Intermetallic compounds and intermetallic layers in AISI 316L to Al 1050 joints

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<th>symbol</th>
<th>meaning</th>
<th>units</th>
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<tbody>
<tr>
<td>$g$</td>
<td>the ratio of the molar volumes of the two intermetallic compounds in different intermetallic layers</td>
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<tr>
<td>$k_0$</td>
<td>chemical control diffusion constant</td>
<td>m s$^{-1}$</td>
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<td>$k_1$</td>
<td>physical control diffusion constant</td>
<td>m s$^{-1}$</td>
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<td>$p, q, r, s$</td>
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<td>$q'$</td>
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<td>thickness of the first intermetallic layer</td>
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<td>$x_{ij}$</td>
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<td>$y_i$</td>
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<td>$A$</td>
<td>intermetallic layer thickness constant</td>
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<tr>
<td>$B$</td>
<td>temperature-thickness constant</td>
<td>m k</td>
</tr>
<tr>
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<td>mol m$^{-3}$</td>
</tr>
<tr>
<td>$C_b$</td>
<td>molar concentration of chromium</td>
<td>mol m$^{-3}$</td>
</tr>
<tr>
<td>$C_c$</td>
<td>molar concentration of nickel</td>
<td>mol m$^{-3}$</td>
</tr>
<tr>
<td>$C_d$</td>
<td>molar concentration of aluminium</td>
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<tr>
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<td>iron diffusion coefficient in aluminium</td>
<td>m$^2$ s$^{-1}$</td>
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<tr>
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<td>chromium diffusion coefficient in aluminium</td>
<td>m$^2$ s$^{-1}$</td>
</tr>
<tr>
<td>$D_c$</td>
<td>nickel diffusion coefficient in aluminium</td>
<td>m$^2$ s$^{-1}$</td>
</tr>
<tr>
<td>$D_d$</td>
<td>aluminium diffusion coefficient in austenite stainless steel</td>
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</tr>
<tr>
<td>$\bar{D}$</td>
<td>Interdiffusion coefficient between stainless steel and aluminium</td>
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<td>$E_a$</td>
<td>the activation at decomposition fraction $\alpha$</td>
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<tr>
<td>$F_1$</td>
<td>forces acting on the stainless steel</td>
<td>N</td>
</tr>
<tr>
<td>$F_2$</td>
<td>forces acting on the sample</td>
<td>N</td>
</tr>
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<td>forces acting on the plastic deformation element</td>
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<td>the Gibbs free energy</td>
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<td>$\Delta H$</td>
<td>enthalpy</td>
<td>kJ mol$^{-1}$</td>
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<td>mixing enthalpy</td>
<td>kJ mol$^{-1}$</td>
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<td>$J_a$</td>
<td>diffusion flux of iron</td>
<td>mol m$^{-2}$ s$^{-1}$</td>
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<td>Symbol</td>
<td>Definition</td>
<td>Units</td>
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<td>--------</td>
<td>------------------------------------------------</td>
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<tr>
<td>$J_b$</td>
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<td>mol m$^{-2}$ s$^{-1}$</td>
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<tr>
<td>$J_c$</td>
<td>diffusion flux of nickel</td>
<td>mol m$^{-2}$ s$^{-1}$</td>
</tr>
<tr>
<td>$J_d$</td>
<td>diffusion flux of aluminium</td>
<td>mol m$^{-2}$ s$^{-1}$</td>
</tr>
<tr>
<td>$L$</td>
<td>thickness of the intermetallic layers</td>
<td>m</td>
</tr>
<tr>
<td>$P$</td>
<td>pressure</td>
<td>MPa</td>
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<tr>
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<td>$R$</td>
<td>gas constant</td>
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<td>$R_a$</td>
<td>surface roughness</td>
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<tr>
<td>$\Delta S_{\text{mix}}$</td>
<td>mixing entropy</td>
<td>J mol$^{-1}$ K$^{-1}$</td>
</tr>
<tr>
<td>$T$</td>
<td>temperature</td>
<td>K</td>
</tr>
<tr>
<td>$T_f$</td>
<td>temperature to form high-entropy alloys at fusion line</td>
<td>K</td>
</tr>
<tr>
<td>$T_w$</td>
<td>temperature to form high-entropy alloys at fusion line</td>
<td>K</td>
</tr>
<tr>
<td>$T_a$</td>
<td>temperature at decomposition fraction $\alpha$</td>
<td>K</td>
</tr>
<tr>
<td>$V_{ij,ia,ja}$</td>
<td>molar volume</td>
<td>mol m$^{-3}$</td>
</tr>
<tr>
<td>$X_a$</td>
<td>concentration fraction of iron</td>
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<tr>
<td>$X_b$</td>
<td>concentration fraction of chromium</td>
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<tr>
<td>$X_c$</td>
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<td>$X_d$</td>
<td>concentration fraction of aluminium</td>
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<tr>
<td>$Z$</td>
<td>frequency factor (pre-exponential factor)</td>
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<td>$\alpha$</td>
<td>decomposition fraction</td>
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<td>$\gamma$</td>
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<tr>
<td>$\lambda$</td>
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<tr>
<td>$\varepsilon$</td>
<td>concentration fraction of aluminium</td>
<td></td>
</tr>
<tr>
<td>$v$</td>
<td>velocity of the lattice plane movement</td>
<td>m s$^{-1}$</td>
</tr>
<tr>
<td>$\Phi_{ij}$</td>
<td>electronegativity</td>
<td>(eV)$^{-1/2}$</td>
</tr>
<tr>
<td>$\Omega_{ij}$</td>
<td>the regular melt model interaction parameter</td>
<td></td>
</tr>
</tbody>
</table>

The units of the rate coefficient ($k$) depend on the kinetics of a reaction:

For order zero, the rate coefficient has units of mol L$^{-1}$ s$^{-1}$
For order one, the rate coefficient has units of s$^{-1}$
For order two, the rate coefficient has units of L mol$^{-1}$ s$^{-1}$
For order $n$, the rate coefficient has units of mol$^{1-a}$ L$^{n-1}$ s$^{-1}$
Chapter 1

Introduction

Many industries are driven by the requirements of developing applicable methods to join aluminium to stainless steel, such as ground transportation, aircraft, shipbuilding and construction companies [1-3]. In fact, aluminium has been applied in many areas as mentioned, to replace steel and stainless steel in structures [3-4]. The intention of joining aluminium to stainless steel is to incorporate the properties of both materials into a product. High strength, high elastic modulus and corrosion resistivity are typical properties of stainless steel. Good electrical conductivity, low density, good corrosion resistivity and ease of fabrication are typical properties of aluminium and its alloys [5-9].

Unfortunately, it is difficult to join aluminium to stainless steel due to large differences in melting temperatures and thermal expansion coefficients, which can introduce hot and cold cracks during or after welding [9]. The brittle intermetallic compounds formed in a fusion joint of aluminium and stainless steel normally degrades the reliability of joint. Cracks usually initiate from these brittle compounds, which is one of the main reasons for poor mechanical properties of the joint. Galvanic corrosion is another problem that should be taken into account when joining aluminium to stainless steel [9-11].

Although, it is hard to join aluminium to stainless steel, there are several methods available. Satisfactory joints can be made by brazing, soldering, diffusion bonding, friction, friction stir, explosive and ultrasonic welding. Some new welding methods like fusion-brazing and impact welding are also under development [12-15].

In many of above mentioned methods, intermetallic compounds are observed at the interface between aluminium and stainless steel. An intermetallic compound is any solid material composed of two or more metal atoms in a definite proportion, which has a crystal structure that differs from those of the constituent metals. Intermetallic compounds are produced during joining processes between dissimilar metals. The compounds are commonly observed in many systems, such as Sn-Ag, Sn-Ni, Sn-Cu, Fe-Al and Cr-Al [16-17]. The limited solubility of the atoms within each other is the main reason responsible for the intermetallic compounds formation. After the solubility limit is reached, the intermetallic compounds will be generated by chemical reactions at the interface of different metals, and intermetallic layers can be constructed from such compounds. It is reported that a thin, continuous and uniform layer indicates that a good metallurgical bond is formed [17]. However, a brittle intermetallic compound has the tendency to generate structure defects. If the intermetallic layer is too thick, it may degrade the reliability of the joint [17-19]. Ideally, if there is no formation of intermetallic compounds at the interface, alloy
formation with a similar microstructure as the base metal will contribute to a good metallic bond.

The typical interfacial structure of steel and aluminium contains Al, FeAl₃, Fe₂Al₅ and Fe in series from aluminium to the steel substrate [20]. Brittle compounds such as FeAl₃ and Fe₂Al₅ construct the different intermetallic layers at the interface. The thickness of these layers is affected by the thermal cycle of a joining process and chemical distributions at the interface [21]. Thermal diffusion of aluminium and iron atoms during joining is the physical mechanism responsible for the formation of the brittle compounds. These atoms also chemically interact with each other during the diffusion process [22]. The formation mechanism of the intermetallic compounds and the growth of the intermetallic layers at certain temperatures have been studied by a few researchers [23-25]. Some of them report that the growth of the intermetallic layer follows a parabolic law. However, Dybokov [4, 8] argued that such a law, developed from mathematical processing of the experimental results based on linear, parabolic, or other relatively simple dependence, is senseless, because the number of such “laws” is infinite in view of the variety of conditions of dissolution of solid material in a liquid melt.

There is no systematic study of the formation mechanism of the intermetallic compounds and the relationship between the thickness of the intermetallic layers with time and temperature at the interface of aluminium and stainless steel. This led to the objectives of the current work, which are:

(1) finding the formation kinetics of the intermetallic compounds;
(2) establishing the intermetallic layer thickness-time-temperature relationship.

The chemical compositions of the intermetallic compounds will be identified and the behaviour of the intermetallic layers will be studied. Since mechanical properties are determined by the microstructures formed [17], metallurgical analysis can help to understand the formation mechanism and compositions of these compounds.

In this work, solid state diffusion bonding and bead-on-plate laser welding were performed separately. To perform this work, it is necessary to study the types of the intermetallic compounds and layers formed at the interface of aluminium and stainless steel from different joining processes. It is also important to be familiar with the chemical and physical reactions that can take place. These aspects are explored in the literature survey presented in chapter 2. In chapter 3, the details of experimental procedures are illustrated. The experimental results are shown in chapter 4. In chapter 5, the reasons, for choosing these two joining processes and stainless steel AISI 316 L and aluminium 1050 as experimental methods and base metals respectively, are discussed. An analysis of the experimental results and a comparison between the solid state bonding and laser welding are also discussed in chapter 5. The conclusions are presented in chapter 6 along with some recommendations for further studies.
Chapter 2

Literature survey

2.1 Intermetallic compounds/layers

A modified metal inert gas welding-brazing process (CMT) has been applied for joining of aluminium-zinc-coated steel; such a system was investigated by Zhang et al. [18]. Hot-dip galvanized steel and a 1 mm thick Al 1060 were joined with a silicon filler metal in their study. Intermetallic layers were formed at the interface between steel and weld metal (figure 2.1). The energy input of sample (b) is 56.8 % higher than sample (a), which leads to the average thickness of the intermetallic layer in sample (b) (~200 μm) being five times that of the layer thickness in sample (a) (~40 μm). This indicates that high heat input increases the thickness of the intermetallic layers. It is clear from this result that the heat input has a strong effect on the thickness of the intermetallic layer. A possible explanation for the formation of the intermetallic layer is that the anisotropic diffusion leads to the intermetallic compounds growing into the weld metal with tongue-like penetrations (figure 2.1 (b)). High energy input encourages this process and as a result a thicker layer is formed. Microhardness test results show that the intermetallic layer at the interface has a high hardness. The excessive thickness of the intermetallic layer in sample (b) results in brittleness and degradation of the joints (figure 2.2) [19].

