MICROSTRUCTURE AND FRACTURE TOUGHNESS OF
THE IN-SITU NiAl-Ni₃Al INTERMETALLIC COMPOSITES

by
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ABSTRACT

An overview of the toughening mechanisms in the intermetallic-base in-situ composites is presented. Based on the literature review and preliminary research, the two phase (β + γ) region of Ni-Al system was chosen as a model in-situ composite to study fracture toughness of the in-situ NiAl-Ni$_3$Al intermetallic composites and explore the fracture toughening mechanisms in these intermetallic materials.

The composition ranges investigated were 25-35 at.% Al for both as-solidified and as-heat-treated composites. To evaluate fracture toughness, a three point bending of Chevron-notched beam (CNB) specimens were used. The values of fracture toughness were calculated either directly from the maximum load at unstable crack propagation or by using a modified $J$-integral approach. Compressive testing was also carried out to obtain yield strength of tested in-situ intermetallic composites. Micromechanical properties of individual phases were probed by Vickers microhardness testing. The relationship between fracture toughness ($K_{h_m}$, $K_{h_c}$) and volume fraction of second phase $V_d$, in the following form: $K_{h_c}=f(V_d^3)$ has been established. Also, boron-doped (0.2 and 0.4 at.%) Ni$_3$Al was fabricated. Fracture mechanisms and boron effect on fracture toughness of the Ni$_3$Al phase were explored.

The obtained results of fracture toughness ($K_{h_m}$, $K_{h_c}$) are compared with the existing models, which describe the second phase toughening mechanisms, and rule of mixtures (ROM). Weibull analysis is also applied for the analysis of the fracture toughness distribution of the investigated Ni$_3$Al/NiAl in-situ composites.

The important features of the $K$-$\Delta a$ and $J$-$\Delta a$ curves by a CNB bend test have been explored in this research. The stress intensity factor $K$ decreases with increasing crack extension ($\Delta a$) and a PLATEAU usually appears with increasing of the crack extension only
until the critical crack extension ($\Delta a_m$), then $K$ starts to increase with increasing crack extension, forming a very special shape which can be called “HOOP HEAD”. Particularly, a critical value ($J_{ KC}$) of the fracture energy for a CNB test can be simply calculated by a horizontal line tangent to the “HOOP HEAD”.

It is shown that fracture toughness of Ni$_3$Al/NiAl increases with increasing volume fraction of Ni$_3$Al in the in-situ composites according to a general formula $K_{ K C} = 6.1 + 0.7V_d^{0.75}$ (Mpa$\sqrt{m}$) (where $V_d$ - volume % of Ni$_3$Al). In some Ni$_3$Al/NiAl composite alloys the Ni$_3$Al$_3$ fine particles are formed (so-called “mat-like structure”) which exhibits very high Vickers microhardness ($=690$ kg/mm$^2$). The significant yield strength of $=1150$ kg/mm$^2$ in the aged Ni$_{63.9}$Al$_{34.1}$ in-situ composite is also attributed to this needle-like structure of Ni$_3$Al$_3$. It is worth of pointing out that a very high yield strength ($\sigma_{YS} = 1150$MPa) is combined in aged alloys with a reasonable value of fracture toughness ($=13$ MPa$\sqrt{m}$). It indicates that such a new promising alloy can be yielded by an economic and simple casting method followed by a proper heat treatment as shown in this research.

The highest Weibull’s modulus $m = 23.8$ for Ni$_{63.7}$Al$_{36.3}$ (=17 vol.% Ni$_3$Al) indicates that this alloy is a very reliable material for engineering design even with lower fracture toughness value ($K_{Km}^{w} = 8$ MPa$\sqrt{m}$). The lowest Weibull’s modulus $m = 5.8$ for Ni$_{71.2}$Al$_{28.8}$ (=99 vol.% Ni$_3$Al) means that the fracture toughness of this alloy is highly variable and no single value for $K_{Km}^{w}$ can be assigned easily.
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DEDICATION

To

my father Jinhan Gao,
my mother Suyuan Xu,
my wife Qihua,
and my daughter Chao
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NOMENCLATURE

\( a \)  
- crack length
\( a^* \)  
- half of the maximum crack length
\( a_0 \)  
- initial crack length
\( a_t \)  
- slot length of CNB notch
\( B \)  
- thickness of CNB specimen
\( b \)  
- ligament length (uncracked length)
\( C \)  
- reciprocal of the degree of constraint on toughening particle
\( c \)  
- volume concentration of toughening particles
\( E \)  
- Young's modulus of composite
\( E' \)  
- plane strain elastic modulus of composite
\( G \)  
- fracture energy (strain energy release rate) of composite
\( h \)  
- height of process or microcrack shielding zone
\( J \)  
- values of the J-integral
\( K_c \)  
- critical stress-intensity factor of composite
\( K_{tc} \)  
- plane strain fracture toughness
\( K_d \)  
- \( K_c \) value of ductile phase
\( K_m \)  
- \( K_c \) value of matrix
\( K_r \)  
- crack growth toughness
\( K_R \)  
- K-resistance curve
\( K_i \)  
- initiation toughness
\( L \)  
- bridging length (projected crack length)
\( <l> \)  
- average length of shear ligaments
\( m \)  
- Weibull modulus

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$N$ slot width of chevron notch
$r_p$ plastic zone size
$S$ half of a single microcrack length
$S_l$ major span
$S_m$ minor span
$S_m$ average value of fracture strength of brittle matrix
$u$ crack opening
$v_p$ critical plastic value of the crack-face displacement
$V$ volume fraction
$W$ width of a specimen
$Y'$ stress intensity factor coefficient
$Y_m$ the minimum value of stress-intensity-factor coefficient

Greek Symbols
$\gamma'$ $L1_2$-ordered crystal structure Ni$_3$Al
$\beta$ $B2$-ordered crystal structure NiAl
$\alpha_l$ orientation of microcrack with respect to the stress axis
$\sigma_r$ residual stress
$\sigma_{ys}$ yield strength
$\sigma_f$ failure stress of toughening particles
$\sigma_{ym}$ yield stresses of matrix
$\sigma_{yd}$ yield stresses of ductile phase
$\sigma(u)$ nominal stress
$\sigma_d$ ultimate stress of ductile phase
$\sigma_s$ shear traction
\(\varepsilon_t\)  total dilatational strain
\(\varepsilon^*_t\)  stress-free strain
\(\varepsilon_{em}\)  effective fracture strain values of matrix
\(\varepsilon_{ed}\)  effective fracture strain values of ductile phase
\(\gamma_r\)  fracture strain in shear
\(\delta^{op}\)  crack opening displacement
\(\phi, \theta\)  crack deflection angle
\(\chi\)  dimensionless work-of-rupture parameter
\(\tau_r\)  fracture stress in shear
\(v\)  Poisson's ratio of composite
\(\lambda\)  toughening ratio

Subscripts

\(m\)  matrix
\(ms\)  microcrack shielding
\(d\)  ductile second phase
\(b\)  crack bridging
\(bl\)  crack blunting
\(el\)  elastic deformation
\(pl\)  plastic deformation
\(l\)  shear ligaments
\(I\)  opening mode

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INTRODUCTION AND LITERATURE REVIEW

Structural alloys based on the ordered intermetallic compounds such as TiAl, Ti3Al, Ni3Al, NiAl and MoSi2 have recently become potential candidate materials for several advanced high-temperature aerospace applications, primarily because of their high specific strength and stiffness which are retained at elevated temperatures exceeding 1000°C. Their structural use, however, is quite limited by low room-temperature ductility and toughness properties; in fact, most of the measured fracture strains under uniaxial tension can be as low as 1% with a fracture toughness below =10 MPa√m. Table 1.1 summarizes the fracture toughness $K_{IC}$ of selected intermetallic alloys and composites. Obviously, most of the single phase intermetallics show low values of $K_{IC}$. The low intrinsic fracture toughness of these materials has not been changed through solid solution elemental additions. A composite approach must then be considered in an effort to increase toughness [1].

These intermetallic compounds closest to commercial utilization, such as Ti3Al, TiAl as
Table 1.1  Room temperature fracture toughness $K_c$ of selected intermetallic alloys and composites.

<table>
<thead>
<tr>
<th>Type of material</th>
<th>Name of material and processing technique</th>
<th>Crystallographic structure</th>
<th>Fracture toughness $K_c$ or $K_O$ (MPa$m^{-1}$)</th>
<th>Refs.</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Single Phase</strong></td>
<td>NiAl [001] (Single crystal)</td>
<td>B2 (CsCl)</td>
<td>10</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>NiAl [011] (Single crystal)</td>
<td>B2 (CsCl)</td>
<td>6</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>NiAl (Power processed)</td>
<td>B2 (CsCl)</td>
<td>2.7-3.8</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td>NiAl (Extruded cast ingot)</td>
<td>B2 (CsCl)</td>
<td>5.4-5.9</td>
<td>4</td>
</tr>
<tr>
<td></td>
<td>Ti$_3$Si$_3$</td>
<td>D8$_8$</td>
<td>2</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td>MoSi$_2$</td>
<td>C11b</td>
<td>4</td>
<td>6</td>
</tr>
<tr>
<td></td>
<td>MoSi$_2$</td>
<td>C11b</td>
<td>4.6</td>
<td>7</td>
</tr>
<tr>
<td></td>
<td>Al$<em>{66}$Ti$</em>{53}$Mn$_8$</td>
<td>L1$_2$</td>
<td>3.5</td>
<td>8</td>
</tr>
<tr>
<td></td>
<td>Al$<em>{66}$Ti$</em>{32}$Cr$_6$</td>
<td>L1$_2$</td>
<td>3.5</td>
<td>8</td>
</tr>
<tr>
<td></td>
<td>Ti$<em>{56}$Al$</em>{27}$Nb$_{15}$</td>
<td>DO$_{19}$</td>
<td>20</td>
<td>9</td>
</tr>
<tr>
<td></td>
<td>Nb$_3$Al</td>
<td>A15</td>
<td>1.1</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td>NiAl+5Nb</td>
<td>B2 + ?</td>
<td>12-2-15.4</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td>NiAl+5Ti</td>
<td>B2 + ?</td>
<td>4.7-14.5</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td>Ti$_3$Si$_3$/Ti$_3$Al</td>
<td>D8$<em>8$+DO$</em>{19}$</td>
<td>12</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td>TiAl$_{52}$</td>
<td>L1$<em>2$+DO$</em>{19}$</td>
<td>10</td>
<td>11</td>
</tr>
<tr>
<td></td>
<td>TiAl$_{18}$ (As-extruded)</td>
<td>L1$<em>2$+DO$</em>{19}$</td>
<td>15</td>
<td>7</td>
</tr>
<tr>
<td></td>
<td>TiAl$_{18}$ (Electrode arc melting)</td>
<td>L1$<em>2$+DO$</em>{19}$</td>
<td>30 $(K_O)$</td>
<td>12</td>
</tr>
<tr>
<td></td>
<td>TiAl$_{18}$/$\beta$Ti, Nb</td>
<td>(L1$<em>2$+DO$</em>{19}$)+20 vol.% $\beta$Ti, Nb</td>
<td>20</td>
<td>7</td>
</tr>
<tr>
<td></td>
<td>MoSi$_2$/Nb</td>
<td>C11b+20 vol.% Nb</td>
<td>5.7</td>
<td>7</td>
</tr>
<tr>
<td></td>
<td>Ti$<em>{56}$Al$</em>{27}$Nb$_{20}$</td>
<td>DO$_{19}$+20 vol.% $\beta$ (B2)</td>
<td>44 $(K_O)$?</td>
<td>9</td>
</tr>
<tr>
<td></td>
<td>Ti$<em>{56}$Al$</em>{27}$Nb$_{15}$</td>
<td>DO$_{19}$+70 vol.% $\beta$ (B2)</td>
<td>26 $(K_O)$?</td>
<td>9</td>
</tr>
<tr>
<td></td>
<td>Nb$_3$Al/Nb</td>
<td>A15+40 vol.%NB</td>
<td>6.5</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td>NiAl/TiB$_2$ (Particulate)</td>
<td>B2+20 vol.% TiB$_2$</td>
<td>6</td>
<td>13</td>
</tr>
<tr>
<td></td>
<td>NiAl/Al$_2$O$_3$</td>
<td>B2+15-25 vol.% Al$_2$O$_3$</td>
<td>9</td>
<td>14</td>
</tr>
</tbody>
</table>
well as Ni$_3$Al, are actually multi-component systems rather than single phases, with highly refined microstructures consisting of a majority strong and sometimes brittle intermetallic phase, in close association with possibly a more ductile phase [1].

These intermetallic compounds closest to commercial utilization, such as Ti$_3$Al, TiAl as well as Ni$_3$Al, are actually multi-component systems rather than single phases, with highly refined microstructures consisting of a majority strong and sometimes brittle intermetallic phase, in close association with possibly a more ductile phase. This is similar to pearlite, the eutectoid microstructure developed between cementite, Fe$_3$C, and ferrite, a microstructure common in many plain carbon steels and known for its toughness. Multiphase systems such as these can be considered composites, since the two constituent phases usually have differing moduli, thermal expansion and ductility. This realization leads to define the term COMPOSITE, which in the present context will not be straightforward. For our purposes, a composite will be defined as:

*any material with multi-component structure for which the phases are manipulated in geometry or volume fraction so as to obtain a desired mix of mechanical properties [1].*

Under this broad definition, many practical engineering materials such as titanium and nickel alloys would be defined as composites. We must make this definition, because for intermetallic based materials to become useful, their properties, especially toughness, will need to be enhanced through the proper manipulation of either artificially manufactured composites
in which particles, whiskers or fibres are added, or through natural or in-situ composites in which the reinforcement can be introduced via either solidification or solid state precipitation. Provided that the phase diagram is well understood, directional solidification and/or various thermomechanical treatments can be used to separate and align the reinforcement into the desired geometry. An in-situ intermetallic composite is then obtained. Additional advantage is that these composites are thermodynamically stable. The in-situ intermetallic composites are limited in their constituents by the phase diagrams, which may limit reinforcement volume fraction, chemistry and morphology [1].

Increases in toughness observed in many multiphase intermetallic composites, including the in-situ ones, are shown in Table 1.1. As mentioned by Ashby [15], a value of $K_{ic}=20$ MPa$\sqrt{m}$ is often quoted as a minimum for conventional design. Also, Jackson et al. [16] stated that a working hypothesis has been offered that once a material exceeds a threshold of $=20$ MPa$\sqrt{m}$. toughness in the make-and-assemble stages is not a major issue. This threshold may eventually be relaxed as further experience is gained. Therefore, an important goal is optimising the structure of many intermetallic alloys to obtain the values of $K_{ic}$ at least about 20 MPa$\sqrt{m}$, if not better. However, in order to achieve this objective a clear understanding of underlying physical mechanisms of second phase toughening and their description in terms of micromechanical models are urgently needed.
1.1 Mechanisms and Micro-Mechanical Modelling of Toughness Improvements in the In-Situ Intermetallic Composites

An overview of the second phase toughening in the in-situ intermetallic composites is presented. The existing models of the second phase toughening of brittle matrix composites such as crack-tip blunting, crack trapping, crack bridging and so on are discussed with the emphasis on their application for the in-situ intermetallic composites. A comparison of available experimental data on fracture toughness of the in-situ intermetallic composites with the theoretical models of fracture toughness enhancement by the second phase toughening is presented.

As discussed before, an in-situ composite is any alloy with multi-component structure for which the phases are separated naturally according to the pertinent phase diagram by solidification, precipitation and/or thermomechanical treatment. In the in-situ composites, macrostructural toughening usually involves the incorporation of a ductile second phase in a brittle matrix. The purpose of the ductile phase is to interact with the progression of cracks through the matrix phase. The ductile second phase can take the form of isolated particles, interpenetrating networks or continuous phases such as lamellae or fibres. While the degree of toughening is generally dependent on the volume fraction and morphology of the second phase, the actual characteristics of the ductile phase that will generate optimum toughness have not
yet been adequately established or modelled. The objective of this section is to present the state-of-the-art in the understanding of relationships between microstructure, toughening mechanism, and fracture resistance. To develop microstructure/toughness relationships, important micromechanical variables affecting fracture resistance are elucidated using micromechanical models.

In general, toughening mechanisms in the in-situ intermetallic composites can be considered either as intrinsic or extrinsic [17-20]. The intrinsic mechanisms, which mainly include crack-tip blunting by a ductile phase [18, 21-27], crack-front trapping [28-30], microcracking renucleation [29, 31-32] and interface delamination (debonding) [32-37], as shown in Figures 1.1a, b, c and d, originate from properties of the constituents [23] and improve the inherent fracture toughness of the material, thereafter enhance the initiation toughness, $K_i$, as shown in Figure 1.2. The term initiation toughness $K_i$ refers to the critical stress intensity at the onset of stable crack growth; it is customarily referred to as the $K_{ic}$ value when the plane strain condition prevails [17-18, 20]. For the purpose of this work the $K_i$ parameter will be later in the text designated $K_{ic}$ assuming that a valid, plane strain test is performed to assess fracture toughness of the in-situ composite. The extrinsic mechanisms, which mainly include crack bridging by a ductile phase [38-47], process zone toughening [48, 49], shear ligament toughening [18, 20, 23, 50-51], crack deflection [18, 36, 52-55] and microcrack shielding [18, 23, 48, 49] as shown in Figures 1.1e, f, g, h and i, impede crack opening in the material and improve fracture resistance by lowering the stress intensity levels in the wake of crack-tip, thereafter affect the crack growth toughness, $K_c$, by inducing a rising
Figure 1.1 Schematic illustration of the possible intrinsic (a to d) and extrinsic (e to i) mechanisms for enhancing the toughness of brittle materials through the addition of a ductile phase [17, 32, 42].
crack-growth resistance curve as shown by a rising solid line in Figure 1.2. The term crack growth toughness $K_r$ is defined as the maximum value of the $K$-resistance, $K_R$, curve at the onset of unstable fracture.

The $K_R$ curve for the single-phase matrix is a lower dotted line with a zero slope (as shown
In this thesis, \( K_m \) designates the fracture toughness \( K_{fc} \) of the matrix. The two-phase intermetallic alloys and composites shows higher toughness than the single-phase matrix because both the initiation and crack growth toughness can be enhanced by the presence of a ductile phase in the microstructure. This fact is supported by many experiments. A typical example was shown by Rigney et al. [56] from the experiments on \( \text{Nb}_2\text{Si}_3/\text{Nb} \) particulate composites compared with the monolithic \( \text{Nb}_2\text{Si}_3 \) (Figure 1.3). The mechanisms by which toughening is achieved and the amount of enhancement, however, vary with the morphology, volume fraction, size, and work-of-fracture of the ductile phase, as well as properties of the interface. The various processes by which toughness can be imparted in brittle intermetallic via the use of a ductile phase are elaborated and modelled as follows.

![Graph showing comparison of toughness between Nb2Si3/Nb and Nb2Si3 particulate composites.](image)

**Figure 1.3** Comparison of \( K \)-resistance curves of \( \text{Nb}_2\text{Si}_3/\text{Nb} \) in-situ composite and the matrix \( \text{Ni}_2\text{Si}_3 \) [17, 56].
1.1.1 Superposition of Toughening Mechanisms

It is interesting to be noted in Figure 1.2 that intrinsic toughening mechanism affect the initiation fracture toughness only, i.e. $K_e$ value [18]. This effect is expressed by Chan [18] by a so-called overall toughening ratio [18]:

$$\lambda = \frac{K_i (\equiv K_\infty \equiv K_{applied})}{K_m} \quad (1.1)$$

In addition, extrinsic toughening mechanisms affect the resistance curve behaviour, e.g. $K_r$ in Figure 1.2. They should not have impact on $K_e$ and $J_e$ [18]. However, in some cases such extrinsic mechanisms as microcrack shielding and crack deflection can also lead to increase in the initiation toughness ($K_{ic}$) value, depending on whether or not a deflected crack tip and shielding microcrack exist prior to crack growth [18].

The main intrinsic and extrinsic mechanisms and their models of ductile dispersion toughening in-situ composites have been discussed separately in Sections 1.1.2 and 1.1.3, respectively. In fact, a few mechanisms (usually, not all of the above mechanisms as shown in Figure 1.1) will always occur in the same material. However, the method to predict the combined effects of multiple toughening mechanisms is still not well established so far. Some selected work on this topic will be presented as follows.
Simple Multiplication

According to Chan [18] the overall toughening ratio for $K_c$ can be calculated theoretically from the following equation (Eq.1.1) [18]:

$$\lambda_c = \lambda_{d} \cdot \lambda_{ms} \cdot \lambda_{b}$$  \hspace{1cm} (1.2)

where $\lambda_{d}$, $\lambda_{ms}$ and $\lambda_{b}$ are toughening ratios for crack deflection, microcrack shielding and crack blunting, respectively. Notice that the summation (multiplication) above is only for those $\lambda$ ratios which increase $K_c$.

Soboyejo et al [7, 54] also proposed that the principle of superposition can be applied to predict the toughening combinations of crack bridging and crack deflection by a simple multiplication of the toughening ratios:

$$K_{lc} = \lambda_{b} \lambda_{d} K_{m}$$  \hspace{1cm} (1.3)

where $\lambda_{b}$ and $\lambda_{d}$ are toughening ratios of crack bridging and deflection, respectively. However, $Eq.(1.3)$ seems to be erroneous because crack bridging, a typical extrinsic mechanism, can not affect $K_c$.

Simple Addition

Another superposition model was suggested by Enoki and Kishi [57]. They [57] considered microfracture process for both fully lamellar and duplex TiAl and found
microcracks and subsequent shear ligament formation from the observations and acoustic emission studies. Instead of a simple multiplication such as in Eq.(1.2), they consider the effects of microcrack shielding and shear ligament mechanisms as a simple addition [57]

\[ K_{fc} = K_m + \Delta K_c + \Delta K_l \]  

(1.4)

where \( \Delta K_c \) and \( \Delta K_l \) are the contributions of microcracking and shear ligaments, respectively. But these two are extrinsic and are responsible for \( K_R \) curve behaviour. Therefore, the correct toughness in Eq.(1.4) is \( K_n \) rather than \( K_{fc} \). Simple addition is good for intrinsic toughening mechanisms plus "microcrack shielding" and "deflection" eventually but extrinsic toughening cannot be additive to \( K_m \) as to get \( K_{fc} \).

So far, there is no standard method available for synthesizing the toughening combinations of several mechanisms in an in-situ composite.

### 1.1.2 Intrinsic Mechanisms

As mentioned above, this type of ductile-phase toughening is expected to improve the initial toughness \( K_i \) of in-situ composites when crack extension commences. It is possible to categorize the typical mechanisms of intrinsic toughening into several distinct classes as follows.

**Crack-Tip Blunting**

Crack-tip blunting as shown in Figure 1.1a occurs when the propagation of a crack tip is
impeded as it intersects a ductile particle with a well-bonded interface. Extensive localized plastic deformation by dislocation movement of the second phase causes the stresses at the crack tip to relax sufficiently to blunt the crack and in the ideal case will prevent the crack from propagating further. The crack tip is shielded from the external load. A second phase material with a low yield strength will tend to maximize this effect [17-18, 21-24]. Toughness enhancement resulting from crack-tip blunting by a ductile phase has been modelled by Chan [17-18, 21-23] using the Hutchinson, Rice and Rosengren (HRR) crack tip field [25-27]. In the HRR-field, the near-tip strains are quite large and it is assumed that the yield stress and effective strain of the two-phase microstructure are related to the corresponding properties of the constituent phases according to the rule of mixtures (for a detailed description, see Appendix A). Therefore, initiation of crack growth in ductile alloys can generally be considered in terms of a critical strain criterion, which assumes that fracture occurs when the strain at a characteristic distance from the crack tip exceeds a critical value.

To model this mechanism, the initiation fracture toughness, \( K_i \), of a two-phase microstructure consisting of a brittle matrix (m), and a ductile phase (d), can be given by [17-18, 21-23]:

\[
\lambda_b = \frac{K_i}{K_m} = \left(1 + V_d (\Sigma - I)^{n+1/2} \right) \left(1 + V_d (\Lambda - I)^{n+1/2} \right) \left(1 + V_d \frac{E_e}{E_m} \right)^{n+1/2}
\]  

(1.5)

with

\[
\Sigma = \frac{\sigma_{yd}}{\sigma_{ym}} \quad \text{(1.6)}
\]

\[
\Lambda = \frac{\varepsilon_{yd}}{\varepsilon_{ym}} \quad \text{(1.7)}
\]
where $K_m$ is the $K_{fc}$ value of the matrix. $V_d$ is the volume fraction of ductile phase. $e_m$ and $e_{pd}$ are effective fracture strain values of matrix and ductile phases, $\sigma_y$ and $\sigma_{yd}$ are their yield stresses, $n$ is the inverse of the strain hardening exponent, $E$ and $E_m$ are elastic moduli of the composite and matrix, respectively.

It is interesting to be noted that the initial fracture toughness $K_i$ increases with the volume fraction of ductile phase $V_d$ generally in a nonlinear fashion for this mechanism. Furthermore, this model remains valid for both continuous or discontinuous ductile phases [18].

As a typical example in experimental research on this mechanism, Chan [18, 23] has identified crack-tip blunting from the toughening mechanisms in the Ti-24Al-11Nb in-situ composites as shown in Figure 1.4.

![Composite in situ scanning electron micrographs](image)

**Figure 1.4** Composite in situ scanning electron micrographs show that the near-tip fracture process in the coarse basketweave microstructure at 25°C is characterized by blunting of the tips of main crack and the microcracks by continuous ductile phase (light phase, β-Ti). The volume fraction of is 39% [23].
Crack-Front Trapping

Crack-front trapping occurs when the crack front interacts with higher toughness reinforcements, requiring the crack to penetrate between the reinforcements. It is most pertinent when the brittle phase is continuous and the ductile particles take the form of rods or spheroids [17, 28]. When a straight crack intersects a row of tough particles, part of the crack front can bow out and loop around the particles as shown in **Figure 1.1b**. The increased crack curvature increases the local stress intensity factor and can lead to fracture of the ductile particles without the formation of bridging particles in the crack wake if the ratio of ductile-phase toughness ($K_d$) to matrix toughness ($K_m$) is less than three [28]. If $K_d$ is considerably greater than $K_m$, intact particles are left in the crack wake by the looping process, which can lead to an additional toughening by crack bridging. The corresponding initiation toughness, $K_i$, attainable from the crack trapping mechanism, is given by [17, 28],

$$
\lambda_I = \frac{K_i}{K_m} = \left(1 + \alpha_I V_d \left(\frac{K_d}{K_m}\right)^2 - 1\right)^{1/2}
$$

(1.8)

where $K_m$ and $K_d$ are the $K_i$ values for the matrix and ductile phase, respectively. $\alpha_I$ is a constant having values of 1 and 1.74 for average and maximum toughening by crack trapping, respectively [17, 28].

It is apparent that the only important variable affecting the initial toughness $K_i$ in crack-front trapping is the volume fraction of ductile phase, $V_d$, which is summarized in **Figure 1.5**.
Figure 1.5 Predictions of the influence of crack trapping on the initiation toughness ratio [29].

Figure 1.6 Comparison of measured and predicted toughness of a brittle matrix reinforced by tough particles [28].
The excellent agreement of measured and predicted toughness of a brittle matrix reinforced by tough particles has been obtained by Bower and Ortiz [28], and Krstic et al. [30] for the toughness of glass reinforced by partially oxidized aluminium particles as shown in Figure 1.6.

As an example, a typical experimental picture of crack-front trapping is also given in Figure 1.7.

![Figure 1.7](image)

**Figure 1.7** Higher-resolution SEM views of the fracture surface of the NiAl/Mo indicating characteristic crack trapping "tails" in the NiAl [29].
Microcrack Renucleation

In a layered in-situ composite as shown in Figure 1.1c, the crack front cannot loop around the ductile phase with well-bonded interface. Consequently, a crack renucleation phenomenon must occur before crack growth proceed [29]. The initiation toughness can be determined by the renucleation of microcrack in the matrix ahead of the main crack [17]. Shaw et al. [31] investigated metal/ceramic multilayers and suggested that for composites with thick brittle matrix layers, the corresponding initiation toughness, $K_i$, can be estimated from

$$K_i = S_m (2\pi h_d)^{1/2}$$

(1.9)

where $S_m$ and $h_d$ are the average value of the fracture strength of the brittle matrix and the thickness of the ductile layer as shown in Figure 1.8, respectively.

| Figure 1.8 | Schematic illustrating the crack geometry and the parameters measured from the multilayered alumina/copper and alumina/aluminum composites [31]. |
Crack-Tip Interface Delamination

Any second phase that is weakly bonded to the matrix has the potential to increase the toughness of the system through crack tip-interface debonding or splitting process [32-37]. As illustrated in Figure 1.1d, when a crack encounters a planar interface, slip and debonding along the interface can cause a stress redistribution that is favourable for initiation toughness enhancement. This stress redistribution produces three important effects [17]:

(1) the triaxial stresses near the crack tip are lowered;

(2) a diffuse microcrack zone is created by enlarging the process zone size;

(3) intact ligaments are generated between the main crack and the microcracks. These processes also increase the fracture resistance by crack bridging or ligament toughening as discussed later.

Unfortunately, there is no a quantitative model available to elucidate microstructure/toughness relationships so far. Even though, crack-tip stress analyses have shown that crack-tip interface debonding significantly reduces the normal stresses near the crack tip and shifts the peak stress away from the crack tip as mentioned above [32-36]. In addition, Deve et al. [37] also found that the work of fracture exhibits a linear dependence on the debond length for the TiAl/Nb laminate composite. As discussed by Anderson [38], a sufficient debonding is a necessary precursor for a subsequent crack bridging.

Figure 1.9 shows a selected instance of crack-interface-debonding mechanism from NiAl/Mo in-situ composite.
1.1.3 Extrinsic Mechanisms

Extrinsic in nature, this type of ductile-phase toughening affects the crack growth toughness $K$, by inducing a rising resistance curve behaviour through the formation of bridged zone and process zone in crack wake or a deflected or tortuous crack path located ahead of the dominant crack tip (e.g., shear ligaments can form as the result of mismatched planes of microcracks). The typical modelling and mechanisms will be summarized in the following sections.
Crack Bridging

The presence of intact ductile particles in the crack wake can significantly increase the fracture resistance of the composite by crack bridging as shown in Figure 1.1e. The mechanics of crack bridging by ductile phase particles are well developed. There are two kinds of popular models available. The earlier ones are spring models proposed by Budiansky et al. [39] and Elliott et al. [40]. The others are energy models suggested by Ashby et al. [41], Mataga [42], and Flinn et al. [43].

Spring Models

The mechanics of ductile-phase toughening have been analyzed by Budiansky et al. [39] by treating the bridging particles as elastic, elastic/perfectly plastic, or rigid/perfectly plastic springs as shown in Figure 1.10. Based on the J-integral approach, Budiansky et al. [39] established a model for the elastic/perfectly plastic case, which is identical to the rigid/perfectly plastic case. as follows

$$\lambda_b = \frac{K_r}{K_m} = [\omega (1 - C) + \frac{2CE\sigma_d \delta}{K_m (1 - \nu^2)}]^{1/2} \quad (1.10)$$

with

$$\omega = \frac{E(1 - \nu^2)}{E_m (1 - \nu^2)} \quad (1.11)$$
Eq.(1.10) increases with increasing of the square root of $V_d$ and the crack opening as fracture resistance $K_r$ of a particulate composite containing a concentration, $C$, of ductile particles subjected to an ultimate stress $\sigma_u$. In Eq.(1.10), $C$ is equivalent to volume fraction of ductile phase, $V_d$. Therefore, it is evident that $K_r$, from displacement, $\delta^{\text{tr}}$, as shown in Figure 1.10b.
Furthermore, based on the $J$-integral approach, the first term within the bracket in Eq.(1.10) is the contribution of the matrix to the overall strain energy release rate of the particle-reinforced composite, while the second term is the contribution due to the plastic work consumed in fracture of the ductile particles in the bridging zone.

Based on stress intensity factor approach, Budiansky et al. [39] also gave an alternative expression for this spring model,

$$\lambda_b = \frac{K_r}{K_m} = 1 + 2\sigma_d \left(\frac{2L}{\pi}\right)^{1/2}$$

(1.12)

which indicates that the fracture resistance $K_r$ caused by crack bridging is proportional to $L^{1/2}$. where $L$ is the length of the bridged zone as shown in Figure 1.10.

Obviously, a very important factor, volume fraction of ductile phase ($V_d$), in the composite was not considered in Eq.(1.12), which definitely limits its application. Therefore, Elliott et al. [40], Chan [18] and Soboyejo et al. [7, 54] modified Eq.(1.12) as,

$$\lambda_b = \frac{K_r}{K_m} = 1 + B V_d \sigma_d L^{1/2}$$

(1.13)

where, $B$ is a constant for this model of crack bridging. $B$ is equal to $2\sqrt{2/\pi} = 0.9$ in Ref.[7, 18, 54]. However, $B$ was also chosen as 1.9 depending on crack geometry by Elliott et al. [40], the reason being not clear.
Energy Model

Relatively ductile particles, when strongly bonded to the brittle matrix, undergo extensive stretching in the crack wake (Figure 1.11) until they fracture or decohere. The work of stretching contributes to the overall toughness of the solid. The crack growth energy in the composite, \( \Delta G_n \), is directly related to the nominal stress, \( \sigma(\dot{u}) \), carried by the stretching particle.

