer})}z)^2dz
\]

After considerable simplification J reduces to (A.12).

\[
\frac{JE_2t^3}{6M^2} = \left[ \frac{\eta^3X^3 + 5\eta^4X^2 + 6\eta^3X + 4\eta^2X^2 + 6\eta^2X + 5\eta X + 1}{(\eta^4X^2 + 4\eta^3X + 6\eta^2X + 4\eta X + 1)^2} \right. \\
\left. - \frac{1}{8\eta^3X + 12\eta^2X + 6\eta X + 1} \right]
\]

The preceding assumed that the cross-sectional dimensions of the beam were approximately equal. For this configuration a plane stress state is appropriate and the moduli in the preceding equation are merely equal to the Young’s moduli. As the dimensions of the
beam in the x direction increase \((b > 3(h+t))\) a plane strain state of stress develops. As such, the stresses in the x and y directions become (A.13).

\[
\sigma_{se}(z) = \frac{E_i}{1 - V_i^2}(\varepsilon_0 + \kappa z_i) = \frac{E_i}{1 - V_i^2} \varepsilon_{se}(z)
\]

\[
\sigma_{ss}(z) = \frac{E_i V_i}{1 - V_i^2} \varepsilon_{ss}(z) = V_i \sigma_{ss}(z)
\]

Substituting (A.13) into the J-integral yields the same result with the exception that \(E_i\) is replaced by the plane strain modulus \(E_i/(1 - V_i^2)\). Thus the plane strain solution is equal to the plane stress solution after making the substitution \(E_i \rightarrow E_i/(1 - V_i^2)\).

In the limit as \(t\) approaches zero the interface energy release rate converges to (A.14).

For the Al\(_2\)O\(_3\)/Ni(Cr)/Al\(_2\)O\(_3\) tri-layer with \(t = 0.25h\) the difference between the actual energy release rate and the approximation (A.14) is significant. The ratio \(J(t=0)/J(t)\) is plotted in Figure A.2. For this reason when conducting fatigue experiments on the Al\(_2\)O\(_3\)/Ni(Cr)/Al\(_2\)O\(_3\) tri-layer the full solution for \(J\) will be used.

\[
J = \frac{21M^2}{4E_i h^3}
\]  

(A.14)

Figure A.2 The ratio of the interface energy release rate for the homogeneous beam \((t=0)\) and the sandwich beam with interlayer thickness \(t\).
Appendix B

Contour Plots of Stress Fields

B.1 Development of In-Plane Stress (plane stress)

Figure B.1 contains three contour plots showing the development of in-plane stress, $\sigma_{yy}$, with temperature change $\Delta T$. Results are for Ni(Cr) with a yield strength of 330 MPa and strain hardening described by a tangent modulus of 1%E. Here contact has not been considered. In a), $\Delta T = 195^\circ$C, the Ni(Cr) is nominally elastic both far ahead of and far behind the crack tip. By b), $\Delta T = 330^\circ$C, the Ni(Cr) has nominally yielded ahead of the crack and at the interface between the lower Al$_2$O$_3$ layer and Ni(Cr). Lastly, by c), $\Delta T = 425^\circ$C, the Ni(Cr) has nearly fully yielded (nominally) both ahead of and behind the crack. Figure B.2 contains a plot of the Mises stress in the vicinity of the crack tip at $\Delta T = 425^\circ$C.

B.2 Out-of-Plane Stress ($\sigma_{xx}$) for Generalized Plane Strain and Plane Strain

The generalized plane strain and plane strain models constrain the out-of-plane deformation during heating or cooling. For plane strain this constraint is simply $\varepsilon_{xx} = \gamma_{xz} = \gamma_{xy} = 0$. For this case, all out-of-plane thermal strain (\(\alpha \Delta T\)) in both the Al$_2$O$_3$ and Ni(Cr) is suppressed and tremendous out-of-plane stress, $\sigma_{xx}$, develops, Figure B.3a.

Generalized plane strain, on the other hand, constrains the out-of-plane deformation only by applying two rigid bounding planes to the model at $x = \pm b/2$; where $b$ is an arbitrary model thickness. During heating or cooling, global out-of-plane deformation (the breathing mode) is not constrained yet stress resulting from differences in thermal properties does develop, Figure B.3b. As the bounding planes are rigid, the out-of-plane deformation both ahead of and behind the crack are linked as suggested in the figure.
Figure B.1 Evolution of $\sigma_{yy}$ with temperature in a $\text{Al}_2\text{O}_3/\text{Ni(Cr)}/\text{Al}_2\text{O}_3$ tri-layer. The Ni(Cr) has a yield strength of $\sigma_0 = 330$ MPa with 1%E strain hardening and the $\text{Al}_2\text{O}_3$ is elastic.
Figure B.2 The Mises stress at the crack tip for $\Delta T = 450^\circ C$. 
Figure B.3 Out-of-plane stress for $\Delta T = 450^\circ$C: a.) plane strain model and b.) the generalized plane strain model. In both cases $\sigma_o = 330$ MPa, $H = 1\%E$ for the plane strain results while $H = 2\%E$ for the generalized plane strain results (necessary for convergence). Note out-of-plane stresses are on the order of GPa for the plane strain model.
Appendix C

Al/Al₂O₃ Interfaces - Supplement

C.1 Liquid Phase Bonded Interfaces

This Appendix contains figures intended to supplement those presented in Chapter 5. Each figure is described by its caption.

**Figure C.1** a) An optical micrograph showing the LPB interface following removal of the top sapphire layer (FeAl₃ appears as dendrites) and b) an SEM micrograph showing fatigue crack growth within the Al.
Figure C.2 Fatigue crack growth along the high purity Al/$\text{Al}_2\text{O}_3$ interface (viewed through the sapphire). During the initial stages of growth "finger-like" cracks travel along both sides of the interface. As the crack gets longer this trend rapidly diminishes giving rise to highly planar growth.
Figure C.3 Fatigue striations observed on the surface of the high purity Al film after removal of the top sapphire layer. Striation spacings of ~ 1, 1.5, and 1.8 μm were found at locations where ΔG ~ 70, 100, and 150 Jm⁻². CTODs, based on σ₀ for 99.999% Al ~20MPa⁹ [114], are ~ 1.75, 2.5, and 3.75μm.

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9. This value is a bulk property. Results vary for thin films. If σ₀ were higher CTOD values would be more in line with the measured striation spacings.
Bibliography


[35] J. Stolken, unpublished research at UCSB.