![Figure 2.1 Microstructure of steel and weld metal, a) with 613.2 J cm⁻¹ heat input; b) with 961.5 J cm⁻¹ heat input [18].](image1)

![Figure 2.2 Microhardness of Al 1060-steel joints using different heat inputs [18].](image2)
TIG welding-brazing of aluminium 5A06 and SUS 321 stainless steel with an Al-Cu 2319 filler metal was investigated by Song et al. [15, 20, 22]. A braze bond was formed on the steel side and a fusion weld on the Al alloy side (figure 2.3).

Figure 2.3 Typical cross section of a butt joint [20].

Figure 2.4 Interface on the stainless steel side [20].

The intermetallic layer formed at the interface of the welded seam and steel containing weld defects such as micro cracks and pores (figure 2.4). The microhardness (figure 2.5) shows that the intermetallic compound is less than the value of 840 HV expected from $\text{Fe}_4\text{Al}_{13}$ [21]. The reason is that Cr, Ni and Cu replace Fe in $\text{Fe}_4\text{Al}_{13}$, which can reduce the hardness of the intermetallic compounds [22].

Figure 2.5 Hardness distribution of the aluminium-steel joint [21].
Laser brazing Al 6016 T4 to a low-carbon steel coated with 10 μm layer of zinc was conducted by Mathieu et al. [23]. Al 4047 filler wire was used in their experiment. The average thickness of the intermetallic layer on the steel side is about 5 μm and the FeAl₃ brittle phase was found at the interface of the weld seam and the steel (figure 2.6). This brittle phase reduces the yield strength of the joint. Alumina (Al₂O₃) was found at the interface of the aluminium and weld seam where the cracks were found to initiate (figure 2.7).

![Figure 2.6 Microstructure of weld seam and steel interface with Al 4047 filler wire [22].](image)

Mathieu et al. [24] also reported laser brazing of the same materials with a zinc-based filler wire. Intermetallic compounds (FeAl₃ and Fe₂Al₅) were found from their experimental results, which are similar to the compounds reported by Kreimeyer and Sepold [25]. Due to the brittle intermetallic compounds formation, cracks were observed at the interface of the aluminium and weld seam. The fracture at the aluminium and the weld seam interface can be explained as the infiltration of Zn in the heat affected zone by grain boundary liquation, which is common for aluminium alloys [26].

Peng et al. [27] reported that by controlling the brazing parameters (time and temperature) appropriately, the formation of intermetallic compounds can be reduced. Experiments were performed in vacuum (5×10⁻⁵ Pa) with a heating power of 45 kW. Al 1060 was brazed to an 18-8 stainless steel (1Cr18Ni9Ti) with an Al-Si filler alloy. It was reported that the Si addition reduced the formation of intermetallic compounds and stopped the diffusion of iron atoms [10]. The thickness of the intermetallic layer formed by these compounds was reported to be related to the temperature distribution.
by both Mathieu et al. [28] and Murakami et al. [29]. However, there is no elemental profile in Peng’s work, which could be useful to track the intermetallic compounds distribution at the interface and to understand the mechanism of intermetallic layer formation.

Besides brazing, intermetallic compounds and layers were also observed in other joining processes. Fukumoto et al. [30-31] reported that short welding time can restrict the formation of the intermetallic layer in friction welding (figure 2.8). The friction welding parameters used were a rotational speed 40 rad s\(^{-1}\), a friction pressure of 50 MPa, an upset pressure of 150 MPa, an upset time of 6.0 s and the friction time varying from 0.1 s to 3.0 s. There is no intermetallic layer formed with a short friction welding time 0.5 s (figure 2.8 (a)).

![Figure 2.8 Friction welding interface of Al 5052 and SUS 304, a) 0.5 s inner region; b) 2.0 s outer region [29].](image)

Hokamoto et al. [32] reported that an intermetallic compound FeAl\(_3\) was formed at the interface while explosive welding Al 5083 to SUS 304. Explosive welding of various aluminium alloys to SUS 304 stainless steel with different thicknesses (0.1–1 mm) of an intermediate plate SUS 304 changes the microstructures at the interface (figure 2.9). It is clear from figure 2.9 (b) that there is no formation of the intermetallic layer. One explanation is that as the thickness of the intermediate plate increases, there is more collision energy absorbed by the intermediate plate while there is less energy for supporting the growth of the intermetallic layer.

![Figure 2.9 Interfacial microstructure in AA 5083/SUS 304 welded by (a) direct explosive welding and (b) by the use of intermediate plate (0.3 mm) [31].](image)

Although satisfactory joints of aluminium and stainless steel were also made from other welding methods [33-35], intermetallic compound formation inevitably appeared at the interface. Ideally, it would be nice to produce a metallic bond at the
interface of aluminium and stainless steel without the formation of an intermetallic layer. In practice, it is reported that as long as the intermetallic layer is less than 10 μm, a reliable joint of aluminium and stainless steel can be produced [21-22].

The reliability of joints is related to the weld structures and service conditions rather than simply depending on the thickness of the intermetallic layer. In order to determine whether a joint is acceptable for a particular application, some understanding of the intermetallic layer formation and its dependency on temperature and time is highly desirable.

2.2 Thermal reactions at the interface of aluminium and stainless steel

Both chemical and physical reactions occur at the interface of aluminium and stainless steel. A chemical reaction is a process that leads to the transformation of one set of chemical substances to another [36]. The physical reaction here mainly refers to the atomic motion; i.e., interdiffusion which occurs without changing the chemical potential of other elements. Due to the complexity of reactions at the interface of aluminium and stainless steel, the thermodynamics, thermal analysis techniques, solid state physics and metallurgical analysis used in this work are introduced here.

2.2.1 Chemical reactions at the interface of aluminium and stainless steel

The products of the chemical reactions appearing at the interface of aluminium and stainless steel are oxides and aluminides [18-36], which can be difficult to quantify accurately when multi-elements are involved. However, it is possible to identify the type of these intermetallic compounds with appropriate technologies, such as X-ray diffraction (XRD) and electron probe micro-analysis (EPMA).

The main elements in stainless steel are iron, chromium and nickel. The limiting solid solubility of these elements in aluminium indicates that once the saturated solubility is reached at a certain time and temperature, chemical reactions will occur at the interface of aluminium and stainless steel. The chemical reactions can be described as

\[ rM\ (Fe, Cr, Ni) + p\ Al \rightarrow M_rAl_p, \] (2.1)

where \( r \) and \( p \) are atomic fractions, \( M_rAl_p \) are intermetallic compound products [37]. The sequence of the intermetallic compounds appearing should be determined by the Gibbs free energy. The compositions of those compounds are expressed by the atomic fraction of the elements. An intermetallic compound with the lowest Gibbs free
energy should appear before other intermetallic compounds [38]. Equation (2.2) describes the chemical reactions and table 2.1 gives the enthalpy of the intermetallic compounds produced at room temperature, which can be used to predict the intermetallic compounds formation.

\[
\begin{align*}
3\text{Al} + \text{Fe} &\rightarrow \text{FeAl}_3 + \Delta H_1 \\
7\text{Al} + \text{Cr} &\rightarrow \text{CrAl}_7 + \Delta H_2, \\
3\text{Ni} + \text{Al} &\rightarrow \text{NiAl}_3 + \Delta H_3
\end{align*}
\]

(2.2)

<table>
<thead>
<tr>
<th>Intermetallic compounds</th>
<th>$\Delta H_{298}$(kJ·mol$^{-1}$)</th>
</tr>
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<tbody>
<tr>
<td>FeAl$_3$</td>
<td>-18.9</td>
</tr>
<tr>
<td>CrAl$_7$</td>
<td>-17.6</td>
</tr>
<tr>
<td>NiAl$_3$</td>
<td>-36.6</td>
</tr>
</tbody>
</table>

Table 2.1 The enthalpy of intermetallic compounds at 298 K [38].

However, mixed intermetallic compounds were reported at the interface of aluminium and stainless steel [4]. One possible explanation could be an interaction between different atoms, which could change the chemical potentials of elements and lead to the formation of the intermetallic compounds. Another explanation could be that Cr and Ni atoms can substitute iron atoms, thus mixed compounds are found at the interface. The growth of the intermetallic layer will be dominated by those compounds. Dybkov [8] reported that two different intermetallic layers formed at the interface of aluminium and stainless steel. He also mentioned that mixed intermetallic compounds formed at the interface and constructed the first layer. The second layer was mainly constructed by the iron-aluminide (FeAl$_3$) intermetallic compounds. Due to the difference of the intermetallic compounds between the two intermetallic layers, the interdiffusion existed between the different intermetallic compounds. Chemical reactions caused by the interdiffusion between these compounds could produce new compounds. It is not easy to describe these processes because of their complexity. Dybkov suggested using the Lorier system to describe the growth of the different intermetallic layers [8]. The system can be mathematically expressed as

\[
\begin{align*}
\frac{dx}{dt} &= \frac{k_1}{x} - \left(\frac{rg}{p}\right) k_0 \\
\frac{dy}{dt} &= k_0
\end{align*}
\]

(2.3)

where $t$ is the time, $k_1$ and $k_0$ are a diffusion (physical) and a chemical constant respectively; $g$ is the ratio of the molar volumes between different chemical compounds, $r$ and $p$ are the sub-indices of the chemical composition (such as $M_1N_p$) and $x$ and $y$ are the thickness of the first and second intermetallic layer respectively. Since, it is hard to acquire the exact value of $r$, $p$ and $g$, the thickness of the initially formed (first) intermetallic layer is used to determine $k_1$ [8]. The details of these mixed compounds and microstructures were not provided, due to the difficulties of quantifying the compositions of the intermetallic layers accurately [4]. Similar
approaches were applied by other researchers in studying the pure aluminium and iron system. Results were reported by Bouayad et al. [39] and Shahverdi et al. [40] with identified intermetallic compounds for different layers.

2.2.2 Theoretical thermal analysis

The oxide layer on the surface of the stainless steel is mainly composed by Cr₂O₃. The Gibbs free energies of the oxides, which can be formed by iron, chromium and nickel, are different (table 2.2).

<table>
<thead>
<tr>
<th>Oxide</th>
<th>Fe₂O₃/Fe₃O₄</th>
<th>Cr₂O₃</th>
<th>NiO</th>
<th>Al₂O₃</th>
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<tr>
<td>The Gibbs free energy (kJ mol⁻¹)</td>
<td>-847.62/-1161.84</td>
<td>-1153.90</td>
<td>-252.14</td>
<td>-1692.37</td>
</tr>
</tbody>
</table>

From table 2.2, the Gibbs free energy indicates that iron oxides should cover on the surface of the stainless steel instead of Cr₂O₃. The existence of the chromium in the stainless steel can change the chemical potential of iron atoms. When the atomic percentage of chromium is over 8 %, it will increase the chemical potential of iron [42-44] indicating that the actual Gibbs free energy of Fe₂O₃/Fe₃O₄ is higher than the values shown in table 2.2 and higher than the Gibbs free energy of chromium oxide. Therefore, the oxide layer on stainless steel is mainly dominated by Cr₂O₃.

Due to the existence of Cr₂O₃ on the surface of stainless steel, a thermite reaction is expected to occur at the interface between aluminium and stainless steel. The reaction is described as,

$$2Al + Cr₂O₃ \rightarrow Al₂O₃ + 2Cr + \Delta H,$$

(2.4)

where $\Delta H = -538.47$ kJ mol⁻¹, is the enthalpy of the reaction. Al₂O₃ dissolves as temperature increases, but some remains at the interface [21].