Figure 1.11 A crack in a brittle matrix, intersected by ductile particles. The particles stretch and fail as the crack opens. The work of stretching contributes to the fracture energy of the composite [41-42].
for a given crack opening, $u$ \[41-42\]

$$\Delta G_r = V_d \int_0^{u^*} \sigma (u) du$$  \hspace{1cm} (1.14)

where $V_d$ is the area-fraction of ductile particles intercepted by the crack and $u^*$ is the total crack opening when the ductile particle fails (Figure 1.11). Both theoretical considerations and model experiments on the glass matrix (brittle)/lead wire (ductile) composites [41] have shown that the crack growth energy due to crack bridging, $\Delta G_r$, over that of the matrix is given by:

$$\Delta G_r = \chi V_d a_0 \sigma_{YS}$$  \hspace{1cm} (1.15)

or using for the plane stress $\Delta K_r = (E\Delta G_r)^{1/2}$

$$\Delta K_r = [\chi a_0 E \sigma_{YS} V_d]^{1/2}$$  \hspace{1cm} (1.16)

where $a_0$ is radius of a spherical second-phase as shown in Figure 1.11 or simply representative microstructural dimension (e.g., lamellar thickness of ductile phase if it is in the lamellar morphology) [44]. The parameter $\chi$ is a dimensionless work-of-rupture parameter which is given by [41, 42]

$$\chi = \int_0^{u^*/a_0} \frac{\sigma (u)}{\sigma_{YS}} \frac{d(u/a_0)}{a_0}$$  \hspace{1cm} (1.17)

$\chi$ depends on interfacial debonding, the reinforcement ductility and the work hardening coefficient. Experimental studies and calculations have indicated that $\chi$ can vary from 0.3 to 8 corresponding to either well-bonded (debonding length, $d=0$) interface or poor-bonded
interface [43-47]. For example, Ashby et al. [41] suggested 1.6 to 6 and Bencher et al. [44] used 2.7 for well-bonded interface, Sun and Yeomans [45] show 0.3 to 1 for well-bonded interface and ductile ligaments that fail by necking to a point.

For plain strain condition elastic modulus in Eq.(1.16) should be modified by factor (1-ν²) where ν is Poisson's ratio of composite. It is interesting to note that Eq.(1.16) suggests a linear relationship between the fracture resistance $K_c$ caused by crack bridging and the square root of ductile-phase volume fraction, $V_d^{1/2}$.

An evidence of crack-bridging zone in an experimental observation is shown in Figure 1.12.

![SEM micrograph of the crack profile in the laminar Nb$_3$Al/Nb composite microstructure under monotonic loading, showing crack bridging by the ductile Nb phase in the crack wake [43].]
Process Zone (Transformation) Toughening

Particles intercepted by the crack, when bonded to the matrix, exhibit extensive plastic stretching in the crack wake as shown in Figures 1.9 and 1.12, and contribute to the toughness by inhibiting crack opening. When such a bridging zone exist, residual stress present in the composite, caused by thermal expansion mismatch, can also contribute to the toughness by means of its influence on the initial crack opening force. Simultaneously, plastic straining of particles in a process zone causes crack shielding. Toughening by crack shielding in the process zone (Figure 1.11) is fundamentally governed by a critical stress for the onset of nonlinearity, \( \sigma_c \), in elements near the crack tip and by the total dilatational strain, \( \varepsilon_t \) [36, 48]. The resulting stress-strain hysteresis of those elements within a process zone then yields fracture-resistance energy given by [36, 48]

\[
G_r = 2 V_d h \sigma_c \varepsilon_t
\]

(1.18)

where \( h \) the process-zone height in steady state (Figure 1.11). Transformation and twin toughening mainly fall into the category of process zone toughening because they are all based on the same simplifying assumption and provide equivalent predictions [36, 48]. Recalling that, \( K^2(1-v^2)/E=G \), it has been demonstrated that \( G_r \) given by Eq.(1.18) is identical to \( K_r \) predicted by the transformation model [48]

\[
K_r = 0.22 E V_d \varepsilon_t h^{1/2}/(1-v)
\]

(1.19)

Sigl et al. [49] also included plastic straining of particles in the process zone as contributing
to the crack tip shielding when particles are very small and have low yield strength. However, the contribution from the latter mechanism usually does not seem to be substantial [49].

It is evident that this mechanism behaves much close relationship with crack bridging because they always occur simultaneously in an in-situ composite toughened by a ductile phase because the bridging zone is always surrounded by a process zone when a crack occurs.

Shear Ligament Toughening

Shear ligament toughening is a process that has been recently identified in both Ti₃Al- and TiAl-base titanium aluminides and used to explain roughness-induced toughness in these alloys [17-18, 23, 50-51]. The toughening mechanism results from deflection of the main crack from the mode I path and the formation of mismatched microcracks ahead of the crack tip. As the main crack zigzags between grains, the angle of deflection and the plane of microcracking are likely to be different among individual grains. As shown schematically in Figure 1.1g, the consequence is that the crack planes in the various grains are unconnected at either grain or phase boundaries and are separated by ligaments, which undergo shear deformation.

A theoretical model of shear ligament toughening is based on an energy balance given by [50, 51]

\[ J_r = J_n + J_l = J_m + \tau_i \gamma_l < l > V_i \]  

(1.20)

where \( J_n, J_m \) and \( J_l \) are the values of the \( J \)-integral supplied by the remote load, exited in the
matrix, and dissipated by the shear ligaments, respectively. \( V_i \) and \( <l> \) are the volume fraction and average length of the shear ligaments \( (=\rho+(L/l)\tan\phi) \), where \( L \) is the projected crack length and \( \phi \) is the crack deflection angle as shown in Figure 1.13, respectively. \( \tau_i \) and \( \gamma_i \) are fracture stress and fracture strain in shear, respectively. Recalling that, \( K^2(1-\nu^2)/E=J \), the fracture resistance \( K_r \) achieved by the crack-wake shear ligaments can be described by [17, 50-51]

\[
K_r = \left[ \frac{E K_m^2}{E_m} + \frac{V_i <l> E \tau_i \gamma_i}{1-\nu^2} \right]^{1/2}
\]  

(1.21)

where \( K_r=K_m \) when shear ligaments are absent \( (V_i=0) \). In other words, the second term in Eq.(1.21) is the contribution of the shear ligament toughening \( (K_i) \). This model indicates that the amount of toughening achieved, increases with the square root of volume fraction, \( V_i \), and the average length, \( <l> \), of the shear ligaments in the crack wake.

Evidence for the formation of shear ligaments by mismatched crack planes is presented in Figure 1.13. Fracture of the shear ligaments requires additional plastic dissipation leading to a tortuous crack path and a resistance-curve behaviour.
Figure 1.13 Composite figures showing the process by which shear ligament toughening occurs in an in-situ composite (Ti-24Al-11Nb) with an equiaxed $\alpha_2 + \beta$ (the lighter phase in (a)): (a) SEM micrograph and (b) a sketch of the ligaments [50].
**Crack Deflection**

The crack is redirected during the deflection process in such a way that the stress intensity at the crack tip becomes significantly reduced or diminished [18, 36, 52-55]. The toughening by crack deflection is the result of a reduction in the local stress intensity factor when a crack deviates from its original path. For a mode I crack that deviates from a straight path by a deflection angle \( \theta \) as shown in **Figure 1.1h**, the fracture resistance \( K_r \) can be assessed [53]:

\[
K_r = \frac{K_m}{\cos^2(\theta / 2)}
\]

(1.22)

where \( \theta \) is the deflection angle in the model analyzed by Suresh [53] as shown in **Figure 1.1h**. Eq.(1.22) was expressed as \( \lambda = K_r/K_m = \cos^2(\theta/2) \) by Soboyejo et al. [55] only if crack deflection increases \( K_m \), i.e. the crack pre-exists as deflection.

**Figure 1.14** shows that the calculated values of the toughening ratio increase with increasing values of the crack deflection angle. Most of the toughening effect occurs at a relatively large deflection angle, however. For example, a 60° angle is required for a 25% increase in the toughness value.

Crack deflection toughening can also be related to the shear ligament toughening identified in both Ti₃Al- and TiAl-base titanium aluminides by Chan [18, 23]. Deflection of the main crack from the mode I path leads to the formation of mismatched microcracks in the grains ahead of the crack tip separated by shear ligaments.
Microcrack Shielding

Microcracks are generally, widely separated and located either ahead of or in wake of the tip of the main crack as shown in Figure 1.14. One approach to assess microcrack shielding given by Chan [18] follows the one proposed by Rose [58]

\[ K_f^p = \sigma_f^p (2\pi R)^{1/2} f_1(S, R, \theta, \alpha, \sigma_f^p) \] (1.23)
where $\sigma_i$ is a shear traction. $S$ is half of a single microcrack length located at a distance $R$ and angle $\theta$ from the tip of the main crack. $\alpha$ is the orientation of the microcrack with respect to the stress axis and $f(s, R, \theta, \alpha, \sigma)$ are complicated mathematics expressions that are given in Rose's article [58].

Furthermore, microcrack interaction with the main crack generally leads a toughening ratio, $\lambda_{ms}$, as following expression [18]:

$$
\lambda_{ms} = \frac{K_i}{K_{ms}} = \frac{K_i}{[(K_i + K_i^p)^2 + (K_i^p)^2]^{1/2}}
$$

but this is correct only if the shielding effect is from a single or two symmetrically disposed secondary cracks in the vicinity of the principal crack tip.

Second approach is given by Evans and Cannon [48] in the following form,

$$
K_r = 1.12(1 + \nu)\sigma R V_{ms} h^{1/2}
$$

where $\nu$ is Poisson's ratio, $\sigma_R$ is the residual stress, $V_{ms}$ is the volume fraction of microcracked grains in the micro shielding zone and $h$ is the height of microcrack shielding zone as shown in Figure 1.1i.

Figure 1.15 shows the formation of microcracks in Ti-24Al-11Nb in-situ composites [18]. It is interesting to be noted that the number and length increase with increasing $K$ levels and crack extension.
Figure 1.15 Composite in situ SEM micrographs show that the near-tip fracture process in the coarse basketweave microstructure at 600°C is characterized by the formation of the microcracks whose number and length increase with increasing $K$ levels and crack extension [18].
1.1.4 Rule of Mixtures (ROM)

Recently, the rule of mixtures for fracture toughness in a composite has been proposed by Davidson et al. [61-62], Krstic [59], Budiansky et al. [39], Flinn et al. [43], Ravichandran [60] and Soboyejo et al. [7, 54].

By analogy with the upper bound of elastic modulus of a composite as shown in Figure 1.16b, Davidson et al. [61-62] suggested a rule of mixtures (ROM) as a straight line (Figure)

![Diagram](image)

**Figure 1.16** For a given density, there exist two values of modulus: an upper bound and a lower bound [63].
1.17) to connect the two points of \((K_{ic})_m\) and \((K_{ic})_d\), which were obtained from the experimental results of the Cr₂Nb-containing the Nb-Cr₂Nb in-situ composites. The straight line is simply mathematically expressed as:

\[
K_{ic} = (1 - V_d) K_m + V_d K_d
\]  \hspace{1cm} (1.26)

where \(V_d\) is volume fraction of ductile phase. As shown in Figure 1.16, all the experimental fracture toughness values of the in-situ composites are lower than the straight line. This fact indicates that the presence of brittle Cr₂Nb in the Nb-Cr₂Nb in-situ composites reduces the fracture toughness of the in-situ composite significantly.

Krstic [59], Budiansky et al. [39], Flinn et al. [43], Ravichandran [60] and Soboyejo et al. [7, 54] used an E-modified rule of mixtures (\(E-ROM\)) for fracture toughness of an in-situ composite. They [7, 39, 43, 54, 59, 60] proposed that fracture energy \(G_{ic}\), i.e., critical strain energy release rate of an in-situ composite can be expressed as:

\[
G_{ic} = (1 - V_d) G_m + V_d G_d
\]  \hspace{1cm} (1.27)

where \(G_m\) and \(G_d\) are fracture energies (critical strain energy release rates) of the matrix and ductile reinforcing phase, respectively.

Recalling \(K_{ic}^2 = E' G_{ic}\) (where \(E' = E\) for plane stress, \(E' = E(1 - \nu^2)\) for plane strain), the \(E-ROM\) for fracture toughness \(K_{ic}\) in an in-situ composite is given in the following form:

\[
K_{ic} = \left\{ E' \left[ \frac{(1 - V_d) K_m^2}{E'_m} + \frac{V_d K_d^2}{E'_d} \right] \right\}^{1/2} \left[ \text{MPa.m}^{1/2} \right] \]  \hspace{1cm} (1.28)

where \(E'_m\) and \(E'_d\) are plane strain elastic moduli of the matrix and ductile second phase,
respectively. As shown in Figure 1.17, $E$-modified ROM is a curve above the straight line of ROM.

**Figure 1.17** Fracture toughness as a function of the vol.% of Cr$_2$Nb. For comparison with measured values, rule-of-mixtures (ROM) and ROM modified by modulus values are shown [61-62].
However, it has to be pointed out that Eq.(1.26) or Eq.(1.27) is a simple assumption without any formal justification or derivation.

Ashby [63] pointed out that Eq.(1.26) and Eq.(1.28) should be treated as the lower and upper limits for fracture toughness, which is similar to a function of the upper and lower bounds for moduli (Figure 1.16), respectively, not as precise formulae for calculating \( K_{lc} \) values.

Furthermore, Ashby [63] modified the ROM of Eqs.(1.26) and (1.28) and considered the worst and best cases for an in-situ composites as shown in Figures 1.18 and 1.11, respectively.

Ashby [63] explained that if the less tough component is thought as the matrix, the most damaging situation, leading to a lower bound, only arises when \( G_m < G_d \) and \( E_m < E_d \), and a crack propagates entirely in the phase of lower toughness avoiding reinforcements (Figure 1.18a). In this case a lower limit for a composite toughness can be expressed as [63],

\[
(G_{lc})_{\text{min}} = G_m \left( \frac{1 + 2V_d}{1 - V_d} \right)^{1/2}, \quad G_{lc} < G_d. \tag{1.29}
\]

From Eq.(1.29), obviously, even in this case the toughness still increases with increasing reinforcement fraction. This is because the crack, in avoiding the reinforcement, is forced into a path of greater area which increases by a factor of approximately \((1+2V_d)^{1/2}\), and also because the rough crack faces tend to interlock or rub, which contributes a factor \(1/(1-V_d)\). It has to be noted that Eq.(1.29) is cut off at \( G_{lc} = G_d \) since the crack will then penetrate in the ductile phase of the composite.
Then the lower bound for fracture toughness, \((K_{lc})_{\text{min}}\), of the composite can be given by the following form,

\[
(K_{lc})_{\text{min}} = K_m \left( \frac{(1 + 2V_d)^{1/2}}{1 - V_d^{1/2}} \right) \frac{E_c}{E_m} \left( \frac{\pi a^*}{E_c'} \right)^{1/2}, \quad K_{lc} < K_d.
\] (1.30)

When \(V_d = 0\), the composite toughness has the value \(K_m\) of the matrix. Definitely, \((K_{lc})_{\text{min}}\) from Eq.(1.30) represents a curve connecting the ends of the straight line but below the straight line marked as ROM (Figure 1.17).

The upper limit was derived by considering crack bridging [63]. Ashby assumed that the characteristic stress exerted by a bridging ligament, cannot be greater than the theoretical strength of the ligament itself, i.e., \(E_d/40\). Based on this assumption, Ashby [63] gave the increment of the stress intensity factor at crack tip, \((K_{lc}) = (1 - V_d)V_d\sigma(\pi a^*)^{1/2} = (1 - V_d)V_d(E_d/40)(\pi a^*)^{1/2}\). Recalling \(G_{lc} = K_{lc}^2/E_c'\) and simply adding this term into Eq.(1.27), Ashby [63] derived the following form for the upper limit of a composite,

\[
G_{lc} = (1 - V_d)G_m + V_d G_d + \left[ \frac{V_d(1 - V_d) E_d'}{40} \right] \frac{\pi a^*}{E_c'}
\] (1.31)

where \(a^*\) is half of the maximum crack length, which can be taken as 5mm in a calculation [63].

Similarly, the upper limit of fracture toughness for a composite can be expressed as,

\[
(K_{lc})_{\text{max}} = \left[ E_c' \left( \frac{(1 - V_d) K_m^2}{E'_m} + \frac{V_d K_d^2}{E'_d} \right) + \left( \frac{V_d(1 - V_d) E'_d}{40} \right)^2 \pi a^* \right]^{1/2}
\] (1.32)
where the first two terms on the right describe the rule-of-mixtures (see Eq.(1.28)); the last term is the additional energy absorbed by the work done against the bridging forces [63].

Obviously, $(K_{IC})_{max}$ from Eq.(1.32), is above the $E$-ROM curve as shown in Figure 1.17.

Figure 1.18 The basis of the lower-limit estimate for composite toughness. The crack propagates entirely in the phase of lower toughness. The apparent toughness increases slowly with volume fraction because of increasing area, and because of an increasing mode II component in its loading [63].
As shown in Figure 1.17 for the Nb-Cr$_2$Nb in-situ composite, the lower bound, $K_{\text{min}}$ model (Eq.(1.32)), predicted values approximately along the experimental Nb-Cr line. In addition, almost all of the experimental data exactly fall into the area surrounded by ROM from Eq.(1.28) and the lower bound ($K_{\text{lc}}$)$_{\text{min}}$ from Eq.(1.32) (Figure 1.17).

1.2 Experimental Observations and Analyses of Fracture

Toughness of the In-Situ Intermetallic Composites

As discussed in Section 1.1, reasonably good correspondence between predicted and measured particle concentration effects on fracture toughening is insightful. However, the properties of the ductile phase that provide optimum toughness are not apparent, either from models or experimental observations. That is because toughening is sufficiently complex and involves a sufficiently large number of independent variables that microstructure optimization only becomes practical when each of the important models has been described by a rigorous model, validated by experiment.

In this section our discussion will be focused on the in-situ intermetallic composites, which were obtained only through liquid or solid state reactions occurring in the metallurgical systems under consideration. In particular, the emphasis will be placed on the dependence of fracture toughness on volume fraction of second phase. It must be pointed out that in the intermetallic
composites listed in Table 1.1 the effect of the volume fraction of the second phase was not
systematically investigated. In fact, the data on the effect of the volume fraction are rather
scarce and confusing.

Strum and Henshall [64] claimed that the fracture toughness $K_Q$ increases linearly with
increasing volume fraction of the ductile phase in the V-V$_3$Si in-situ composites (Figure 1.19).
In fact, the fit is not that linear. Power-law fit yields (broken line in Figure 1.19) the following
equation:

$$K_Q = 2.824 + 0.003 V^2 \text{ [MPa.m}^{1/2}] \tag{1.33}$$

The result can not be expected by any toughening model discussed before.

Bewlay et al. [65] investigated in-situ intermetallic composites in the binary system of Nb-
Si. They used directional solidification (DS) to process the alloys. The DS hypoeutectic alloys
with compositions less than 18.2% Si were found to contain primary Nb dendrites and the
(Nb+Nb$_3$Si) eutectic. The hypereutectic alloys with compositions of 18.7% Si and greater were
found to contain primary Nb$_3$Si dendrites with the inter-dendritic eutectic. Alloys with
compositions between 20 and 22 at.% Si contained additionally primary Nb$_5$Si$_3$ dendrites.
Bewlay et al. [65] observed the linear increase of fracture toughness with decreasing Si
concentration (increasing Nb volume fraction) as shown in Figure 1.20.
The average fracture toughness of $V-V_3Si$ composites as a function of ductile phase fraction (All the castings were arc melted. To minimize hydrogen absorption from requisite acid cleaning and to attempt further minimization of interstitial levels from the melt stock, high-purity vanadium chips were substituted for melting stock in the series-2 castings) [64].
The effect of Si concentration on the fracture toughness of binary DS Nb-Si alloys with composition from 12 to 22% Si (D.S.: directly solidified; Extr.: extrusion; A.M.: arc melting; H.T.: heat treatment) [65].

To explain the linear rather than proportional to $V_d^{1/2}$ (Eq.1.16) increase of $K_Q$ with increasing Nb volume fraction, Bewlay et al. [65] put forward several possible factors for this behaviour. The first is that crack bridging by the ductile phase is not the predominant
toughening mechanism and that other mechanisms, such as micro-cracking, crack deflection and crack blunting are playing more significant roles. The second factor is that not all the Nb contributes the same specific work of fracture, since the latter is dependent on the scale of the Nb. In attempting to correlate the above ductile phase toughening theory with fracture toughness, it is assumed that all the Nb fails in a ductile manner. This is true for the eutectic and some of dendritic Nb, but much of the dendritic Nb failed by cleavage. Third, the degrees of constraint of the different types of Nb may be different. For example the shape of the high aspect ratio DS eutectic Nb may lend itself to interface decohesion more readily than the DS dendrites; in addition, the relative volume fractions of the eutectic and dendritic Nb change with Si concentration. Measurements of the eutectic alloy made by Bewlay et al. [65] indicate that the toughening increment that the eutectic possesses over the single phase Nb₅Si₃ is =3 MPa√m, assuming that the contributions from the individual toughening mechanisms are additive. Because of its fine scale, the eutectic Nb cannot be expected to contribute a much larger toughening increment [65].

In the hypereutectic region, where the eutectic matrix is reinforced by the brittle Nb₃Si, the fracture toughness increases linearly with increasing Si content, i.e., with increasing volume fraction of Nb₃Si and Nb₅Si₃ (Figure 1.20), which is quite surprising because both the Nb₃Si and Nb₅Si₃ are rather brittle phases. So far, the reason for such a behaviour is still not clear. A major improvement in the fracture toughness of the extruded alloys is also clearly seen in Figure 1.20. Extrusion makes several major modifications to the microstructure including phase alignment, reduced grain size, Nb hardness, Nb-Nb₅Si₃ interface orientation relationship.
and the reduction of flaws, such as pores and cracks. It is also to be pointed out that the arc-melted (A.M.) alloys exhibit noticeably lower fracture toughness than the directionally solidified (D.S.) ones (Figure 1.20).

![Fracture toughness as a function of volume fraction of particles in σ+X microstructures, where X designates each phase such as β, γ and σ phase [66].](image)

Figure 1.21

Fracture toughness as a function of volume fraction of particles in σ+X microstructures, where X designates each phase such as β, γ and σ phase [66].
Ebrahimi et al. [66] observed approximately the linear increase of fracture toughness, $K_I$, of $\sigma$ phase (Nb$_2$Al(Ti)) in the Nb-Ti-Al ternary system, with increasing volume fraction of $\beta$ (Ti-Nb BCC disordered solid solution), $\gamma$ (TiAl(Nb)) and orthorhombic (Ti$_3$NbAl) ($\omega$) phases (Figure 1.21). Based on the fractographic studies various toughening mechanisms were proposed by Ebrahimi et al. [66]. In the case of the $\beta$ and orthorhombic phases the particle-matrix interface was strong and toughening was achieved by crack tip trapping in the particle (crack blunting), crack front impediment, reinitiation of the crack ahead of the impeded crack front, crack bridging and separation of the crack surfaces by cleavage of the particle. The $\gamma$ phase was associated with large tensile internal stresses and perhaps a low interfacial energy allowing for the crack deflection and following the $\sigma$-$\gamma$ interface. The latter mechanism results in a lower level of toughening (Figure 1.21).

The fracture toughness of the NiAl-Ni$_3$Al in-situ intermetallic composite seems to increase linearly with increasing content of Ni (Figure 1.22). This suggests that fracture toughness could increase with the volume fraction of Ni$_3$Al ($\gamma'$) because the latter increases with increasing Ni content. However, fracture toughness of the alloys in the region from about 62 to 75 at.% Ni is not well researched. As seen in Figure 1.22 only several data points exist, mostly grouped at around 62 at.% Ni and the broken line up to 75 at.% Ni in Figure 1.22 is essentially an extrapolation [67].
Varin and Li [68] also obtained a linear increase of $K_{IC}$ with increasing volume fraction of minority phases, such as Ni(Si), MgNi$_2$ and Ni$_3$Si$_2$ formed in the brittle Mg$_6$Ni$_{16}$Si$_4$ ($\eta$ phase) [69] intermetallic matrix of the in-situ intermetallic composites based on the Ni-Mg-Si ternary system (Figure 1.23). Interestingly, Ni$_3$Si$_2$, which is a rather brittle intermetallic phase, gives approximately the same amount of toughening as Ni(Si) which by its nature is a more ductile
phase (compare alloy 4 and 5 in Figure 1.23). Such a result is unexpected and difficult to explain by the existing models discussed in Section 1.1. Such a behaviour is similar to the one discussed for the DS hypereutectic Nb-Si composite alloys by Bewlay et al. [65]. Again, an apparently brittle intermetallic phase embedded in the intermetallic (rather brittle) matrix provides a respectable amount of toughening.

![Graph showing dependence of fracture toughness on volume fraction of Ni-rich microconstituent](image)

**Figure 1.23** Dependence of $K_{IC}$ on the volume fraction of Ni-rich microconstituent; matrix is a brittle intermetallic of the $Mg_2Ni_6Si$-type ($Mn_2Th_6$ structure type) [68, 69].

49
It can be speculated that a weak interface between the matrix and reinforcing material aids the bridging mechanism. When a matrix crack encounters such an interface, this interface experiences Mode II loading; debonding occurs if the fracture energy of the interface is low [38].

So far the only case of the dependence of fracture toughness on the $V_d^{1/2}$ (Eq. 1.16) is the result obtained by Rao et al. [70] on the intermetallic $\gamma$-TiAl reinforced with TiNb particles (Figure 1.24). This is not an in-situ intermetallic system because the composite was obtained

![Figure 1.24](image_url)

**Figure 1.24** Variation in crack-initiation toughness, $K_i$, with volume fraction, $V_d$, for both Nb/TiAl and TiNb/TiAl composites (open and filled symbols are separately face and edge of the pancakes-shaped particles) [70].
artificially by blending the \(\gamma\)-TiAl powder with TiNb particles, and consolidated under vacuum at high temperature followed by high temperature forging [70]. As a result the TiNb particles were shaped in a pan-cake form. With respect to volume fraction of TiNb, power-law fit yielded

\[
K_I = 8 + 26.8 V_d^{\frac{1}{2}} \quad [\text{MPa} \cdot \text{m}^{\frac{1}{2}}] \tag{1.34}
\]

However, it must be pointed out that the scatter of data points in Figure 1.24, would probably give a reasonable fit to \(V_d\).

Chan [23] tried to correlate experimental values of \(K_c\) in TiAl-base alloys with his crack-tip blunting model expressed by \(Eq.(1.5)\). The value of \(K_n=12.5 \text{ MPa} \sqrt{m}\), for a single phase \(\alpha_2\) alloy [71], was used in \(Eq.(1.5)\). Chan [18] used \(n=18\) because most of the alloys exhibited relatively low strain breaking at 25°C. Varying the \(n\) value from 8 to 18 resulted in insignificant changes in \(\lambda_b\) ratio. The comparison is shown in Figure 1.25. As seen, the scatter of experimental \(K_c\) values is quite substantial which precludes any firm statement about the predictability of \(Eq.(1.5)\) with respect to fracture toughness. The only conclusion that can be drawn from Figure 1.25 is that the initiation fracture toughness shows a trend to increase with increasing volume fraction of the ductile phase.
Li and Schulson [73] used the model (Eq. (1.16)) to check whether the increment of fracture toughness ($\Delta K_c$) is proportional to the square root of the product of the particle strength, volume fraction and size of particles ($L = a_0$, as shown schematically in Figure 1.26) for boron-free and boron-doped Ni-23 at.% Si alloys. However, no effect is apparent as shown in Figure 1.27. They stated that possibly, it can be explained in terms of an attendant reduction in the strength of the composite particles, for as the product $(V_d L)^{1/2}$ increased, the volume fraction of the harder Ni$_3$Si rim decreased, correspondingly, $\sigma_y$ should have decreased, because hardness and strength are related.
Figure 1.26  Schematic sketch defining the microstructural parameters for a complex nickel silicide containing particles of a ductile phase [73].

Figure 1.27  Fracture toughness increment as a function of $(V_{dL})^{1/2}$. (O, □) Boron-free and (●, ■) boron-doped alloys. Points were obtained using (O, ●), $L=L_{Ni3Si}$ and (□, ■), $L=L_{Ni3Si}+L_{Ni3Si}$ [73].
Bencher et al. [44] also used Eq.(1.16) to calculate the increase in toughness of the Nb/Nb$_2$Al composite. Using $V_d = 0.4$, $\sigma_y = 90$ MPa, $E = 123$ GPa, Nb lamellar thickness $a_0 = 1$ $\mu$m and $\chi = 2.7$ (assuming a well bonded interface), the predicted elevation in toughness from bridging is $\approx 3.5$ MPa$\sqrt{m}$. Taking $K_{fc}$ for monolithic Nb$_2$Al as 1.1 MPa$\sqrt{m}$ [10] and $K_{fc} = K_m + \Delta K_{fc}$, the toughness of the Nb/Nb$_2$Al in-situ composite is $\approx 4.6$ MPa$\sqrt{m}$, which is slightly lower than the experimental value (5.5 MPa$\sqrt{m}$). However, it must be noted that according to Chan's rule for extrinsic toughening mechanism [17-18, 23], crack bridging of Eq.(1.16) cannot effect the $K_{fc}$ value of the composite. Obviously, Bencher et al. [44] did not take into account of the Chan's rule [17-18, 23].

Kumar et al. [13] investigated the role of brittle TiB$_2$ particulates and/or Al$_2$O$_3$ whiskers in affecting the toughness of stoichiometric and Ni-rich NiAl as shown in Figure 1.28, in which fracture toughness of about 10 vol.% TiB$_2$ composite is less than that of the matrix (Figure 1.28a) but additions of up to 25 vol.% Al$_2$O$_3$ whiskers improved the $K_{fc}$ of stoichiometric NiAl (Figure 1.28b).

Enoki and Kishi [57] also found another example in an arc-melted Ti-48 at.% Al composite with a duplex microstructure consisting of equiaxed $\gamma$ grains and $\gamma/\alpha_2$ (TiAl/Ti$_3$Al) lamellar grains, in which the static fracture toughness decreased with increasing volume fraction of equiaxed $\gamma$ as shown in Figure 1.29. In other words, the toughness of the in-situ composite decreases with increasing volume fraction of brittle $\gamma$ reinforcement.
Figure 1.28  
Effect of reinforcement type and volume fraction on fracture toughness. (a) Stoichiometric NiAl-TiB₂ particulate composites, (b) stoichiometric NiAl-Al₂O₃ whisker composites, (c) Ni-rich (61.5 at.% Ni) NiAl-Al₂O₃ whisker composites [13].
Chan [51] used Eq.(1.21) to calculated the crack growth toughness, $K_r$, in the $K$-resistance curve (Figure 1.2) for the TiAl-base alloys. Comparison of the calculated and observed $K_r$ values is presented in Figure 1.30, which shows good overall agreement between theory and experiment. In other words, the crack growth toughness, $K_r$, also depends on volume fraction as predicted by shear ligament toughening.
Figure 1.30
(a) Comparison of model calculation and experimental data of crack growth toughness, $K_r$. (b) Dependence of $K_r$ on the product of volume fraction and width of the crack-wake ligament in TiAl-base alloys [51].
1.3 Alloy System Selection and Statement of Objectives

To meet the demand for new structural materials to be employed in advanced jet engines and other high performance applications, alloys based on several intermetallic systems have been targeted for research [74-76]. One of the most important intermetallics is NiAl which has been targeted for an extensive research over the last five years because the NiAl-based intermetallic composites have a great potential for commercial applications. Fracture toughness evaluations of the NiAl-based materials have been a major topic of recent emphasis [67]. The fracture toughness of polycrystalline NiAl seems to increase by going to Ni-rich composition, within the two phase $\beta+\gamma'$ (NiAl+Ni$_3$Al) field as shown in Figure 1.22. The behaviour in Figure 1.22 suggests a certain relationship between fracture toughness and the volume fraction of a more ductile Ni$_3$Al ($\gamma'$) phase embedded in the more brittle NiAl ($\beta$) matrix. However, fracture toughness of the alloys in the region from about 62 to 75 at.% Ni is not well researched. As seen in Figure 1.22 only limited data are available, mostly grouped at around 62 at.% Ni and as mentioned previously the broken line up to 75 at.% Ni in Figure 1.22 is essentially an extrapolation.

Another problem pertinent to the NiAl-Ni$_3$Al system is the transformation of $\beta$ NiAl into martensite upon cooling and formation of the Ni$_3$Al$_3$ phase upon subsequent annealing in the Ni-Al system, in the composition range from about 62 to 74 at.% Ni [71-79]. Figure 1.31 shows a portion of recently evaluated Ni-Al binary system. In this system the nickel-rich NiAl
Figure 1.31  Approximate positions of boundaries in the nickel-aluminum phase diagram involving the Ni$_5$Al$_3$ [77].

Phase existing in the range greater than about 61 at.% Ni, transforms martensitically upon cooling from elevated temperatures [77-79]. As seen, the field of the existence of Ni$_5$Al$_3$ is indicated by a broken line. This phase is formed in both 63 and 70 at.% nickel-aluminum alloys on annealing below about 700°C from the martensitically transformed NiAl [77]. In view of the above, the in-situ intermetallic composite alloys existing in the approximate range from 60 to 70 at.%
=65 at.% [77] in Figure 1.22 could be in reality the mixture of martensitic NiAl and Ni₅Al₃ or regular NiAl and Ni₅Al₃, rather than NiAl and Ni₃Al. Similarly, the alloys in the range from 65 to 74 at.% Ni (Figure 1.31) could be the mixture of martensitic NiAl and Ni₃Al or Ni₅Al₃+Ni₃Al rather than NiAl and Ni₃Al.

The third problem is that polycrystalline Ni₃Al is extremely brittle in tension and apt to fail along grain boundaries at room temperature [80-81]. The low ductility of monolithic Ni₃Al, however, has been improved dramatically by microalloying with a small amount of boron. Subsequent studies [82-83] suggested that the role of boron, which was observed to segregate along the grain boundaries, is to enhance the bonding between nickel atoms and result in improvement of grain-boundary cohesion and reduction of the tendency toward brittle intergranular fracture. This is because boron alleviates the effects of moisture in air which in reaction with Al releases atomic hydrogen with, in turn, penetrates the crack tip embrittling it [83]. The boron-doped Ni₃Al exhibited a fracture toughness exceeding 30 MPa·√m [81], however, the toughening mechanisms are still not clear so far.

Therefore, the two phase region NiAl or Ni₅Al₃ + Ni₃Al in Figure 1.31 was selected as a model in-situ composite system for preliminary investigations of the processing and resulting microstructures. The principal objective of this research is to understand the relations of microstructures, fracture toughness and fracture mechanisms in view of the toughening mechanisms discussed in Sections 1.1 and 1.2 on the selected system with or without boron doping. In particular, the focus will be on establishing the effect of volume fraction of Ni₃Al on the fracture toughness of the in-situ NiAl/Ni₃Al composites.
1.4 Ni-Rich Part of The Ni-Al Binary System

1.4.1. Phase Diagram

The generally-accepted Al-Ni phase diagram is shown in Figure 1.32, in which the Ni rich
part has been given the conventional names used in the superalloy literature, $\beta$ (NiAl), $\gamma'$ (AlNi$_3$), Al$_3$Ni$_5$ and $\gamma$ (Ni). The equilibria between these phases involve the following three reactions,

1. peritectic: \[ L + \beta (\text{AlNi}) \leftrightarrow \gamma' (\text{AlNi}_3) \] at 1395°C;

2. eutectic: \[ L \leftrightarrow \gamma (\text{Ni}) + \gamma' (\text{AlNi}_3) \] at 1385°C;

3. peritectoid: \[ \beta (\text{AlNi}) + \gamma' (\text{AlNi}_3) \leftrightarrow \text{Al}_3\text{Ni}_5 \] at 700°C.

The compositions of phase boundaries between these phases are approximately 58.8 at.% Ni at $\beta$+(Al$_3$Ni$_5$), 63.9 at.% Ni at $\beta$+(Al$_3$Ni$_5$)/Al$_3$Ni$_5$, 67.9 at.% Ni at Al$_3$Ni$_5$/(Al$_3$Ni$_5$+$\gamma'$), and 73.3 at.% Ni at (Al$_3$Ni$_5$+$\gamma'$)/$\gamma'$, in Figure 1.32. However, some recent studies [85-87] agree with the older Ni-rich portion of the diagram due to Schramm [88], which show

1. peritectic: \[ L + \beta (\text{AlNi}) \leftrightarrow \gamma' (\text{AlNi}_3) \] at 1362°C;

2. eutectic: \[ L \leftrightarrow \gamma (\text{Ni}) + \gamma' (\text{AlNi}_3) \] at 1360°C;

3. peritectoid: \[ \beta (\text{AlNi}) + \gamma' (\text{AlNi}_3) \leftrightarrow \text{Al}_3\text{Ni}_5 \] at 700°C.

Along the increasing of Ni at.% content, the eutectic reaction occurs first instead of the peritectic one as shown in Figure 1.33.

In 1991, Verhoeven et al. [87] proposed a portion of the Ni-Al phase diagram (Figure 1.34), which supports the result in Figure 1.33. However, as shown in Figure 1.34, the eutectic and peritectic temperatures are higher than those in Figure 1.33, but lower than those in Figure 1.32.

In 1994, Lee et al. [89] estimated the position of the $\gamma'$/$\beta$ eutectic in the Ni-Al system. It is
found that the equilibrium $\beta/\gamma'$ eutectic is located at 75.4% Ni (24.6% Al) and the metastable $\beta/\gamma'$ eutectic is at 75.5% Ni (24.5% Al) as shown in Figure 1.35.

Khadikar et al. [90] also carried out a quantitative phase analysis to establish the (NiAl + Ni$_5$Al$_3$)/Ni$_5$Al$_3$ phase boundary location as shown in Figure 1.36. The composition of the phase boundary is around 59.5 at.% Ni at (NiAl + Ni$_5$Al$_3$)/Al$_5$Ni$_3$. Obviously, the established
Figure 1.34  Ni-rich portion of the Al-Ni phase program taken from Verhoeven et al. [87].
Figure 1.35  Estimated position of the metastable $\gamma'/\beta$ eutectic in the Ni-Al system [89].

Figure 1.36  Portion of the Al-Ni phase program established by Khadkikar et al. [90].
phase boundary is on the nickel-rich side compared to Figure 1.32. It must be mentioned that the alloys used by Khadkikar et al. [90] were produced by a powder metallurgy process.

As mentioned above, the more recent proposition for the complete Al-Ni phase diagram is shown in Figure 1.37. This is essentially the same one as developed by Singleton et al. [84] with the following modifications. Comparing Figure 1.37 and Figure 1.32, we could see that the melting point of stoichiometric NiAl, while still assumed to be congruent, is approximately 44K greater than previously reported [91]. This higher liquidus temperature also has been confirmed by Noebe [24] on both single crystal and prealloyed powder NiAl materials. The peritectoid reaction, resulting in the formation of Ni5Al3, is approximately 25K higher in temperature [92] (725°C vs 700°C as in Refs. [86, 90]) and the boundary for the Al-rich side of the Ni5Al3 phase has been modified based on the result by Khadkikar [90] (Figure 1.36). The most significant changes in this version of the phase diagram, however, concern the Ni3Al region. The position of the eutectic and peritectic reactions are reversed. The changes to the Ni3Al portion of the phase diagram are based on significant experimental work by Bremmer et al. [86] and are in agreement with previous work by Schramm [88].

So far, however, the exact equilibrium positions of β/(β+Al3Ni5), (β+Al3Ni5)/Al3Ni5, Al3Ni5/(Al3Ni5+γ'), and (Al3Ni5+γ')/γ' boundaries are still uncertain.
Figure 1.37  Al-Ni phase diagram taken from Noebe [24].
1.4.2. Transformations and Microstructures in the Ni-Rich Ni-Al System

Martensitic Transformation on Cooling

The martensitic transformation upon cooling results in the formation of L1₀ martensite with either ABC (3R) stacking or ABCABAC (7R) stacking [86, 90]. The β and 3R structures are the same except for the c/a ratio (f.c.t. indexing) [90]. The transformation sequence from NiAl to Ni₅Al₃ is depicted in Figure 1.38. The Ni-rich B2 NiAl, with excess nickel atoms on aluminum sites, undergoes Bain distortion and transforms to L1₀ martensite upon quenching. A simple ordering of the nickel atoms on the aluminum sublattice (which can take place at low temperatures) is required to transform the martensitic structure to Ni₅Al₃. A summary of the available data for the dependence of the measured $M_s$ temperatures on NiAl alloy composition is shown in Figure 1.39. A compilation of the literature data on transformation temperature as a function of composition indicates large discrepancies (120K) in the measured $M_s$ temperatures in NiAl alloys. A rather steep dependence of the $M_s$ temperature on alloy composition exacerbates the error in measurement of both the $M_s$ temperature and the alloy composition [90].
Nickel
Aluminurn
Nickel - Aluminurn

Figure 1.38 Transformation sequence from NiAl to Ni$_5$Al$_3$ [93].

Figure 1.39 Summary of available data on the dependence of $M_s$, temperature on alloy composition [90].
Annealing and Aging

A typical example of the microstructure that results from annealing of an arc-melted alloy (Ni$_{54}$Al$_{36}$) for 10 hours at 727°C to increase the amount of γ' present (the method of cooling, i.e., furnace or air cooling is not given in Ref.[24]), is shown in Figure 1.40. It is evident that γ' preferentially nucleates at the grain boundaries forming a continuous film around the β grains, a microstructure that is now commonly referred to as a "necklace microstructure" [94].

Figure 1.40 Backscatter SEM micrograph of an extruded alloy Ni$_{54}$Al$_{36}$ annealed at 727°C for 10 hours resulting in a necklace microstructure of γ'. The alloy was processed by directional solidification or extrusion (927°C) of prealloyed metal powders [24].
The particles within the NiAl grains are Ni$_2$Al. This result is consistent with the NiAl portion of the Ni-Al diagram in Figures 1.22 and 1.40. However, peritectoid temperature is 725°C in Figure 1.37. It means that the annealing at 727°C would occur almost at peritectoid temperature and it is not clear why it might not have led to the formation of Ni$_5$Al$_3$.

Robertson and Wayman [93, 95, 96] investigated the Ni$_{63}$Al$_{37}$ and Ni$_{70}$Al$_{30}$ alloys (at.%) which were obtained in the form of cast rods [95]. After annealing at temperatures of 1100°C for the 63% Ni alloy and 1300°C for the 70% Ni alloy and water-quenching, as pointed out by the authors [96], the former was entirely β phase, while the latter contained both β and γ phases. Then, according to the authors [96], the 63% Ni sample aged at 505°C became single-phase Ni$_5$Al$_3$, which was found to be stable below about 700°C.

Khadkikar et al. [78-79] investigated microstructures in Ni$_{70.3}$Al$_{24.8}$ and Ni$_{64.4}$Al$_{34.7}$ (at.%) alloys, also containing less than 0.9 at.% of Hf and 0.1 at.% of boron, as well as Ni$_{63.05}$Al$_{36.95}$ (with major impurity of 0.045 wt.% oxygen) alloy, produced by a powder metallurgy process. These hot-extruded microstructures can be modified dramatically by suitable heat treatments. Figure 1.41 shows the microstructures of the alloy A (Ni$_{70.3}$Al$_{24.8}$) and alloy B (Ni$_{64.4}$Al$_{34.7}$) after various heat treatments. At the homogenization temperature of 1250°C, according to phase diagrams in Figure 1.32 and Figure 1.37, the alloy A transforms to a mixture of Ni$_3$Al plus NiAl phases with the compositions of the respective phase boundaries and the alloy B completely transforms to Ni-rich NiAl. Upon rapid cooling from this temperature, the alloy A transforms to a two phase mixture of NiAl martensite (3R-type) plus NiAl (Figure 1.41a) whereas the Ni-rich β-phase in alloy B transforms completely to 3R martensite (Figure 1.41d).
After the above heat treatments and upon additional aging at 850°C (above the peritectoid temperature, see Figures 1.32 and 1.37), both of alloys A and B should be transformed to Ni₅Al plus NiAl phase mixtures (Figures 1.41b and e) as one would expect from the phase diagrams presented in Figures 1.32 and 1.37. Unfortunately, it is not clear in Figure 1.41e where the Ni₃Al phase is located. However, aging at 600°C (below the peritectoid temperature in Figure 1.37) after quenching will result in the formation of Ni₅Al₃ phase. Hence, the alloy A transforms to Ni₅Al₃ plus Ni₃Al (Figure 1.41c) whereas, the alloy B transforms to Ni₅Al₃ plus NiAl (Figure 1.41f). The proportions of the two phases vary and approach equilibrium with aging time. All of the above resultant microstructural phases were detected by X-ray diffraction [78]. However, the exact volume fractions of each of the phases and the compositions of the Ni₅Al₃ phase are in question since the phase boundaries between $\beta/(\beta+\text{Al}_3\text{Ni}_5)$, $(\beta+\text{Al}_2\text{Ni}_5)/\text{Al}_3\text{Ni}_5$, $\text{Al}_3\text{Ni}_5/(\text{Al}_3\text{Ni}_5+\gamma')$, and $(\text{Al}_3\text{Ni}_5+\gamma')/\gamma'$ in Figures 1.32 and 1.41 are not exactly known and are based on only a few data points [96].
Figure 1.41 
Microstructures of alloys A (Ni$_{70.3}$Al$_{28.8}$) and B (Ni$_{64.4}$Al$_{34.7}$) after various heat treatments. (a) and (d) 1250°C/24 hr, water quenched, (b) and (e) 1250°C/24 hr, water quenched plus 850°C/24 hr, (c) and (f) 1250°C/24 hr, water quenched plus 600°C/24 hr [78]. However, the method of cooling after aging was not mentioned in ref.[78].
Figure 1.42 illustrates typical microstructures in alloy B (Ni$_{64.4}$Al$_{34.7}$), which was annealed at 1250°C for 4h, water-quenched (Figure 1.42a) and aged at 550°C for 15 days (Figure 1.42b) [79]. The NiAl martensite is heavily twinned (Figure 1.42a) and the Ni$_5$Al$_3$ has a very distinct needle-like microstructure (Figure 1.42b). This sequence of transformation can be

![Figure 1.42 Optical microstructure of the Ni$_{64.4}$Al$_{34.7}$ alloy for (a) specimen homogenized at 1250°C for 4h and probably water quenched according to the text; (b) specimen homogenized at 1250°C for 4h and probably water quenched according to the text, and aged at 550°C for 15 days [79].]
described in such a manner that the Ni₅Al₃ phase results from a transformation of L₁₀ martensite upon aging at lower temperatures (up to approximately 700°C) whereas the martensite was formed by water-quenching the Ni-rich NiAl alloy that is stable at high temperature. The interesting point is that a small amount of NiAl was found to retain in equilibrium with Ni₅Al₃ even after aging for 15 days at 550°C. According to the phase diagrams in Figures 1.32 and 1.37, no NiAl should exist at equilibrium at the composition of 64.4 at.% nickel after aging at 550°C only single phase Ni₅Al₃. These observations indicate that the position of the Ni₅Al₃/(Ni₅Al₃ + NiAl) phase boundary is uncertain. This is no surprise since the phase boundary indicated in Figures 1.32 and 1.37 is actually based on only a few data points for the Ni₅Al₃ phase from the original study [96]. Also the transformation to Ni₅Al₃ might be very sluggish and aging time at 550°C was insufficient.

The microstructures of Ni₆₃.₅Al₃₆.₃ alloy in water-quenched (after homogenizing at 1250°C for 4h) and aged (550°C, 600°C and 650°C for 720h; 550°C for 1 to 360h) conditions are shown in Figures 1.43-1.45. The presence of parent B₂-NiAl phase in the optical micrograph shows that the martensitic transformation has not been completed at room temperature (Figure 1.43a). Of particular interest are the clean (i.e., no grain boundary phase) grain boundaries seen in the SEM micrograph of Figure 1.43b.

The SEM micrographs show that mat-like microstructures are observed in the specimens aged at both 600°C and 650°C (Figure 1.44), the aging at the higher temperature results in a coarser microstructure. X-ray diffraction traces showed that a nearly complete transformation
Figure 1.43  (a) Optical micrograph and (b) SEM images showing the microstructure of the Ni$_{63.05}$Al$_{36.93}$ alloy in the as-quenched condition after 1250°C/4h) [90].

Figure 1.44  SEM images showing the microstructure of the Ni$_{63.05}$Al$_{36.93}$ alloy in the as-aged conditions (720h), (a) 550°C and (b) 650°C after homogenizing at 1250°C/4h and water-quenching [90].
to $\text{Ni}_5\text{Al}_3$ occurred with only a minor amount of NiAl but a two-phase microstructure consisting of most probably $\text{Ni}_5\text{Al}_3$ and NiAl is still observed upon aging at 600°C and 650°C (Figure 1.44). The short-time aging was carried out in order to understand the microstructural evolution of transformation to $\text{Ni}_5\text{Al}_3$. The short-time aging produced a very complex microstructure due to the presence of multiple phases (Figure 1.45). Two distinct phases, a blocky grain boundary phase and a platelet-like grain interior phase, appear to grow with aging time. According to the authors [90], these platelet-like precipitates in the grain interior were identified from electron diffraction patterns to be new variants of the $3R$ martensite. The $3R$ martensite increased in number as a function of aging time. The matrix surrounding the platelet $3R$ precipitate was identified as $7R$ martensite, as shown in the BF image of Figure 1.46 with its corresponding diffraction pattern [90].

The blocky grain boundary phase were identified as to $\text{Ni}_5\text{Al}_3$. The volume fraction of NiAl transformed to the $\text{Ni}_5\text{Al}_3$ phase plotted versus aging time at 550°C is shown in Figure 1.47. The transformation curve generated has an S shape indicating cellular transformation kinetics [90].

As discussed above, transformation to $\text{Ni}_5\text{Al}_3$ can occur either from B2-NiAl or L1$_0$ martensite as the parent phase aging below 700°C for the alloy of 63-70 at.% Ni content. In addition, simultaneous hot-stage microscopy experiments indicated that the nucleation of $\text{Ni}_5\text{Al}_3$ occurs at the NiAl grain boundaries after 2 hours of exposure at 600°C [90].
SEM images showing the microstructure of the Ni$_{63.05}$Al$_{36.95}$ alloy in the short-time, as-aged conditions (550°C), (a) 1h, (b) 4h, (c) 12h, and (d) 72h. Note the mat-like structure in (c) and (d) and grain boundary precipitation [90].

Figure 1.45
Figure 1.46  BF TEM image showing the 7R martensite matrix observed in the specimen aged for 12h at 550°C. A selected area diffraction pattern of the 7R martensite is also shown [90].

Figure 1.47  (111) peak area as a function of aging time at 550°C indicative of the increase in volume fraction of the Ni$_3$Al$_3$ phase [90].
CHAPTER 2

EXPERIMENTAL PROCEDURE

2.1 The Specimen-Dimension Design for a Bending Test

According to the existing ASTM standards E 399-90 [97], E 1304 [98] and E 813-89 [99], a small-size notch-bend test as shown in Figure 2.1 will be prepared for the investigation of the fracture toughness of the in-situ composites. The reason is that this specimen configuration is much simpler to fabricate and test, the least amount of material required and more flexible with respect to size compared to other specimen configurations [97-99].

The bend specimen can be loaded in three-point or four-point loading. In four-point loading the specimen alignment is not very critical because of the constant moment between the inner loading points (Figures 2.1b and d). Also, additional interaction between the load roller stress field and the crack stress field, which can happen in three-point loading (Figure 2.1a), is avoided [38, 100, 101]. However, more material will be needed because of the additional span ($S_2$) and the diameter of the rollers. A three-point loading is preferred for this test as will be discussed further.
The profiles of the two specimen types: (a) single-edge-precrack-beam (SEPB) by three-point loading [38] (b) chevron-notch-beam (CNB) by four-point loading [101]. Bending and tensile stress formulae and distribution: (c) three-point loading (d) four-point bending [100].
2.1.1 The Validity Requirements for a $K_{IC}$ test

The concept of plane-strain fracture toughness $K_{IC}$ of materials has been widely used since it was first formulated by Irwin in 1958 [102-103]. So far, for small-size notch-bend specimen tests to measure $K_{IC}$ directly, there are two different notch-producing fracture testing methods more popular recently such as (1) Single-Edge Precracked Beam (SEPB) [38, 104] as shown in Figure 2.2, (2) Chevron-Notch Beam (CNB) (Figure 2.1b), since for both specimens costly fatigue precracking could be avoided [104-106].

![Diagram of SEPB test](image)

**Figure 2.2** Schematic of single-edge-precracked-beam (SEPB) [38, 104]. A crack starter, i.e., a Vickers indentation or a straight-through notch [104].
Plastic Zone Size in an Elastic-Plastic Material

There seems to be general agreement that properly designed and tested bend specimens should provide good measurements of $K_i$, provided the specimen conforms sufficiently well to the assumptions of linear elastic fracture mechanics (LEFM). For the in-situ composites, the most important LEFM assumption is that there is negligible plasticity in the specimen. In other words, the LEFM criterion is satisfied only when the specimen size is very large compared to that of crack-tip plastic zone size which is characteristic of the material of which the specimen is made. Then it is essential to know the plastic zone size in a real material before designing a fracture toughness test.

Based on the theory of linear-elasticity, the stress field caused by tension loading (opening mode I), near the crack tip in a linear-elastic, isotropic and infinite plate as shown in Figure 2.3, can be shown as the following equations [38, 107-108]:

\[
\sigma_x = \frac{K_I}{(2\pi r)^{1/2}} \cos \frac{\theta}{2} \left[ 1 - \sin \frac{\theta}{2} \sin \frac{3\theta}{2} \right] + \ldots
\]  
(2.1)

\[
\sigma_y = \frac{K_I}{(2\pi r)^{1/2}} \cos \frac{\theta}{2} \left[ 1 + \sin \frac{\theta}{2} \sin \frac{3\theta}{2} \right] + \ldots
\]  
(2.2)

\[
\tau_{xy} = \frac{K_I}{(2\pi r)^{1/2}} \cos \frac{\theta}{2} \sin \frac{\theta}{2} \sin \frac{3\theta}{2} + \ldots
\]  
(2.3)

\[
\sigma_z = 0 \quad (plane \ stress)
\]  
(2.4)

\[
\sigma_z = \nu (\sigma_x + \sigma_y) \quad (plane \ strain; \ \varepsilon_z = 0)
\]  
(2.5)

\[
\tau_{yz} = \tau_{zx} = 0
\]  
(2.6)
However, it was noted that real materials cannot support the theoretically infinite stresses at the tip of a sharp crack. Upon loading the crack tip becomes blunted and a region of yielding, crazing, or microcracking forms as shown in Figure 2.4.

For such an elastic, perfectly plastic, isotropic and infinite plate, Tresca predicts yielding to occur if the maximum yield stress $\tau_{\text{max}}$ exceeds the yield stress in shear, $\sigma_{yS}/2$. The Von Mises criterion, in terms of the principal stresses, follows from [108]

$$
(\sigma_1 - \sigma_2)^2 + (\sigma_2 - \sigma_3)^2 + (\sigma_3 - \sigma_1)^2 = 2\sigma_{yS}^2
$$

where, $\sigma_{yS}$ is the uniaxial yield strength of the material. In the crack plane ($\theta = 0$), the size of the crack tip yielding zone $r_\gamma$ (Figure 2.4) as a function of $\theta$ follows from substitution of Eqs. (2.1-2.6) into Eq. (2.7):

$$
\begin{align*}
    r_{\gamma\sigma} &= \frac{l}{2\pi} \frac{K_I^2}{\sigma_{yS}^2} & \text{(plane stress)} \\
    r_{\gamma\varepsilon} &= \frac{l}{6\pi} \frac{K_I^2}{\sigma_{yS}^2} & \text{(plane strain)}
\end{align*}
$$

where $\nu = 0.3$; the subscripts $\sigma$ and $\varepsilon$ designate plane stress and plane strain conditions, respectively. It is clear that the crack tip yielding zone size $r_{\gamma\varepsilon}$ for plane strain is only one third of that $r_{\gamma\sigma}$ for plane stress. The yielding zone $r_\gamma$ can be called a first order estimate of plastic zone $r_p$ because it was based on an elastic crack tip solution. For a real elastic-plastic material, the stresses are lower than the values from the elastic stress field equations because of yielding within the plastic zone.
Figure 2.3  (a) An infinite plate containing a through-thickness central crack. (b) Three-dimensional coordinate system for the region of a crack tip [107].
The yielded material thus offers resistance that expected, and large deformation occurs, which in turn causes yielding to extend even farther than $r_y$, as illustrated in Figure 2.4. A simple force balance leads to a second order estimate of the plastic zone size, $r_p$ [38]:

$$\sigma_{ys} r_p = \int_0^{r_p} \sigma_{yy} dr = \int_0^{r_p} \frac{K_I}{(2\pi r)^{1/2}} dr$$

Integrating and solving for $r_p$ gives that yielding actually extends to about $2r_y$, called real plastic-zone size $r_p$ in this thesis,

$$r_{p\sigma} = 2r_{y\sigma} = \frac{1}{\pi} \frac{K_I^2}{\sigma_{ys}^2} \quad (plane \ stress) \quad (2.11)$$
\[ r_{pe} = 2 r_{ye} = \frac{1}{3\pi} \frac{K_I^2}{\sigma_{ys}^2} \quad \text{(plane strain)} \] (2.12)

where \( r_{pe} \) and \( r_{ye} \) represent the real plastic zone sizes in an elastic-plastic material under plane stress and plane strain, respectively.

**The Validity Requirements in ASTM Standard E 399-90**

If the plastic zone is sufficiently small, there will be a region outside of it where the elastic stress field Eqs. (2.1) to (2.6) still apply, called \( K \)-field as shown in Figure 2.5a. The existence of such a region is essential for linear elastic fracture mechanics (LEFM) theory to be applicable because the \( K \)-field surrounds and controls the behaviour of the plastic zone and crack tip area.

As a practical matter, it is necessary that the plastic zone be small compared to the distance from the crack tip to any boundary of the member, such as distance \( a \), \((W-a)\), and \( h \) for a cracked plate as in Figure 2.5b. Generally, a distance larger than twelve times the plastic zone size \( r_{pe} \) is sufficient. Hence, an overall limit on the use of LEFM applicable for opening mode is [107]

\[ a, (W - a), h \geq \frac{4}{\pi} \left( \frac{K_I}{\sigma_{ys}} \right)^2 \quad \text{(LEFM applicable)} \] (2.13)

From Eqs.(2.12) and (2.13), it is clear that \( (K_I/\sigma_{ys})^2 \) is a characteristic dimension of the
Figure 2.5 (a) A crack and its plastic zone, and the larger K-field that must exist for LEFM to be applicable. Small plastic zone compared to planar dimensions (b), and situations where LEFM is invalid due to the plastic zones being too large compared to (c) crack length, (d) uncracked ligament, and (e) member height [107].
plastic zone that should be useful in estimating specimen dimensions. The pertinent dimensions of plate specimens for $K_c$ bend-testing are crack length ($a$), thickness ($B$), and ligament length (uncracked length: $W-a$, $W$ is the width of the specimen as shown in Figure 2.1). For a critical fracture toughness $K_c$ which is independent on size parameters, these parameters must be greater than a certain multiple ($\alpha$) of $(K_c/\sigma_{ys})^2$ (Figure 2.6), these multiples to be determined by an adequate number of trial $K_c$ tests [109].

Figure 2.6 showed effects of thickness and crack size on measured $K_c$ of a maraging steel [108, 109]. According to Figure 2.6 consistent $K_c$ values are obtained if $\alpha \geq 2.5$, the value adopted in the ASTM size requirement [97]

$$B, a, (W - a), h \geq 2.5 (\frac{K_{ic}}{\sigma_{ys}})^2 \quad \text{(plane strain)} \quad (2.14)$$

Comparing Eq.(2.12) to Eq.(2.14) indicates that specimen dimension must be $2.5 \times 3\pi = 24$ times larger than the plastic zone size $r_{pc}$ for plane strain in order to obtain a size-independent critical $K_c$ value. In addition, the requirements on the in-plane dimensions of Eq.(2.13) are less stringent than Eq.(2.14), so that the limits on the use of LEFM are automatically satisfied if plane strain is satisfied.

Although plane strain as shown in Eq.(2.14) is necessary condition for a valid $K_c$ test, it is not sufficient. The validity requirements in ASTM Standard E 399-90 [97] are very stringent because it is possible that a fracture-toughness test displays considerable plastic deformation prior to failure as shown in Figure 2.7. A $K_Q$ value computed from $P_Q$ [97] may just barely
Figure 2.6  Effects of (a) thickness, (b) crack size on measured $K_c$ of a maraging steel [108, 109].
satisfy the size requirements of Eq. (2.14), however, such a quantity would have little relevance to the fracture toughness of the material. Since the specimen fails well beyond $P_Q$, the $K_Q$ value in this case would grossly underestimate the true toughness of the materials. Therefore, another requirement is essential to a $K_{ic}$ test as described in E 399-90 [97]:

$$P_{\text{max}} \leq 1.10 P_Q$$  \hspace{1cm} (2.15)

The meaning of $P_Q$ can be explained by Figure 2.8.

As shown in Figure 2.8, three types of the load-displacement curves could be obtained during $K_{ic}$ testing. The critical load, $P_Q$, is defined in one of several ways, depending on the type of curve. A smooth curve as in Type I can be caused by a steady tearing type of fracture called slow-stable crack growth, plastic zone effects, or both. In other cases, the crack may suddenly grow a short distance, which is called pop-in (II), or it may suddenly grow to complete failure (III). A line from origin with a slope equal to 95% of the initial elastic loading slope must be constructed to determine $P_S$ (Figure 2.8) because it corresponds to crack growth through approximately 2% of the ligament in test specimens with $a/W = 0.5$ [38]. In the case of Type I behaviour, $P_Q = P_S$. With a Type II curve, a small amount of unstable crack growth occurs before the curve deviates from linearity by 5%. In this case, $P_Q$ is defined at the pop-in. For Type III behaviour, a specimen fails completely before achieving 5% nonlinearity. In this case, $P_Q = P_{\text{max}}$. 

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Figure 2.7  A schematic load-displacement curve for an invalid $K_c$ test, where ultimate failure occurs well beyond $P_Q$ [38].

Figure 2.8  Major types of load-displacement records during $K_c$ testing. For the valid test, $P_{\text{max}} \leq 1.10 P_Q$ [97].
2.1.2 Preliminary Estimation of the Bend-Specimen-Size of the Selected System

The values of yield strength $\sigma_{ys}$, elastic modulus $E$, Poisson's ratio $\nu$ and fracture toughness $K_{fc}$ of polycrystalline NiAl, monolithic Ni$_3$Al and boron-doped Ni$_3$Al at room temperature are listed in Table 2.1. The alloy processing method (APM) and alloy grain size are also shown in Table 2.1 if they are available in references because the values of $\sigma_{ys}$ and $K_{fc}$ are different depending on various alloy processing method (APM) and alloy grain size as shown in Table 2.1.

For example, Rigney et al. [81] explained that the compressive yield strengths of NiAl were significantly higher than expected, resulting from possible interstitial contamination during hot pressing. That is the only case that the values are not considered in the following specimen-size design. Taking the average values of $\sigma_{ys}$ and $K_{fc}$, the specimen sizes for polycrystalline NiAl, boron-free and boron-doped monolithic Ni$_3$Al should be:

\[ \text{NiAl: } B, a, (W - a) \geq 2.5\left(\frac{6}{244}\right)^2 \times 10^3 = 1.5mm \]  \hspace{1cm} (2.16)

\[ \text{Ni}_3\text{Al: } B, a, (W - a) \geq 2.5\left(\frac{20}{294}\right)^2 \times 10^3 = 11.6mm \]  \hspace{1cm} (2.17)

\[ \text{Ni}_3\text{Al + B: } B, a, (W - a) \geq 2.5\left(\frac{30.5}{304}\right)^2 \times 10^3 = 25.2mm \]  \hspace{1cm} (2.18)

For the specimens containing 50 vol.% NiAl + 50 vol.% Ni$_3$Al with assumption of the averages of $\sigma_{ys}$ and $K_{fc}$ for each phase, the specimen size could be:
Table 2.1  The values of $E$, $v$, $\sigma_{ys}$ and $K_{ic}$ of polycrystalline NiAl and monolithic Ni$_3$Al (with and without boron doping) at room temperature.

<table>
<thead>
<tr>
<th>Alloys</th>
<th>$E$ (GPa)</th>
<th>$\sigma_{ys}$ (MPa)</th>
<th>$K_{ic}$ (MPa$\cdot$m)</th>
<th>Grain Size ($\mu$m) and APM</th>
<th>Poisson's Ratio $v$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni$_3$Al</td>
<td>179 [110]</td>
<td>100$\leftrightarrow$450 [112] 236$\leftrightarrow$389 [81]</td>
<td>20 [111] 18.7$\leftrightarrow$20.9 [81]</td>
<td>9, $HPP^<em>$ [111] 8$\leftrightarrow$69, [112] 9$\leftrightarrow$25, $HPP^</em>$ [81]</td>
<td>0.305</td>
</tr>
<tr>
<td>Ni$_3$Al+B</td>
<td>-</td>
<td>280 [113] 283$\leftrightarrow$374 [81]</td>
<td>&gt;28.1 [111] 28 $\leftrightarrow$ 33 [81]</td>
<td>9, $HPP^<em>$ [111] 9$\leftrightarrow$150 $HPP^</em>$ [81]</td>
<td>-</td>
</tr>
</tbody>
</table>

Note: Alloy processing method (APM) are marked by references. $HPP$: hot-pressed powders; $CP$+$AE$: conventional purity induction melted casting + as-extruded; $PE$: powder extruded.
Obviously, in order to get valid $K_c$ values the size of the bend specimens can be designed as very small, e.g. from 1.5 to 6 mm, only for polycrystalline NiAl to the polycrystalline NiAl containing less than 50 vol.% Ni$_3$Al (not sure how much less than 50 vol.% now) in the in-situ composites. However, for the polycrystalline NiAl with more than 50% Ni$_3$Al to approximately 100% Ni$_3$Al which shows higher $K_c$ values and almost the same $\sigma_{YS}$ values, the size of the bend specimens could be very large, from 5.8 to 25.2 mm. Therefore, the maximum length of the specimens could be more than 4x25.2=100.8 mm because the standard loading span for the bend specimen should be four times the width ($W$) [97] (Figure 2.1). Such a huge specimen is completely impractical for fabrication in our lab. Definitely, an alternative bending method, $J$-integral method, for fracture-toughness determination is needed for the selected system.

2.1.3 The specimen-Size Requirements for a Valid $J_c$

To determine $K_c$ indirectly since linear elastic fracture mechanics ($LEFM$) is valid only as long as nonlinear material deformation is confined to a small region surrounding the crack tip, there is only one experimental technique appropriate, i.e., $J$-integral method [38, 99, 100].
Obviously, the design of the specimen size and geometries for a valid \( K_c \) test needs a thorough understanding of applications of LEFM and elastic-plastic fracture mechanics (EPFM).

In ASTM standard E 813-89 [99], a provisional \( J_0 = J_c \) as long the following size requirements are satisfied:

\[
B, (W - a) \geq \frac{25 J_0}{\sigma_{YS}}
\]  

(2.20)

It is instructive to compare specimen size requirements associated with valid \( K_c \) and \( J_c \) test procedures. The upper-bound specimen sizes of NiAl and Ni3Al can be calculated for a valid \( J_c \) test by substituting data for \( \sigma_{YS} \) from Table 2.1 into Eq.(2.20) and recalling that \( J_c = (1 - v^2)K_c^2/E \) [38, 100]:

\[
\text{NiAl: } B, (W - a) \geq 25 \frac{J_c}{\sigma_{YS}} = \frac{25 \times 6^2}{241.5(1 - 0.315^2)244} = 0.017 \text{mm}
\]  

(2.21)

\[
\text{Ni3Al: } B, (W - a) \geq 25 \frac{J_c}{\sigma_{YS}} = \frac{25 \times 20^2}{179(1 - 0.305^2)312.5} = 0.2 \text{mm}
\]  

(2.22)

\[
\text{Ni3Al + B: } B, (W - a) \geq 25 \frac{J_c}{\sigma_{YS}} = \frac{25 \times 30.5^2}{179(1 - 0.3^2)328.5} = 0.4 \text{mm}
\]  

(2.23)

Where, \( E \) and \( \sigma_{YS} \) are the average values of elastic moduli and yield strengths taken from Table 2.1. Obviously, the \( J_c \) size requirements are much more lenient than the \( K_c \) requirements.
2.2 Geometrical Criteria for the Design of Small-Size Bend Specimen

Fracture mechanics theory applies to cracks that are infinitely sharp prior to loading. While laboratory specimens invariably fall short of this ideal, it is possible to introduce cracks that are sufficiently sharp for practical purposes. A fatigue-precracking method is adopted in ASTM E 399-90 [97], which requires the peak value of stress intensity in a single cycle, $K_{\text{max}}$, should be no larger than 0.8 $K_c$ during the initial stages of fatigue precracking and less than 0.6 $K_c$ as the crack approaches its final size [38, 97]. The user must specify fatigue loads based on the anticipated toughness of the material. If one is conservative and selects low loads, precracking could take a very long time. On other hand, if precracking is conducted at high loads, the user risks an invalid result, in which case the specimen and the user's time are wasted. Therefore, people have been trying to develop other techniques in order to replace costly fatigue-precracking method. SEPB and CNB are such types of fracture specimens developed recently.