Reaction (2.4) is likely to proceed before reaction (2.2), because of the lower enthalpy. Another reason is that the activation energy for aluminium atomic diffusion in Cr₂O₃ is around 405 kJ mol⁻¹[45-46]. This means that the oxide layer on the surface of stainless steel becomes a barrier for aluminium atom diffusion into the stainless steel. The interdiffusion of aluminium atoms with iron, chromium and nickel atoms only take place after the oxide layer is removed.

To investigate reaction (2.4), there are many techniques available including thermal analysis techniques, such as thermogravimetry (TG), differential thermal analysis (DTA) and differential scanning calorimetry (DSC). In these techniques, a physical property of a substance is measured as a function of temperature whilst being subject to a controlled temperature program [47]. Thermogravimetry and differential thermal
analysis are useful techniques for studying the kinetics of solid-state thermal reactions [47]. Based on these analysis technologies, Coats and Redfern [48] deduced equations that describe the mechanism of a thermal reaction and suggested using graphical techniques to fit experimental data into equations. Based on the work of Coats and Redfern and other available literature [44-49], the relationship between the kinetics of reactions time and temperature can be generalized as

\[
\begin{align*}
g(\alpha) &= BP(X) \\
X &= \frac{E_a}{RT_\alpha},
\end{align*}
\]

(2.5)

where \( \alpha \) is the decomposition fraction of the materials, \( g(\alpha) \) is the kinetic function of the reaction, \( P(X) \) depends on its activation energy, \( B \) is a constant determined by the heating rate and activation energy, \( E_a \) and \( T_\alpha \) are activation energy and temperature. \( T_\alpha \) is the temperature when the decomposition fraction is \( \alpha \).

The function \( g(\alpha) \) can be defined as

\[
g(\alpha) = \int \frac{d\alpha}{f(\alpha)} = \int k dt,
\]

(2.6)

where \( f(\alpha) \) is the decomposition rate function and depends on the reaction mechanism and \( k \) is a rate constant expressed as

\[
k = Z \exp \left( -\frac{E_a}{RT} \right),
\]

(2.7)

where \( Z \) is frequency factor, \( E_a \) is the activation energy for a thermal reaction, \( R \) is gas constant and \( T \) is the temperature. The right hand side of equation (2.5) can be substituted by (2.6) and (2.7) as

\[
\begin{align*}
g(\alpha) &= \frac{Z E_a}{Rq} P(X) = \frac{Z E_a}{Rq} \int \exp \left( -\frac{E_a}{RT} \right) dt = \frac{Z}{B} \left( e^{-X} - \int_{X}^{\infty} \frac{e^{-u}}{u} du \right) \\
X &= \frac{E_a}{RT_\alpha}, \\
u &= \frac{E_a}{RT}
\end{align*}
\]

(2.8)

where \( \frac{Z E_a}{Rq} = B \), the constant mentioned above and \( q' \) is a constant heating rate,

\[
q' = \frac{dT}{dt}.
\]

(2.9)

The theoretical values of \(-\log(P(X))\) have been tabulated by Zsako [50] for the temperature range from 100 to 430 °C and activation energy range from 41.84 to 276.14 kJ mol\(^{-1}\). An approximation formula of \( P(X) \) can be used as long as \( X > 50, \)
which is expressed as

\[ P(X) \approx e^{-X} \left( \frac{1}{x^2} - \frac{2}{x^3} \right); \quad (2.10) \]

however, the accuracy of this approximation is reported to be lower than other approximations by Starink [51].

To investigate the kinetics of a thermal reaction and determine the activation energy, several models were proposed by different researchers, which can be characterized as mainly of two types. One is rate-isoconversion methods, which do not make any approximation of \( P(X) \), but requires data at the determination temperature. The determination temperature is the point where maximum temperature is reached during the reaction for various heating rate. Another is \( P(X) \)-isoconversion methods, which rely on choosing appropriate \( P(X) \) approximation to determine the activation energy for a reaction. Most of these models were summarized and evaluated by Starink [51]. Starink concluded that for real experimental data, determination of a base-line of the thermal analysis data is never perfect and accuracy of determination of transformation rates is hence limited. In such cases, the \( P(X) \)-isoconversion methods are more accurate than the rate-isoconversion methods [51]. As Starink suggested, the most accurate model to approximate \( P(X) \) is

\[ P(X) = \frac{\exp(-1.0008X - 0.312)}{X^{1.92}}, \quad (2.11) \]

which will be used in the discussion chapter to calculate the start temperature of the thermite reaction reported above. Starink also reported that the accuracy of this approximation was more than 99.75%. However, due to the changes in the experimental conditions and experimental errors, the actual results can hardly reach such a high level of accuracy.

Combining the equations (2.8) and (2.11), equation (2.5) can be expressed as

\[ g(\alpha) = \frac{ZE_a}{Rq} P(X) = \frac{ZE_a \exp(-1.0008X - 0.312)}{X^{1.92}}. \quad (2.12) \]

The left part of equation (2.12), \( g(\alpha) \) is the integral of the function \( f^{-1}(\alpha) \), which is a kinetic function of a thermal reaction. In order to find the proper reaction mechanism to describe a certain type of thermal reaction, Sestak and Berggren [52] explored the possible mechanisms of individual cases for the solid state reactions. They suggested that the preliminary appraisal of possible reaction mechanism can be described as

\[ M = \frac{da}{dt} = k\alpha^m (1 - \alpha)^n (-\ln(1 - \alpha))^p = kf(\alpha), \quad (2.13) \]
where the parameters of $m$, $n$ and $p$ are determined by different reaction mechanisms. The reaction mechanisms can be characterized as phase boundary controlled processes, nucleation according to an exponential law, processes governed by nucleation followed by bulk growth of nuclei, processes controlled by nucleation followed by linear growth of nuclei and diffusion controlled reactions. Based on these reaction mechanisms, the parameters $m$, $n$ and $p$ can be determined and the function $f(\alpha)$ can be generated. The functions $f(\alpha)$ and $g(\alpha)$ from different reaction mechanisms are summarized in table 2.3.

Table 2.3 The most important rate equations used in kinetic analyses of solid state reactions [53].

<table>
<thead>
<tr>
<th>1. Acceleratory $\alpha$ - time</th>
<th>1 - Acceleratory $\alpha$ - time</th>
<th>1 - Acceleratory $\alpha$ - time</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pn power law</td>
<td>$\alpha^{1/n}$</td>
<td>$n\alpha^{(n-1)/n}$</td>
</tr>
<tr>
<td>E1 exponential law</td>
<td>$\ln \alpha$</td>
<td>$\alpha$</td>
</tr>
</tbody>
</table>

2. Sigmoid time

| A2 Avrami-Erkeev                | $[-\ln (1 - \alpha)]^{1/2}$  | $2(1 - \alpha)[1 - \ln (1 - \alpha)]^{1/2}$ |
| A3 Avrami-Erkeev                | $[-\ln (1 - \alpha)]^{1/2}$  | $3(1 - \alpha)[(-\ln (1 - \alpha)]^{2/3}$ |
| A4 Avrami-Erkeev                | $[-\ln (1 - \alpha)]^{1/4}$  | $4(1 - \alpha)[(-\ln (1 - \alpha)]^{3/4}$ |
| An Avrami-Erkeev                | $[-\ln (1 - \alpha)]^{1/2}$  | $n(1-\alpha)[-\ln(1-\alpha)]^{(n-1)/n}$ |
| B1 Prout-Tompkins               | $\ln [(1 - \alpha)^{-1/\alpha}]$ | $\alpha(1-\alpha)$ |

3 Deceleratory $\alpha$ - time
3.1 Geometrical $\alpha$ - time

| R2 conraction area              | $1 - (1 - \alpha)^{1/2}$     | $2(1 - \alpha)^{1/2}$ |
| R3 contracting volume           | $1 - (1 - \alpha)^{1/3}$     | $3(1 - \alpha)^{2/3}$ |

3.2 diffusion models

| D1 One-dimensional             | $\alpha^2$                    | $(1/2)\alpha$ |
| D2 Two-dimensional             | $(1 - \alpha)[\ln(1 - \alpha) + \alpha]$ | $[-\ln (1 - \alpha)]^1$ |
| D3 Three-dimensional           | $[1 - (1 - \alpha)]^{1/3}$     | $3(2)/(1-\alpha)^{2/3}[1-(1-\alpha)^{1/3}]$ |
| D4 Ginstling-Broushtstein      | $1-(2\alpha/3)-(1-\alpha)^{2/3}$ | $3(2)/(1-\alpha)^{1/3}.1^{-1}$ |

3.3 ‘order of reaction’

| F0 zero order                  | $\alpha$                      | 1 |
| F1 first order                 | $-\ln (1 - \alpha)$           | $1 - \alpha$ |
| F2 second order                | $[(1 - \alpha)^{-2} - 1]$      | $(1 - \alpha)^2$ |
| F3 third order                 | $[(1 - \alpha)^{-3} - 1]$      | $(1 - \alpha)^3$ |

$\alpha = h(t)$

$kt$
2.3 Interdiffusion between aluminium and stainless steel

The chemical reactions are related to the diffusion of the elements and ultimately result in changing the chemical concentration. Once the concentration of these atoms reaches a certain value (limiting solubility), the atomic interaction can change the chemical potential leading to the formation of intermetallic compounds. These compounds construct the intermediate layers, and the growth of the layers is controlled by solid state diffusion. This is a commonly occurring phenomenon during the joining of dissimilar metals [54].

It is reported that the growth of the intermetallic layer formed at the interface follows a parabolic law [55-57],

\[ X^2 = Kt, \]  

(2.14)

where \( K \) is a temperature dependent constant proportional to the interdiffusion coefficient \( D \). The interdiffusion coefficient \( D \) can be deduced from the empirical Arrhenius equation,

\[ D = D_0 \exp \left( - \frac{Q}{RT} \right), \]  

(2.15)

where \( Q \) is the activation energy, \( D_0 \) is a pre-factor, \( R \) is gas constant and \( T \) is the absolute temperature [58].

Iron, chromium, nickel and aluminium atoms are the main diffusion elements in the system of aluminium and stainless steel (figure 2.10). \( J_a, J_b, J_c \) and \( J_d \) are diffusion fluxes formed by Fe, Cr, Ni and Al atoms, the subscripts \( a, b, c \) and \( d \) refer to iron, chromium, nickel and aluminium, respectively. Due to the similar atomic radii, the substitutional diffusion mechanism dominates the atomic interdiffusion process. A net flux forms at the interface of aluminium and stainless steel. The activation energies for atomic diffusion of different atoms in \( \gamma \)-Fe and in aluminium determine the final interdiffusion coefficient (table 2.4).

![Figure 2.10 Interdiffusion fluxes between aluminium and stainless steel.](image)
Table 2.4 Atomic radii and activation energy in γ-Fe and in aluminium [58, 59].