2.2.1 Single-Edge-Precracked-Beam (SEPB)

As a substitute for the fatigue-precracked-beam method prescribed in ASTM E399 A2, this method involves testing of straight through notched specimens that have been precracked in bridge-compression method as shown in Figure 2.2. A crack starter, i.e., a Vickers indentation or a straight-through notch (0.1 mm wide by 1.5 mm deep) can be placed at the center of the
bottom surface [104]. The precrack length is varied by changing the groove width in bridge configuration and loading greater than the pop-in load, and can be controlled by a pop-in sound detected by a sonic sensor attached to the pusher framework. A dye penetrant mixed with acetone can be used before the bending test to distinguish the difference between the precrack and the final fracture [104].

However, this method has the following disadvantages: (1) Secondary microcracks in a specimen might be introduced during the precracking by bridge-compression for very brittle material; (2) Cannot easily be used to obtain crack growth data; (3) The length of pre-crack may not be fully reproducible from specimen to specimen due to difficulty with controlling load.

The author has tried several specimens by SEPB technique. The problems are (1) it is very hard to introduce precrack for the relatively tougher material in the selected system such as Ni$_{72.2}$Al$_{26.8}$ in-situ composite, even at the maximum groove width and highest load closed to 500 kg. (2) A dye penetrant mixed with acetone was used for precracked Ni$_{67.3}$Al$_{32.7}$ specimens but it was hard to distinguish the difference between the precrack and the final fracture. Therefore, the method was abandoned in this research.
2.2.2 Chevron-Notched-Beam (CNB) Test

The geometry of Chevron-notched bending specimens can be seen in Figure 2.9. The main advantages of CNB are: (1) no pre-cracking essentially necessary; (2) condition. \( a \geq 1.25(K_{1C}/f_{c})^2 \) is irrelevant. Similar condition \( a \geq 2.5(K_{1C}/f_{c})^2 \) which must be obeyed in SENB and SEPB, makes notching and pre-cracking more time consuming procedure particularly for materials of unknown \( K_{IC} \); (3) More likely to obtain a load-displacement records as shown in Figure 2.10, which can be used to calculate work-of-fracture (\( \gamma_{WOF} \)) and other.

\[
\begin{align*}
\alpha &= a/W \\
\alpha_0 &= a_0/W \\
\alpha_1 &= a_1/W
\end{align*}
\]

**Figure 2.9** Chevron-notched, three-point flexure test geometry [120].
Figure 2.10  Examples of load-displacement curves for CNB specimens, (a) stable crack growth fracture test of silicon nitride at room temperature [120], and (b) stable crack growth fracture test of martensitic stainless steel at room temperature [125].
parameters \((J\text{-integral})\); (4) specimen size is much smaller than for a \textit{SEN}B \textit{SEP}B because for \textit{CN}B: \(B \geq 1.25(K_E/\sigma_y)^2\) [98].

One of the important assumptions of the chevron-notch geometry is that the crack growth occurs in a stable manner prior to the attainment of a peak load. The apex of the chevron-notch gives rise to a high stress concentration and propagation occurs at relatively low loads. Because of the low initiation load, the stored elastic strain energy in the specimen and the test machine (probably negligible if machine is stiff enough) is also low which promotes the stable crack growth. This is also due to the fact that as the crack progresses through the chevron the crack front continually increases promoting stable crack growth [121-123]. Load-displacement curve for such a situation exhibits an initially linear behaviour until the crack propagation commences and then becomes nonlinear just before it reaches \(P_{\text{max}}\). This non-linearity is caused by the stable crack propagation. The extent of this non-linearity on the load \((P)\) - displacement curve before \(P_{\text{max}}\) seems to depend on the material. In materials which can be called "linear elastic" (flat \(R\)-curve) or "nonlinear elastic" (rising \(R\)-curve) [120], (non-linear elastic behaviour, e.g. in ceramics, is due to the development of nonelastic processes in the crack tip region such as microcracking phase transformations, or grain interlock [124] or fracture mechanisms which develop in the wake of region as the crack propagates [120]), the extent of the non-linearities before \(P_{\text{max}}\) is rather minimal (Figure 2.10a). However, in materials which also develop some plasticity during stable crack growth this extent can be much more substantial (Figure 2.10b).
At $P_{\text{max}}$, a balance is achieved between the increasing crack area and the resistance to crack propagation by the material and the crack driving force from the external loading. Once the maximum load for the load-displacement curve is achieved, then in the ideal case the further crack growth is stable where the increasing resistance of the specimen to crack extension is just balanced by the crack driving force so that the crack propagates in a quasistatic, stable manner, instead of catastrophically. This results in a characteristic "tail" on the load-displacement curve (Figure 2.10a).

However, there is a strong experimental evidence that on many occasions despite predictions to the contrary, the presence of a chevron notch in a bend or short-bar specimen does not always guarantee the formation of a stably growing crack at low loads. Instead, a sharp drop in the load occurs immediately at the end of a linear portion of the load-displacement record, at $P_{\text{max}}$ [106, 124, 125-129].

Usually this kind of behaviour is related to a relatively wide chevron-notch slot width [106, 124]. Chuck et al. [124] argued that the problem with a wide notch is not the difficulty of initiating a crack at the apex of the chevron, but rather of propagating a "proper" chevron crack (that is, a crack that is in the proper plane and not pinned by the notch groove). Barker [130, 131] recommended for chevron-notched short-rod and short-bar specimens the notch width gap less than 0.03B and ideally, the slots forming the chevron should have sharply pointed slot bottoms ($\leq 60^\circ$) to maintain good plane strain constraint along the crack front. However, data listed in Table 2.2 for specimens exhibiting a fully linear load-displacement record and unstable
crack growth do not convincingly show that a stable crack growth can always be obtained for the slot width $N/B$ ratios smaller than 0.03 as suggested by Barker [130, 131]. The Barker's notch width criterion was established for short-bar or short-rod specimens and it is not clear whether or not it applies to a bend specimen (3 or 4 point loading). In trialuminides tested in bending [129] it was impossible to obtain a stable crack growth despite that the chevron slot width ratio was only 0.022 (Table 2.2), i.e. much less than that recommended by Barker [130, 131]. However, the fracture toughness values obtained from chevron-notch-beam (C NB) specimens were conservative and almost identical as those obtained from single-edge-precracked-beam (SEPB) specimens [129]. Similarly, Horton and Schneibl [128] obtained

Table 2.2 Slot widths in chevron-notch testing of various materials at room temperature exhibiting a fully linear load-displacement record and unstable crack growth.

<table>
<thead>
<tr>
<th>Material</th>
<th>Chevron Slot Width $N$ (mm)</th>
<th>Slot Width Ratio $N/B$</th>
<th>Loading Mode</th>
<th>Validity of Test</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glass</td>
<td>0.50</td>
<td>0.125</td>
<td>4PB</td>
<td>Invalid</td>
<td>[124]</td>
</tr>
<tr>
<td>Steel</td>
<td>0.37</td>
<td>0.031</td>
<td>3PB</td>
<td>Invalid</td>
<td>[126]</td>
</tr>
<tr>
<td>Glass</td>
<td>2.38</td>
<td>0.170</td>
<td>3PB</td>
<td>Valid</td>
<td>[106]</td>
</tr>
<tr>
<td>Steel</td>
<td>0.14</td>
<td>0.005</td>
<td>T (Short Bar)</td>
<td>Invalid</td>
<td>[127]</td>
</tr>
<tr>
<td>Trialuminide</td>
<td>0.11</td>
<td>0.022</td>
<td>4PB</td>
<td>Valid</td>
<td>[129]</td>
</tr>
</tbody>
</table>
rather conservative fracture toughness values calculated from the maximum load for a 
Nd2Fe14B intermetallic despite that the load-displacement record in three-point bending was 
fully linear up to $P_{\text{max}}$ with the following unstable crack growth. In conclusion, it seems that as 
long as the chevron slot width in bend specimens is smaller than 0.03B the maximum load at 
the fully linear load-displacement record indicating unstable crack propagation can be utilized 
for the calculation of conservative (valid) fracture toughness value. Because of the unique 
features of CNB specimen as discussed above, some of these specimens such as short rod and 
short bar in tension test have been considered by ASTM [98]. Unfortunately there is no ASTM 
standard file available for CNB specimen in bending, which obviously can save more material 
and be tested in easier way than short-bar or rod in tension. But more and more investigators 
have been working on it recently because it is fairly well based theoretically and has much more 
attractive advantages than other conventional methods [120-128]. Furthermore, the bending 
tests on CNB can be performed by analogy with the ASTM standards E 1304-89 [98], E 399-
90 [97] and E 813-89 [99].

**Determination of Specimen-Size and Loading Mode**

Considering the dimension and cast-quality of the ingot and numbers of specimens for the 
test, the specimen-dimensions will be designed as follows: $B=3.5\text{mm}$, $W=4\text{mm}$ and $WB=1.14$, 
which are decided on the basis of the references ($WB=1.25$ [124, 132], $WB=1.5$ [126, 133],
WB=1.0 [120], WB=1.25-2.5 [135], WB=1.6 [136], WB=1.8 [106]) and analogy with the requirement in E 399-90: 1 ≤ W/B ≤ 4 [97]. A nominal support span will be equal to 16 mm for a bending test according to E399-90 (S/W=4) [97] and references [106, 126, 133, 134-136]. The diameter $D$, of the roller will be 4.8 mm, which is close to the requirement of E399-90: $W > D > W/2$ [97].

No clear preference is seen for the mode of loading from the references. Most researchers used three-point bending (3PB). Munz et al. [132] indicated that in four-point bending (4PB) the specimen alignment is not very critical because of the constant moment between the inner loading points as shown in Figures 2.1 b and d. Additionally interaction between the load roller pins stress field and the crack stress field, which can happen in 3PB is avoided in 4PB. Therefore 4PB might be preferred for a bending test. But in testing small-size specimens the above concerns don't seem to be too important. From references [106, 120, 124, 126, 132-136], the most preferred geometry seems to be $S/W = 4$ for 3PB and $S/W = 8$ for 4PB. Therefore, for a four-point loading as shown in Figure 2.1b, the major span, $S_1$, the distance between the support rollers, would be at least 40 mm if considering $S_2 = 10$ mm and the diameter of the rollers, $D = 4.8$ mm in our case. Thus the total length of the specimen would be approximately 45 mm, which would definitely increase the difficulty to prepare the ingots, and more than twice as much material would be used comparing to the three-point loading. Therefore, the 3PB flexure loading arrangement will be preferred in this research.
Notch-Parameter Design

There are six parameters \((N, \theta, a_o, a_i, \alpha_o, \text{ and } \alpha_i)\) as shown in Figure 2.9 that must be considered for chevron-notch-geometry design, but only three of them are independent.

The Slot Width \(N\) of the Notch

Notch preparation is critical in the determination of the plane-strain fracture toughness of materials with notched bend specimen. Measured chevron fracture toughness values \((K_{hm})\) decrease with decreasing slot width, \(N\) [132]. Below a critical slot width \(N_c\) (or notch root radius \(r_o\)), "\(K_{hm}\)" is constant and presumably equal to the plane-strain fracture toughness that would be obtained from specimens with sharp cracks. In *E 1304-89* [98], the slot width is recommended as \(N \leq 0.03B\). Wu [126, 133] chose \(N/B=0.013\) in a three-point loading CB and obtained a very good result: \(K_{hm} = K_c\), where \(K_c\) was determined by ASTM E399 Standard method. However, Wu [126] observed a change to completely linear load-load line displacement (LLD) and unstable crack growth with \(N/B = 0.031\). Probably, the best choice would be to have it at \(N/B = 0.01\) but that might be difficult to machine. In our case, an electric discharge machine (EDM) thinner wire of 0.1 \(mm\) thickness will be used in this experiment to yield the notch width of \(\approx 0.11 \text{ mm}\) and notch ratio of \(N/B = 0.031\).
The Slot Angle $\theta$ of the Notch

Bar-on et al. [134], Nakamura and Kobayashi [137] suggested the optimum sharpness of the notch because stable crack growth must occur easily when the notch tip angle is relatively sharp. In $E 1304-89$ [98], two small slot angles ($\theta = 54.6^\circ$ or $34.7^\circ$) were used. Wu [126, 133] used $\theta = 60^\circ$ and obtained a stable crack growth up to $P_{\text{max}}$. In this research, $\theta = 60^\circ$ (Figure 2.9) will be chosen as the slot angle of the notch.

The Initial Crack Length $a_0$

Bar-On et al. [134] pointed out that the larger value of $a_0$ promotes stable crack propagation after reaching maximum load. Wu [126, 133] also recommended the depth ratio of chevron notch $\alpha_0$ ($a_0/W \geq 0.3$ because the fracture toughness values $K_{fm}$ determined by CNB and $K_c$ from ASTM E 399 Standard method were in good agreement with one another. However, Munz et al. [132] obtained very good agreement between $K_{fm}$ from CNB and $K_c$ determined by ASTM E 399-90 [97], which appeared to be independent of the initial crack length $a_0$. Chuck et al. [124], and Merkel and Messerschmidt [136] also obtained pretty good results ($K_{fm}=K_c$) by choosing $a_0=0.2W$. In other words, $K_{fm}$ seems not to be sensitive to $a_0$. In this experiment, $a_0$ will be dependent on other three parameters because of the EDM processing. $a_0$ could vary from 0.4 to 1.6 mm ($a_0/W = 0.1$ to 0.4) which was measured on broken specimens.
The Slot Length $a_t$ of the Notch

Bar-On et al. [134] pointed out that interaction of the stress field arising from the loading pin with the stress field of the advancing crack was avoided by locating the base of the triangle far enough away from the loading point. Therefore, $a_t = 0.75W$ was used in their three-point loading CNB test. Jenkins et al. [120] chose $a_t=W$ for their three point CNB to investigate work-of-fracture. Merkel and Messerschmidt [136] also used $a_t=W$ for their three-point CNB and obtained a lower $K_{hm}$ with much better reproducibility than $K_e$ values obtained from tests using straight-notched specimens [136]. Thereby, $a_t = 0.8W$ is chosen in this research.

Thus, the dependent ratios of the notch parameters of the CNB are as follows: $\alpha_y = 0.1-0.4$, $\alpha_t = 0.8$ and $N/B = 0.031$ as shown in Figure 2.9.

2.2.3 Evaluation of Fracture Toughness Parameters in CNB Bend Testing

Evaluation of Fracture Toughness $K_{hm}$

Munz et al. [132] and Barker [121] developed a basic relation of evaluating $K_{hm}$, which denotes the fracture toughness of CNB calculated from the $P_{max}$ and $Y^*_m$, by use of the energy approach of linear elastic fracture mechanics as follows (Appendix B):

$$K_{Oe} = \frac{P_{max}}{BW^{1/2}} Y^*_m$$ (2.24)
where $Y_m^*$ is the minimum value of the dimensionless stress-intensity-factor coefficient (Figure 2.11) when the crack length, $a$, increases to a critical value, $a_m$, and the load reaches a maximum $P_{\text{max}}$ in the meantime if the crack growth resistance curve of the tested material is flat [126, 133]. The $Y^*$ parameter depends only on the geometry of the specimens [122, 126, 132-133],

$$Y^* = \left( \frac{1}{2} \frac{dC_v(\alpha)\alpha}{d\alpha} \alpha - \alpha_0 \right)^{1/2}$$

(2.25)

![Diagram showing comparison on normalized stress-intensity factor coefficients for chevron-notched and straight-through crack specimens [121].](image)
where \( C_c(\alpha) = E'BC \) (\( C \) denotes the compliance of the material, \( E' = E \) for plane stress and \( E' = E(1-\nu^2) \) for plane strain), is the dimensionless compliance. \( \alpha, \alpha_o \) and \( \alpha_i \) are normalised depths by \( \alpha = a/W \), \( \alpha_o = a_o/W \) and \( \alpha_i = a_i/W \) as shown in Figure 2.9, respectively. For the occurrence of \( P_{\text{max}} \) at approximately \( a_m \) for \( \chi' \) function it is important that the chevron crack must grow in a stable fashion before the load reaches \( P_{\text{max}} \).

There are three methods for determination of \( \chi' \) coefficient. The first one is the direct experimental calibration of \( \chi' \) with \( K_c \) value obtained by ASTM E 399-90 [97]. However, the direct calibration is dependent on the behaviour of the calibrated material and is restricted to a single specimen geometry. The second one is the experimental calibration of \( C_c(\alpha) \) [138]. The compliance calibration is dependent on the loading device used in the calibration. In addition, the results of \( \chi' \) are dependent on the fitting functions of \( C_c(\alpha) \). The third method is a calculation of \( C_c(\alpha) \) based on the straight-through-crack assumption (STCA) proposed by Munz et al. [132, 139]:

\[
\frac{dC_v(\alpha)}{d\alpha} = \frac{dC_s(\alpha)}{d\alpha}
\]  

(2.26)

or a more refined "slice model" proposed by Bluhm [140]

\[
\frac{1}{C_v(\alpha)} = \frac{\alpha - \alpha_o}{\alpha_1 - \alpha_o} \frac{1}{C_s(\alpha)} + \frac{k}{\alpha_1 - \alpha_o} \int_{\alpha}^{\alpha_i} \frac{1}{C_s(\xi)} d\xi
\]  

(2.27)

where \( k \) is the shear transfer coefficient. \( C_c(\alpha) \) is defined as follows:
\[ C_s(\alpha) = \gamma + \beta \tan^2\left(\frac{\pi\alpha}{2}\right) \]  \hspace{1cm} (2.28)

with (Wu [126, 133], hereafter called as "Wu's solution")

\[ \gamma = \frac{I}{4} \left(\frac{S}{W}\right)^3 \left[ 1 + 3(1+\nu)\left(\frac{W}{S}\right)^2 \right] \]  \hspace{1cm} (2.29)

\[ \beta = 2 \frac{S}{\pi 4W} \left[ 7.31 + 0.21\left(\frac{S}{W} - 2.9\right)^{1/2} \right]^2 \]  \hspace{1cm} (2.30)

or (Bluhm [140], Munz [132], and Withey and Bowen [141], hereafter called as "Bluhm's solution")

\[ \gamma = \frac{I}{4} \left(\frac{S}{W}\right)^3 \left[ 1 + 2(1+\nu)\left(\frac{W}{S}\right)^2 \right] \]  \hspace{1cm} (2.31)

\[ \beta = 2.7 \left(\frac{S}{W}\right)^2 \]  \hspace{1cm} (2.32)

Thus an analytical expression of the dimensionless compliance of CNB specimen can be deduced by substituting Eq.(2.28) into Eq.(2.27),

\[ \frac{I}{C_v(\alpha)} = \frac{\alpha - \alpha_0}{\alpha_1 - \alpha_0} \gamma + \beta \tan^2\frac{\pi\alpha}{2} + \frac{k}{(\alpha_1 - \alpha_0)(\gamma - \beta)} \left(\frac{\alpha_1 - \alpha}{\pi} - 2\right) \]

\[ \frac{\beta}{\gamma} \left[ \arctan\left(\frac{\beta}{\gamma} \tan\frac{\pi\alpha}{2}\right) - \arctan\left(\frac{\beta}{\gamma} \tan\frac{\pi\alpha}{2}\right) \right] \]  \hspace{1cm} (2.33)

where the value of \(k\) is given as [133].
for $\phi \geq 1$: \[ k = 1 + 0.444(\alpha_i)^{3.12} \] (2.34)

$\phi < 1$: \[ k = 1 + \alpha_i^{3.12}(2.236\phi - 4.744\phi^2 + 4.669\phi^3 - 1.77\phi^4) \] (2.35)

where $\phi=0.5(\pi-\theta)$ (for definition of $\theta$ see Figs. 2.9 and 2.12). It must be pointed out that the expressions provided by Eqs.(2-34) and (2.35) for the shear coefficient $k$, are semi-empirical and must be treated with caution.

From the references [126, 132, 133, 140, 141], it is hard to see which solution is correct. Therefore, the two solutions will be used by Maple software to calculate $K_{h_m}$. These two solutions will be used for calculation of the fracture toughness values which will be designated $K_{h_m}^W$ (Wu's solution) and $K_{h_m}^B$ (Bluhm's solution), respectively. The experimental results of the two solutions will be compared and analyzed in Chapters 3 and 4.

In addition, the stress-intensity factor coefficient $Y'$ is very sensitive to the $V$-notch geometry. The two sides of the $V$-notch machined by the preceding method may cause a deviation of $f$ from the midthickness plane as shown in Figure 2.12. Wu [133] derived a formula to calculate the dimensionless compliance, $C'_v(\alpha)$, of the specimen with a deviation of $f$ by use of the slice model as follows,

\[
\frac{1}{C'_v(\alpha)} = \frac{1}{C_v(\alpha)} + \Delta(F)
\] (2.36)

where

\[
\Delta(F) = \frac{k}{\pi(\alpha_1 - \alpha_0)(\gamma - \beta)} \left( \frac{\beta}{\gamma} \right)^{\frac{\mu^2}{2}} \arctan\left( \frac{\beta}{\gamma} \right)
\]
\[-\arctan\left(\frac{\beta}{\gamma}\right) \tan \frac{\pi(\alpha_1 + F)}{2} \right) \right) - \arctan\left(\frac{\beta}{\gamma} \tan \frac{\pi(\alpha_1 - F)}{2} \right) \right] \tag{2.37}

with

\[ F = \frac{f}{W} \cot \frac{\theta}{2} \tag{2.38} \]

\[ \alpha_1 = \frac{a_1}{W} = \frac{B}{2W} \cot \frac{\theta}{2} + \alpha_0 \tag{2.39} \]

The size requirement for a valid \( K_{hm} \) in a CNB bending test is \([98, 122]\),

\[ B \geq 1.25 \left( \frac{K_{\alpha_0}}{\sigma_{rs}} \right)^2 \tag{2.40} \]

Here it has to be pointed out that \( K_{hm} \) values are not necessarily, automatically equivalent to \( K_c \) obtained from \textit{ASTM E 399} \([97]\).

Figure 2.12  Cross section of deviated chevron notch \([133]\).
**Evaluation of Apparent Fracture Toughness $K_{WOF}$ in CNB Bend Testing**

At the point of complete fracture through the chevron section, the work-of-fracture can be determined from the total energy consumed during the entire fracture process divided by the total, projected fracture area, $2A_T$, of the specimen such that \([120]\) (under the condition that the load-displacement curve has the shape as shown in Figure 2.10a):

$$\gamma_{WOF} = \frac{\int_0^{LFD} Pd(LLD)}{2A_T} \quad (2.41)$$

where the integral can be calculated directly from the area under the load-displacement curve. $\gamma_{WOF}$ can be used as an estimate of the fracture energy. Extending the assumption of linear elastic behaviour to \(LEFM\), the apparent fracture toughness can be calculated from the $\gamma_{WOF}$ such that \([120]\),

$$K_{WOF} = \left[ E' (2\gamma_{WOF}) \right]^{1/2} \quad (2.42)$$

where $K_{WOF}$ is the apparent fracture toughness, which can be used to predict fracture toughness of linear or sometimes nonlinear elastic materials. However, if the energy consumed by the nonlinear elastic fracture processes of the composite is too large, total work-of-fracture cannot be used to predict the \(LEFM\) $K_c$.

In addition, because the work-of-fracture is related to nonlinear elastic fracture mechanisms its determination will be dependent upon such conditions as crack velocity (displacement or
loading rate), size of the chevron section, and other testing variables [120]. Despite these limitations in non-LEFM materials, $\gamma_{\text{WOF}}$ is still a useful nonlinear elastic fracture parameter for comparative purposes for the same material and test conditions.

**2.2.4 J-Integral Method in a CNB Test**

Unfortunately, there is no ASTM Standard file available for J-integral method for a CNB test so far and also not much experimental work on this subject. However, the J-integral test for a CNB can be performed by analogy with the fundamental concepts and methods as described above in the ASTM Standards E 813-90 [99], E 1304-89 [98] and E 399-90 [97]. Besides, this is also the reason why we choose this approach: we are trying to establish a new, maybe not perfect, but reasonable approach for J-integral method as applied for a CNB test.

**Evaluation of J-Integral in ASTM Standard E 813-89**

This method is an energy approach and has been developed to define the fracture conditions in a component experiencing both elastic and plastic deformation. J-integral is a mathematical expression, a line or surface integral that encloses the crack front from the one crack surface to the other, used to characterize the local stress-strain field around the crack front.
The $J$-$\Delta a$ data can be generated by either multiple specimen (at least five) or single specimen techniques.

With the multiple specimen technique, a series of nominally identical specimen are loaded to various levels and then unloaded. These samples should reveal various amounts of crack extension, which is marked by heat tinting to discolour the existing fracture surface after the test. Each specimen is then broken open and the crack extension is measured. $\Delta a$ is given by the average of nine readings taken across the crack front from one surface to the other (Figure 2.13b). The area under the load-displacement plot for each sample is measured, and $J_{pl}$ is computed as shown below.

The ASTM Standard E 813-89 [99] defines the $J$ value at a given measured point $i$ ($1 \leq i \leq n$) on the load-displacement line corresponding to a load $P_i$ and displacement $\delta_i$. For three-point bending with a span/width ratio of four, the elastic and plastic components of $J$ can be estimated from the following expression [99]:

$$J_i = J_{el(i)} + J_{pl(i)} = \frac{K_i^2(1-\nu^2)}{E} + \frac{2A_i}{Bb}$$

(2.43)

where $b (=W-a)$ is the initial uncracked ligament and $B$ is thickness of the specimen as shown in Figure 2.1a. $A_i$ is the plastic area under the load-displacement curve as shown in Figure 2.13c.

The $J$-integral is determined and plotted against physical crack growth, $\Delta a$, using at least four data points within specified limits of crack growth. In ASTM Standard E 813-89 [99], the crack length was not measured directly from the bent specimen but calculated from a
Figure 2.13 Procedures for multi-specimen determination of $J_{IC}$ [100].
relationship with crack opening displacements, which measured at the notched edge. These data reflect the materials resistance to crack growth.

The $J$ versus crack extension behaviour is approximated with a best-fit power law relationship (Figure 2.13d). In Figure 2.13d, the blunting line has a slope of $2\sigma_y$ (where effective yield strength $\sigma_y = (\sigma_{ys} + \sigma_{rs})/2$, $\sigma_{rs}$ denoting the ultimate tensile strength), which takes into account strain hardening in the material. A 0.2 mm offset line parallel to the blunting line is drawn and the intersection of this line and the power law fit defines $J_{lc}$, provided the validity requirements of this test method are satisfied.

Obviously, the multiple specimen technique involves the testing of numerous specimens, which makes the procedure both tedious and very expensive. Particularly, it is very difficult to machine several specimens with absolutely identical dimensions. As a substitute of it, another technique has been developed from multiple loadings of a single sample, which is illustrated in Figure 2.14. After the sample is loaded to a certain load and displacement level, the load is reduced by approximately 10%. By measuring the specimen compliance during this slight unloading period, the crack length corresponding to this compliance value can be defined [99]. As the crack grows, the specimen becomes more compliant. Relatively deep cracks ($0.50 \leq a/W \leq 0.70$) are required in $E 813$-90 [99] because the unloading compliance technique is not sufficiently sensitive to $a/W < 0.5$ [99].
Evaluation of J-Integral for a CNB Test

Before the ASTM standard E 813-89 [99] for J-integral method was available, Sakai et al. [142] successfully used such a similar loading-unloading procedure on polycrystalline graphite by tensile testing of chevron-notched specimens and proved that the energy method for determining nonlinear fracture mechanics parameters from load-displacement diagrams was very effective and feasible in studying the elastic-plastic fractures of various materials.
According to Eq.(2.24) and analogy with Eq.(2.43), the elastic and plastic components of $J$-integral in a CNB test can be assessed by:

$$J_i = J_{el(i)} + J_{pl(i)} = \frac{P_i^2 Y_i^2 (1 - v^2)}{B^2 W E} + \frac{4 A_i}{B(2W - a_i - a_0)}$$  (2.44)

For monitoring crack growth and calculating the plastic area $A_i$, the unloading compliance method for a single specimen can be used as illustrated by Figure 2.15.

Figure 2.15a shows the special case of negligible plasticity, which exhibits a load-displacement curve deviating from its initial linear shape because the compliance continuously changes. If the specimen were unloaded prior to fracture, the curve would return to the origin, as the dashed lines indicate [38]. The instantaneous crack length can be inferred from the compliance through relationships given in Eq.(2.33) with $\alpha = a/W$ and $C = C/E'B$ or from assumed linear relationship between load-line-displacement (LLD) and a crack extension as it is calculated in this work (see Section 4.8 and 4.9).

Figure 2.15b illustrates the case where a plastic zone forms ahead of the growing crack. The nonlinearity in the load-displacement curve is caused by a combination of crack growth and plastic deformation. If the specimen is unloaded prior to fracture, the load-displacement curve does not return to the origin; crack tip plasticity produces a finite amount of permanent deformation in the specimen [38]. The stress intensity should be corrected for plasticity effects by substituting $C_{eff}$ into Eq.(2.33) to determine an effective crack length.
Figure 2.15 Load-displacement curve for crack growth (a) in the absence of plasticity, (b) with plasticity, (c) the unloading compliance method for monitoring crack growth and calculate the plastic area $A_i (1 \leq i \leq n)$ [38].
Figure 2.15c shows the most common case where the crack length is computed at regular intervals during the single specimen test by partially unloading the specimen and measuring the compliance. As the crack grows, the specimen becomes more compliant (less stiff) [38]. The plastic area $A_i$ can be calculated by

$$A_i = A_{i-1} + \frac{P_i (P_i C_i - P_{i-1} C_{i-1})}{2}$$

where $1 \leq i \leq n$. When $i = 1$, the $A_0$ could be measured directly from the load-displacement curve.

Thereafter, according to the ASTM Standard E 813-90 [99] the $J$-integral is determined and plotted against physical crack extension, $\Delta a$, using at least four data points. The $J$ versus crack extension behaviour can be simulated by a power law curve, which reflect the materials resistance to crack growth. Thereby, a $J_{Q_e}$ value can be obtained from this curve. After verifying the validity of $J_{Q_e}$ by Eq.(2.20), a $J_{xc}$ value would be obtained and used to calculate the $K_{xc}$ [38, 99-100],

$$K_{xc} = \left[ \frac{J_{xc} E}{(1-v^2)} \right]^{1/2}$$

Obviously, the $J$-integral, unloading-reloading method in a CNB test by three-point bending has more advantages than a customary CNB test for $K_{xc}$ because this method needs exceptionally small amount of materials as discussed in Section 2.1.3 and is much more useful for non-elastic materials.
2.3 Alloy Processing and Microstructure Measurement Techniques

The in-situ boron-free and boron-doped composite alloys investigated were prepared from pure elements (nickel (99.98 pct) and aluminum (99.99999 pct)) and a master alloy of Al-3.2 wt.% B, and had a composition of Ni<sub>1-x</sub>Al<sub>100-y</sub>B<sub>x</sub>, x = 0.2 or 0.4 at.% for boron-doped alloys; y = 65, 67, 69, 70, 73, 75 and 77 at.%). The pure elements were melted by a high frequency induction melting method in a graphite crucible coated inside with a boron nitride aerosol lubricant and then poured into a stainless steel mould under a high-purity argon atmosphere. The details of the melting procedure are given in Table 2.3.

In addition, the maximum temperature of the melt was measured by a thermocouple (W-5%Rh and W-26%Rh) inserted into the graphite crucible. Temperature had to be controlled accurately (within ±5°C) to avoid the reaction between the melting solution and the crucible at elevated temperature.

An additional homogenizing heat treatment was performed at 1000°C/100h (furnace cooling) for all the ingots in a tube furnace. Some additional annealing or quenching was also done for some of the samples to investigate the changes in the microstructure. To reveal the grain-boundaries, the polished surface of the specimen was etched by Nital (4% HNAI<sub>3</sub>+ alcohol) for 20 to 90 seconds.
Table 2.3  Details of melting and casting processing procedure.

<table>
<thead>
<tr>
<th>In-situ Composite</th>
<th>Method no.</th>
<th>Description</th>
</tr>
</thead>
</table>
| Ni₆₅Al₃₅          | 1          | (i) Evacuating the chamber of the induction furnace to 0.05 atm.  
|(ii) Heating up to ≈400°C in vacuum  
| (iii) Evacuating again to 0.05 atm. or below  
| (iv) Pressurize the chamber with high purity argon gas (1.7x10⁻³ MPa)  
| (v) Slow heating up to max. temperature ≈1520°C in 10 min.  
| (vi) Holding at ≈1520°C for 6 min.  
| (vii) Pouring into a stainless steel mould  
| (viii) Furnace cooling (20°C) |
| Ni₆₇Al₃₃          |            |             |
| Ni₆₉Al₃₁          | 2          | Almost the same steps as above except:  
| (v) Slow heating up to max. temperature ≈1500°C in 15 min.  
| (vi) Holding at ≈1500°C for 6 min. |
| Ni₇₁Al₂₉          |            |             |
| Ni₇₃Al₂₇          | 3          | Almost the same steps as above except:  
| (v) Slow heating up to max. temperature ≈1485°C in 15 min.  
| (vi) Holding at ≈1485°C for 6 min. |
| Ni₇₄Al₂₇B₀.₂      |            |             |
| Ni₇₅Al₂₅          |            |             |
| Ni₇₄₄Al₂₅B₀.₂     |            |             |
| Ni₇₄₆Al₂₅B₀.₄     |            |             |
| Ni₇₇₇Al₂₃         | 4          | Almost the same steps as above except:  
| (v) Slow heating up to max. temperature ≈1485°C in 15 min.  
| (vi) Holding at ≈1485°C for 6 min. |
| Ni₇₅₈Al₂₃B₀.₄     |            |             |
The microstructure, crystal structure and composition of the alloys were investigated by optical microscopy (Nomarski interference contrast), scanning electron microscopy, X-ray diffraction (XRD) patterns carried out in a Siemens D500 diffractometer equipped with a nickel filter and graphite monochromator using Cu-Kα radiation (λ=1.54060 Å) and a fully quantitative X-ray energy dispersive spectroscopy (EDS) analysis (QX2000 Link system). The volume fractions of the second phase was measured on the monitor's screen attached to the optical microscope by the linear intercept method [143]. Vickers indentations were made in the proximity of grain boundary under load of 2000g as to induce intergranular cracking at the grain boundaries in the B-free and B-doped Ni3Al specimens. This in a qualitative manner would test the effect of boron addition on the brittleness of grain boundaries in Ni3Al. These intergranular microcracks were also measured on some specimens by an automated Java image analysis system [144].

2.4 Preparation and Procedures of the Fracture Toughness Test

This test method involves testing of chevron-notched specimens by three-point loading. The cross head speed was 0.05 mm/min, which was the lowest one of the Instron machine (Model 4206). Load versus load-line displacement (LLD) was recorded either digitally by a computer or autographically on an x-y recorder. The $K_{\text{Im}}$ value is calculated from the
maximum load by equations that have been established on the basis of elastic stress analysis of CNB specimens described in Chapter 2.

The single specimen technique involves using an elastic compliance technique as discussed in Section 2.2 to obtain the $J$-$\Delta a$ curve from a single specimen. At least five specimens for each in-situ composite were tested. The load/reload sequences of a single-specimen technique produce $J$ versus crack extension data points evenly spaced over the prescribed test region. A minimum of six $J$ versus crack-extension data points were obtained.

The validity of the determination of the calculated $K_{\text{nc}}$ and $J_{\text{nc}}$ from this test would be discussed in Chapter 4.

### 2.4.1 Specimen Preparation

The bend specimen is a chevron notched beam with dimensions: (3.5 to 5) x (4 to 5) x 20 mm$^3$, which is machined by an EDM. The ratio $WB$ of the rectangular beam is nominally equal to 1.14→1.45. The dimensional tolerances and surface roughness satisfied the requirements of $E$ 399-90 FIG. A3.1 [97] by medium emery paper polishing. The CNB was loaded in three-point bending with a support span, $S$, nominally equal to four times the width, $W$, as shown in Figure 2.9.

The specimen must be installed in the fixture properly. The test fixture was set up so that the line of action of the applied load shall pass midway between the support roller centres within 1\% of the distance between these centres. The load point was aligned right in the middle of the specimen using a magnifying glass with light. The span was measured within 0.5\% of
nominal length. The specimen was located with the crack tip midway between the rollers to within 1% of the span, and squared to the roller axes within 2°. The specimen was loaded at a rate of 0.0008s⁻¹ such that the rate of increase of stress intensity is within the range 0.007 to 0.017 MPa.√m/s. At least five specimens were tested for each alloy.

2.4.2 Fixture Design and Fabrication

The primary requirements of all alignment devices are that the load is applied axially, uniformly and with negligible "slip-stick" friction [145]. In order to ensure uniaxial loading, a ball-joined fixture was designed and processed by a lathe and a milling machine for a CNB test. This fixture is designed to minimize frictional effects by allowing the support rollers to rotate and move apart slightly as the specimen is loaded, thus permitting rolling contact as shown in Figure 2.16.

The precise feedings step by step for ball surface was calculated using Matlab software. The fixture was made from Hot Rolled-SPS steel. Before machining, its surface Rockwell "C" hardness was approximately 22, which is easy to machine to any shape. After machining, its surface hardness was increased to 55 HRC when it was heated to 830° for 50 minutes followed by oil quenching in order to avoid its deformation during loading.
Figure 2.16 Schematically drawings of ball-joined loading parts and span-adjustable support parts, of three-point bending fixture.
This fixture is more adjustable with respect to the size of the specimen because the span can be adjusted continuously to any value that is within its capacity from 8 to 40 mm as shown in Figure 2.16. Thus CNB specimens with a wide range of thicknesses can be tested with the single fixture.

2.5 Some Additional Tests

2.5.1 Compression Testing

The yield strength $\sigma_{YS}$ of each broken specimen was obtained by a compression test according to ASTM standard E 9-89a [145]. The rectangular specimen with 4x4x6.8 mm$^3$ (the ratio of specimen length over equivalent diameter is 1.5, which is recommended in E 9-89a [145]) was subjected to an increasing axial compressive load under a constant strain rate of $10^{-4}$ s$^{-1}$: both load and strain were monitored and recorded digitally by a computer.

Both ends of the compression specimen shall bear on blocks with surfaces flat and parallel within 0.0002 in/in and with a surface finish less than 1.6 $\mu$m by grinding. The two hardened steel blocks with =50 HRC after heat treatment 870°C for 30 minutes and brine quenching were carefully centred with respective to the testing machine heads.

To reduce friction, which can effect test results by barrelling, molybdenum disulfide was
applied on the surfaces. The specimens were carefully polished to obtain a surface roughness of 1.6 μm, flatness and parallelism within 0.0005 mm/mm, which was perpendicular to the lateral surface. The specimen was placed in the test fixture and carefully aligned to ensure concentric loading. The strain range was set less than 0.05 because only yield strength was acquired in this test.

2.5.2 Vickers Microhardness Test

The micro-mechanical properties of individual phases were investigated by a Vickers microhardness test. The Shimadzu Micro Hardness Tester HMV-2000 was used to carry out Vickers microhardness test. Its automation of loading, holding of loads, unloading and selection of the test load eliminate individual errors during loading [146]. As well, the additional low weights of 5 gf and 10 gf, and the built-in data processing capability permit the high reliability and controllability of this hardness test.
CHAPTER 3

EXPERIMENTAL RESULTS

3.1.1

3.1.2 As discussed in the previous Chapters, fracture toughness of in-situ composites is very dependent on the microstructural features, which include: morphology of structure, volume fraction of reinforcement, composition and grain size. Therefore, a general investigation and thorough understanding of microstructural features in the as-cast and homogenized, boron-free and boron-doped in-situ NiAl-Ni$_3$Al composites produced by induction melting method is essential before a discussion of the fracture toughness test results can begin.

3.1 Microstructural Features

3.1.1 The As-Cast, Boron-Free and Boron-Doped In-Situ Composites

Figure 3.1 shows a group of typical photographs obtained from the as-cast, boron-free in-situ composites. A few local twin-structures obviously exist in the NiAl matrix of the as-cast
Figure 3.1  Optical micrographs of the etched microstructures of the as-cast, boron-free in-situ composites with Nomarski interference contrast: (a) Ni$_{64.6}$Al$_{35.4}$ and (b) Ni$_{65.5}$Al$_{34.5}$.
Figure 3.1  Optical micrographs of the etched microstructures in the as-cast, boron-free in-situ composites with Nomarski interference contrast: (c) Ni$_{67.1}$Al$_{32.9}$ and (d) Ni$_{70.3}$Al$_{29.7}$. 
Ni$_{64.6}$Al$_{35.4}$ composite alloy as shown in Figure 3.1a. The Ni$_3$Al phase is distributed as an envelope at the grain boundaries and intragranular precipitates. Compared to Figure 3.1a, it can be seen that the Ni$_{66.5}$Al$_{34.5}$ alloy shows almost fully twinned-structures (Figure 3.1b) while the overall Ni content in the two composites only differs by 0.9 atomic percent, which demonstrates that the phase morphologies of the Ni-rich in-situ composites are very sensitive to the increase of Ni content. In addition, the volume fraction of Ni$_3$Al phase in Ni$_{66.5}$Al$_{34.5}$ distributed as precipitates and at grain boundaries simultaneously increases up to 21%. This is because these structures are in as-cast materials where cooling rates were not in controlled. In other words, these structures are non-equilibrium. The compositions of each phase are shown in Table 3.1.

When the overall Ni-content again increases by 1.6 at.% to 67.1 at.% in the in-situ composite Ni$_{67.1}$Al$_{32.9}$, the microstructure exhibits a round, discontinuous morphology of Ni$_3$Al phase with a fully twin structure of the NiAl matrix (Figure 3.1c). The size of the ductile second phase of Ni$_3$Al, especially in grain boundaries (as shown in Figures 3.1a to c), gradually increases from approximately 0.6 to 5 μm with increasing Ni content from 64.6 at.% to 67.1 at.%, respectively. The total volume fraction of the ductile Ni$_3$Al phase also increases from 5% to 26%, as shown in Table 3.2.

Almost equal distribution of Ni$_3$Al and NiAl, volume fractions of 54% to 46%, respectively is seen in Ni$_{70.3}$Al$_{29.7}$ as shown in Figure 3.1d. It can be seen that the sharp NiAl phase is continuously distributed in the matrix of Ni$_3$Al (Figure 3.1d). Furthermore, increasing the Ni
### Table 3.1

Target composition and quantitative EDS results of the as-cast, boron-free and boron-doped in-situ composites (at.%).

<table>
<thead>
<tr>
<th>Target Ni (at.%)</th>
<th>Element</th>
<th>Overall</th>
<th>Matrix</th>
<th>Grain boundary</th>
<th>Precipitates</th>
</tr>
</thead>
<tbody>
<tr>
<td>63</td>
<td>Ni</td>
<td>64.6±0.5</td>
<td>62.5±0.9</td>
<td>71.0±1.0</td>
<td>71.7±0.8</td>
</tr>
<tr>
<td></td>
<td>Al</td>
<td>35.4±0.5</td>
<td>37.5±0.9</td>
<td>29.0±1.0</td>
<td>29.3±0.8</td>
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<td>65</td>
<td>Ni</td>
<td>65.5±0.3</td>
<td>63.6±0.9</td>
<td>73.5±0.4</td>
<td>73.5±0.4</td>
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<tr>
<td></td>
<td>Al</td>
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<td>36.4±0.9</td>
<td>26.5±0.4</td>
<td>26.5±0.4</td>
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<tr>
<td>67</td>
<td>Ni</td>
<td>67.1±0.9</td>
<td>65.7±0.5</td>
<td>74.9±0.7</td>
<td>74.8±0.3</td>
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<tr>
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<td>Al</td>
<td>32.9±0.9</td>
<td>34.3±0.5</td>
<td>25.1±0.7</td>
<td>25.2±0.3</td>
</tr>
<tr>
<td>69</td>
<td>Ni</td>
<td>70.3±0.6</td>
<td>73.4±0.6</td>
<td>-</td>
<td>64.2±0.7</td>
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<tr>
<td></td>
<td>Al</td>
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<td>65.4±0.8</td>
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<td>94.2±0.7</td>
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<td>5.8±0.7</td>
</tr>
<tr>
<td>72.8-0.2B</td>
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<td>75.4±0.6</td>
<td>-</td>
<td>65.0±0.6</td>
</tr>
<tr>
<td></td>
<td>Al</td>
<td>26.6±1.1</td>
<td>24.4±0.6</td>
<td>-</td>
<td>34.8±0.6</td>
</tr>
<tr>
<td>74.6-0.4B</td>
<td>Ni</td>
<td>74.5±0.7</td>
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<td>-</td>
</tr>
<tr>
<td></td>
<td>Al</td>
<td>25.1±0.7</td>
<td>24.9±0.6</td>
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</tr>
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</table>
Figure 3.1  Optical micrographs of the etched microstructures in the as-cast, boron-free in-situ composites with Nomarski interference contrast: (e) Ni$_{72.4}$Al$_{27.6}$ and (f) Ni$_{73.1}$Al$_{26.9}$.
Table 3.2 The mean grain size of the material and volume fraction of second phase with standard deviations of the as-cast, boron-free and boron-doped in-situ composites.

<table>
<thead>
<tr>
<th>In-situ composites (at.%)</th>
<th>Type of matrix phase</th>
<th>Matrix grain size (μm)</th>
<th>Type of the second phase</th>
<th>second phase</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni$<em>{64.6}$Al$</em>{35.4}$</td>
<td>NiAl</td>
<td>163 ± 87.4</td>
<td>Ni$_3$Al</td>
<td>0.8 ± 0.2</td>
</tr>
<tr>
<td>Ni$<em>{65.5}$Al$</em>{34.5}$</td>
<td>NiAl</td>
<td>121.2 ± 34.7</td>
<td>Ni$_3$Al</td>
<td>0.9 ± 0.3</td>
</tr>
<tr>
<td>Ni$<em>{67.1}$Al$</em>{32.9}$</td>
<td>NiAl</td>
<td>-</td>
<td>Ni$_3$Al</td>
<td>-</td>
</tr>
<tr>
<td>Ni$<em>{70.3}$Al$</em>{29.7}$</td>
<td>Ni$_3$Al</td>
<td>-</td>
<td>NiAl</td>
<td>3.5 ± 1.1</td>
</tr>
<tr>
<td>Ni$<em>{72.4}$Al$</em>{27.6}$</td>
<td>Ni$_3$Al</td>
<td>-</td>
<td>NiAl</td>
<td>5.2 ± 2.4</td>
</tr>
<tr>
<td>Ni$<em>{73.1}$Al$</em>{26.9}$</td>
<td>Ni$_3$Al</td>
<td>-</td>
<td>NiAl</td>
<td>5.1 ± 2.6</td>
</tr>
<tr>
<td>Ni$<em>{77.2}$Al$</em>{22.8}$</td>
<td>Ni$_3$Al</td>
<td>168.2 ± 89.4</td>
<td>Ni</td>
<td>-</td>
</tr>
<tr>
<td>Ni$<em>{73.2}$Al$</em>{25.6}$B$_{0.2}$</td>
<td>Ni$_3$Al</td>
<td>-</td>
<td>NiAl</td>
<td>5.5 ± 2.5</td>
</tr>
<tr>
<td>Ni$<em>{74.5}$Al$</em>{25.1}$B$_{0.4}$</td>
<td>Ni$_3$Al</td>
<td>35.6 ± 42.4</td>
<td>NiAl</td>
<td>-</td>
</tr>
</tbody>
</table>
content from 70.3 to 73.1 (Figures 3.1d to f) results in a gradual decrease of the sharp, locally twinned-structure of the NiAl phase from 46 vol.% to 33 vol.% as indicated in Table 3.2.

Figure 3.1g shows the Ni$_{77.2}$Al$_{22.8}$ alloy which is almost a pure single-phase Ni$_3$Al (only 0.6 vol.% of Ni found). To check the effect of boron-doping on the investigated in-situ composites, two alloys were produced as shown in Figures 3.2a and b. The compositions, grain size and volume fraction of each phase are summarised in Tables 3.1 and 3.2. It is clear that the Ni$_{73.3}$Al$_{26.6}$B$_{0.2}$ in-situ composite shown in Figure 3.2a exhibits the same structure as
Figure 3.2  Optical micrographs of the etched microstructures in the as-cast, boron-doped in-situ composites with Nomarski interference contrast: (a) Ni$_{73.2}$Al$_{26.6}$B$_{0.2}$ and (b) Ni$_{74.5}$Al$_{25.1}$B$_{0.4}$. 

Ni$_{3}$Al  

20μm
Ni$_{73.1}$Al$_{26.9}$ (Figure 3.1f). However, the boron-doped Ni$_{74.5}$Al$_{25.1}$B$_{0.4}$ alloy is almost pure single-phase Ni$_3$Al (Figure 3.1l), which is similar to the structure of the Ni$_{77.2}$Al$_{22.8}$ (Figure 3.1g).

3.1.2 The Homogenized, Boron-Free and Boron-Doped In-Situ Composites

The as-cast in-situ composites were homogenized at 1000°C for 100h followed by a slow furnace cooling. Figure 3.3 shows another group of typical, optical micrographs of the as-annealed, boron-free in-situ composites, corresponding to Figure 3.1. To show homogenized structure in detail, lower magnification photos are also included for each composite. After the heat-treatment at 1000°C for 100h followed by a slow furnace cooling, the overall Ni-content was the same as that of the as-cast specimens (see Table 3.3). The volume fraction of Ni$_3$Al increased for every in-situ composite (Table 3.4). Such an obvious increase of Ni$_3$Al phase is demonstrated by the coarsening of the intergranular and grain boundary precipitates (Figures 3.3a to f) or by the larger area of the Ni$_3$Al matrix (Figures 3.3g to l). In particular, the Ni$_{73.2}$Al$_{26.8}$ in-situ composite became almost pure Ni$_3$Al single phase (91.2%). Obviously, the increase of the volume fraction of relatively more ductile γ (Ni$_3$Al) phase after homogenization may lead to fracture toughening of these in-situ composites.

Another obvious change is that the twinned-structure in the NiAl phase decreased dramatically (Figures 3.3a to f) and the local twin structure in particular almost disappeared in Figures 3.3g to l. This is probably due to the lower cooling rate.
Figure 3.3  Optical micrographs of the etched microstructure of the homogenized Ni<sub>63.7</sub>Al<sub>36.3</sub> in-situ composite at: (a) lower and (b) higher magnification with Nomarski interference contrast.
Figure 3.3  Optical micrographs of the etched microstructure of the homogenized Ni_{63.3}Al_{36.7} in-situ composites at: (c) lower and (d) higher magnification with Nomarski interference contrast.
Figure 3.3 Optical micrographs of the etched microstructure of the homogenized Ni$_{67.2}$Al$_{32.8}$ in-situ composite at: (e) lower and (f) higher magnification with Nomarski interference contrast.
Figure 3.3  Optical micrographs of the etched microstructure of the homogenized Ni$_{70.5}$Al$_{29.5}$ in-situ composite at: (g) lower and (h) higher magnification (Nomarski interference contrast).
Table 3.3  Target composition and quantitative EDS results of the homogenized, boron-free and boron-doped in-situ composites (at.%).

<table>
<thead>
<tr>
<th>Target Ni (at.%)</th>
<th>Element</th>
<th>Overall</th>
<th>Matrix</th>
<th>Phase</th>
<th>Grain boundary</th>
<th>Precipitates</th>
<th>Phase</th>
</tr>
</thead>
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<tr>
<td>63</td>
<td>Ni</td>
<td>63.7±0.4</td>
<td>60.7±1.0</td>
<td>NiAl</td>
<td>73.2±0.2</td>
<td>Ni$_3$Al</td>
<td>Ni$_3$Al</td>
</tr>
<tr>
<td></td>
<td>Al</td>
<td>36.3±0.4</td>
<td>39.3±1.0</td>
<td></td>
<td>26.8±0.2</td>
<td>27.5±0.3</td>
<td></td>
</tr>
<tr>
<td>65</td>
<td>Ni</td>
<td>65.3±0.5</td>
<td>63.9±0.4</td>
<td>NiAl</td>
<td>73.8±0.1</td>
<td>Ni$_3$Al</td>
<td>Ni$_3$Al</td>
</tr>
<tr>
<td></td>
<td>Al</td>
<td>34.7±0.5</td>
<td>36.1±0.4</td>
<td></td>
<td>26.2±0.1</td>
<td>26.5±0.4</td>
<td></td>
</tr>
<tr>
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<td>Ni</td>
<td>67.2±0.4</td>
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<td>NiAl</td>
<td>74.4±0.2</td>
<td>Ni$_3$Al</td>
<td>Ni$_3$Al</td>
</tr>
<tr>
<td></td>
<td>Al</td>
<td>32.8±0.4</td>
<td>36.7±0.7</td>
<td></td>
<td>25.6±0.2</td>
<td>25.9±0.5</td>
<td></td>
</tr>
<tr>
<td>69</td>
<td>Ni</td>
<td>70.8±0.4</td>
<td>73.2±0.3</td>
<td>Ni$_3$Al</td>
<td></td>
<td>-</td>
<td>62.0±0.5</td>
</tr>
<tr>
<td></td>
<td>Al</td>
<td>29.2±0.4</td>
<td>26.8±0.3</td>
<td></td>
<td>-</td>
<td>38.0±0.5</td>
<td></td>
</tr>
<tr>
<td>71</td>
<td>Ni</td>
<td>72.8±0.6</td>
<td>73.7±0.5</td>
<td>Ni$_3$Al</td>
<td></td>
<td>-</td>
<td>63.0±0.7</td>
</tr>
<tr>
<td></td>
<td>Al</td>
<td>27.2±0.6</td>
<td>26.3±0.5</td>
<td></td>
<td>-</td>
<td>37.0±0.7</td>
<td></td>
</tr>
<tr>
<td>73</td>
<td>Ni</td>
<td>73.2±0.4</td>
<td>73.7±0.3</td>
<td>Ni$_3$Al</td>
<td></td>
<td>-</td>
<td>62.2±0.5</td>
</tr>
<tr>
<td></td>
<td>Al</td>
<td>26.8±0.4</td>
<td>26.3±0.3</td>
<td></td>
<td>-</td>
<td>37.8±0.5</td>
<td></td>
</tr>
<tr>
<td>77</td>
<td>Ni</td>
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<td>Ni$_3$Al</td>
<td></td>
<td>-</td>
<td>95.1±0.6</td>
</tr>
<tr>
<td></td>
<td>Al</td>
<td>22.3±0.4</td>
<td>22.4±0.7</td>
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<td>-</td>
<td>4.9±0.6</td>
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</tr>
<tr>
<td>72.8-0.2B</td>
<td>Ni</td>
<td>73.2±0.5</td>
<td>74.9±1.1</td>
<td>Ni$_3$Al</td>
<td></td>
<td>-</td>
<td>64.2±0.4</td>
</tr>
<tr>
<td></td>
<td>Al</td>
<td>26.6±0.5</td>
<td>24.9±1.1</td>
<td></td>
<td>-</td>
<td>35.6±0.4</td>
<td></td>
</tr>
<tr>
<td>74.6-0.4B</td>
<td>Ni</td>
<td>74.8±0.5</td>
<td>75.0±0.4</td>
<td>Ni$_3$Al</td>
<td></td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Al</td>
<td>24.8±0.5</td>
<td>24.6±0.4</td>
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<td>-</td>
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<td>-</td>
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</table>
Figure 3.3 Optical micrographs of the etched microstructure of the homogenized Ni\textsubscript{72.8}Al\textsubscript{27.2} in-situ composite at: (i) lower and (j) higher magnifications with Nomarski interference contrast.
Figure 3.3  Optical micrographs of the etched microstructure of the homogenized Ni$_{73.2}$Al$_{26.8}$ in-situ composite at: (k) lower and (l) higher magnifications with Nomarski interference contrast.
Table 3.4  The mean grain size of the materials and volume fraction of second phase with standard deviations of the homogenized, aged and boron-free and boron-doped in-situ composites.

<table>
<thead>
<tr>
<th>In-situ composites (at.%)</th>
<th>Type of matrix phase</th>
<th>Matrix grain size (μm)</th>
<th>Type of the second phase</th>
<th>second phase</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
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<td></td>
<td>Thickness or size (μm)</td>
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<td>183.8±56.2</td>
<td>Ni₃Al</td>
<td>1.2±0.9</td>
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<tr>
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<td>NiAl</td>
<td>167.5±29.6</td>
<td>Ni₃Al</td>
<td>1.5±0.7</td>
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<td>NiAl</td>
<td>-</td>
<td>Ni₃Al</td>
<td>1.8±0.8</td>
</tr>
<tr>
<td>Ni₇₂.₈Al₂₇.₂</td>
<td>Ni₃Al</td>
<td>-</td>
<td>NiAl</td>
<td>5.5±2.4</td>
</tr>
<tr>
<td>Ni₇₂.₈Al₂₇.₂</td>
<td>Ni₃Al</td>
<td>-</td>
<td>NiAl</td>
<td>6.7±1.1</td>
</tr>
<tr>
<td>Ni₇₃.₂Al₂₆.₈</td>
<td>Ni₃Al</td>
<td>269±82.4</td>
<td>NiAl</td>
<td>3.3±1.5</td>
</tr>
<tr>
<td>Ni₇₇.₇Al₂₂.₃</td>
<td>Ni₃Al</td>
<td>194±67.2</td>
<td>Ni</td>
<td>-</td>
</tr>
<tr>
<td>Ni₇₃.₂Al₂₆.₆B₀.₂</td>
<td>Ni₃Al</td>
<td>275±93.9</td>
<td>NiAl</td>
<td>11.5±7.6</td>
</tr>
<tr>
<td>Ni₇₄.₈Al₂₄.₈B₀.₄</td>
<td>Ni₃Al</td>
<td>54.7±39.5</td>
<td>NiAl</td>
<td>-</td>
</tr>
</tbody>
</table>

148
In addition, the grain sizes for all of the in-situ composites are relatively unchanged after homogenization. A group of microstructures of the boron-doped in-situ composites is also shown in Figure 3.4. After homogenization, the Ni_{71.2}Al_{26.6}B_{0.2} in-situ composite has only around 5% of the NiAl second phase, which is evenly distributed in the Ni_3Al matrix.

It is also worthy of note that the sharp NiAl phase (shown in Figures 3.1e to f, and Figure 3.2a) has become round (shown in Figures 3.3i to l, and Figure 3.4a), which might also improve the fracture toughness behaviour for the in-situ composites.

![Figure 3.3m](image)

**Figure 3.3m** A typical micrograph of the etched microstructure of the homogenized, boron-free Ni_{77.7}Al_{22.3} in-situ composite with Nomarski interference contrast.
Figure 3.4  Optical micrographs of the etched microstructure of the homogenized, boron-doped in-situ composites (Nomarski interference contrast): (a) $\text{Ni}_{73.2}\text{Al}_{26.6}\text{B}_{0.2}$ and (b) $\text{Ni}_{14.8}\text{Al}_{24.8}\text{B}_{0.4}$. 
3.1.3 Some Additional Heat Treatments

In order to form Ni₅Al₃, the homogenized Ni₆₅₃Al₃₄₇ in-situ composite (Figures 3.3c and d) was aged at 550°C for 100h followed by a slow furnace cooling. A typical microstructure of the aged in-situ composite is shown in Figure 3.5. A very distinct needle-like, cross-matched structure, called "mat structure", is clearly seen in Figure 3.5. However, X-ray analysis must be used to determine whether or not this mat-like structure is the Ni₅Al₃ phase. The overall composition after ageing was measured by EDS giving: 65.9 ± 0.5 at.% Ni and 34.1 ± 0.5 at.% Al (included in Table 3.4).

Figure 3.5  An optical micrograph of the etched microstructure of the Ni₆₅₃Al₃₄₇ in-situ composite (Nomarski interference contrast) homogenized at 1000°/100h plus aged at 550°/100h followed by furnace cooling.
To check the possible grain-boundary brittleness of the polycrystalline Ni$_3$Al, the homogenized, boron-free Ni$_{77.7}$Al$_{22.3}$ in-situ composite was reheated to 1000°C for 15 min. followed by water quenching. Local grain-boundary cracking due to quenching (Figure 3.6a) was found for this kind of Ni$_3$Al single-phase alloy. The ratio of the crack length over the total measured area in Ni$_{74.3}$Al$_{25.7}$ was $0.0055 \pm 0.0037$ µm/µm$^2$, as measured by the Java image analysis system [144]. For the water-quenched boron-doped Ni$_{73.5}$Al$_{26.5}$B$_{0.5}$ alloy (Figure 3.6b) grain-boundary cracking could also be found but seems to be much less pronounced ($0.0041 \pm 0.0025$ µm/µm$^2$). For the water-quenched boron-doped Ni$_{74.8}$Al$_{25.2}$B$_{0.4}$ alloy the ratio of the crack length over the total measured area was $0.0043 \pm 0.0019$ µm/µm$^2$, almost the same as that in the 0.2 at.% B alloy. This decrease in the extent of grain boundary cracking might be attributed to the boron segregation effect at grain boundaries.

The water-quenching after homogenization was also used for other in-situ composites. However, no grain boundary cracking was found.
Figure 3.6 The typical micrographs of the grain boundary cracking of (a) the boron-free Ni$_{77.3}$Al$_{22.7}$ and (b) the boron-doped Ni$_{73.2}$Al$_{26.8}$B$_{0.8}$ alloys after re-heating treatment of 1000°C/15min followed by water quenching (Nomarski interference contrast).
3.2 X-Ray Analysis

Typical results of X-ray analysis of the homogenized Ni$_{63.7}$Al$_{36.3}$ in-situ composite are shown in Table 3.5. It is clear that only two phases Ni$_3$Al (L1$_2$) + NiAl (B2) exist in the Ni$_{63.7}$Al$_{36.3}$ composite, as expected.

The homogenized (1000°C/100h) plus aged (550°C/100h) Ni$_{65.9}$Al$_{34.1}$ in-situ composite was also investigated by X-ray analysis and the results are listed in Table 3.6. Definitely, the orthorhombic D$_{2h}^{19}$ Ni$_5$Al$_3$ [93] exists in the Ni$_{65.9}$Al$_{34.1}$ in-situ composite.

Table 3.5 A typical X-ray analysis of the homogenized Ni$_{63.7}$Al$_{36.3}$ in-situ composite.

<table>
<thead>
<tr>
<th>Position 2θ (deg)</th>
<th>Observed intensity (I/I₀)</th>
<th>Observed d$_{hkl}$ [Å]</th>
<th>Standard d$_{hkl}$ [147] [Å]</th>
<th>Reflection (hkl)</th>
<th>Type of structure</th>
</tr>
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<td>38.146</td>
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<td>2.547</td>
<td>110</td>
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<td>43.668</td>
<td>100.0</td>
<td>2.0712</td>
<td>2.077</td>
<td>111</td>
<td>Fundamental L1$_2$ Ni$_3$Al</td>
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<td>44.472</td>
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<td>2.0355</td>
<td>2.074</td>
<td>110</td>
<td>Fundamental B2 NiAl</td>
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<td>50.750</td>
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<td>64.817</td>
<td>18.7</td>
<td>1.4373</td>
<td>1.434</td>
<td>200</td>
<td>Fundamental B2 NiAl</td>
</tr>
<tr>
<td>74.950</td>
<td>16.6</td>
<td>1.2661</td>
<td>1.285</td>
<td>210</td>
<td>Superlattice B2 NiAl</td>
</tr>
</tbody>
</table>
Table 3.6  A typical X-ray analysis of the aged, boron-free Ni$_{65.9}$Al$_{34.1}$ in-situ composite.

<table>
<thead>
<tr>
<th>Position 2θ (deg)</th>
<th>Observed intensity ($I/I_0$)</th>
<th>Observed $d_{hl}$ [Å]</th>
<th>Standard $d_{hl}$ [Å]</th>
<th>Reflection {hkl}</th>
<th>Type of structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>24.796</td>
<td>6.1</td>
<td>3.5916</td>
<td>3.6</td>
<td>100</td>
<td>Superlattice L1$_2$ Ni$_3$Al</td>
</tr>
<tr>
<td>33.183</td>
<td>6.8</td>
<td>2.6976</td>
<td>2.641</td>
<td>100</td>
<td>Superlattice B2 NiAl</td>
</tr>
<tr>
<td>35.650</td>
<td>5.7</td>
<td>2.5164</td>
<td>2.500</td>
<td>220, 021</td>
<td>Orthorhombic $D_{2h}^{19}$</td>
</tr>
<tr>
<td>43.777</td>
<td>100.0</td>
<td>2.0662</td>
<td>2.074</td>
<td>111</td>
<td>Fundamental L1$_2$ Ni$_3$Al</td>
</tr>
<tr>
<td>44.700</td>
<td>39.8</td>
<td>2.0257</td>
<td>2.02</td>
<td>110</td>
<td>Fundamental B2 NiAl</td>
</tr>
<tr>
<td>47.736</td>
<td>15.1</td>
<td>1.9037</td>
<td>1.869</td>
<td>200</td>
<td>Orthorhombic $D_{2h}^{19}$</td>
</tr>
<tr>
<td>65.000</td>
<td>10.7</td>
<td>1.4336</td>
<td>1.434</td>
<td>200</td>
<td>Fundamental $D_{2h}^{19}$</td>
</tr>
<tr>
<td>69.850</td>
<td>7.4</td>
<td>1.3455</td>
<td>1.320</td>
<td>402</td>
<td>Orthorhombic $D_{2h}^{19}$</td>
</tr>
<tr>
<td>74.983</td>
<td>10.5</td>
<td>1.2656</td>
<td>1.250</td>
<td>422</td>
<td>Orthorhombic $D_{2h}^{19}$</td>
</tr>
<tr>
<td>78.140</td>
<td>17.5</td>
<td>1.2222</td>
<td>1.229</td>
<td>440</td>
<td>Superlattice L1$_2$ Ni$_3$Al</td>
</tr>
</tbody>
</table>
3.3 Micro-Mechanical Properties

After Vickers microhardness tests, no cracks in the matrix were found for all the as-cast and homogenized in-situ composites under the maximum load of 2000g. However, some serious grain boundary cracking under various indentations were observed for a water-quenched, near-Ni$_3$Al single-phase in-situ composite as shown in Figure 3.7a. In contrast, no cracks were found for boron-doped in-situ composites under various indentations (Figure 3.7b). Obviously, boron is shown again to have some positive effect on the room temperature grain boundary cohesiveness of polycrystalline Ni$_3$Al.