<table>
<thead>
<tr>
<th>Atom</th>
<th>Radii (pm)</th>
<th>Activation energy in γ-Fe (kJ Mol⁻¹)</th>
<th>Activation energy in aluminium (kJ Mol⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>126</td>
<td>284.1</td>
<td>193</td>
</tr>
<tr>
<td>Cr</td>
<td>128</td>
<td>335</td>
<td>257</td>
</tr>
<tr>
<td>Ni</td>
<td>124</td>
<td>282.5</td>
<td>Varies with temperature</td>
</tr>
<tr>
<td>Al</td>
<td>143</td>
<td>184</td>
<td>142</td>
</tr>
</tbody>
</table>

The growth of the intermetallic layer is determined by the net flux at the interface between aluminium and stainless steel. These atomic fluxes can be described as

\[
\begin{align*}
J_a &= -D_a \frac{\partial C_a}{\partial x} \\
J_b &= -D_b \frac{\partial C_b}{\partial x} \\
J_c &= -D_c \frac{\partial C_c}{\partial x} \\
J_d &= -D_d \frac{\partial C_d}{\partial x}
\end{align*}
\]  
(2.16)

where \( D_a, D_b, D_c \) and \( D_d \) are diffusion coefficients, \( C_a, C_b, C_c \) and \( C_d \) are the concentrations of iron, chromium, nickel and aluminium respectively. The concentrations change with time and distance from the aluminium side to the stainless steel side. But the total concentration of all elements \( C_0 \) in the system should be a constant (mass conservation), which indicates that the sum of all the elements is a constant and described as

\[
C_0 = C_a + C_b + C_c + C_d.
\]  
(2.17)

By differentiation the equation (2.17), the left side of the equation equal to zero, and the relationship between aluminium concentration and the concentrations of other atoms can be expressed as

\[
\frac{\partial C_d}{\partial x} = - \left( \frac{\partial C_a}{\partial x} + \frac{\partial C_b}{\partial x} + \frac{\partial C_c}{\partial x} \right).
\]  
(2.18)

Since the concentrations of the atoms from stainless steel can be represented by the concentration of aluminium atoms, it is much easier to describe a problem with less variables. As the atomic diffusion creates vacancies, the diffusion flux created by atoms is equal to the flux of the vacancies [59-60]. If there is a net flux of aluminium atoms in one direction, there is an equal flux \( (J_v) \) of vacancies in the opposite direction. Define the vacancy flux is \( J_{v1} = -J_d \) created by aluminium atoms diffusing from aluminium to stainless steel. Another vacancy flux is \( J_{v2} = -(J_a + J_b + J_c) \) created by Cr, Ni and Fe atoms diffusing from stainless steel to aluminium. The total vacancy flux is described as
\[ J_v = J_{v1} + J_{v2} = -J_a - J_b - J_c, \]  
\hspace{1cm} (2.19)

which can be substituted with (2.16) and (2.18) to obtain

\[ J_v = (D_a - D_d) \frac{\partial c_a}{\partial x} + (D_b - D_d) \frac{\partial c_b}{\partial x} + (D_c - D_d) \frac{\partial c_c}{\partial x}. \]  
\hspace{1cm} (2.20)

The growth of the intermetallic layers is determined by the movement of atoms at the interface and these atoms construct the lattice plane at the front of the intermetallic layer. The travel velocity of the lattice plane is equal to the growth rate of the intermetallic layer and also equal to the travel velocity of the vacancies.

Assuming that the lattice plane moves at a velocity of \( u \), which is the same as the velocity of the vacancies. The movements of the lattice plane can be expressed as the vacancy flux which can be described as

\[ J_v = C_0 u. \]  
\hspace{1cm} (2.21)

Combining equations (2.20) and (2.21), \( u \) can be written as

\[ u = (D_a - D_d) \frac{\partial X_a}{\partial x} + (D_b - D_d) \frac{\partial X_b}{\partial x} + (D_c - D_d) \frac{\partial X_c}{\partial x} \]  
\hspace{1cm} (2.22)

where \( X_a = C_a/C_0 \), \( X_b = C_b/C_0 \) and \( X_c = C_c/C_0 \), also define \( X_d = C_d/C_0 \), \( X_a \), \( X_b \), \( X_c \), and \( X_d \) are concentration fractions.

As the lattice plane movement defines the growth of the intermetallic layer and the movement of the lattice plane can be evaluated by interdiffusion of atoms, it is necessary to calculate the interdiffusion coefficient. Several steps should be followed to acquire the interdiffusion coefficient. The interdiffusion coefficient will be a parameter used to describe the behaviour of the intermetallic layer.

---

![Figure 2.11](image-url)

**Figure 2.11 The interdiffusion flux at the interface of aluminium and stainless steel.**

The vacancies created by aluminium atoms are occupied by the atoms of iron, chromium and nickel diffusing from stainless steel. It is easier to use the flux of
aluminium to address the diffusion process than flux of other atoms. Consider a thin slice of material with the thickness of $\Delta x$ at a fixed distance from the interface on the aluminium side (figure 2.11). If the total flux of aluminium atoms entering the slice across plane 1 is $J_d^i$, the total flux leaving is $J_d^i + (\partial C_d/\partial x) \Delta x$, which gives the change of aluminium atoms during diffusion is

$$\frac{\partial C_d}{\partial t} = -\frac{J_d^i}{\partial x}. \quad (2.23)$$

The total flux of aluminium atoms across a stationary plane with respect to the specimen is the sum of two contributions: (1) the aluminium diffusive flux is $J_d = -D_d (\partial C_d/\partial x)$, due to atomic diffusion relative to the lattice plane; (2) a flux $\nu C_d$ due to the movement of the lattice plane in which diffusion is occurring. Therefore

$$J_d^i = -D_d \frac{\partial C_d}{\partial x} + \nu C_d. \quad (2.24)$$

Then, assume that the concentration fraction of iron, chromium, nickel and aluminium is

$$X_a : X_b : X_c : X_d = \beta : \gamma : \lambda : \varepsilon \quad (2.25)$$

and

$$X_a + X_b + X_c + X_d = 1. \quad (2.26)$$

Based on this assumption, equations (2.22) and (2.24) can change into equations (2.27) and (2.28)

$$\nu = \left\{ \frac{(D_a - D_d) \beta}{\varepsilon} + \frac{(D_b - D_d) \gamma}{\varepsilon} + \frac{(D_c - D_d) \lambda}{\varepsilon} \right\} \frac{\partial x_d}{\partial x} \quad (2.27)$$

And

$$J_d^i = -D_d \frac{\partial C_d}{\partial x} + \nu C_d = X_d \left\{ \left( \frac{\beta + \gamma + \lambda}{\varepsilon} + \frac{1}{x_d} \right) D_d - \frac{\beta D_a + \gamma D_b + \lambda D_c}{\varepsilon} \right\} \frac{\partial C_d}{\partial x} = -\bar{D} \frac{\partial C_d}{\partial x}. \quad (2.28)$$

Finally, from the equation (2.28) and by the definition of diffusion coefficient, the interdiffusion coefficient between the aluminium and the stainless steel is

$$\bar{D} = -X_d \left\{ \left( \frac{\beta + \gamma + \lambda}{\varepsilon} + \frac{1}{x_d} \right) D_d - \frac{\beta D_a + \gamma D_b + \lambda D_c}{\varepsilon} \right\}, \quad (2.29)$$

which can be evaluated from experimental results.
Chapter 3

Experiments

3.1 Sample preparation and chemical composition

Al 1050 and AISI 316L were used to study the interfacial behaviour between aluminium and stainless steel. The chemical compositions of these materials are shown in tables 3.1 and 3.2.

<table>
<thead>
<tr>
<th>Material</th>
<th>Mn</th>
<th>Mg</th>
<th>Fe</th>
<th>Si</th>
<th>Ti</th>
<th>Cu</th>
<th>Ni</th>
<th>Al</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al 1050</td>
<td>0.004</td>
<td>0.008</td>
<td>0.236</td>
<td>0.120</td>
<td>0.025</td>
<td>0.020</td>
<td>0.030</td>
<td>Balance</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Material</th>
<th>Al</th>
<th>Mg</th>
<th>Cu</th>
<th>Si</th>
<th>Cr</th>
<th>Ni</th>
<th>Mo</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>AISI 316L</td>
<td>0.072</td>
<td>0.023</td>
<td>0.245</td>
<td>0.66</td>
<td>17.09</td>
<td>10.53</td>
<td>1.85</td>
<td>Balance</td>
</tr>
</tbody>
</table>

Two groups of samples were prepared for solid-state diffusion bonding and laser experiments (bead-on-plate). The first group of samples for solid-state diffusion bonding were cut into the required round cake shape with a thickness of 2 mm and a diameter of 20 mm. The second group of samples for laser experiments were 10×10 mm² AISI 316L with a thickness of 2 mm. Al 1050 filler wire with 1.2 mm diameter was applied in the bead-on-plate experiments.

The first group of samples were ground using abrasives of grades 600, 800, 1200, 2400, and polished with diamond suspension up to 1 μm. A metallographically flat surface was prepared for chemical cleaning. The AISI 316L samples were cleaned with 10 ml HNO₃ (10 % solution), 10 ml H₂SO₄ (6 % solution) and 10 ml HF (20 % solution) for 10 min and washed with 60 °C hot distilled water and dried. The Al 1050 samples were cleaned with 10 % Na(OH) water solution for 10 ~ 15 s and washed with 60 °C hot distilled water and dried.

The surface of the second group of samples were cleaned with a steel brush and washed with ethanol. Then, a chemical reagent Villela was used to remove the oxide on the surface of the stainless steel. The chemical composition of Villela is 45 ml Glycerol (87 % solution), 30 ml HCl (32 % solution) and 15 ml HNO₃ (65 % solution). After etching for 30 s with Villela, samples were cleaned with ethanol and dried.
3.2 Solid-state diffusion bonding

Solid-state diffusion bonding is a joining process in which a bond is formed as a result of the interdiffusion of atoms across the bond interface (figure 3.1) [61]. The process from (a) to (d) shows the formation of an ideal metallic bond by solid-state diffusion bonding. Compressing the two cleaned surfaces of the base metals results in an interface between two components. Plastic deformation caused by compressive force ($P$) leads to the appearance of new grains at the interface. These new grains can change into the same structure as the base metal by atomic diffusion.

![Figure 3.1 Schematic diagram of the solid-state bonding processes.](image)

In reality, however, new phases, such as intermetallic compounds, often appear at the interface and degrade the strength of the bond.

3.2.1 Clamping

A controllable and reproducible clamping device is required to meet the required experimental conditions of solid-state diffusion bonding. A clamping device was designed and used in this work as shown in Figure 3.2.

![Figure 3.2 Schematic diagram of the clamping device.](image)

There are carbon steel (1 in figure 3.2), stainless steel (2 in figure 3.2) and plastic deformation element (3 in figure 3.2) used in this device. The samples (4 and 5 in figure 3.2) were assembled as shown and a steel ring (6 in figure 3.2) was placed around the samples to prevent extrusion of the aluminium component during high temperature compression. The difference of the thermal expansion coefficient between carbon steel (12 µm K$^{-1}$) and stainless steel (16–18 µm K$^{-1}$) introduces a
compressive force during heating of the device. Due to lower thermal coefficient of carbon steel, it expands less than the stainless steel during heating. By constraining both sides of this device, a compressive stress will build up in the device. The compressive stress is limited by a plastic deformation element. The loading of the plastic deformation element was examined in this work. The stress-strain curve of this element was obtained by compression tests at 600 °C (figure 3.3).

![Stress-strain curve](image)

Figure 3.3 Stress-strain curve of the deformation element from compression tests at 600 °C.

The principle of the device was tested and the changes in length (\(\Delta l\)) of the plastic deformation element was measured at different temperatures, which can be calculated as

\[
\Delta l = \alpha_{ss} \Delta T L_{ss} - \alpha_{cs} \Delta T L_{cs},
\]

where \(\alpha_{ss}\) and \(L_{ss}\) are the thermal coefficient and length (170 mm) of the stainless steel, \(\alpha_{cs}\) and \(L_{cs}\) the thermal coefficient and length (215 mm) of the carbon steel.

<table>
<thead>
<tr>
<th>Test No.</th>
<th>temperature (K)</th>
<th>Calculated length (mm)</th>
<th>Measured length (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>723</td>
<td>0.140</td>
<td>0.141</td>
</tr>
<tr>
<td>2</td>
<td>773</td>
<td>0.155</td>
<td>0.152</td>
</tr>
<tr>
<td>3</td>
<td>823</td>
<td>0.171</td>
<td>0.167</td>
</tr>
<tr>
<td>4</td>
<td>873</td>
<td>0.186</td>
<td>0.175</td>
</tr>
<tr>
<td>5</td>
<td>913</td>
<td>0.198</td>
<td>0.184</td>
</tr>
<tr>
<td>6</td>
<td>873</td>
<td>0.186</td>
<td>0.179</td>
</tr>
</tbody>
</table>

Note: the length was measured with an electronic micrometer.

The calculated and measured changes in lengths are compared in table 3.3. The average thermal expansion coefficient (17 \(\mu m\) K\(^{-1}\)) of the stainless steel was used in the calculation. The first five absolute length changes of the plastic deformation element were measured after solid-state diffusion bonding experiments. The sixth was
measured without the experimental samples to validate the principle of this device. Table 3.3 shows that the plastic deformation in the experiments was approximately 0.01 %, indicating that the compressive stress in the system was around 300 MPa (refer to figure 3.3). The compressive stress acting on the samples can be calculated from the following equation.

\[
\begin{align*}
F_1 &= A_1 \sigma_1 \\
F_2 &= A_2 \sigma_2 \\
F_3 &= A_3 \sigma_3 \\
F_1 &= F_2 = F_3
\end{align*}
\] (3.2)

where \( F_1, F_2 \) and \( F_3 \) were the forces acting on the stainless steel, samples and plastic deformation element, \( A_1, A_2 \) and \( A_3 \) were the cross-section areas of the stainless steel, samples and plastic deformation element, and \( \sigma_1, \sigma_2 \) and \( \sigma_3 \) were the stresses acting on the stainless steel, samples and plastic deformation element, respectively. The stress acting on the samples was \( \sigma_2 \) (48 ± 5 MPa) in these experiments.

### 3.2.2 Surface roughness tests

Surface roughness is quantified by the vertical deviations of a real surface from its ideal flat form. If these deviations are large, the surface is rough; if they are small the surface is smooth. The surface roughness plays an important role in determining how the real surfaces interact with each other at the interface of aluminium and stainless steel [62]. The irregularities on the surface provides the nucleation sites of the intermetallic compounds at the interface.

The arithmetic average of absolute values of \( R_a \) is one of the common parameters employed to describe the roughness profile of the surface [62]. The \( R_a \) can be calculated with equation 3.3.

\[
R_a = \frac{1}{n} \sum_{i=1}^{n} |y_i|
\] (3.3)

where \( n \) is the number of tested points, \( y_i \) is the height of each point. Samples were compressed at room temperature and the roughness was tested with a Taylor Hobson and a Talysurf-120 roughness profile machines. Experimental results are provided in chapter 4 and further discussion in chapter 5.
3.2.3 Heat treatments

It is reported that there were intermetallic compounds appearing around 500 °C at the interface of aluminium and stainless steel in the study of the interdiffusion between AISI type 316 and aluminium [63]. It is also reported that two regions of the intermetallic layer formed at the interface between aluminium and stainless steel above 600 °C in a study of the diffusion bonding of stainless steel to alumina using an aluminium interlayer [64].

Solid-state diffusion bonding experiments were conducted in a Nabertherm® furnace, model 35/SH 1997 and experiments were repeated in a Heraeus K750/1 furnace to study the formation and growth of the intermetallic layer. The heating and cooling schemes examined are shown in table 3.4.

<table>
<thead>
<tr>
<th>Experimental Number</th>
<th>Furnace heating time (min)</th>
<th>Holding period</th>
<th>Furnace cooling time (h)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Time (min)</td>
<td>Temp (°C)</td>
</tr>
<tr>
<td>1</td>
<td>120</td>
<td>60</td>
<td>450</td>
</tr>
<tr>
<td>2</td>
<td>95</td>
<td>45</td>
<td>500</td>
</tr>
<tr>
<td>3</td>
<td>105</td>
<td>45</td>
<td>550</td>
</tr>
<tr>
<td>4</td>
<td>115</td>
<td>45</td>
<td>600</td>
</tr>
<tr>
<td>5</td>
<td>117</td>
<td>45</td>
<td>610</td>
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<td>6</td>
<td>119</td>
<td>45</td>
<td>620</td>
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<td>7</td>
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<td>45</td>
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</tr>
<tr>
<td>8</td>
<td>122</td>
<td>45</td>
<td>635</td>
</tr>
<tr>
<td>9</td>
<td>123</td>
<td>45</td>
<td>640</td>
</tr>
</tbody>
</table>

Note: 1) temperature accuracy is ± 5 °C, heating rate is 5 °C min⁻¹; 2) Samples were cooled in the furnace till 60 °C; 3) Three samples were tested for each temperature.

3.3 Bead-on-plate laser brazing

Lasers were used as a heat source for the brazing of aluminium and stainless steel because they can produce localized fusion with a high energy density [23-24]. To understand the mechanism of the intermetallic compound formation and the growth of the intermetallic layers, bead on plate experiments were carried out (figure 3.4).

The high heating and cooling rate is an advantage to study the mechanism in laser welding, because the intermetallic compounds formed at high temperature may remain after the components cool to room temperature. Laser experiments were carried out within 5 min after the sample preparation. Several tests were performed before the experiments to acquire the welding parameters. The welding length, wire feeding speed and angle are 75 mm, 19.5 mm s⁻¹ and 15°, respectively. Other welding
parameters are shown in table 3.5. Argon shielding gas was applied to protect the focal lens and the gas flow pressure was 3 bar. The focal length of the lens was 150 mm. The laser spot diameter was 4 mm.

![Schematic diagram of the laser brazing process.](image)

**Figure 3.4 Schematic diagram of the laser brazing process.**

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Laser power (kW)</th>
<th>Laser travel speed (mm s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.2</td>
<td>3</td>
</tr>
<tr>
<td>2</td>
<td>1.5</td>
<td>3</td>
</tr>
<tr>
<td>3</td>
<td>1.7</td>
<td>10</td>
</tr>
<tr>
<td>4</td>
<td>1.9</td>
<td>10</td>
</tr>
<tr>
<td>5</td>
<td>2.0</td>
<td>10</td>
</tr>
</tbody>
</table>

**Table 3.5 Parameters of bead on plate laser welds.**

3.4 Sample preparation for optical microscopy/SEM/XRD

Samples were cut through the cross section and prepared following a standard metallographic procedure. Samples were ground using abrasives of grades 600, 800, 1200, 2400, and polished with diamond suspension up to 1 μm. Samples were etched with Kelling’s reagent and washed in an ultrasonic cleaner for 5 minutes and dried with hot air.

Optical microstructures of samples were observed with a Leica DMLM microscope. Further examination of the samples was performed with an JEOL JSM-6500F scanning electron microscope (SEM) and chemical distribution were obtained from Energy Dispersive Spectrometer (EDS). XRD was performed in the PANalytical Xpert PRO X-ray diffraction system.

Microhardness testing was performed with an automatic microhardness tester. The microhardness of solid-state diffusion bonds was tested across the intermetallic layer with a load of 10 gf. The microhardness around the fusion line of the bead-on-plate laser welds and the light and dark phases in the weld pool were also tested.
Chapter 4

Experimental Results

4.1 Surface roughness

The surface roughness of samples was measured within 15 min after preparation and the results of AISI 316L and Al 1050 are shown in tables 4.1 and 4.2.

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>The Ra before compression</th>
<th>Ra after compressed at 50 MPa</th>
<th>Ra after compressed at 352 MPa</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2.03</td>
<td>2.03</td>
<td>4.21</td>
</tr>
<tr>
<td>2</td>
<td>1.98</td>
<td>1.96</td>
<td>4.14</td>
</tr>
<tr>
<td>3</td>
<td>1.97</td>
<td>1.95</td>
<td>4.23</td>
</tr>
<tr>
<td>4</td>
<td>1.93</td>
<td>1.98</td>
<td>4.03</td>
</tr>
<tr>
<td>5</td>
<td>2.08</td>
<td>1.97</td>
<td>4.09</td>
</tr>
</tbody>
</table>

Table 4.1 The surface roughness of AISI 316L (Ra μm).

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>The Ra before compression</th>
<th>Ra after compressed at 50 MPa</th>
<th>Ra after compressed at 352 MPa</th>
</tr>
</thead>
<tbody>
<tr>
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<td>6.41</td>
<td>4.58</td>
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<td>5.97</td>
<td>4.21</td>
</tr>
<tr>
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<td>9.02</td>
<td>5.56</td>
<td>4.49</td>
</tr>
<tr>
<td>5</td>
<td>8.95</td>
<td>5.74</td>
<td>3.96</td>
</tr>
</tbody>
</table>

Table 4.2 The surface roughness of Al 1050 (Ra μm).

The yield strength of AISI 316L and AL 1050 are 105 and 170 MPa respectively. As tables 4.1 and 4.2 show, the roughness of stainless steel barely changes with the lower compressive force (50 MPa), but it increases from around 2.0 μm to around 4.0 μm at higher compressive force (352 MPa). The similar roughness between aluminium and stainless steel at higher compressive force indicates that the oxide layer on the aluminium side is broken and aluminium is attached on the surface of the stainless steel. This may explain the roughness increase of the stainless steel.

The roughness of the aluminium decreases as the compressive force increases. Plastic deformation appears at lower compressive force on the aluminium side because of the lower yield strength of aluminium compare to stainless steel. The roughness ultimately reaches the same value as on the stainless side.

Three dimensional surface profiles of samples after compressing to 50 MPa were measured and results are shown in figures 4.1 and 4.2. The same position (A) on the surfaces of AISI 316L and Al 1050 are compared in figure 4.3 to illustrate that the surface on the aluminium side is plastically deformed. The blue areas also indicate plastic deformation on the surface of the aluminium (figure 4.3 (b)).
Figure 4.1 Surface roughness of AISI 316L after compression (50 MPa).

Figure 4.2 Surface roughness of Al 1050 after compression (50 MPa).

Figure 4.3 Surfaces profile of stainless steel and aluminium, a) AISI 316L; b) Al 1050.
4.2 Optical microscopy

4.2.1 Optical microscopy of Solid-state bonds

The microstructures at the interface between aluminium and stainless steel from the solid-state diffusion bonds were observed with an optical microscope. Intermetallic compounds appear above 500 °C and form layers. The intermetallic layers grow as the temperature increases and layers with a different composition appear above 600 °C. The layers grow faster on the aluminium side than on the stainless steel side. Iron precipitates in the aluminium matrix. The interface on the stainless side is more uniform than the interface between aluminium and the intermetallic layer.

![Image](image_url)

Figure 4.4 The interface of Al 1050/AISI 316L after a) holding at 500 °C for 45 min; b) holding at 550 °C for 45 min.

Figure 4.4 shows the intermetallic layer formed at the interface between Al 1050 and AISI 316L at 500 and 550 °C. In figure 4.4 (a), there is a clear interface between the aluminium and the stainless steel, but no obvious intermetallic has formed. In figure 4.4 (b), an intermetallic layer has grown into the aluminium side. Over etching causes the dark regions and the white marks on stainless steel side in figure 4.4 (b) are scratches.

![Image](image_url)

Figure 4.5 Intermetallic layers at the interface of Al 1050/AISI 316L after a) holding at 600 °C for 45 min; b) holding at 610 °C for 45 min.
As the temperature increases, the intermetallic layer grows and the interface of the aluminium and the stainless steel is replaced by the intermetallic layer. Although it is not clear in figure 4.5 (a) that a second intermetallic layer is already present on top of the first layer, the chemical distribution examined with EDS indicates that the second layer is present above 600 °C. In addition to the intermetallic layers, dark spots of the iron precipitates were observed in the matrix of the aluminium (figure 4.5 (b)).