It is worth noting that the mat-like Al$_5$Ni$_3$ structure obtained from aging at 550°C/100h exhibits a much higher hardness value (Table 3.7) than that of any other structures, as shown in Figure 3.8a by the difference in the size of indentation for aged and homogenized alloys. The Vickers hardness values of Ni$_3$Al and NiAl are almost the same (=350 kg/mm$^2$) for all of the homogenized, boron-free in-situ composites (Table 3.7). The boron-doped composites, however, show slightly lower Vickers hardness values of =290 kg/mm$^2$ than the boron-free in-situ composites (Table 3.7). Vickers hardness of both Ni$_3$Al and NiAl is almost independent of the load (Figure 3.9).
Figure 3.7  Typical micrographs of (a) a grain boundary cracking under 2000g load for the boron-free Ni$_{77.7}$Al$_{22.3}$ alloy, and (b) no grain-boundary cracking under 2000g load for the boron-doped Ni$_{74.8}$Al$_{25.8}$B$_{0.4}$ alloy (Nomarski interference contrast). Both were re-heated at 1000°C/15min followed by water quenching before the microhardness testing.
Figure 3.8  Typical micrographs of Vickers microhardness testing on (a) the "mat-
structure" of the aged Ni₆₅.₉Al₃₄.₁ (1000°C/100h + 500°C/100h both followed by a slow furnace cooling), and (b) the twin-structure of the homogenized Ni₆₃.₇Al₃₆.₃ (1000°C/100h followed by a slow furnace cooling) in-situ composites under 2000g load.
Figure 3.9  Vickers microhardness on the phases of NiAl and Ni₃Al for (a) as-cast and (b) as-homogenized composites.
Table 3.7  Vickers microhardness values with standard deviations of the homogenized and aged*, in-situ composites under 10g load (kg/mm²).

<table>
<thead>
<tr>
<th>In-situ composites (at.%)</th>
<th>Ni₃Al</th>
<th>NiAl</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni₆₃.₇Al₉₆.₃</td>
<td>386 ± 10</td>
<td>359 ± 6</td>
</tr>
<tr>
<td>Ni₆₅.₃Al₃₄.₇</td>
<td>378 ± 9</td>
<td>370 ± 10</td>
</tr>
<tr>
<td>Ni₆₅.₉Al₃₄.₁</td>
<td>337 ± 19</td>
<td>690 ± 15¹</td>
</tr>
<tr>
<td>Ni₆₇.₂Al₂₉.₈</td>
<td>384 ± 9</td>
<td>351 ± 10</td>
</tr>
<tr>
<td>Ni₇₀.₈Al₂₉.₂</td>
<td>364 ± 7</td>
<td>355 ± 8</td>
</tr>
<tr>
<td>Ni₇₂.₈Al₂₇.₂</td>
<td>362 ± 10</td>
<td>384 ± 11</td>
</tr>
<tr>
<td>Ni₇₃.₂Al₂₆.₈</td>
<td>344 ± 7</td>
<td>373 ± 8</td>
</tr>
<tr>
<td>Ni₇₇.₇Al₂₂.₃</td>
<td>323 ± 9</td>
<td>316 ± 9</td>
</tr>
<tr>
<td>Ni₇₃.₂Al₂₆.₆B₀.₂</td>
<td>278 ± 11</td>
<td>-</td>
</tr>
<tr>
<td>Ni₇₅.₈Al₂₄.₈B₀.₄</td>
<td>297 ± 7</td>
<td>-</td>
</tr>
</tbody>
</table>

1) Ni₅Al₃ precipitates in the NiAl matrix (Figure 3.8a).

3.4 Compression Testing

After fracture toughness testing, half of the tested specimens were cut by EDM into a parallelepiped beam (4x4x6.8mm), which was polished properly and compressed by a hydraulic compression machine. The average yield strength and standard deviations for each in-situ composite are listed in Table 3.8.
Table 3.8  The average yield strength with standard deviations of the homogenized and aged in-situ composites.

<table>
<thead>
<tr>
<th>In-situ composites (at.%)</th>
<th>Yield strength (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni&lt;sub&gt;63.7&lt;/sub&gt;Al&lt;sub&gt;36.3&lt;/sub&gt;</td>
<td>423 ± 35</td>
</tr>
<tr>
<td>Ni&lt;sub&gt;55.9&lt;/sub&gt;Al&lt;sub&gt;34.1&lt;/sub&gt;</td>
<td>1151 ± 148</td>
</tr>
<tr>
<td>Ni&lt;sub&gt;67.2&lt;/sub&gt;Al&lt;sub&gt;22.8&lt;/sub&gt;</td>
<td>819 ± 66</td>
</tr>
<tr>
<td>Ni&lt;sub&gt;70.8&lt;/sub&gt;Al&lt;sub&gt;29.2&lt;/sub&gt;</td>
<td>539 ± 139</td>
</tr>
<tr>
<td>Ni&lt;sub&gt;72.8&lt;/sub&gt;Al&lt;sub&gt;27.2&lt;/sub&gt;</td>
<td>431 ± 51</td>
</tr>
<tr>
<td>Ni&lt;sub&gt;73.2&lt;/sub&gt;Al&lt;sub&gt;26.8&lt;/sub&gt;</td>
<td>374 ± 55</td>
</tr>
<tr>
<td>Ni&lt;sub&gt;77.7&lt;/sub&gt;Al&lt;sub&gt;22.3&lt;/sub&gt;</td>
<td>222 ± 93</td>
</tr>
<tr>
<td>Ni&lt;sub&gt;73.2&lt;/sub&gt;Al&lt;sub&gt;26.6&lt;/sub&gt;B&lt;sub&gt;0.2&lt;/sub&gt;</td>
<td>535 ± 14</td>
</tr>
<tr>
<td>Ni&lt;sub&gt;74.8&lt;/sub&gt;Al&lt;sub&gt;54.8&lt;/sub&gt;B&lt;sub&gt;0.4&lt;/sub&gt;</td>
<td>382 ± 72</td>
</tr>
</tbody>
</table>

*) Aged at 550°C for 100h followed by a slow furnace cooling.

3.5 Fracture Toughness Testing

3.5.1 Fractography

Fracture surfaces broken in three-point bend test, were studied by scanning electron microscopy (SEM). A typical group of SEM fractographs is shown in Figures 3.10 to 3.18.
Figure 3.10  Typical scanning electron microscope (SEM) fractographs of the homogenized Ni$_{63.7}$Al$_{36.3}$ specimens (1000°C/100h followed by a slow furnace cooling). (a) transgranular fracture in the NiAl phase and intergranular Ni$_3$Al grain facets, and (b) two elongated envelops and precipitates of Ni$_3$Al in the NiAl grains, which shows a river-pattern cleavage fracture.
Figure 3.11  Typical scanning electron microscope (SEM) fractographs of the homogenized and aged Ni$_{65.9}$Al$_{34.1}$ in-situ composite (1000°/100h + 500°/100h both followed by a slow furnace cooling): (a) local cleavage fracture in the grains, and (b) elongated and broken Ni$_3$Al reinforcements.
Figure 3.12 Typical scanning electron microscope (SEM) fractographs of the homogenized Ni$_{67.2}$Al$_{32.8}$ specimens (1000°/100h followed by a slow furnace cooling). (a) stretched ductile second phases, and (b) delamination at interfaces.
Typical scanning electron microscope (SEM) fractographs of the homogenized Ni₇₀Al₂₉ specimens (1000°/100h followed by a slow furnace cooling). (a) debonding at interfaces of NiAl and Ni₃Al (b) intergranular fracture of Ni₃Al.
Figure 3.14 Typical scanning electron microscope (SEM) fractographs of the homogenized Ni$_{72.8}$Al$_{27.2}$ specimens (1000°/100h followed by a slow furnace cooling). (a) delamination at grain boundary of Ni$_3$Al and at interfaces of Ni$_3$Al and NiAl, and (b) a whole fracture surface of a bent specimen.
Figure 3.15  Typical scanning electron microscope (SEM) fractographs of the homogenized Ni$_{73}$Al$_{27}$ specimens (1000°C/100h followed by a slow furnace cooling). (a) intergranular fracture with clear secondary cracks along the grain boundaries, and (b) twin structures clearly marked in the Ni$_3$Al grains.
A mixed transgranular-intergranular fracture (TIF) mode in NiAl phase was observed in the Ni\textsubscript{63.7}Al\textsubscript{36.3} specimens (Figure 3.10a). The NiAl matrix exhibits typical river-patterns on each facet (corresponding to a single grain) of cleavage fracture as shown in Figure 3.10b. Delamination can be observed at grain boundaries of NiAl and also at Ni\textsubscript{3}Al/NiAl interfaces (Figure 3.10b).

Figure 3.11a shows primarily transgranular fracture of aged Ni\textsubscript{3}Al in Ni\textsubscript{65.9}Al\textsubscript{34.1} alloy. In addition, Figure 3.11a clearly shows that two propagating cleavage facets of NiAl phase stop at the grain boundaries of Ni\textsubscript{3}Al phases in the aged Ni\textsubscript{65.9}Al\textsubscript{34.1} in-situ composite. Delamination can be clearly seen at the Ni\textsubscript{3}Al/NiAl interfaces as shown in Figure 3.11b. It is interesting to note that the ductile Ni\textsubscript{3}Al reinforcements embedded in the NiAl grains were elongated and broken after fracture toughness testing (Figure 3.11b). Since this process consumes more energy than crack propagation without precipitates, the effects of Ni\textsubscript{3}Al reinforcements are evident. In the Ni\textsubscript{67.5}Al\textsubscript{32.5} in-situ composite, a precipitate of Ni\textsubscript{3}Al was stretched into a tip (see arrow in Figure 3.12a). This definitely demonstrates the crack bridging effect of the relatively ductile second phase of Ni\textsubscript{3}Al. Debonding at the Ni\textsubscript{3}Al/NiAl interface can also be more clearly observed in this alloy. A different direction of alignment of Ni\textsubscript{3}Al phase is shown in Figure 3.12b, which is a typical example of how complex a composite is. From Figures 3.10 to 3.12, it is clear that the NiAl matrix shows a mixed mode of transgranular/intragranular fracture and that the second phase and grain boundary of Ni\textsubscript{3}Al phase show partly intergranular fracture with smooth facets.
Figure 3.16  Typical scanning electron microscope (SEM) fractographs of the homogenized Ni$_{77.7}$Al$_{22.3}$ specimens (1000°/100h followed by a slow furnace cooling). (a) smooth intergranular fracture with grain-boundary cracks, and (b) a lot of tiny dimples on the fracture surfaces.
Figure 3.17  Typical scanning electron microscope (SEM) fractographs of the homogenized Ni$_{32}$Al$_{36.6}$B$_{0.2}$ in-situ composite (1000°/100h followed by a slow furnace cooling): (a) delamination at the Ni$_{3}$Al/NiAl interface, and (b) some voids at the grain boundaries.
Figure 3.18  Typical scanning electron microscope (SEM) fractographs of the homogenized Ni$_{34.8}$Al$_{34.8}$B$_{0.4}$ specimens (1000°/100h followed by a slow furnace cooling). (a) cracks extended along grain boundaries, and (b) square stair-dimple in the grain.
From Figures 3.13 to 3.18, it is easy to distinguish that the matrix of Ni$_3$Al showing intergranular fracture with very smooth grain facets will become dominant in the fracture surfaces of the specimens. A large amount of relatively brittle reinforcements of NiAl in the Ni$_{70.8}$Al$_{29.2}$ in-situ composite were cleavage fractured during the bend testing (Figure 3.13b). A high magnification fractograph in Figure 3.14a shows delamination at grain boundary of Ni$_3$Al and at interfaces of Ni$_3$Al and NiAl in the Ni$_{72.8}$Al$_{27.2}$ in-situ composite. A whole fracture surface of a bent specimen was also given by a lower magnification fractograph as shown in Figure 3.14b. It will be very helpful to analyze the whole process of crack initiation, growth and termination behaviour during the bending test for this composite. The two symmetric sides of the surfaces cut by the electronic discharge machine (EDM) can be clearly seen in Figure 3.14b.

The grain boundary brittleness of the Ni$_3$Al phase in the Ni$_{72.2}$Al$_{25.8}$ in-situ composite can be clearly seen in Figure 3.15a. The distinct plastic deformation markings can also be clearly seen in the Ni$_3$Al grain facets at a higher magnification fractograph (Figure 3.15b).

The fracture behaviour of the boron-free polycrystalline Ni$_3$Al in the Ni$_{77.7}$Al$_{22.3}$ bent specimens is seen in Figure 3.16. The grain facets are extremely smooth and free from any deformation marks, indicating the brittleness of the boundaries (Figure 3.16a). However, the SEM fractograph of the Ni$_{77.7}$Al$_{22.3}$ bent specimens in Figure 3.16b also shows some tearing type fracture regions, indicating potential for some plasticity at room temperature.

The fracture behaviour of the boron-doped polycrystalline Ni$_3$Al in the Ni$_{72.3}$Al$_{25.6}$B$_{0.2}$ and
Ni$_{74.8}$Al$_{24.8}$B$_{0.4}$ in-situ composite can be seen in Figures 3.17 and 3.18, respectively. A delamination at the Ni$_3$Al/NiAl interface can be seen in Figure 3.17a. Figure 3.17b shows some secondary cracks and pre-existing voids appeared at the grain boundary in the Ni$_{73.2}$Al$_{26.6}$B$_{0.2}$ in-situ composite. Serious secondary cracks along grain boundaries can still be seen in the Ni$_{74.8}$Al$_{24.8}$B$_{0.4}$ surface fractured by bending (Figure 3.18a).

Some square stair-dimples seem to show some ductile potential in the Ni$_{74.8}$Al$_{24.8}$B$_{0.4}$ alloy. Further discussion on the fracture behaviour of the investigated in-situ composite will be given in the next Chapter. More examples of fractographs for the investigated in-situ composites are shown in Appendix C.

### 3.5.2 Fracture Toughness of the Investigated In-Situ Composites

**Shapes of Load-Load line Displacement (P-LLD) and Y'-a Curves**

In general, according to Munz [101] four possible and principal types of load-displacement records could be observed during a bending test (Figure 3.19), which can be related to unstable and stable crack extension.

Type I in Figure 3.19 shows a linearity up to the maximum load without any stable crack extension. In this case, fracture toughness $K_{IC}$ could be calculated from maximum load, $P_{max}$. However, a delicate problem arises here because Eq.(2.24) requires that stable crack growth
must precede $P_{\text{max}}$ and then $Y_m^{*}$ in Eq.(2.24) corresponds to a certain finite crack length, $a_m$ (or $\alpha_m$). If load-load line displacement is linear up to $P_{\text{max}}$ then obviously the crack length is $a_0$ at $P_{\text{max}}$ rather then $a_m$. From the formal point of view the $Y'$ function has almost an infinite value at $a_0$. It seems, however, that one would be on the rather safe side by still using Eq.(2.24) with a calculated $Y_m^{*}$ which would give quite a conservative value of $K_{f_m}$. This might be particularly true if the $Y'=f(a)$ curve would have a “flat bottom” as shown in Figure 3.20.

In the case in Figure 3.20, even a minimal crack growth from $a_0$, sometimes unrecognizable on the load-load line displacement curve, leads to the value of $Y'=Y_m^{*}$. It is to be pointed out that Withey and Bowen [2] showed that for relatively brittle materials tested by
Figure 3.20  A schematic of a \( Y' = f(\alpha) \) curve with a "flat bottom".

\[ Y^* \]
\[ Y_m^* \]
\[ \alpha_0 \]
\[ \alpha_m \]
\[ \alpha \]

\( CNB \) (\( K_{ovm} = 4 \text{ MPa}\sqrt{\text{m}} \)) valid toughness values were obtained even without any indication of non-linear compliance changes prior to failure.

A near-type I curve was observed in the present work for a \( \text{Ni}_{65.9}\text{Al}_{34.1} \) alloy (Figure 3.21a) which was aged at 550°C for 100h and contained needle-like precipitates of the \( \text{Ni}_5\text{Al}_3 \) phase in the NiAl matrix (Figure 3.5). It was also observed for \( \text{Ni}_{67.2}\text{Al}_{32.8} \), which was a homogenized alloy (Figure 3.21b). However, as seen in Figures 3.21a and 3.21b, the curves exhibit a minimal non-linearity just prior to \( P_{\text{max}} \). Also, the homogenized \( \text{Ni}_{63.7}\text{Al}_{36.3} \) and \( \text{Ni}_{73.2}\text{Al}_{26.8} \) alloys
showed near-type I behaviour with the modification that the stable crack growth occurred after $P_{\text{max}}$ (Figure 3.22). Similarly, boron-doped Ni$_{73.2}$Al$_{36.6}$B$_{0.2}$ and Ni$_{74.8}$Al$_{24.8}$B$_{0.4}$ alloys showed near-type I behaviour with the modification that small pop-ins occurred only prior to the maximum load, and stable crack growth occurred after the maximum load (Figure 3.23). Type IV behaviour was exhibited by homogenized alloys Ni$_{70.8}$Al$_{29.3}$, Ni$_{73.4}$Al$_{27.2}$ and Ni$_{77.7}$Al$_{22.3}$ (Figure 3.24).
Figure 3.21 A group of near-type I curves was observed in the present work for (a) the aged Ni$_{65.9}$Al$_{34.1}$ and (b) the homogenized Ni$_{67.2}$Al$_{32.8}$ alloys. exhibiting a minimal non-linearity just prior to $P_{\text{max}}$. 
A group of near-type I curves was observed in the present work for the homogenized (a) Ni3Al36.3 and (b) Ni23Al88.3 alloys, showing the modification that the stable crack growth occurred after $P_{\text{max}}$. 
Figure 3.23 A group of near-type I curves was observed in the present work for boron-doped (a) Ni\textsubscript{13.2}Al\textsubscript{66.6}B\textsubscript{0.2} and Ni\textsubscript{14.8}Al\textsubscript{24.8}B\textsubscript{0.4} alloys, exhibiting the modification that small pop-ins occurred only prior to the maximum load and a stable crack growth after the maximum load.
Type IV behaviour was exhibited by homogenized alloys (a) Ni_{70.8}Al_{29.2}, (b) Ni_{72.8}Al_{27.2} and (c) Ni_{77.7}Al_{22.3}.
It must be pointed out that the shapes of the load-load line displacement curves were the same for each group of alloys (Figures 3.21 to 3.24) with a specified composition, despite that individual specimens in this group could contain slightly different volume fractions of Ni$_3$Al (Appendix D).

**Evaluation of Fracture Toughness Values $K_{I_m^W}$ and $K_{I_m^B}, K_{WOF}$**

The measured ($B, W, a_0$ and $a_1$ from each specimen) and calculated ($\Delta a_m$ and $Y'_m$) geometrical parameters and volume fraction of Ni$_3$Al for each CNB specimen of the investigated in-situ composites are listed in Appendix D. The $\Delta a_m$ parameter was calculated from Eq.(2.25) taking the first derivative of $Y'$ as equal to zero ($dY'/d\alpha = 0$) and taking for calculation the measured geometrical parameters of each individual specimen. Elastic moduli for calculation of $C_e(\alpha)$ were taken from Table 2.1.

The mechanical properties such as $E_c$ and $\sigma_{ys}$, and the experimental results of $K_{I_m}$, work of fracture $\gamma_{WOF}$ and $K_{WOF}$ values from each CNB bend specimen are summarized in Appendix E.

To obtain a conservative estimate, the elastic modulus $E_c$ of each CNB bend specimen is calculated from the lower bound of the rule of mixtures for composites [63, 100]:

$$E_c = \frac{1}{\frac{V_d}{E_d} + \frac{1 - V_d}{E_m}}$$

(3.1)

where the moduli of monolithic alloys are: $E_d = 179$ GPa for Ni$_3$Al and $E_m = 294$ GPa for NiAl.
These values are taken from Ref.[110] (see Table 2.1).

The yield strength $\sigma_{YS}$ (offset = 0.2%) is determined by the compression test (see sections 2.5.1 and 3.4).

The values of $K_{hm}^W$ and $K_{hm}^B$ were calculated from Eqs.(2.29) to (2.32) from Wu's solution [126, 133] and Bluhm's solution [132, 140, 141], respectively, as mentioned in Chapter 2. It is clear that Wu's solution [126, 133] is more conservative than Bluhm's solution [126, 140, 141] because almost all of the $K_{hm}^W$ values are greater than the $K_{hm}^B$.

The values of $\gamma_{WOF}$ and $K_{WOF}$ were calculated from Eqs.(2.41) and (2.42), respectively. Obviously, the values of the apparent fracture toughness $K_{WOF}$ are greater than those of $K_{hm}$.

The invalid values of $K_{hm}^W$ and $K_{hm}^B$ were also distinguished according to the validity requirements in Chapter 2. The invalid values are marked in bold face in Appendix E.

**Effects of Slot Geometries of CNB Bend Specimens on the Values of $K_{hm}^W$**

As indicated in Eqs.(3.25), (3.27) and (3.33), stress intensity factor coefficient $Y'$ is a function of the slot geometries of CNB. The values of $Y'_m$ increase with the increasing of the initial crack length $a_0$, as shown in Figure 3.25a, which is in agreement with the results calculated by Wu [133]. However, $Y'_m$ seems not to be sensitive to the slot length $a_1$ (Figure 3.25b). The independence of $K_{hm}^W$ values on the slot geometries of $a_0$ and $a_1$ can be seen in Figure 3.26.
Figure 3.25 The relationship of the stress intensity factor coefficient, $Y_m^*$, with (a) the initial crack length, $a_0$, and (b) the slot length, $a_1$, of the CNB bend specimens produced by the investigated in-situ composites.
Figure 3.26 The independence of the $K_{I_{0}}^W$ values on (a) the initial crack length, $a_0$, and (b) the slot length $a_1$, of the CNB bend specimens produced by the investigated in-situ composites.
The Relationship between \( LLD \) and \( Aa \) in a CNB Test

As described in Chapter 2, the partial unloading compliance method was used for monitoring crack extension (\( \Delta a \)) (Figure 2.15c) and calculating the plastic area \( A_i \) (1 \( \leq i \leq n \)) (see Eq.(2.45)).

However, the compliance \( (C_{LLD}) \) obtained from each load-load line displacement \( (LLD) \) curve (Figures 3.21 to 3.24) is almost ten times greater than the that compliance \( (C_{ai}) \) calculated from Eq.(2.33). This result indicates that instantaneous crack extension of each bend specimen cannot be monitored by this method in a CNB bend test because values of \( C_{LLD} \) and \( C_{ai} \) did not simultaneously correspond to each other at the unloading points. The reason is not clear.

Therefore, an alternative method to estimate crack extension was used in this research. The alternative method is to assume that a linear relationship exists between \( LLD \) and \( \Delta a \) prior to and after the maximum load \( P_{\text{max}} \). As shown in Figures 3.27a and 3.27b, this method is very reliable for type IV (see Figures 3.19 and 3.24, including Ni\(_{70.8}\)Al\(_{29.2}\), Ni\(_{72.8}\)Al\(_{27.2}\) and Ni\(_{77.7}\)Al\(_{22.3}\) alloys), and most of the near-type I \( P-LLD \) curves (see Figures 3.22 and 3.23) because stable crack growth happened both prior to and after \( P_{\text{max}} \). The method is also accurate enough for the near-type I curves as shown in Figure 3.21 because a small stable crack growth always exists prior to \( P_{\text{max}} \) for all the CNB specimens and the experimental values of \( J_{\text{fc}} \) and \( K_{\text{fc}} \) would be calculated in this section (prior to \( P_{\text{max}} \)) as explained in the following section.
Figure 3.27  The typical linear relationships between load-load line displacement (LLD) and crack extension (Δa) for (a) Ni$_{77.7}$Al$_{22.3}$, (b) Ni$_{65.9}$Al$_{34.1}$, and (c) Ni$_{63.7}$Al$_{36.3}$ alloys.
**Evaluation of Fracture Toughness Values $J_{hc}$ and $K_{hc}$**

*Figure 3.28* shows a typical relationship between the parameters $Y'$, $P_{max}$, $K_{hm}^w$ and the crack extension ($\Delta a$) for the homogenized Ni$_{63.7}$Al$_{36.3}$ in-situ composite. This figure is a typical example to show all the features in a CNB bend test of this research: crack initiates before $P_{max}$ (*Figure 3.28a*), flat-bottom part of $Y'$ (*Figure 3.28b*) and a decreasing parameter $K_h$ with a plateau of $K_{hm}$ at $\Delta a_m$ (*Figure 3.28c*). As a comparison, more examples of such features for each in-situ composite are summarized in Appendix G.

The energy parameters of the CNB bend specimens, $J_{el}$, $J_{pl}$ and $J$ are calculated by *Eq.(2.44)*. A typical group of shapes of $J_{el}$, $J_{pl}$ and $J$, versus crack extension is shown in *Figure 3.29a*, 3.29b and 3.29c, respectively. As expected, $J_{el}$ is predominant only up to $\Delta a_m$ while $J_{pl}$ will take over after $\Delta a_m$ and show a much greater values than $J_{el}$. However, the shape of $J-\Delta a$ seems surprising but very reasonable if one checks the procedure carefully. It is very interesting to note that the $J-\Delta a$ fracture resistance curves showed a "hook" shape for all the CNB bend specimens (Appendix F). Therefore, to determine the $J_{hc}$ of each specimen, a "minimum-line method", instead of "blunting-line method" [99], was used for the determination of $J_{hc}$. Thereafter, $K_{hc}$ can be calculated by *Eq.(2.46)*. The values of $J_{hc}$, $K_{hc}$ for each CNB bend specimen of the investigated in-situ composite were calculated and summarized in Appendix G. For purely comparative purposes the parameters $\Delta a_c$ $Y'_c$, $P_c$, and $LLD_c$ and (where c - means "critical") were also calculated from the $J-\Delta a$ curve at the minimum point of $J$, and are
Figure 3.28  A typical relationship between the parameters (a) $P_{max}$, (b) $Y^*$ and (c) $K$, and the crack extension ($\Delta a_m=0.65\text{mm}$) for the homogenized Ni$_{63.7}$Al$_{36.3}$ in-situ composite.
Figure 3.29: A typical group of shapes of the parameters, (a) $J_{ct}$, (b) $J_{pl}$ and (c) $J$, versus the crack extension ($\Delta a_m=0.65\text{mm}$).
listed in Appendix G. Most of the values of "critical" parameters are exactly equal to the same parameters calculated purely from the geometry of CNB specimens and listed in Appendix D. The only exceptions are found for some of the 70.8, 72.8, 77.7, 73.2-0.2B and 74.8-0.4B alloys. The validity of experimental values of $J_{hc}$ and $K_{hc}$ ($K_{hm}$) were verified using Eqs. (2.20) and (2.40), respectively.

The "hook" shape of the $J$-$\Delta \alpha$ fracture resistance curve shows an exceptionally important feature of a CNB bend specimen. This feature make it much easier to determine the values of $J_{hc}$. In addition, the values of $J_{hc}$ and $K_{hc}$ are more reasonable because this method can automatically avoid either overestimating fracture toughness (see Appendix F3) or underestimating fracture toughness (Appendix F6).

It is important to note that the $Y'$ versus $\Delta \alpha$ curves show a wide, flat range at the bottom (approximately 0.3mm to 1.2 mm as shown in Figure 3.28b) for all the investigated in-situ composites (Appendices F1 (b) thro F8 (b)). In this section of the curve $Y'$ changes very little as $\Delta \alpha$ changes. This stability will result in more reliable values when using Eq.(2.24) to calculate $K_{hm}$. 

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CHAPTER 4

DISCUSSION

4.1 Microstructural Characterization

In this study, the overall composition of the as-cast, homogenized and aged in-situ composites ranges from Ni$_{63.7}$Al$_{36.3}$ to Ni$_{77.7}$Al$_{22.3}$, which covers the two phase ($\beta+\gamma'$) (NiAl/Ni$_3$Al) field in the Al-Ni phase diagrams (Figures 1.32 and 1.37). Due to fast cooling rate the as-cast alloys show non-equilibrium structures (Figures 3.1 and 3.2), which are not suitable for a fracture toughness test. The homogenized and aged microstructures conform in general to the phase diagrams as shown in Figures 1.32 and 1.37. The fracture toughness values of the homogenized and aged in-situ composites are highly sensitive to their microstructures. Therefore, the toughening mechanisms of the in-situ composites can be explored by analysing their microstructure and fracture surface characterizations. The effects of homogenization at 1000°C for 100h as well as ageing at 550°C for 100h (both followed by a slow furnace cooling), can be summarized as follows:
(1) It is evident that the relatively ductile phase of Ni$_3$Al preferentially nucleates at the grain boundaries forming a continuous film around the NiAl grains as shown in Figures 3.1 and 3.3a to d. These results are in agreement with the results from Kumar et al. [13] and Noebe [24]. In addition, the thickness of Ni$_3$Al phase increases after homogenization from approximately 0.8 μm to 1.5 μm. Such an existence and thickness increment of “necklace microstructure” may toughen the grain boundaries of brittle NiAl phase and thereafter may increase the fracture resistance of the alloys. This is because NiAl does not have enough slip systems to satisfy grain boundary compatibility and the continuous film of γ'-Ni$_3$Al has multiple independent <110>[111] slip systems, which may enable grain-to-grain compatibility to be restored [114]. Therefore, the continuous, ductile grain boundary film would thus act as a compliant layer between NiAl grain facets.

(2) After homogenization the thickness or size of the Ni$_3$Al precipitates also increases greatly (Tables 3.2 and 3.4), which benefits crack blunting (Figure 1.1a) or crack front trapping (Figure 1.1b) toughening mechanisms and thereafter increases the fracture toughness of the in-situ composites.

(3) The fully twinned-structure in the NiAl grains, which is most probably a result of martensitic transformation, only appears in the non-equilibrium, as-cast alloys. This is because of the fast cooling rate (=300°C/h) for the as-cast alloys. After homogenization with much slower cooling rate of approximately 50°C/h (furnace cooling), the occurrence of this twinned-structure (martensitic) of NiAl is reduced but still noticeable (Figures 3.3b, 3.3d, and 3.8b). This observation might indicate that the NiAl phase is still in a slight non-equilibrium even after furnace cooling from the homogenization temperature.
(4) The most important phenomenon from comparison of morphologies in Figure 3.1 with Figure 3.3, or data in Table 3.2 with Table 3.4 is that the volume fraction of ductile Ni$_3$Al phase increased greatly after homogenization for all the alloys, which may potentially benefit both ductility and toughness of the material.

(5) The morphologies of the in-situ composites are highly sensitive to composition. As shown in Figure 3.3, the morphologies after homogenization change greatly when the overall Ni-content increases only a little. After homogenization at 1000°C for 100h followed by a slow furnace cooling, the main distinct structures of the selected system include:

- locally twinned NiAl matrix grains (=180 μm) with embedded rod-like particles and “necklace” of Ni$_3$Al (=17 vol.%l) at grain boundaries (Figures 3.3a and b), for the 63.7-Ni content alloy;

- continuous NiAl matrix (without twinned-structure) surrounded by fine and round semi-continuous Ni$_3$Al particles (=32 vol.%) as shown in Figures 3.3e and f, for the 67.2-Ni content alloy;

- continuous Ni$_3$Al matrix containing approximately 40 volume percent of sharp NiAl particles (Figures 3.3g and h), for the 70.8-Ni content alloy;

- continuous Ni$_3$Al matrix containing 23 volume percent of round NiAl phase (Figures 3.3i and j), for the 72.8-Ni content alloy;

- continuous Ni$_3$Al matrix containing only 8.8 volume percent of round or rod-like NiAl phase (Figures 3.3k and l), for the 73.2-Ni content alloy.

(6) Of particular interest is the aged, in-situ composite Ni$_{65.5}$Al$_{34.5}$, which was heated at 1000°C for 100h and aged at 550°C for 100h followed by a slow furnace cooling (Figure 3.5).
In this alloy, a partial plate-like structure of Ni₃Al₅ [77] rather than 3-R martensite [78, 79, 90] was confirmed by X-ray analysis (Table 3.6). The obtained result is in agreement with the work done by Robertson and Wayman [77] but contrary to the result by Khadkikar et al. [78, 79, 90]. They reported (see Figure 1.46) that the plate-like precipitates in the grain interior were identified from electron diffraction patterns to be new variants of the 3R martensite [90].

(7) For the boron-doped in-situ composites, it can be observed that there is a very little microstructural change for the Ni₇.2Al₅₆.6B₀.₂ and Ni₇.2Al₅₆.₈ alloys by comparing Figure 3.4a with Figure 3.3k and data in Table 3.4. The Ni₇₄.₈Al₃₄.₈B₀.₄ alloy is almost a monolithic Ni₃Al with only 0.1 vol.% of NiAl phase as shown in Figure 3.4b.

(8) Very little compositional change for overall composition and the composition of each phase in all the in-situ composites was found after homogenization (as shown by comparing Table 3.1 with Table 3.3), which also indicates the reproducibility of EDS measurements.

(9) Compositions of the Ni₃Al phase as listed in Table 3.3 approximately conform to the most accurate equilibrium Ni-Al binary phase diagram in Figure 1.34, although some small discrepancies should be noted. The maximum nickel content in Ni₃Al reported in Table 3.3 is at 77.6 at.%. However, the data points for the maximum Ni content in Ni₃Al from Figure 1.34 are no greater than 77 at.%. This is quite satisfactory agreement taking into account that the error in the EDS measurements is not smaller than 0.5 at.%. The minimum nickel content in Ni₃Al in Table 3.3 is 72.5 at.%, which can be compared to about 73.5 at.% in Figure 1.34. The discrepancy is now slightly greater but still within 1 at.%. Less satisfactory agreement between data in the present work and those reported in the literature occurs for the NiAl phase. The maximum nickel content in this phase measured in the present work and listed in Table 3.3
is 64.2 at.%. From Figure 1.36 the maximum nickel content in NiAl is given as approximately 60 at.% and in Figure 1.32 and 1.37 the maximum nickel solubility content line is drawn at slightly less than 60 at.%. Such a discrepancy between the results obtained in the present work and the literature cannot be simply accounted for by the relative inaccuracy of the EDS method used in this work. It is possible that the NiAl phase which is a microconstituent of the investigated in-situ composites still has a slightly non-equilibrium composition most probably owing to a furnace cooling after homogenization (=50°C/h) which was still too high to allow full compositional equilibration. The highest nickel content of 64.2 at.% found in NiAl in the present work almost corresponds to the nickel content in NiAl at about 1000°C (Figures 1.32 and 1.37). Also, another argument supporting the notion about a non-equilibrium furnace cooling rate after homogenization is the occurrence of a twinned martensite in NiAl (martensitic transformation) (e.g. Figure 3.8).