![Figure 4.6 Intermetallic layers at the interface of Al 1050/AISI 316L after a) holding at 620 °C for 45 min; b) holding at 640 °C for 45 min.](image)

It is clear from figure 4.6 (a) that the intermetallic layer grows into both the aluminium and the stainless steel. The red line in figure 4.6 (a) indicates the original interface position between the aluminium and stainless steel. The thicker intermetallic layer on the aluminium side indicates that the intermetallic layer grows faster on the aluminium side than on the stainless steel side, which also suggests that the atomic diffusion of iron, chromium and nickel in the aluminium matrix is easier than that of aluminium in the austenitic stainless steel. In figure 4.6 (b), the two different intermetallic layers can be distinguished. The average thickness of the first intermetallic layer observed from experimental results is approximately 10 μm. From 600 to 645 °C, the thickness of the first intermetallic layer is almost constant at 10 μm, while the second intermetallic layer grows as the temperature increases. In figure 4.6 (b), it is hard to determine where the interface between these two intermetallic layers is precisely. It is possible that a transition zone (1~2 μm thick) has formed between the two intermetallic layers. The chemical distributions from EDS will indicate whether this interpretation is correct.
4.2.2 Optical microscopy from bead-on-plate laser welds

The microstructures appearing at the fusion line and in the weld pool of the laser weld are the main interests in this work. The aim is to observe the evolution of the intermetallic compounds and layers with increasing laser powers. Optical images of microstructures were acquired for further analysis. The behaviour of the intermetallic compounds and layer at the interface and in the weld pool of Al 1050 and AISI 316L were observed.

Figure 4.7 Laser weld made at 1.2 kW, a) Interface between aluminium and stainless steel; b) weld pool.

At low laser power (1.2 kW), cracks initiated next to the fusion line between the aluminium and the stainless steel (figure 4.7 (a)). A weak metallic bond might form at the fusion line but this breaks due to the stress build up during cooling. Bamboo-leaf shape phases (intermetallic compounds) were observed in the weld pool (figure 4.7 (b)). The hardness of the bamboo-leaf shape phases reaches 750 HV, indicating that the brittleness of these phases is responsible for the crack. The hardness of the light region is around 50 HV which indicates that almost pure aluminium is retained in the weld pool.

Figure 4.8 Interface between Al 1050 and AISI 316L with 1.5 kW laser power.

With 1.5 kW laser power, the microstructures at the fusion line and in the weld pool are different from laser welds made at 1.2 kW. A continuous bond is observed at the
fusion line and the crack has moved away from the fusion line and initiated in the weld pool (figure 4.8). The crack probably originates as a result of the differences between the thermal coefficients of the stainless steel and the weld. The bamboo-leaf shape phases changed into island-like dark phases and flowed into the weld pool. The high laser power provided enough energy for the interdiffusion between the bamboo-leaf shape and white phases in the weld pool (see figure 4.7 (b)). As a result the island-like phases and light phases are formed and constructed in the laser weld (see figure 4.8). The hardness of the dark phases dropped to around 650 HV but the light phases increased to 450–500 HV. The cracks probably originate as a result of the difference between the thermal coefficients of the stainless steel substrate and the weld.

It is interesting to find that a weld can be obtained from laser welding aluminium to austenitic stainless steel.

![Figure 4.9 Microstructures of the weld made with 1.7 kW laser power, a) cracks and pores in laser weld; b) microstructures at the fusion line of the weld; c) microstructures in the weld pool area \( \Lambda_2 \); d) microstructures at the fusion line area \( \Lambda_3 \).](image)

The geometry of the 1.7 kW laser weld is shown in figure 4.9 (a), about 50 % of the filler metal is mixed with AISI 316L in the weld pool. Cracks and pores appear in these welds. The microstructures at the interface between weld and stainless steel are shown in figure 4.9 (b). In the weld pool, butterfly phases appear and distribute more or less uniformly in the weld pool (figure 4.9 (c)). At the fusion line, no obvious intermetallic layer can be observed (figure 4.9 (d)), but on the left side of the weld (area \( \Lambda_3 \) shown in figure 4.9 (a)), an intermetallic layer has been found (figure 4.10).
The average thickness of the intermetallic layer is around 5 μm. This suggests that, by controlling the welding parameters appropriately, it is possible to join austenitic stainless steel to aluminium with laser fusion welding. In addition to the intermetallic layer, the results of atomic diffusion of aluminium into AISI 316L along the grain boundaries can also be observed (figure 4.10). Because of the high cooling rate of laser welding, the growth of the intermetallic layer should be constrained within a certain thickness. Whether this thickness is acceptable to the formation of a satisfactory weld should be determined by the geometry and application purposes of the weld.

Figure 4.10 The intermetallic layer appeared between the weld and AISI 316L (1.7 kW laser power).

Based on the microstructures of the laser welds made at 1.7 kW, intermetallic compounds were expected to appear in the weld pool and intermetallic layer growth was also expected at the fusion line at higher laser power. However, in the 1.9 kW laser power experiments, no intermetallic layer was observed at the fusion line in this work (figure 4.11). The chemical distributions will be examined later.

Figure 4.11 Bead-on-plate of laser weld of AISI 316L/Al 1050 with 1.9 kW laser power.

As laser power increased to 2.0 kW, the size of the weld pool increased indicating that mixing ratio between AISI 316L and Al 1050 was also increased (figure 4.12 (a)). At the fusion line, there was no intermetallic layer formation (figure 4.12 (b)). In the weld pool, dark phases appear in area B1, which could be the oxide on the surface of
the stainless steel driven by fluid flow into the weld pool. Gas can also be trapped inside of the weld generating porosity during cooling (figure 4.12 (c)). At the fusion line between AISI 316L and the weld, it is clear that the columnar grains grow perpendicular to the fusion line (figure 4.12(d)). There were no intermetallic compounds or intermetallic layer at the fusion line or in the weld pool. The microhardness tests results show that in these regions the hardness varies from 400 to 500 HV indicating that alloys instead of intermetallic compounds have formed.

Figure 4.12 Microstructures of the weld with 2.0 kW laser power, a) geometry of the laser weld; b) microstructures at the fusion line of the weld; c) microstructures in the weld pool area B1; d) microstructures at the fusion line area B2.

Figure 4.13 Microstructures in the weld pool with 2.0 kW laser power.

In the weld pool, aluminium diffusion along the grain boundaries of the solid austenite was observed (figure 4.13). The right side of the weld was close to the centre of the laser weld, indicating that the temperature on the right side is higher than
on the left side during welding. Aluminium atomic diffusion is faster at higher temperature. As shown in figure 4.13, the aluminium has already diffused into the grains of the stainless steel on the right side, while aluminium has mostly diffused along the grain boundaries on the left side. The fast cooling rate of laser welding makes it possible to observe these microstructures, which are produced at high temperatures.

4.3 Results from SEM examinations

4.3.1 Examination of intermetallic layer from solid-state diffusion bonds

EDS measurements were carried out along with SEM to examine the chemical distributions at the interface of aluminium and stainless steel.

![Figure 4.14 Examination of the intermetallic layer formed at 550 °C (solid-state diffusion bonding).](image)

The intermetallic layer formed at 550 °C with solid-state diffusion bonding was examined (figure 4.14). The chemical distributions from EDS tests shows that iron precipitates around 50 μm away from the intermetallic layer in the aluminium matrix. The atomic proportion at the interface illustrates that iron, chromium and nickel diffused into the aluminium. It is therefore possible to form iron-aluminides, chromium-aluminides or nickel-aluminides at the interface. Iron-aluminides are expected in this system because iron and aluminium are the most abundant elements present. As mentioned in section 2.1, the similar atomic size of iron, chromium and nickel allows chromium and nickel atoms to substitute iron atoms in the iron-aluminides. Thus, mixed intermetallic compounds are expected in this intermetallic layer.

Different intermetallic layers appeared at 640 °C during solid-state diffusion bonding. The EDS results show that the thickness for the first layer next to the stainless steel
side is approximately 10 µm (figure 4.15). The thickness of the first intermetallic layer on the stainless steel side is independent of real temperature because the layer became a barrier for aluminium atom diffusion into the stainless steel, which reduced the growth speed of the intermetallic layer on the stainless steel side. The atoms from the stainless side diffuse more easily into the aluminium side not only because the atomic radii of iron, chromium and nickel (approximately 125 pm), are smaller than aluminium (148 pm) but also because the activation energy for iron, chromium and nickel diffusion is lower in aluminium than the aluminium activation energy for diffusion in austenitic stainless steel (discussed in the next chapter). The second layer grows into the aluminium on the top of and after the formation of the first layer.

![Image](image_url)

Figure 4.15 Examination of intermetallic layers formed at 640 °C (solid state diffusion bonding).

Due to the aluminium diffusion, the first intermetallic layer grows into both the stainless steel and aluminium matrix. According to the elemental distribution from the EDS results, Fe2Al5 formed on the stainless steel side and the first intermetallic layer is constructed from Fe2Al5 together with the mixed intermetallic compounds mentioned above. The second intermetallic layer was mainly formed from FeAl3.

![Image](image_url)

Figure 4.16 Hardness profile of the specimen produced at 640 °C (10 gf).

Microhardness tests (figure 4.16) across the interface show that the hardness is lower than expected form FeAl3 or Fe2Al5, which are 1025 HV and 730 HV respectively
[72]. One possible reason is that during the hardness tests, cracks were introduced at the edge of the indentations, the measured hardness was therefore reduced. The actual value can be acquired from nano-indentation. Another possible cause in the absence of cracking is that iron atoms can be replaced by chromium and nickel atoms leading to a drop in hardness. Cracking was observed at some but not all of the measurement locations.

4.3.2 Examination of the fusion welded Al 1050 to AISI 316L

It is interesting to find a continuous metallic bond between aluminium and stainless steel at the fusion line in the laser weld samples. The butterfly-like phases in the weld pool also deserve further investigation. An EDS examination was therefore carried out to observe the chemical distributions at the fusion line and inside the weld pool.

Figure 4.17 Chemical distributions across weld fusion line into weld pool (1.2 kW laser power).

Figure 4.17 (a) shows the microstructure at the interface of the fusion line, the anisotropic diffusion of Fe, Cr and Ni from stainless steel to aluminium leads to the intermetallic growing into the weld metal with tongue-like penetrations. A metallic bond is formed at the fusion line of AISI 316L and Al 1050 laser welds and an intermetallic layer with a thickness of approximately 20 μm is formed. Based on EDS results (figure 4.17 (b)), the metallic bond contains around 40 at. % Fe, 40 at. % Al, 12 at. % Cr and 8 at. % Ni. In the weld pool, iron-aluminium intermetallic compounds, such as FeAl₃, mixed with nickel-aluminium intermetallic compounds are present, due to the changes of the iron, aluminium and nickel contents. Due to the high cooling rate in laser welding, the 1.2 kW laser power was not able to support the interdiffusion between different phases. The matrix of the weld remained primarily aluminium and the EDS examination results show that the concentration of aluminium increases when moving away from the fusion boundary into the weld pool.
Figure 4.18 Chemical distributions across weld fusion line into weld pool (1.5 kW laser power).