4.2 Microhardness and Compressive Mechanical Properties

It is interesting to note that the mat-like structure of Ni₅Al₃ phase showed a significant microhardness value of 690 kg/mm² (Table 3.7), which shows an obvious smaller indentation area as shown in Figure 3.8a. This value is almost twice as much as those of any other structures in the in-situ composites. This behaviour is in agreement with Vickers microhardness measurements by Khadkikar et al. [90]. It is reasonable to assume that the extremely high yield strength of $\sigma_{YS} = 1150$ MPa (all $\sigma_{YS}$ values are tabulated in Appendix E) in Ni₆₇.₉Al₃₄.₁ in-situ
composite also results from this special mat-like structure of \textit{Ni}_3\textit{Al}_3 phase because very high values of neither yield strength (Table 3.8) nor Vickers microhardness (Table 3.7) can be found for any other in-situ composites without \textit{Ni}_3\textit{Al}_3 phase. It is worth of pointing out that a very high yield strength ($\sigma_{YS} \approx 1150\text{MPa}$) and a reasonable value of fracture toughness ($\approx 13 \text{MPa} \sqrt{\text{m}}$) (Appendix E) of the aged Ni$_{65.9}$Al$_{34.1}$ alloy indicate that such a new promising alloy can be yielded by an economic and simple casting method followed by a proper heat treatment as shown in this research.

4.3 Dependence of Fracture Toughness on Microstructure

4.3.1 Grain Size Effects

It has to be pointed out that the grain sizes of the matrix for all the in-situ composites as shown in Table 3.4 are approximately one forth of the critical crack length of the chevron-notch specimens as shown in Appendix D. This fact seems to indicate that the fracture toughness values obtained from the critical crack length of the in-situ composites might be affected by only a very few matrix grains in the materials. In other words, the small size of bend specimens might be unsuitable from the stand point of the size of matrix grains and should not be used to test the fracture toughness of the in-situ composites when the matrix grain size is relatively large. On the other hand, the linear elastic fracture mechanics (LEFM) assumes that
fracture toughness should be obtained from only a continuous material (i.e. many grains in the crack front). However, it might not necessarily be limiting factor for the real materials. In fact, there is no such a grain-size limitation in any ASTM Standard document such as $E\ 399-90$ [97], $E\ 1304-89$ [98] or $E\ 813-89$ [99]. Furthermore, a lot of small-size bending tests were performed without any grain-size limitation. For example, the grain size of NiAl in Rigney and Lewandowski’s work [81] was approximately 2000 μm and the single-edge-notched, three-point-bend specimen size was also small with dimensions: 6mm x 6mm x 50mm [81], which satisfies the size requirements of ASTM Standard $E\ 399$ [97] for plane strain. Rigney and Lewandowski [81] obtained a very reasonable toughness of 6.6 MPa$\sqrt{m}$ for NiAl. Therefore, the toughness values obtained in this research might not necessarily be affected by the relative sizes of the matrix grains and the critical crack lengths of the bend specimens.

### 4.3.2 The Effect of the Volume Fraction of Ni$_3$Al on the Fracture Toughness of the Boron-Free, In-Situ Composites

Figures 4.1 and 4.2 shows that both valid $K_{fma}^{w}$ and $K_{fc}$ values of homogenized alloys increase with increasing volume fraction of ductile Ni$_3$Al phase in the boron-free in-situ composites. The best fit curves in Figures 4.1 and 4.2 describe exactly the relationship of $K_{fc} = A + BV_d^n$ type which is similar to the results for both Ni/TiAl and TiNb/TiAl in-situ composites obtained by Rao et al. [70] (Figure 1.24).

Furthermore, comparing Figure 4.1 with Figure 4.2, it also can be seen that valid fracture
toughness values of $K_{hm}$ calculated from Eq.(2.24) give very consistent results with $K_{hc}$ obtained from the $J$-integral method of Eq.(2.46). The best fit curves establishing the precise relationship between fracture toughness and volume fraction of Ni$_3$Al for the in-situ, boron-free composites, can be given as follows:

$$K_{hm} = 6.12 + 0.7 V_d^{0.74} \text{ (MPa} \sqrt{\text{m}})$$  \hspace{1cm} (4.1)

$$K_{hc} = 6.05 + 0.714 V_d^{0.749} \text{ (MPa} \sqrt{\text{m}})$$  \hspace{1cm} (4.2)

where, $V_d$ is in ($\%$) and the residual mean-square correlation coefficients of $R^2$ are 0.95 and 0.92, for Eq.(4.1) and Eq.(4.2), respectively, and are pretty close to 1, showing that the best fit curves give a very good fit to the experimental data for the boron-free, in-situ composites.

When $V_d = 0$, the fracture toughness values of $K_{hm}$ or $K_{hc}$ represent the fracture toughness of NiAl phase, $= 6.1$ MPa$\sqrt{\text{m}}$, which is in a very good agreement with the results obtained by Kumar et al. [13].

In Figures 4.1 and 4.2, the solid symbols, representing the fracture toughness values obtained from the aged Ni$_{65.9}$Al$_{34.1}$ alloy, are very close to the best fit curves, which are yielded by homogenized in-situ composites (half-solid symbols). This fact actually indicates that ageing does not adversely affect the fracture toughness of the in-situ composites because Ni$_5$Al$_3$ phase only exists in the grains and does not embrittle the Ni$_3$Al/NiAl interfaces in the aged Ni$_{65.9}$Al$_{34.1}$ in-situ composite.

It has to be pointed out that the validity of $K_{hm}$ values (see the bold values of $K_{hm}$ as shown in Appendix E) is definitely limited for higher volume fraction of Ni$_3$Al (only one valid point for volume fraction higher than 80% of Ni$_3$Al as shown in the right part of Figure 4.1)
Figure 4.1  The dependence of valid $K_{fvm}^W$ values on the volume fraction of Ni$_3$Al phase in the boron-free, in-situ composites. The solid symbols show the aged alloy of Ni$_{65.9}$Al$_{34.1}$ and the open ones designate the homogenized alloys. The best fit line is labelled by squares. 

$K_{fvm}^W = 6.12 + 0.7V_d^{0.74}$  

$R^2 = 0.95$
Figure 4.2  The dependence of valid $K_{Ic}$ values on the volume fraction of Ni$_3$Al phase in the boron-free, in-situ composites. The solid symbols show the aged alloy of Ni$_{65.9}$Al$_{34.1}$ and the open ones designate the homogenized alloys. The best fit line is labelled by squares.

$$K_{Ic} = 6.05 + 0.714V_d^{0.749}$$

$$R^2 = 0.92$$
while the $K_{hc}$ values are all valid as shown in Appendix G and more points of $K_{hc}$ values are shown in the right part of Figure 4.2. This arises from the limitation imposed by the CNB specimen-thickness ($B \geq 1.25(K_d/\sigma_{ys})^2$ for a conventional $K_{fm}$ bending test. In other words, the $J$-integral unloading-reloading method for a single specimen of a CNB bend test is a much more convenient and useful tool to obtain valid fracture toughness values for the more ductile in-situ composites because the size requirement ($B \geq 25(J_d/\sigma_{ys})$ as shown in Eq.2.20) for valid-$J_{lc}$ of the $J$-integral unloading-reloading method is much more lenient than the conventional $K_{hc}$ requirements as discussed in Section 2.1.2.

Dependence of fracture toughness of the “in-situ” NiAl/Ni$_3$Al composite on volume fraction of toughening phase (Ni$_3$Al) can also be analysed in terms of the rule of mixtures (ROM) as reported by Davidson and Chan [61-62] for the Nb-Cr$_2$Nb system.

For comparison with the experimental results, the calculated rule of mixtures (ROM), both with and without considering the differences in modulus between NiAl ($E_m = 294$ GPa [110]) and Ni$_3$Al ($E_d = 179$ GPa [110]), are represented by dashed lines and designated “$E$-ROM” and “ROM”, respectively. The lower bound, $K_{min}$, and upper bound, $K_{max}$, of the modified ROM by Ashby [63] are also shown as solid lines in Figure 4.3. The typical points on the $E$-ROM, ROM, $K_{min}$ and $K_{max}$ lines are calculated by Eqs.(1.26), (1.28), (1.30) and (1.32), respectively. The parameters for calculating $E$-ROM, ROM, $K_{min}$ and $K_{max}$ are summarized in Table 4.1.
Table 4.1 The parameters used for calculating $E$-$ROM$, $ROM$, $K_{max}$ and $K_{min}$.

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Note: Poisson's ratio, $v$, taken for calculations of $E'_m$ (NiAl) is equal to 0.315 [119] and for $E'_d$ (Ni$_3$Al) is equal to 0.305 [119]. Values of $E_d$ and $E_m$ are taken from Table 2.1.
Figure 4.3  The valid $K_{hm}$ and $K_{inc}$ fracture toughness of the boron-free in-situ composites as a function of volume fraction of Ni$_3$Al. A regular ROM (straight broken line), modulus-modified (E-ROM) as well as upper bound ($K_{max}$) and lower bound ($K_{min}$) of Ashby's modified ROM [63] are shown. The solid symbols designate the aged alloy of Ni$_{65.9}$Al$_{34.1}$ and the unsolid ones represent the homogenized alloys. The numbers in parentheses indicate overlapping data points.
In either case, the values of the fracture toughness of the investigated in-situ composites are almost within the \textit{ROM} and \(K_{\text{max}}\) (or \textit{E-ROM}) lines. In particular, this behaviour experimentally confirms the validity of either \textit{E-ROM} or \(K_{\text{max}}\) by Ashby’ approach [63]. Furthermore, all the data from the NiAl-Ni\(_3\)Al are close to the upper bound, which is contrary to the results from the Nb-Cr\(_2\)Nb in-situ composites obtained by Davidson and Chan [61-62]. In their results [61-62], all the data from the Nb-Cr\(_2\)Nb in-situ composites were close to the \(K_{\text{max}}\) lower bound line (Figure 1.17).

4.3.3 Comparison with Existing Toughening Models

\textbf{The Alloys Containing a Continuous NiAl Matrix and a Discontinuous Ni\(_3\)Al Phase}

Crack bridging is probably one of the pronounced toughening mechanisms for the in-situ composites containing a continuous NiAl matrix and a discontinuous Ni\(_3\)Al phase (Figures 3.3a thro f, and Figure 3.5) because the stretched ductile Ni\(_3\)Al particles could be clearly observed from the typical fractographs of these alloys as shown in Figures 3.10b, 3.11b, 3.12a and b. This is because when they are intercepted by a crack, the ductile Ni\(_3\)Al particles could undergo extensive plastic stretching in the crack wake and contribute to the toughness of the in-situ composites by inhibiting or making further crack opening very difficult.

A quantitative analysis of crack bridging mechanism can be given by \textit{Eq.}(1.16) although according to Chan’s rule for \textit{extrinsic} toughening mechanism [17-18, 23], crack bridging model described by \textit{Eq.}(1.16) cannot effect the \(K_{\text{fc}}\) value of the composite, as discussed in Chapter 1.
Disregarding the Chan’s rule [17-18, 23] one can try to use simple addition rule: $K_c = K_m + \Delta K_r$, where $\Delta K_r$ designates the toughness contribution by crack-bridging toughening mechanism as shown in Eq.(1.16). This rule has been applied several times by other researchers for an in-situ Nb-reinforced Nb₃Al intermetallic composite [44] and both fully lamellar and duplex TiAl system [57]. The quantitative analysis of crack-bridging toughening mechanism can be given as follows.

The parameters to calculate crack-bridging toughening mechanism for the in-situ composites containing a continuous NiAl matrix and a discontinuous Ni₃Al phase (Figures 3.3a thro f, and Figure 3.5) are listed in Table 4.2. The elastic modulus of the in-situ composites, $E$, as shown in Eq.(1.16), is calculated from the lower bound of the rule of mixtures for composites as Eq.(3.1) [63, 100] and listed in Appendix E (this is a conservative estimate of the elastic modulus of a composite).
Table 4.2 The parameters for quantitative analysis of crack-bridging toughening mechanism in the alloys containing the NiAl matrix and a discontinuous Ni$_3$Al phase.

| Ni $\text{at.\%}$ | $V_{d}$ vol.$\%$ | $E$ GPa | $\sigma_{TS}$ MPa | $\chi$ | $a_0$ $\mu$m | $\Delta K_R$ MPa m$^{1/2}$ | $K_m$ MPa m$^{1/2}$ | $K_{ic}$ MPa m$^{1/2}$ | $K_{ivm}$ W
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<td>11.45734</td>
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<td>17.65734</td>
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</tbody>
</table>

Note: 1. $K_{ic} = K_m + \Delta K_R$

2. $K_{ivm}$ is experimental.
The work-of-fracture parameter $\chi$ can vary from the interface debonding of the two phases, e.g., Ni$_3$Al/NiAl in the in-situ composites. For a well-bonded interface (debonding length, $d = 0$) and for ductile ligaments that fail by necking to a point, the resultant $\chi$ is in the range 0.3 to 1 [45]. For various extents of debonding at the interface of the cylindrical specimens of Pb in glass, experiments show that $\chi$ can vary from 0.5 to 6 (Figure 4.4) For the network structure of Al$_2$O$_3$/Al composites, $\chi$ is in the range of 2 to 3.5 [43]. For the particulate ductile phase toughened brittle materials, since the maximum debonding that can be achieved is appreciably smaller than that of the other two microstructures, the $\chi$ value is comparatively small [45]. Therefore, by analogy with references [43-45] and according to the typical fractographs as shown in Figures 3.10, 3.11 and 3.12, the $\chi$ values of 0.4, 0.6, and 1.1 for the homogenized Ni$_{63.7}$Al$_{36.3}$ alloy, the aged Ni$_{65.9}$Al$_{34.1}$ alloy and the homogenized Ni$_{67.2}$Al$_{32.8}$ (Table 4.2), respectively, can be arbitrarily assumed as reasonable approximations for $\chi$.

The average values of thickness of Ni$_3$Al, $a_0$, are taken from Table 3.4. The $K_{ic}$ value of the matrix, $K_m = 6.2$ MPa$\sqrt{m}$ for monolithic NiAl in Table 4.1, is taken from Eqs.(4.1) and (4.2) when $V_d = 0$.

The results by simple addition rule ($K_{ic} = K_m + \Delta K_{ic}$) as shown in Table 4.2, seem to fit well to the Ni$_{63.7}$Al$_{36.3}$ ($K_{ic} = 9.22 \pm 0.14$ MPa$\sqrt{m}$ vs. $K_m^{w} = 8.25 \pm 0.27$ MPa$\sqrt{m}$) and Ni$_{65.9}$Al$_{34.1}$ ($K_{ic} = 13.89 \pm 0.34$ MPa$\sqrt{m}$ vs. $K_m^{w} = 13.30 \pm 1.30$ MPa$\sqrt{m}$) alloys but overestimate the fracture toughness of the Ni$_{67.2}$Al$_{32.8}$ in-situ composite ($K_{ic} = 17.69 \pm 0.68$ MPa$\sqrt{m}$ vs. $K_m^{w} = 14.80 \pm 1.07$ MPa$\sqrt{m}$). These results might indicate that the crack bridging model of Eq.(1.16) be only suitable for the homogenized Ni$_{63.7}$Al$_{36.3}$ and aged Ni$_{65.9}$Al$_{34.1}$ in-situ composites, but not for
the Ni₆₇.₆₃Al₂₉ in-situ composite. This is most probably because the interfacial/grain boundary fracture of Ni₅Al becomes more (dominant) in the Ni₆₇.₆₃Al₂₉ alloy over crack bridging by the Ni₅Al particles. Such a scenario seems to agree with the fractographs of the Ni₆₇.₆₃Al₂₉ alloys in Figure 3.12.

![Diagram](image)

**Figure 4.4** \( \chi \) "work of rupture" parameter against maximum normalized displacement [41].

Crack blunting could be another evident toughening mechanism for the in-situ composites containing the continuous NiAl matrix and a discontinuous Ni₅Al phase (Figures 3.3a thru f, and Figure 3.5) since the impeded "river-pattern" crack at the grain boundaries could be observed in the typical fractographs of Figures 3.10b, 3.11 and 3.12. This is due to the
impediment of the propagation of cleavage crack forming river-pattern in the NiAl grains as they intersected the "necklace", i.e., ductile $\gamma'$-Ni$_3$Al at the grain boundaries. The extensive localized plastic deformation of the second $\gamma'$ phase may cause the stresses at the crack front to relax sufficiently to blunt the crack in the ideal case, and therefore would prevent the crack from propagating further. As indicated in crack blunting model Eq.(1.5), the fracture toughness caused by this mechanism would be more significant when the volume fraction of ductile Ni$_3$Al phase increases. Unfortunately, since the effective fracture strain values of matrix and ductile phase ($\varepsilon_{fm}$ and $\varepsilon_{pl}$ in Eq.(1.7)) as required in this model are hard to measure for the in-situ composites, the quantitative analysis of this toughening mechanism on the in-situ composites could not be given in this work.

**The Alloys Containing a Continuous Ni$_3$Al Matrix and a Discontinuous NiAl Phase**

As shown in Appendices E and G, the in-situ composites containing a continuous Ni$_3$Al matrix and a discontinuous NiAl phase (Figures 3.3j thro m, and Figures 3.4a, b) showed higher fracture toughness values of $K_{fm}^{\text{w}}$ and $K_{fca}$ than the ones for the in-situ composites containing a continuous NiAl matrix and a discontinuous Ni$_3$Al phase (Figures 3.3a thro h, and Figure 3.5).

It can also be seen that the Ni$_3$Al grain facets show intergranular fracture mode in all the in-situ composites with the Ni$_3$Al matrix (Figures 3.13 to 3.16) as well as in the boron-doped in-situ composites (Figures 3.17 to 3.18). Although the Ni$_3$Al matrix was shown to fail by brittle intergranular fracture, toughness values in excess of 20 MPa$\sqrt{m}$ (Appendices E and G) were still obtained from the in-situ composites containing a continuous Ni$_3$Al matrix and a
discontinuous NiAl phase (Figures 3.3h thro m, and Figures 3.4a and b). These results are consistent with Rigney and Lewandowski' earlier work [81]. This is because of several factors, including interfacial delamination, crack tip blunting or plastic deformation on the grain facets and in the specimen bulk. As indicated by Rigney and Lewandowski' earlier work [81], the intergranular cracks of Ni\textsubscript{3}Al phase are clearly stable and significant plasticity develops at the crack tip, which may result in the observed high toughness values as shown in Appendices E and G. In addition, with increase in load, dislocation motion is promoted in the Ni\textsubscript{3}Al grains contained within the plastic zone at the crack tip, and owing to high stresses and strains attained ahead of the chevron notch, the blunting of the crack tip causes further yielding along the grain facets neighbouring the crack faces.

The reason that the in-situ composites with higher volume fraction of $\gamma'$-Ni\textsubscript{3}Al phase shows higher potential ductility, can be explained by comparing the slip systems of NiAl phase and Ni\textsubscript{3}Al phase.

It is well known that only three independent slip systems are available for polycrystalline NiAl deformation by $<110>$ slip, regardless of the operative slip planes [24, 67, 82-83, 111-115]. Because this is less than the five independent deformation modes considered necessary for extensive, uniform, crack free deformation of a polycrystalline aggregate, NiAl is considered to have little potential for exhibiting substantial room temperature tensile ductility and fracture toughness. This view is supported by experimental evidence (only zero to a maximum of about 4% room-temperature tensile ductility [24, 114] and 4 to 7 MPa$\cdot$\text{m} of fracture toughness of polycrystalline NiAl [81, 111]). Therefore, simply speaking, monolithic NiAl is a slip system limited material.
In contrast to NiAl, the ordered fcc $\text{Ni}_3\text{Al}$ phase has enough independent slip system to accommodate plastic deformation in polycrystalline form since its low temperature deformation occurs by $<110>\{111\}$ slip [82-83, 113]. $\gamma'$-$\text{Ni}_3\text{Al}$ has inherent tensile ductility at room temperature as demonstrated by single crystal behaviour (over 98% elongation) and even with intrinsic grain-boundary brittleness, monolithic $\text{Ni}_3\text{Al}$ has superior toughness of 20 MPa$\sqrt{\text{m}}$ [81]. This makes higher volume fraction of $\gamma'$-$\text{Ni}_3\text{Al}$ phase a higher contributor of fracture toughness in the in-situ composites. Besides, the effect of volume fraction of $\text{Ni}_3\text{Al}$ ductile phase on fracture toughness on the in-situ composites would be discussed in detail in the following sections because of its exceptional importance.

**Figure 4.5** schematically show the toughening mechanism proposed to be responsible for the high toughness in $\text{Ni}_3\text{Al}$. The dislocation emission results in local plastic deformation along grain facets neighbouring the extending macrocrack. The tip of the precrack blunts during loading, while intergranular microcracking develops in the process zone on the sample surface (only). Intergranular macrocracking occurs along grain boundaries after significant crack opening displacement, while intergranular macrocrack propagation occurs in a stable manner accompanied by significant local plasticity in the grains and at grain boundary regions. The mechanism proposed supports initiation of stable intergranular macrocracks, followed by energy dissipation through dislocation activity in the vicinity of grain boundaries and grain interiors, thereby contributing significantly to the high toughness and resistance curve behaviour in $\text{Ni}_3\text{Al}$.

Additionally, **Figure Appendix C1** (p.222) shows that grain boundary facets (in reality semi-dendritic boundaries) are interconnected by most probably secondary dendritic arms.
Schematic diagrams of the mechanisms contributing to high toughness and resistance curve behaviour in Ni$_3$Al. (a) With increasing in load, dislocation motion is promoted in grains contained within the plastic zone owing to high stresses and strains attained ahead of the precrack. (b) The blunting of the crack tip causes further yielding along the grain facets neighbouring the crack facets. A high degree of yielding in grains on the sample surface away from the macrocrack causes prior particle boundary and intergranular cracking. This process continues with crack growth [81].
which fracture last acting similarly to crack bridging mechanism. This may be somehow additive to the toughness resulting from the local plasticity developing during grain (semi-dendritic) boundary fracture (Rigney and Lewandowski [81]).

The Alloy after Ageing

As indicated in Section 4.1, the Ni$_5$Al$_3$ phase in the Ni$_{65.9}$Al$_{34.1}$ in-situ composite, was not observed nucleating at the grain boundaries, which is inconsistent with the results by Khadkikar et al. [78, 79, 90]. This fact indicates that the Ni$_5$Al$_3$ phase would not affect the intergranular fracture pattern in Ni$_{65.9}$Al$_{34.1}$ in-situ composite but might be beneficial for bowing or crack front trapping in the grains during the fracture toughness test. That is probably why this needle-like mat structure of fine Ni$_5$Al$_3$ particles is not embrittling the alloy and simultaneously increases the yield strength of the Ni$_{65.9}$Al$_{34.1}$ in-situ composite.

The Alloy with Ni Reinforcements

The non-catastrophic fracture and significant plasticity of the Ni$_{77.7}$Al$_{22.3}$ alloy with near-single Ni$_5$Al phase, as shown in Figure 3.16, prompted additional toughness testing utilizing $J$-integral technique in a CNB test. The present results from $J$-integral technique as shown in Appendix G, indicate that despite the observed intergranular fracture (Figure 3.16a) this alloy possesses extremely high toughness (=85 MPa√m as shown in Appendix G). This might be due to the Ni phase residing within the grains as shown in Table 3.3 and Table 3.4 and seen in Figure 3.3m. The significant plastic deformation on the grain facets and in the specimen bulk, especially local tearing fracture mode as shown in Figure 3.16b, is definitely beneficial for such
high fracture toughness value of this alloy.

4.4 The Dependence of the Fracture Toughness on the Yield Strength for the Boron-Free, In-situ Composites

Materials with higher yield strength usually exhibit a lower tensile ductility and thus a lower fracture resistance (fracture toughness) [107, 108]. This general behaviour as shown in Figure 4.6 is also true for the investigated boron-free, in-situ composites (Figures 4.7 and 4.8).

Figures 4.7 and 4.8 show the influence of the yield strength on the valid $K_{fm}^w$ and $K_{fc}$ for the boron-free in-situ composites, respectively. It can be seen that the fracture toughness values decrease with increasing yield strength for most of the investigated in-situ composites. In addition, this rule can be expressed as follows for the boron-free, in-situ composites:

$$K_{fm}^w = 1609.2 \sigma_{YS}^{-0.6859} \quad (R^2=0.7767) \quad (4.3)$$

$$K_{fc} = 953.18 \sigma_{YS}^{-0.6084} \quad (R^2=0.8625) \quad (4.4)$$

where $\sigma_{YS}$ is in MPa, and $K_{fm}^w$ and $K_{fc}$ in MPa$\cdot$m.$^3$

However, it is interesting to note that the Ni$_{63.7}$Al$_{36.3}$ alloy (the circle symbols as shown in Figures 4.7 and 4.8) does not conform to this rule, which shows lower fracture toughness dependence on the lower rather than higher yield strength. The reason for such a behaviour is not clear.
Figure 4.6  (a) Fracture toughness as a function of yield strength [108]. (b) Fracture toughness vs. yield strength for AISI 4340 steel quenched and tempered to various strength levels [107].
Figure 4.7  The valid $K_{\text{hom}}^\infty$ as a function of the yield strength for the boron-tree, in-situ composites. The solid symbols show the aged alloy of Ni$_{65.9}$Al$_{34.1}$ and the open ones designate the homogenized alloys.
Figure 4.8  The valid $K_{ic}$ as a function of the yield strength for the boron-free, in-situ composites. The solid symbols show the aged alloy of Ni$_{68.5}$Al$_{31.5}$ and the unsolid ones designate the homogenized alloys.
4.5 Engineering Implications-the Weakest Link Theory

The weakest link theory (WLT) originally proposed by Weibull [150, 151] was conventionally used to explain the large strength variation of ceramics by many researchers. Recently, Rogers et al. [152] first applied it for the analysis of fracture toughness results of fully lamellar γ-based titanium aluminides.

The WLT or so called Weibull analysis, assumes that the failure of the weakest element among all the elements which comprise an isotropic and statistically homogeneous component would cause the whole component to fail. The most important parameter in the WLT is Weibull modulus \( m \). For fracture toughness the parameter \( m \) can be obtained as the slope of a \( \ln [1/(1-F)] \) versus \( \ln K_t \) curve, where \( F \) represents a probability of failure. A high \( m \) value gives a narrow fracture-toughness range and little scatter, i.e. a high fracture reliability. Conversely, a low \( m \) value means a large scatter in fracture toughness. The function of \( m \) is somehow similar to that of the standard deviation or root mean square deviation from a normal distribution. The only difference is that when the standard deviation or root mean square deviation is large, the scatter of the properties is large and when the standard deviation or root mean square deviation is small, the variation of the properties is also small.

In the WLT, \( F \) is defined as follows [150, 151],

\[
F = n/(1+N)
\]  \hspace{1cm} (4.5)

where \( n \) is the ordered data to rank the values of \( K_t \) from the small value to the large value, \( N \)
is the total number of the values.

The results of Weibull analysis on each in-situ composite are summarized in Table 4.3 in detail. The three pairs of typical examples are shown in Figures 4.9 to 4.11. In particular, it is very interesting to note that the values of \( m=23.8 \) and \( m=5.8 \) are obtained for \( \text{Ni}_{63.7}\text{Al}_{36.3} \) with lower fracture toughness \( (K_{\text{f},w} = 8.7 \text{ MPa}\sqrt{\text{m}}) \) and \( \text{Ni}_{73.2}\text{Al}_{26.8} \) with a higher value of \( K_{\text{f},w} = 23.6 \text{ MPa}\sqrt{\text{m}} \), respectively. The obtained results of \( m \) indicate that:

1. The alloys \( \text{Ni}_{63.7}\text{Al}_{36.3}, \ \text{Ni}_{67.2}\text{Al}_{32.8}, \ \text{Ni}_{70.8}\text{Al}_{29.2} \) and \( \text{Ni}_{72.8}\text{Al}_{27.2} \) are very reliable materials for engineering design even \( \text{Ni}_{63.7}\text{Al}_{36.3} \) with a lower value of average fracture toughness;

2. The alloys \( \text{Ni}_{65.9}\text{Al}_{34.1} \) and \( \text{Ni}_{73.2}\text{Al}_{26.8} \) exhibit rather low Weibull modulus \( (m=5.9) \). This means that the fracture toughness values of these alloys are highly variable and no single value for \( K_{\text{f},w} \) can be assigned easily. This has very important implications for engineering design with these in-situ composites since safety factors will have to be high due to the uncertainty in the \( K_{\text{f},w} \).

There is no microstructural indication to explain such a difference in behaviour of these alloys.
Figure 4.9 Two typical examples of Weibull analysis on the investigated boron-free in-situ composites: (a) Ni$_{37.7}$Al$_{36.3}$, and (b) Ni$_{73.2}$Al$_{26.8}$. 
Figure 4.10 Two typical examples of Weibull analysis on the investigated boren-free in-situ composites: (a) Ni$_{67.3}$Al$_{32.7}$, and (b) Ni$_{65.9}$Al$_{34.1}$. 

\[ y = 12.054x - 32.924 \quad R^2 = 0.9152 \]

\[ y = 8.871x - 23.378 \quad R^2 = 0.9889 \]
Figure 4.11 Two typical examples of Weibull analysis on the investigated boron-free in-situ composites: (a) Ni_{79.8}Al_{29.2}, and (b) Ni_{72.8}Al_{27.2}. 

\[ y = 15.703x - 50.138 \]
\[ R^2 = 0.8477 \]
\[ x = \ln(\lambda_{1vm}) \]

\[ y = 13.779x - 45.012 \]
\[ R^2 = 0.869 \]
\[ x = \ln(\lambda_{1vm}) \]
Table 4.3  Weibull analysis on each boron-free, in-situ composite.

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<th>Ni$<em>{73.2}$Al$</em>{26.8}$</th>
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4.6 The Influence of the Boron-Doping on the Fracture Toughness of the In-Situ Composites

As shown in Figures 3.17 and 3.18, in the boron-doped in-situ composites the fracture mode of Ni$_3$Al was not changed from intergranular failure to transgranular tearing as reported by Rigney and Lewandowski [81]. That is why the fracture toughness values (=25 MPa) obtained from the boron-doped in-situ composites are almost equal to the ones (= 24 MPa) obtained from the boron-free in-situ composites (Appendices E and G).

Comparing the micrographs of the boron-free Ni$_{77.3}$Al$_{22.7}$ alloy (Figures 3.6a and 3.7a) with the boron-doped in-situ composites of Ni$_{72.2}$Al$_{56.6}$B$_{0.2}$ and Ni$_{74.8}$Al$_{54.8}$B$_{0.4}$ (Figures 3.6b and 3.7b), much less grain-boundary cracking can be seen for the water-quenched, 0.2 at.% boron-doped alloy (Figure 3.6b) and no grain-boundary cracking can be observed for Vickers indentation fracture testing under the highest load (2000g) on the 0.4 at.% boron-doped in-situ composites as shown in Figure 3.7b. The obtained results indicate that boron doping seems to be beneficial for the grain-boundary cohesion of polycrystalline Ni$_3$Al, which agrees with the work by Liu et al. [82, 110, 113]. In their research [82, 110, 113], due to boron addition (=0.2 at.%) the ductility increases dramatically for the boron-doped Ni$_3$Al with less than 25 at.% Al. This is because boron is less electronegative with respect to the base metals of Ni and Al. Therefore, boron would share electrons with the metal atoms rather than draw charge off them and thus enhance bonding in the grain boundary of monolithic Ni$_3$Al.

However, the fractographs (Figures 3.17 and 3.18) and fracture toughness results (Figure
4.12) in this research indicated that the fracture toughness of Ni$_3$Al as shown in Figure 4.12, seems to be insensitive to boron addition. This might be because boron addition did not change the fracture mode of Ni$_3$Al from intergranular to transgranular as shown in Figures 3.17 and 3.18. The obtained results are obviously contrary to the recent results obtained by Rigney and Lewandowski [81, 115] and Liu et al. [82, 110, 113]. In their work [81, 115], 0.2 at.% boron doping raised the toughness value of monolithic Ni$_3$Al from 20 MPa$\sqrt{m}$ to 30 MPa$\sqrt{m}$ and the load-displacement curve showed much higher plastic deformation (Figure 4.13a) than that from Ni$_3$Al. Furthermore, Liu et al. [82] found that ductility increases dramatically and fracture mode changes from intergranular to transgranular due to boron doping (Figure 4.13b).

However, Table 3.3 shows that the Ni$_3$Al matrix in boron-doped alloys contain 24.9 at.% Al and 24.6 at.% Al for 0.2 at.% B and 0.4 at.% B, respectively. These Al contents are relatively high being close to a border-line content of 25 at.% Al. It is well-known [153] that Al contents much lower than 25 at.% are needed for full ductilizing effect of boron.
Figure 4.12  The dependence of (a) the valid $K_{\text{int}}$ and (b) $K_{\text{inc}}$ values on the boron content.
Figure 4.13 (a) Typical load-crack opening displacement toughness test traces for monolithic materials [81, 115]. (b) SEM fractographs of Ni$_3$Al doped with 0.05 wt.% B, showing tensile fractured surface of 24 at.% Al [82].
4.7 Work-of-Fracture and Apparent Fracture Toughness

In this research, critical stress intensity factors were also calculated from the work of fracture analyses performed simultaneously on the same specimen. This involved measuring the area under the load-load line displacement curve of an in-situ composite beam through integration and dividing by the total, projected area of the specimen to obtain the effective surface energy or "work of fracture", $\gamma_{WOF}$, as described by Eq(2.42). The designation of apparent fracture toughness [120] (or so called average fracture toughness in some references [154]) $K_{WOF}$ is used to denote the work of fracture critical stress intensity factor in order to avoid confusion with the maximum load derived parameters, $K_{hm}$ or the $J$-integral obtained values, $K_{hc}$.