With an increase of laser power to 1.5 kW, the microstructures at the fusion line and in the weld pool are different from the laser weld made at 1.2 kW. There is no obvious intermetallic layer formed at the fusion line of AISI 316L and Al 1050. Based on figure 4.8 (b) there is a continuous metallic bond (approximately 10 μm thick) formed at the fusion line. The elemental distribution is different from that of the 1.2 kW weld shown in figure 4.17 (b). The elemental distributions vary more slowly with distance from fusion line for the 1.5 kW samples than for the 1.2 kW samples. If there is an intermetallic layer at the fusion line, then the thickness might be expected to increase as the laser power increases. If this supposition is valid, then the chemical distributions inside of weld pool will be similar for both laser powers. However, the EDS results show that in the weld pool, the concentration of aluminium in the 1.5 kW laser weld is almost equal to the concentration of iron (figure 4.18 (b)), while the concentration of aluminium in the 1.2 kW laser weld is higher. This probably occurs because of interdiffusion between the bamboo-leaf phases and aluminium at higher laser power. The bamboo-leaf phases change into the island-like phases shown in figure 4.19. The island-like phases are iron rich and the remaining material is aluminium rich, both phases are homogeneously distributed in the weld pool.

Figure 4.19 The microstructure in the weld pool (1.5 kW).
At 1.7 kW laser power, a clear intermetallic layer formed at the fusion line of the weld with a thickness around 5 µm (figure 4.20). The EDS results indicate that the layer is mainly formed from Fe₂Al. The chemical distribution (figure 4.20 (b)) inside the weld pool was similar to the laser weld made at 1.5 kW.

![Figure 4.20 Chemical distributions across weld fusion line into weld pool (1.7 kW laser power).](image)

With a further increase of the laser power to 1.9 kW, the chemical distribution (figure 4.21 (b)), inside the weld pool differs substantially from laser welds made with lower powers. The phase formed inside the weld pool is constant with approximately 45 at. % iron, 32.5 at. % aluminium, 12.5 at.% chromium and 7.5 at. % nickel. The literature suggests that it is possible to form a high-entropy alloy with this chemical composition [65]. High-enthalpy alloys with simple crystal or amorphous structures are therefore expected to form inside the weld pool.

![Figure 4.21 Chemical distributions at the fusion line (1.9 kW).](image)

Similar chemical distributions were observed in the laser welds made at 2.0 kW (figure 4.22 (b)). Columnar grains grow perpendicularly from the fusion line into the weld. The chemical concentration in a grain is shown in the figure 4.22. The small changes between 30 and 110 µm in figure 4.22 (b) occur because the chemical concentration at grain boundaries is slightly different from the chemical concentration.
inside the grains. Comparing figures 4.22 (b) and 4.21 (b), the aluminium concentration in the laser weld made at 2.0 kW is lower than in the laser weld made at 1.9 kW, which may be caused by increased dilution. As the laser power increase to 2.0 kW more stainless steel substrate is melted and mixed with the filler metal (Al 1050), the relative aluminium concentration therefore falls.

Figure 4.22 Chemical distributions across weld fusion line (2.0 kW laser power).

4.4 Results from XRD examinations

The experimental samples were examined using X-Ray diffraction with CoKα radiation. Figure 4.23 shows an XRD pattern of a solid-state diffusion bond at 640 °C, whilst figure 4.24 shows an XRD pattern of a laser weld made at 1.9 kW. Because the diameter of the XRD spot (1 mm) was larger than the thickness of the intermetallic layer of interest (~20 µm thick), signals from the matrix of the base metal (AISI 316L and aluminium) are stronger than the signals from the intermetallic layers. To determine if the expected intermetallic compounds (FeAl₃, Fe₂Al₅ and FeAl) appeared in the intermetallic layer, it is helpful to study published XRD patterns from iron-aluminium intermetallic compounds. Standard iron and aluminium XRD patterns [66-67] are provided in figure 4.25 to help distinguish the XRD pattern that came from intermetallic layers in figure 4.23. The positions of X-Ray peaks for intermetallic compounds are pointed out with red arrows in figures 4.23 and 4.24 [68-74].

XRD patterns from the solid-state diffusion bond confirmed that intermetallic compounds formed at the interface of aluminium and stainless steel. The chemical proportions of different intermetallics were determined from EDS results. FeAl₃ and Fe₂Al₅ are the intermetallic compounds mainly present in the intermetallic layers; the relevant XRD patterns in this work match those in the literature [66-74]. The chromium and nickel aluminides did not appear in the XRD pattern because their volume fractions were far lower than those of iron aluminides.
XRD patterns in figure 4.24 indicate that Fe$_{1.3}$Al$_{0.7}$ formed in the bead-on-plate laser weld, having a Pearson’s B2 crystal structure. In this crystal structure, chromium and nickel atoms can substitute iron atoms due to similar atomic radii. Based on the chemical concentration of chromium and nickel, intermetallics containing these elements should also be detected with X-Ray diffraction; however, the XRD pattern only shows Fe and Al. It is possible that the similar atomic radii of iron, chromium and nickel were identified as iron in XRD patterns. The high-entropy alloys reported have a simple crystal structure [65], this indicates that a FeAlCrNi alloy forms in the laser weld. Supporting arguments are provided in the next chapter (section 5.2).
Figure 4.25 Standard XRD patterns, a) Aluminium; b) Iron [66-67].
Chapter 5

Discussions

The evolution of the intermetallic compounds and intermetallic layers at the interface of aluminium and stainless steel is expected in the solid-state diffusion bonding experiments. From the intermetallic compound formation to the growth of the intermetallic layers, the processes can be characterized in several distinct stages. In this work, five different stages are identified. The first stage involves the breaking down of oxide layers on the surface of aluminium by thermal expansion and compression force, which is introduced by the clamping device designed in this work. Pure aluminium is compressed through the broken oxides and forced into contact with the Cr₂O₃ on the stainless steel surface. The second stage involves the reaction of the pure aluminium with the oxide layer on the surface of the stainless steel. A thermite reaction is expected during the heating process and chemical reaction energy is absorbed by the surrounding material. The third stage is characterised by atomic interdiffusion at the interface between aluminium and stainless steel. Aluminium atoms diffuse into the austenitic stainless steel and iron, chromium and nickel atoms diffuse into the aluminium until the limiting solubilities are reached. The mobility of these atoms determines which elements can reach saturation solubility firstly. The fourth stage involves mixed intermetallic compound formation at the interface. After the limiting solubilities are reached, chemical reactions take place and interactions between different elements ultimately lead to mixed intermetallic compound formation. In the fifth stage, two different intermetallic layers appear at the interface of the aluminium and the stainless steel. Mixed intermetallic compounds construct the first intermetallic layer, which grows as temperature increases. But the thickness of this layer is limited by the chemical concentration of the different elements, which causes the second intermetallic layer to grow on top of the first layer.

Bead-on-plate laser welding was carried out to observe the reactions between melting aluminium and stainless steel, taking advantage of the highly localized heat density of the laser to study localized intermetallic compounds formation. The high heating rate of the laser makes it possible to study the solid-state diffusion at the fusion line. The high cooling rate makes it possible to study the remaining microstructures of the intermetallic compounds from high temperature in the weld pool and at the fusion line. Because the molten aluminium reacts with the oxide layer on the surface of the stainless steel during laser welding, the oxide layer is easier to remove than during solid-state diffusion bonding. A high laser power increases the size of the weld pool and promotes the dissolution of the aluminium oxide. Mixing of the aluminium with the stainless steel base metal is also increased with higher laser powers. Interactions occur between the aluminium atoms and the atoms from stainless steel, and the lowest Gibbs free energy, determines the intermetallic compound or high-entropy alloy that forms at the fusion line and inside the weld pool.
5.1 Solid-state diffusion bonding

5.1.1 Intermetallic formation

5.1.1.1 Breaking down oxide layer

Stainless steel and aluminium easily form oxide layers in air. Cr₂O₃ and Al₂O₃ are the main oxide compositions on the surface of stainless steel and aluminium, respectively. The hardness of Cr₂O₃ and Al₂O₃ are very high (more than 2000 HV) [75-76], and these oxides cover softer base metals. The elasticity modulus of AISI 316L is higher than Al 1050 (71 and 193 GPa respectively) [76-77].

The oxide layer fracture processes are schematically shown in figure 5.1. The stainless steel and aluminium are compressed by a clamping device, in which the compressive force (P) increases as temperature increases until approximately 50 MPa is reached. The oxide layer on the surface of the aluminium is broken by this compressive force, which is represented by the steps from (a) to (b) in figure 5.1. The aluminium oxide layer breaks rather than the stainless steel because of the lower elastic modulus of aluminium, which leads to easier deformation of the aluminium. The process from (b) to (c) indicates that pure aluminium is compressed through the breaking oxide layer against the oxide layer on the surface of stainless steel. The hard aluminium oxide is then separated by the compressed pure aluminium. This aluminium oxide remains at the interface or dissolves into molten aluminium at high temperatures [61-62].

![Figure 5.1 Schematic diagram of the broken oxide layer.](image)

It is hard to observe the oxide layer break down process during the solid-state diffusion bonding experiments because the oxide layers on the surface of the samples are rather thin (several nm) after polishing. By testing the surface roughness after the experimental samples were compressed at room temperature, the surface profiles may indicate the similarity of the surface roughness produced by the clamping device at high temperature. The rough surface provides potential nucleation sites for the formation of intermetallic compounds i.e., location A in figure 4.1 and 4.2, which grow into both the aluminium and stainless steel. The SEM results reveal the morphologies at the aluminium-stainless steel interface (Figure 5.2).
5.1.1.2 Thermite reaction at the interface of AISI 316 L/Al 1050

5.1.1.2.1 Calculation method

After breaking down the oxide layer, the pure aluminium is compressed against the oxide layer on the surface of the stainless steel. In theory, a thermite reaction should take place before the interdiffusion of the iron, chromium, nickel and aluminium atoms. However, due to the thin oxide layer (Cr$_2$O$_3$) on the surface of SS 316 L, it is also hard to observe this thermite reaction. Theoretical approaches are needed to describe this reaction.

Based on the study of the Cr$_2$O$_3$-Al thermite reaction by Ray et al. [45], a calculation can be made concerning the layer thickness in this work. In their experiment, 15 mg of the Cr$_2$O$_3$-Al sample with different molar ratios were tested [45]. To use the experimental data of the differential thermal analysis (DTA) peak from their work, the mass of the thin Cr$_2$O$_3$ oxide layer in this work needs to be calculated. An assumption needs to be made in order to calculate the reacted mass of this oxide layer. Based on the report from Ohmi et al. [78], the thickness of chromium oxide formed on SS 316 L can be predicted to lie between 10 and 30 nm. A thickness of 15 nm was employed to calculate the mass of the thin Cr$_2$O$_3$ layer in this work because the thickness of the Cr$_2$O$_3$ layer should be close to the minimum thickness (10 nm) under the current experimental conditions (time and temperature). The simple mass calculation can be expressed as

\[
\begin{align*}
M_{\text{Cr}_2\text{O}_3} &= V_{\text{Cr}_2\text{O}_3} \rho_{\text{Cr}_2\text{O}_3} \\
V_{\text{Cr}_2\text{O}_3} &= A_{\text{Cr}_2\text{O}_3} h
\end{align*}
\]

(5.1)

where $M_{\text{Cr}_2\text{O}_3}$ is the mass, $V_{\text{Cr}_2\text{O}_3}$ is the volume, $\rho_{\text{Cr}_2\text{O}_3}$ is the density of Cr$_2$O$_3$, $A_{\text{Cr}_2\text{O}_3}$ is the area of the sample surface and $h$ is the thickness of the oxide layer. The values and calculated mass are shown in table 5.1.
Table 5.1 Mass of the Cr₂O₃ oxide layer [78].