Figure 4.14 shows a plot of apparent fracture toughness $K_{WOF}$ and the valid $K_{hm}^w$ versus volume fraction of the ductile Ni$_3$Al phase ($V_d$) for the boron-free in-situ composites. It is worth noting that for every composite, $K_{WOF} > K_{hm}^w$, and that the magnitude of the separation becomes larger with increasing $V_d$. This is in very good agreement with the results obtained from the polymeric sintered Ni/\alpha-Al$_2$O$_3$ composites [154]. It was found that there is an increasing separation between $K_{WOF}$ and $K_{hm}^w$ with increasing content of Ni in the Ni/\alpha-Al$_2$O$_3$ composite [154]. This separation between $K_{WOF}$ and $K_{hm}^w$ clearly indicates that the energy consumed by the non-linear fracture processes of the in-situ composite is too large and the apparent fracture toughness $K_{WOF}$ cannot be used to predict the LEFM $K_{ic}$. However, because the plastic deformation increased with increasing volume fraction of the ductile Ni$_3$Al phase,
the non-linear fracture would cause a separation of the $K_{WOF}$ and $K_{hm}$ since the two distinct stress intensity factors are probing different critical crack lengths (i.e. different regimes of beam failure) [120, 154]. This feature can be explained in the following.

In relation to this work, in the case of maximum load derived stress intensity factor, $K_{hm}$, primarily the early portion of the $K_{hm} - \Delta a$ is being probed. This is because the maximum loads in the load/load line displacement plots occur at relatively small displacements or critical crack extension when compared to the total displacement at beam failure. The work of fracture stress intensity factor, $K_{WOF}$, on the other hand, serves more as an average fracture toughness in relation to the overall fracture resistance curve since its determination relies on integration of the entire load/load line displacement curve from start to finish. Furthermore, due to the unique geometry of the chevron notches (i.e. the crack encounters more and more material as it progresses), this “average” fracture toughness is also weighted in favour of the larger crack lengths.
Figure 4.14 A comparison of the apparent fracture toughness $K_{WOF}$ and valid $K_{Ivm}^W$ versus volume fraction of ductile Ni$_3$Al phase for the boron-free in-situ composites. The solid symbols show the aged alloy of Ni$_{65.9}$Al$_{34.1}$ and the void ones designate the homogenized alloys.
4.8 The Unique Features of $K-\Delta a$ and $J-\Delta a$ Curves for a CNB Bending Test

The important characterizations of the fracture resistance $K-\Delta a$ and $J-\Delta a$ curves derived from a $J$-integral method by a chevron-notch-beam (CNB) bending test could be observed in Figure 3.28c, Appendices F1 (c) thro F8 (c) and Figure 3.29c. Appendices F1 (f) thro F8 (f), respectively, and summarized as follows:

1. As shown in Figure 3.28c and Appendices F1 (c) thro F8 (c), the stress intensity factor $K$ decreases with increasing crack extension $\Delta a$ and besides, a PLATEAU usually appears right up to the critical crack extension $\Delta a_m$.

The fracture energy $J$ decreases with increasing crack extension $\Delta a$ only until the critical crack extension $\Delta a_m$, then starts to increase with increasing crack extension, forming a very special shape which can be called "HOOP HEAD" as shown in Figure 3.29c and Appendices F1 (f) thro F8 (f). It is very interesting to note that this feature is distinct from the conventional power-law regression curve of $J-\Delta a$ defined by ASTM Standard E 813-89 [99] as shown in Figure 2.13d. Particularly, a critical value ($J_{hc}$) of the fracture energy for a CNB test can be now simply calculated by a horizontal line tangent to the "hoop head", i.e., a minimum value of $J$. It has to be pointed out that the above important features of $K-\Delta a$ and $J-\Delta a$ curves from a $J$-integral method for a CNB test has never been found in any other references so far up to best of author’s knowledge.

To elucidate the main reasons for such special characterizations as pointed out above, it is
essential to consider the parameters $P$ and $Y'$ because the stress intensity factor $K$ and the fracture energy $J$ are directly calculated from the product of the applied load $P$ and the stress intensity factor coefficients $Y'$. As discussed in Chapter 2, the stress intensity factor $K$ and the fracture energy $J$ are calculated from

$$K = PY'(B\sqrt{W})$$

and

$$J = (PY')^2(S-1)/(B^2WE)+4A/[B(2W-a_1-a_0)]$$

respectively. Where, $Y'$ is calculated from Eq.(2.25) for a CNB specimen and $Y' = f(a/W)/W$ [97] for a single-edge-straight-through (SEST) specimen. Therefore, the three important features as mentioned above are actually resulting from the following:

1. The load-load line displacement ($P$-$LLD$) curves as shown in Figures 3.21 thro 3.24) start from zero, but the load-crack extension ($P$-$\Delta a$) curves (Figure 3.28a and Appendix F (a)) start from a load value much higher than zero, which corresponds to the end of elastic portion (straight line) of the $P$-$LLD$ curve. This difference between the curves of $P$-$LLD$ and $P$-$\Delta a$ arises because the precrack in a CNB specimen can begin a stable growth only under a certain applied load, which is usually beyond the maximum elastic load on the $P$-$LLD$ curve.

2. When crack-length-to-width-ratio equals to $a_0/W$ (i.e. $\Delta a_0=0$), $Y' = \infty$ for a CNB specimen (a solid line as shown in Figure 2.11), however, $Y' = f(a_0/W)/W$ for a SEST specimen (a dashed line as shown in Figure 2.11). This difference of the normalized stress-intensity factor coefficients ($Y^*$) between CNB and SEST specimens comes from the CNB's and SEST's configurations as shown in Figure 2.11. The detailed derivations for $Y^* = f(\Delta a)$ can be seen in Section 2.2.3 and references [97, 121-122].
Due to a peculiar shape of \( Y^* = f(\Delta a) \) and \( P-\Delta a \) curves for a CNB specimen, Eqs.(4.6) and (4.7), either a \( K-\Delta a \) or \( J-\Delta a \) curve would obviously not start from zero but a \( K-LLD \) or \( J-LLD \) curve would start from zero. In addition, a fracture resistance curve of either \( K-\Delta a \) or \( J-\Delta a \) for a CNB specimen would start from INFINITY rather than from a certain value (Figure 1.2) or zero (Figure 2.13d). In other words, the conventional fracture resistance curve of either \( K-\Delta a \) or \( J-\Delta a \) as schematically shown in Figure 1.2 or Figure 2.13d is only suitable for any other specimen's geometries such as a single-edge-straight-through (SEST) specimens, but not for a CNB specimen.

Similarly, a PLATEAU in a \( K-\Delta a \) curve (Figure 3.28c and Appendices F1 (c) thro F8 (c)), or a flat bottom “HOOP HEAD” in a \( J-\Delta a \) curve (Figure 3.29c and Appendices F1 (f) thro F8 (f)), also results from a flat bottom \( Y^*-\Delta a \) curve (Figure 3.28b and Appendices F1 (b) thro F8 (b)).

4.9 Methodology of the Assessment of the Relationship between \( LLD \) and \( \Delta a \)

In this research crack extension \( \Delta a \) was not measured directly because of substantial experimental difficulties. Therefore, the load-crack extension \( (P-\Delta a) \) curves (Figure 3.28a and Appendices F1 (a) thro F8 (a)) were actually obtained from the experimental load-load line displacement \( (P-LLD) \) curves (Figures 3.21 thro 3.24) using three well-known points from the
In order to further elucidate the fundamental relationship between load-load line displacement \( LLD \) and crack extension \( \Delta a \) for a tested specimen, the technique used in this work can be summarised in more detail as follows:

**Defining three pairs of points between the \( P-LLD \) and \( P-\Delta a \) curves:**

Point 1 is crack extension starting point: \((LLD_0, P_0)\), which is the end of the straight line portion (elastic) of the \( P-LLD \) curve in Figures 3.21 thro 3.24, and \((\Delta a_0, P_0)\), where \( \Delta a_0 = 0 \);

Point 2 is maximum load point: \((LLD_m, P_m)\) and \((\Delta a_m, P_m)\), where \( \Delta a_m \) is calculated from Eq.(2.25);

Point 3 is maximum extension point: \((LLD_w, P_w)\), where \( LL_{Dw} \) is the load line displacement taken at the load \( P_w =0 \), and \((\Delta a_w, P_w)\), where \( \Delta a_w = W - a_0 \), and \( W \) is the width of a CNB specimen.

Since a constant and very low cross-head speed of 0.05 mm/min (as pointed in Section 2.4) was used in the three-point bend test, a smoothly increasing \( P-LLD \) curve would be seen at the first stable section just after linear portion of the \( P-LLD \) curve. Therefore, the crack extension starting point of \((LLD_0, P_0)\) can be found directly from the \( P-LLD \) curve because the \( P-LLD \) curve would show a pop-in phenomena, i.e., the applied load \( P \) would stop to increase suddenly when crack extension starts (Figures 3.21 thro 3.24). This is because the resistance stress in the bending specimen would not keep a balance with increasingly applied load since crack extension occurs suddenly.

The maximum load point of \((LLD_m, P_m)\) and maximum extension point of \((LLD_w, P_w)\) can be easily obtained from the highest point and the last point on the \( P-LLD \) curve, respectively.
Thereafter, the corresponding extension value of $\Delta a_m$ can be calculated correspondingly from the minimum stress intensity factor coefficient of $Y_m$ by Eq.(2.25). This is because when the applied load reaches its maximum value of $P_m$, the stress intensity factor coefficient $Y'$ would decrease to its minimum value of $Y'_m$ and the corresponding crack extension $\Delta a$ could be defined as $\Delta a_m$ if the crack growth resistance curve of the tested material is flat [126, 133]. This assumption would be also true when the bottom part of stress intensity factor coefficient $Y'$ of are flat (Figure 3.28b and Appendices F1 (b) thro F8 (b)) because the fracture toughness value of $K_{hm}$ would not be sensitive to $\Delta a_m$.

**Connecting the three points on the LLD-\Delta a curve - simple linear assumption:**

The two straight lines to connect point 1 ($LLD_0$, $\Delta a_0$) to point 2 ($LLD_m$, $\Delta a_m$), then to point 3 ($LLD_w$, $\Delta a_w$) are schematically shown in Figure 4.15. The two lines can be mathematically expressed as following:

For $0 \leq \Delta a \leq \Delta a_m$: \[ LLD = (LLD_m-LLD_0)\Delta a/\Delta a_m + LLD_0 \] (4.8)

For $\Delta a_m \leq \Delta a \leq \Delta a_w$: \[ LLD = (LLD_m-LLD_w)(\Delta a-\Delta a_m)/(\Delta a_m-\Delta a_w) + LLD_m \] (4.9)

These lines are made actually based on such an assumption that the crack extension $\Delta a$ has the same average speed as the load-line-displacement ($LLD$) during bending. This assumption is true for a medium ductile material. In other word, a curved assumption could be more accurate for a material with different speed between load-line-displacement $LLD$ and crack
extension $\Delta a$. For instance, crack extension could be much faster than load-line-displacement in a movement for a brittle material.

**Calculating more data points according to the linear $LLD-\Delta a$ curve**

To obtain accurate shape of the parameters ($P$, $K$, $J$) vs. $\Delta a$ curves, more data points must be calculated according to the $LLD-\Delta a$ curve. According to Eqs.(4.8) and (4.9), the inserting values (usually 6 (or 7) and 9 (or 10) points inserted between point 1 to 2 and point 2 to 3, respectively, as shown in Figure 3.27) can be calculated by the following formulas:

For $0 \leq \Delta a \leq \Delta a_m$: 

$$LLD_i = (LLD_m - LLD_0) \Delta a / \Delta a_m + LLD_0$$  \hspace{1cm} (4.10)

For $\Delta a_m \leq \Delta a \leq \Delta a_w$: 

$$LLD_i = (LLD_m - LLD_w)(\Delta a_i - \Delta a_m)/(\Delta a_m - \Delta a_w) + LLD_m$$  \hspace{1cm} (4.11)

where $i = 1, \ldots, n$.

From the discussion above, it can be seen that the corresponding technique is very simple, useful and reliable method to overcome the difficulty of measuring crack extension directly in an experiment. Obviously, the patent to such an advanced approach should be applied soon.
Figure 4.15 A schematic showing the fundamental relationship between load-load line displacement $LLD$ and crack extension $\Delta a$. 
4.10 Future Research

The first area for future research is an effort to improve the \( J \)-integral method for a chevron notched bend specimen test:

1. Validity of \( K_{hc} \) and \( J_{hc} \):

In this research, the fracture toughness values of \( K_{hc} \) were calculated from \( J_{hc} \) by Eq.(2.46) and confirmed by the agreement with fracture toughness values of the valid \( K_{hm} \) rather than any validity requirement. The values of \( J_{hc} \) were obtained automatically from lines tangent to the "hoop head" of the \( J-\Delta a \). The experimental values of \( J_{hc} \) and \( K_{hc} \) (\( K_{hm} \)) were validated using Eqs.(2.20) and (2.40), respectively. These requirements might not be good enough for validity of \( K_{hc} \) and \( J_{hc} \) in a formal ASTM Standard document of the \( J \)-integral method for a CNB bend test. Some additional validity requirements such as validation of \( J_c \) as \( J_{hc} \) might be necessary by analogy with ASTM Standard document [99] for a CNB specimen. In addition, the critical unloading slope ratio (\( r_c \)) as described in ASTM Standard document [98] or the value of plasticity \( p \) [98, 122] as shown in Figure 4.16 might be also needed to be considered for such an unloading/reloading \( J \)-integral method used in this research. Limited by the difficulty to obtain the critical unloading slope ratio (\( r_c \)) and theoretical confirming of \( K_c = [(1+p)/(1-p)]^{1/2}K_0 \) [122], the parameter \( r_c \) or \( p \) was not considered in this research.

2. Experimentally establishing the relationship between a real compliance from unloading/reloading a load-load line displacement curve and a geometry compliance from
Eq.(2.33) for the same CNB bend specimen:

In this research, a compliance from unloading/reloading the load-load line displacement curve is approximately at least ten times greater than the compliance calculated from Eq.(2.33) for the same CNB bend specimen for all the investigated in-situ composites. The reason why the two compliances are not equal to each other at the mean time, is unclear. The establishment of the experimental relationship between these two compliances might be necessary;

Other areas for the toughening mechanisms of the NiAl/Ni3Al in-situ composites include:

1. Influence of grain size on fracture toughness:

   In this research, grain size effect of reinforcements and matrix on the in-situ composites are still not clear. An effort for a proper etching method of the in-situ composites might be essential;

2. Boron effect on Ni3Al grain-boundary embrittlement:

   In this research, the microscopy and surface indentation testing from the water-quenched alloys showed that boron looks beneficial for improving the Ni3Al grain-boundary embrittlement because less grain boundary cracking for water-quenched alloys and no grain-boundary cracking under surface indentation were observed. However, the fractography and fracture toughness test from homogenized alloys indicated that boron appears no effect on the Ni3Al grain-boundary embrittlement because no changes of fracture mode and toughness values for the alloys with or without boron addition. The reason for such contrary results is uncertain. An effort on confirming boron content in the in-situ composites by some advanced measuring technique looks necessary.
Figure 4.16 Schematic of a load-displacement illustrating the method of determining the plasticity. $p = \Delta x_0 / \Delta x$ [122].
CHAPTER 5

SUMMARY

An overview of the toughening mechanisms in the intermetallic-base in-situ composites is presented. The toughening mechanisms and corresponding modelling formulas such as crack-tip blunting, crack trapping, microcrack renucleation, interface debonding, crack bridging, shear ligament toughening, crack deflection, microcrack shielding and so on have been discussed in detail.

The use of NiAl as a structural material has been hindered by its lack of tensile ductility or toughness at room temperature. The operative flow and fracture mechanisms in monolithic NiAl leading to these poor low temperature properties, demonstrate the need for ductile phase toughening. Based on the literature review and preliminary research, the two phase ($\beta + \gamma'$) region of Ni-Al system with and without boron adoption has been chosen as a model in-situ composite. This is because Ni$_3$Al is a good candidate for ductile phase toughening of NiAl since the two phase systems can be readily formed in-situ from the melt or by heat treatment.
The advantage for using Ni₃Al (γ') as a reinforcing second phase is its superior ductility and toughness compared to β-NiAl. A study of fracture toughness of the in-situ NiAl-Ni₃Al intermetallic composites is presented. The composition ranges investigated are 25-35 at.% Al for both as-solidified and as-heat-treated composites. Also, boron-doped (0.2 and 0.4 at.%) Ni₃Al is studied.

To evaluate fracture toughness, a non-linear fracture method such as J-integral unloading/reloading method, has been applied for the investigated in-situ composite. The method is based on a three point bending of chevron-notched specimens. Additionally, compression testing as well as Vickers microhardness testing are also used for the investigated composites.

The main results can be summarized as follows:

1. The volume fraction of ductile phase Ni₃Al increases with increasing Ni content in the investigated intermetallic composites under either the as-cast or as-annealed condition.

2. The volume fraction of ductile phase Ni₃Al of the as-cast composites increases after homogenization at 1000°C for 100h followed by a slow furnace cooling. The increment of the relatively more ductile γ' (Ni₃Al) phase by the heat treatment is an important means of modifying the local fracture processes in Ni-rich NiAl.

3. The grain boundary cracking was found for the boron-free Ni₃Al alloy after water quenching using Vickers indentation fracture testing under the highest load (2000g). Less grain boundary cracking was found for the boron-doped Ni₃Al alloy after both water quenching and Vickers indentations. The possible boron effect
might be attributed to boron increasing the grain boundary cohesive strength and allowing the deformation of grain interiors without premature intergranular failure. However, no effect was found on the fracture toughness of the in-situ composites.

4. The Orthorhombic \( D_{2h}^{19} \) \( \text{Ni}_5\text{Al}_3 \) in the aged alloy \( \text{Ni}_{65.9}\text{Al}_{34.1} \) at 1000\(^\circ\)C/100h + 550\(^\circ\)C/100h both followed by a slow furnace cooling, was identified by X-ray analysis method.

5. The mat-like structure of fine particles of \( \text{Ni}_5\text{Al}_3 \) exhibits very high Vickers microhardness (=690 kg/mm\(^2\)). The significant yield strength of =1151 MPa in \( \text{Ni}_{65.9}\text{Al}_{34.1} \) in-situ composite is also contributed to this needle-like structure of \( \text{Ni}_3\text{Al}_5 \). It has to be pointed out that very high yield strength (=1150MPa) and reasonable value of fracture toughness (=13 MPa\(\sqrt{\text{m}} \)) of \( \text{Ni}_{65.9}\text{Al}_{34.1} \) is a new promising alloy. To the contrary, this needle-like mat structure (\( \text{Ni}_5\text{Al}_3 \)) is not embrittling to the alloy but is very beneficial for yield strength.

6. The brittle \( \text{NiAl} \) presents not much higher Vickers hardness of =400 kg/mm\(^2\) than the ductile \( \text{Ni}_3\text{Al} \) phase (=280 kg/mm\(^2\)) for both the as-cast and as-annealed composites. All of the Vickers hardness values for the investigated composites are almost independent on the load.

7. Delamination at interfaces of \( \text{Ni}_3\text{Al} \) and \( \text{NiAl} \), crack bridging in the wake of \( \text{Ni}_3\text{Al} \) and crack-tip blunting are predominant toughening mechanisms in the in-situ composites.

8. The volume fraction of \( \text{Ni}_3\text{Al} \) in the in-situ composites has a significant effect on the fracture toughness. The valid \( K_{\text{t}} \) and \( K_{\text{f}} \) values increase with increasing of
the volume fraction of ductile Ni$_3$Al phase in the boron-free in-situ composites. The power curve, describing exactly the relationship of $K_{hc}=f(V_d^a)$, is $K_{hc}=6.1+0.7V_d^{0.7}$.

9. All the values of the fracture toughness of the investigated in-situ composites are within the $K_{max}$ and $K_{min}$ models (or upper and lower bound) [63]. This behaviour experimentally conformed the $E$-modified ROM modes which was theoretically proposed by Ashby [63]. Furthermore, all the data are close to the upper bound ($K_{max}$), which is contrary to the results from the Nb-Si in-situ composites obtained by Davidson and Chan [61-62].

10. Weibull analysis was applied into the fracture toughness distribution of the investigated Ni$_3$Al/NiAl in-situ composites. Weibull’s modulus $m = 23.8$ for Ni$_{63.7}$Al$_{36.3}$ indicates that this alloy is a very reliable material for engineering design even with lower fracture toughness value; however, $m = 7.0$ was also found in the in-situ composite of Ni$_{73.2}$Al$_{26.8}$. This means that the fracture toughness is highly variable and no single value for $K_{km}$ can be assigned easily.

11. A mixed transgranular-intergranular fracture mode was observed in most of the representative photographs of the boron-free and boron-doped in-situ composites. This behaviour is consistent with the results obtained by Rigney and Lewandowski [81].

12. The important characterizations of the $K$-$\Delta a$ and $J$-$\Delta a$ curves derived from a $J$-integral method by a chevron-notch-beam (CNB) bend test have been obtained first by this research. The stress intensity factor $K$ decreases with increasing the crack
extension $\Delta a$ and a PLATEAU usually appears right up to the critical crack extension $\Delta a_m$. The fracture energy $J$ decreases with increasing of the crack extension $\Delta a$ only until the critical crack extension $\Delta a_m$, then starts to increase with increasing of the crack extension, forming a very special shape which can be called "HOOP HEAD", which is obviously distinct from the conventional power-law regression curve of $J-\Delta a$ defined by ASTM Standard E 813-89 [99] as shown in Figure 2.13d.

13. Particularly, a critical value ($J_{hc}$) of the fracture energy for a CNB test can be simply calculated by a horizontal line tangent to the "hoop head", i.e., a minimum value of $J$, which is much more simple than a blunting-line approach defined in ASTM Standard E 813-89 [99].

14. In this research, a simple corresponding-insertion technique was successfully developed for exploring the fundamental relationship between load-load line displacement $LLD$ and crack extension $\Delta a$. This advanced approach effectively solved the measuring problem caused by a small bend specimen.
REFERENCES


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ASTM Standard E 399-90.

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ASTM Standard E 813-89.


149. ASTM Standard E 8M-96.
APPENDIX A
THE DEDUCTION OF THE CRACK-TIP BLUNTING MODEL

The crack-tip blunting model of Eq.(1.5) resulted from the Hutchinson, Rice and Rosengren (HRR) crack tip field [25-27]. From the HRR theory [25-27], the near-tip effective strain distribution can be described by [18, 25-27]

\[
\varepsilon_m = \alpha' \varepsilon_y^m \left[ \frac{J_m}{\alpha' \varepsilon_y^m \sigma_y^m I_n r} \right]^{n/(n+1)} \varepsilon(\theta, n) \tag{A1}
\]

for the matrix and

\[
\varepsilon_c = \alpha' \varepsilon_y^c \left[ \frac{J_c}{\alpha' \varepsilon_y^c \sigma_y^c I_n r} \right]^{n/(n+1)} \varepsilon(\theta, n) \tag{A2}
\]

for a composite containing a brittle matrix, \(\alpha\), reinforced with a ductile second phase, \(\beta\), when the hardening exponents, \(n\), for the matrix and composite are identical. In Eqs.(1) and (2), \(I_n\) is a constant value corresponding to \(n\), given by Hutchinson [25]; \(\alpha'\) is a coefficient in the tensile stress-strain relations of certain metals: \(\varepsilon=\sigma+\alpha \sigma^\beta\); \(r\) and \(\theta\) are cylindrical co-ordinates.

Dividing Eq.(A2) by Eq.(A1) leads to

\[
\frac{\varepsilon_c}{\varepsilon_m} = \frac{\varepsilon_y^c}{\varepsilon_y^m} \left[ \frac{J_c}{J_m} \right]^{n/(n+1)} \left[ \frac{\varepsilon_y^m \sigma_y^m}{\varepsilon_y^c \sigma_y^c} \right]^{n/(n+1)} \tag{A3}
\]

or,

\[
\frac{\varepsilon_c}{\varepsilon_m} = \left[ \frac{J_c}{J_m} \right]^{n/(n+1)} \left[ \frac{\sigma_y^m}{\sigma_y^c} \right]^{(n-1)/(n+1)} \left[ \frac{E_m}{E_c} \right]^{1/(n+1)} \tag{A4}
\]
when the relations $\epsilon_*=\sigma_*/E_c$ and $\epsilon_**=\sigma_**/E_m$ are invoked. Eq. (A4) can be combined with $J=(1-v^2)K^2/E$ to give

$$\begin{align*}
\frac{K_c}{K_m} &= \left[ \frac{\varepsilon_c}{\varepsilon_m} \right]^{(n+1)/2n} \left[ \frac{\sigma_y^c}{\sigma_y^m} \right]^{(n-1)/2n} \left[ \frac{E_c}{E_m} \right]^{(n+1)/2n}
\end{align*}$$

(A5)

based on the assumption that the rule of mixtures for composite materials is applicable to a two-phase alloy: $\sigma_y=V_\alpha \sigma_\alpha+V_\beta \sigma_\beta$ and $\varepsilon_y=V_\alpha \varepsilon_\alpha+V_\beta \varepsilon_\beta$. Eq. (1.5) can be deducted.
APPENDIX B
A BASIC RELATION OF THE EVALUATING $K_{lvm}$ IN CNB BEND TESTING

A three-point-bend specimen with a chevron notch is characterized by the dimensions shown in Figure 2.9. The length of the crack front $b$ at crack length $a$ is

$$ b = B[(a - a_0)/(a_1 - a_0)] = B[(\alpha - \alpha_0)/(\alpha_1 - \alpha_0)] \tag{B1} $$

The relation between load $P$ and fracture toughness $K_{fc}$ is obtained by considering the available and the necessary energies for crack propagation. The available energy for the extension of the crack by $\Delta a$ is

$$ \Delta U = (P^2/2W)(dC_v/d\alpha)\Delta a \tag{B2} $$

where $C_v$ is the compliance of the specimen with a trapezoidal crack front. Extending the crack by the increment $\Delta a$ increases the crack area by $\Delta A = b\Delta a$. The necessary energy for crack extension is

$$ \Delta W = G_{lve} b\Delta a = (K_{lve}^2/E')b\Delta a \tag{B3} $$

with $E'=E$ for plane stress and $E'=E(1-\nu^2)$ for plane strain. During crack extension, $\Delta U=\Delta W$:

$$ K_{lve} = P[(dC_v/d\alpha)E']^{1/2} = \frac{P}{B W^{1/2} \sqrt{2d\alpha}} \frac{C_v \alpha - \alpha_0}{2d\alpha \alpha - \alpha_0} \tag{B4} $$

where the term in brackets $Y'=\{(1/2)dC_v(\alpha)/d\alpha\}/[(\alpha_1-\alpha_0)(\alpha-\alpha_0)]^{1/2}$, is stress-intensity factor coefficient. For a stable crack growth of CNB bend testing, $K_{c}=K_{hmc}$, which could be calculated from $P_{\max}$, which occurs at the minimum value of $Y'$, i.e., $Y'_m$.
APPENDIX C
MORE EXAMPLES OF FRACTURE SURFACES FROM
THE INVESTIGATED IN-SITU COMPOSITES

Typical scanning electron microscope (SEM) fractographs of the homogenized Ni_{70.8}Al_{29.2}: small transgranular fractures occurred on the smooth intergranularly fractured grain boundary facets.
Appendix C2

Typical scanning electron microscope (SEM) fractographs of the homogenized Ni$_{63.7}$Al$_{36.3}$: (a) intergranular fracture of Ni$_3$Al phase, (b) secondary grain boundary cracks and (c) transgranular crack-path-deflection of cleavage fracture plane.
Appendix C3  Typical scanning electron microscope (SEM) fractographs of the homogenized Ni₆₇.₂Al₃₂.₈: (a) a mixed mode of transgranular/intergranular fracture, (b) delamination at interfaces.
Appendix C4  Typical scanning electron microscope (SEM) fractographs of the homogenized Ni\textsubscript{72.8}Al\textsubscript{27.2}: (a) deep dimples surrounded by cleavage fracture with river pattern, (b) debonding occurs at interfaces.
APPENDIX D
THE MEASURED AND CALCULATED GEOMETRICAL PARAMETERS FOR EACH CNB BEND SPECIMEN.
### Appendix D1
The Measured and Calculated Geometrical Parameters for Each CNB Bend Specimen.

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<th>Ni (at.%)</th>
<th>Ni$_3$Al (vol.%)</th>
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<th>$\Delta a_m$ (mm)</th>
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Appendix D2
The Measured and Calculated Geometrical Parameters for Each CNB Bend Specimen.

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Note:
The bold and italic values were obtained using Bluhm's solution since Wu's solution did not work for these specimen geometries because S/W in Eq.(2.30) was greater than 2.9.
APPENDIX E
THE MECHANICAL PROPERTIES
AND FRACTURE TOUGHNESS VALUES
FOR EACH CNB BEND SPECIMEN.
Appendix E1

The Mechanical Properties, Maximum Load and Fracture Toughness Values for Each CNB Bend Specimen.

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Note:

1. The bold values are invalid according to the validity requirements.
2. The $K_{Ivm}^W$ values were calculated using Wu's solution.
3. The italic values of $K_{Ivm}^B$ were obtained by Bluhm's solution.
Appendix E2

The Mechanical Properties and Fracture Toughness Values for Each CNB Bend Specimen.

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| 73.2-0.2B | 93.7 | 183.52 | 543 | 34.38 | 27.48 | 30.21 | 35.26 | 3387.28 |
| 73.2-0.2B | 93.6 | 183.6 | 517 | 29.11 | 25.86 | 28.37 | 32.78 | 2926.28 |
| 73.2-0.2B | 94.6 | 182.86 | 532 | 26.97 | 19.14 | 13.27 | 28.91 | 2285.32 |
| 74.8-0.4B | 99.8 | 179.14 | 355 | 43.7 | 22.82 | 25.25 | 53.21 | 7902.49 |
| 74.8-0.4B | 99.8 | 179.14 | 350 | 65.31 | 24.59 | 27.46 | 55.07 | 8464.62 |
| 74.8-0.4B | 99.9 | 179.07 | 75.84 | 25.24 | 25.31 | 52.51 | 7698.94 |
| 74.8-0.4B | 99.9 | 179.07 | 334 | 66.58 | 25.28 | 22.71 | 48.36 | 6530.1 |
| 74.8-0.4B | 99.9 | 179.07 | 489 | 46.97 | 25.24 | 27.85 | 56.72 | 8982.96 |

Note:

1. The bold values are invalid according to the validity requirements.
2. The $K_{fvm}^{W}$ values were calculated using Wu's solution.
3. The italic values of $K_{fvm}^{B}$ were obtained using Bluhm's solution.
APPENDIX F
TYPICAL RELATIONSHIPS BETWEEN
THE PARAMETERS (a) $Y^*$, (b) $P_{max}$, (c) $K$,
(d) $J_{el}$, (e) $J_{pl}$, (f) $J$ AND THE CRACK EXTENSION
FOR EACH ALLOY.
Appendix F1  A typical relationship between the parameters (a) $P_{max}$, (b) $Y'$ and (c) $K$, and the crack extension of Ni$_{67.2}$Al$_{32.8}$. 
Appendix F1  
A typical relationship between the parameters (d) $J_{dl}$, (e) $J_{pl}$ and (f) $J$, and the crack extension of Ni$_{67.3}$Al$_{32.7}$. 

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Appendix F2  A typical relationship between the parameters (a) $P_{max}$, (b) $Y^*$ and (c) $K$, and the crack extension of Ni$_{65.9}$Al$_{34.1}$. 
Appendix F2

A typical relationship between the parameters (d) $J_{dl}$, (e) $J_{pl}$ and (f) $J$, and the crack extension of Ni$_{65.9}$Al$_{34.1}$.
Appendix F3

A typical relationship between the parameters (a) $P_{\text{max}}$, (b) $Y^*$ and (c) $K$, and the crack extension of Ni$_{70}$Al$_{30}$.2.
Appendix F3 A typical relationship between the parameters (d) $J_{el}$, (e) $J_{pl}$ and (f) $J$ and the crack extension of Ni$_{70.3}$Al$_{29.7}$. 
Appendix F4  A typical relationship between the parameters (a) $P_{\text{max}}$, (b) $Y'$ and (c) $K$, and the crack extension of Nb$_{72.8}$Al$_{27.2}$. 

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Appendix F4  A typical relationship between the parameters (d) $J_{\text{ef}}$, (e) $J_{\mu}$ and (f) $J$, and the crack extension of Ni$_{73.3}$Al$_{26.7}$. 

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Appendix F5  A typical relationship between the parameters (a) $P_{max}$, (b) $Y$ and (c) $K$, and the crack extension of Ni$_{73.2}$Al$_{26.8}$. 
Appendix F5  

A typical relationship between the parameters (d) $J_{el}$, (e) $J_{pl}$ and (f) $J$ and the crack extension of Ni$_{73.5}$Al$_{26.5}$. 

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Appendix F6 A typical relationship between the parameters (a) $P_{\text{min}}$, (b) $Y'$ and (c) $K$, and the crack extension of Ni$_{77.7}$Al$_{22.3}$. 
Appendix F6  A typical relationship between the parameters (d) $J_{cl}$, (e) $J_{pl}$ and (f) $J$ and the crack extension of Ni$_{77.7}$Al$_{22.3}$. 

279
Appendix F7  A typical relationship between the parameters (a) $P_{max}$, (b) $Y^*$ and (c) $K$, and the crack extension of Ni$_{73.2}$Al$_{26.8}$B$_{0.2}$.
A typical relationship between the parameters (d) $J_{cd}$, (e) $J_{pl}$ and (f) $J$, and the crack extension of Ni$_{73.2}$Al$_{16.6}$B$_{0.2}$. 

Appendix F7
Appendix F8

A typical relationship between the parameters (a) $P_{\text{net}}$, (b) $Y^*$ and (c) $K$, and the crack extension of Ni$_{34.8}$Al$_{34.8}$B$_{0.4}$. 
Appendix F8  A typical relationship between the parameters (d) $J_d$, (e) $J_{pl}$ and (f) $J$, and the crack extension of Ni$_{74.3}$Al$_{34.8}$B$_{0.4}$. 
APPENDIX G
THE CALCULATED $J_{lvc}$ AND $K_{lvc}$, AND CORRESPONDING PARAMETERS FOR EACH CNB BEND SPECIMEN
Appendix G

The Calculated $J_{Ic}$ and $K_{Ic}$, and Corresponding Parameters for Each CNB Bend Specimen.

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<td>J/m$^2$</td>
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Note: The values of $P_{c}$, $Y_e$ and $LLD_c$ are the load, stress-intensity-factor coefficient and load-line-displacement corresponding to $J_{Ic}$, respectively.