<table>
<thead>
<tr>
<th>A₀₂O₃ (m²)</th>
<th>h (m)</th>
<th>ρ₀₂O₃ (kg m⁻³)</th>
<th>V₀₂O₃ (m³)</th>
<th>M₀₂O₃ (kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.14×10⁻⁴</td>
<td>1.50×10⁻⁸</td>
<td>5210</td>
<td>4.71×10⁻¹²</td>
<td>~2.5×10⁻⁸</td>
</tr>
</tbody>
</table>

As a standard definition from metallurgy, a thermal reaction starts once the decomposed fraction of a reaction is 1 % [79]. In Ray’s study [45], they define the starting point of the thermite reaction in the Cr₂O₃-Al system to be 993 K (figure 5.3), and calculated the relationship between the decomposition fraction α and temperature T for different heating rates as shown in figure 5.4. The molar ratio for the reactants in a completed reaction is 1:9 (Cr₂O₃ : Al) [45], which indicates that the mass of reactants in the present work accounting for 1 % of the reaction is approximately 0.06 mg. The calculated mass is approximately 0.4 % of the mass in the Ray’s experiments [45], which is below the reacted mass required to define the starting point of the reaction. Additionally, as the sensitivity to detect mass changes is only 0.1 mg [79], it is impossible to detect the reaction at such a low level (0.06 mg) with current technologies. Analogy methods are therefore needed if the experimental data from Ray’s work is to be employed.

It is hard to define the start temperature for a reaction but easier to measure the completion temperature. A theoretical deduction based on the completion temperature is used to find the start temperature for this thermite reaction and this is defined as the start point of atomic interdiffusion between the aluminium and the stainless steel.

The calculated mass (0.06 mg) is 1 % of 6 mg Cr₂O₃-Al reactants. In order to apply the data from figure 5.3 and 5.4, 6.0 mg of Cr₂O₃-Al is defined as the completed reaction mass for the thermite reaction. The start temperature is defined as the point where 1 % of the reactants (0.06 mg) has completely reacted. The 6.0 mg total mass of the reactants represents 40 % of the reaction mass (15 mg) in Ray’s work. Therefore, it is reasonable to employ the data from figure 5.4 to determine the start temperature in the present work.

Normally, it is easier to find the relationship between the activation energy and kinetics than to find the start temperature for a reaction. Several methods can be applied to determine the activation energy for a reaction. The traditional method is to use the decomposition fraction to compare the reaction mechanisms graphically, determine the reaction mechanism and calculate the activation energy. A model-free method, or differential thermal analysis (DTA peak), uses the peak temperature without involving the reaction model f(α) to determine the activation energy and reaction mechanism. Mathematically processing the experimental data in the model-free method usually introduces a parameter to calibrate the calculation [80].
Figure 5.3 Determination of DAT peak area due to the aluminothermic reduction of Cr₂O₃ [45].

Figure 5.4 α-T plots for thermite reaction of Cr₂O₃ and Al [45].

This work combines the traditional method with the DTA peak method to calculate the start temperature for the Cr₂O₃-Al thermite reaction, which is compared graphically to different reaction mechanisms at different decomposition fractions to deduce the start temperature form the peak temperature and determine the most appropriate reaction mechanism.

An approximation is proposed to determine the start temperature of the thermite reaction. As equation (2.5) indicates that the slope of the log (g(α)) vs. T-curve should be the same as the slope of the log(P(K)) vs. T-curve, this can be expressed as the slope ratio
\[ \Delta_i = \frac{\log(p(\alpha_2)) - \log(p(\alpha_1))}{T_2 - T_1} \frac{T_2 - T_1}{\log(p(\alpha_2)) - \log(p(\alpha_1))}. \]  

(5.2)

Comparing the root mean square (RMS) of \( \Delta_i \) from different reaction mechanisms (Table 2.3), the minimum value of RMS indicates that the mechanism describes the most appropriate kinetics of the reaction. The relationship between the decomposition fraction \( \alpha \) of the reactants and temperature is calculated based on the mechanism determined by the RMS of \( \Delta_i \), which can be expressed as

\[ RMS(\Delta_i) = \sqrt{\frac{\sum_{i=1}^{n} (\Delta_i - \bar{A})^2}{n-1}}, \quad (i \geq 1, \text{integer}), \]  

(5.3)

where \( \Delta_i \) are the values calculated from equation (5.2), \( \bar{A} \) is the expected average value of \( \Delta_i \), which should ideally be 1.

![Figure 5.5 Calculated results based on average activation energy compared with the data from figure 5.4 [45].](image)

Comparing the calculated results in this work with the results calculated by Ray et al. [45], which are shown in the curves of figure 5.4 and by the red points in figure 5.5, the start temperature of the reaction in this work (933 K) is 60 K lower than the start temperature in Ray’s work (993 K). As shown in figure 5.5, the calculated results match at high temperature and decomposition fraction ranges but not at low temperature. It was reasonable for Ray et al. to define the 993 K as the start temperature in their work because the total reacted mass in their experiments is 15 mg, but it is not applicable in this work. Both calculated results are consistent above 30\% of the decomposition fraction, thus it is valid to use the temperature at 40\% decomposition fraction which represents the completion temperature in the present work to deduce the start temperature. The calculation procedure and an assessment of the validity of the method applied in this work are presented in the next section.
5.1.2.2 Calculation method and its validity

From the theory of thermal analysis (section 2.2.2), the calculation method for the start temperature applied in this work is evaluated. Ozawa et al. [81] reported that the average activation energy for the aluminothermal reduction of Cr₂O₃ is 290 kJ mol⁻¹ (figure 5.6). The activation energy $E_a$ at different decomposition fraction $\alpha$ is applied in the following evaluation processes to calculate the initial reaction temperature.

![Ozawa plots for the aluminothermal reduction of Cr₂O₃ ($q = 5{°C \, min}^{-1}$) [81].](image)

The decomposition fraction $\alpha = 0.2$ occurs at a temperature of 1105 K (see figure 5.4). The $\alpha = 0.2$ curve from figure 5.6 is plotted as the $-\log (P(X))$ curve in figure 5.7. Calculations were carried out for the thermite reaction mechanisms $-\log (g(\alpha))$ curve, over the temperature range 373 to 1105 K, to determine whether these match the experimental ($\alpha = 0.2$) curve. Because the reaction mechanism was not known at the beginning, nine different reaction mechanisms from table 2.3, as suggested by Sharp et al. [82], were employed for the calculation.

Comparing the slopes of these curves (figure 5.7), the average slope ratios are shown in table 5.2, none of them are close to the expected value of 1, indicating that within this temperature range the reaction mechanisms do not match experimental results. In order to find the appropriate mechanism to describe the reaction, the same calculation was repeated for different reaction mechanisms until a slope ratio close to 1 and a temperature close to 1105 K at $\alpha = 0.2$ was determined. Both criteria determine the end of the calculation and the most appropriate reaction mechanism can be obtained. In this case at $\alpha = 0.2$, calculation stops after six repeated calculations and the calculated average slope ratios $\bar{\Delta}$ are shown in table 5.3. As discussed before, the $\bar{\Delta}$
should ideally be 1 but it is impossible in real case. Thus, the mechanism D3 is
determined as the most appropriate mechanism to describe this reaction because the
\( \bar{\Delta} \) of mechanism D3 is closer to 1 than other mechanisms. The lowest \( RMS (\Delta_i) \) value
suggests that most of the points on both curves (\( - \log (P(X)) \) and \( -\log (g(\alpha)) \)) share
the same slope.

![Figure 5.7 Compare different reaction mechanisms with \(- \log (P(X))\).](image)

### Table 5.2 Average \( \bar{\Delta} \) of first calculation.

<table>
<thead>
<tr>
<th>Mechanism</th>
<th>F1</th>
<th>A2</th>
<th>A3</th>
<th>R2</th>
<th>R3</th>
<th>D1</th>
<th>D2</th>
<th>D3</th>
<th>D4</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \bar{\Delta} )</td>
<td>16.3</td>
<td>32.7</td>
<td>49.1</td>
<td>19.7</td>
<td>18.4</td>
<td>12.5</td>
<td>10.7</td>
<td>9.2</td>
<td>10.1</td>
</tr>
</tbody>
</table>

### Table 5.3 \( \bar{\Delta} \) and RMS (\( \Delta_i \))

<table>
<thead>
<tr>
<th>Mechanism</th>
<th>F1</th>
<th>A2</th>
<th>A3</th>
<th>R2</th>
<th>R3</th>
<th>D1</th>
<th>D2</th>
<th>D3</th>
<th>D4</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \bar{\Delta} )</td>
<td>1.976</td>
<td>3.953</td>
<td>5.929</td>
<td>2.546</td>
<td>2.325</td>
<td>1.757</td>
<td>1.430</td>
<td>1.162</td>
<td>1.324</td>
</tr>
<tr>
<td>RMS(( \Delta_i ))</td>
<td>0.993</td>
<td>1.735</td>
<td>2.229</td>
<td>1.247</td>
<td>1.155</td>
<td>0.869</td>
<td>0.657</td>
<td><strong>0.406</strong></td>
<td>0.569</td>
</tr>
</tbody>
</table>

With the appropriate reaction mechanism D3 determined by the calculation above,
similar calculations are repeated to check the consistency between the reaction
mechanism and the data \( T'_{a} \) at different decomposition fractions. Here \( T'_{a} \) represents
the temperature at different decomposition fractions taken from the 5 °C min\(^{-1}\) heating
curve in figure 5.4. The relationship between the reaction mechanism and the
temperature can be derived from equation (5.2) and expressed as

\[
\ln \left( \frac{g(\alpha_2)}{g(\alpha_1)} \right) = \frac{1.0008E_a}{R} \left( \frac{1}{T_{\alpha_1}} - \frac{1}{T_{\alpha_2}} \right) + 1.98 \ln \frac{T_{\alpha_1}}{T_{\alpha_2}}
\]

(5.4)

where \( T_{\alpha_1} < T_{\alpha_2} \), \( \alpha_1 \) and \( \alpha_2 \) are the decomposition fractions; if the reaction
mechanism \( g (\alpha) \) is determined and \( T_{\alpha_2} \) is the completion temperature, then \( T_{\alpha_1} \) can be
deduced from this equation. The calculated temperature based on the mechanism D3 are summarized in table 5.4.

<table>
<thead>
<tr>
<th>Decomposition fraction α %</th>
<th>Calculated $T_{α=20}$ (K)</th>
<th>Experimental data $T_{α}$ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>1058</td>
<td>1075</td>
</tr>
<tr>
<td>20</td>
<td>1095</td>
<td>1105</td>
</tr>
<tr>
<td>30</td>
<td>1117</td>
<td>1125</td>
</tr>
<tr>
<td>40</td>
<td>1134</td>
<td>1140</td>
</tr>
<tr>
<td>50</td>
<td>1156</td>
<td>1155</td>
</tr>
<tr>
<td>60</td>
<td>1174</td>
<td>1165</td>
</tr>
<tr>
<td>70</td>
<td>1185</td>
<td>1183</td>
</tr>
<tr>
<td>80</td>
<td>1200</td>
<td>1200</td>
</tr>
<tr>
<td>90</td>
<td>1217</td>
<td>1230</td>
</tr>
<tr>
<td>95</td>
<td>1228</td>
<td>1250</td>
</tr>
</tbody>
</table>

The comparison in table 5.4 indicates that calculated temperatures at different fractions match the data from figure 5.4 in the temperature range between 1095 K and 1200 K. This also indicates that the determined reaction mechanism is not applicable both at low and high temperatures.

To validate this calculation method, approximations are repeated at different decomposition fractions to deduce the temperature at other fractions; i.e., the reaction mechanism at $α = 0.4$ is used to deduce the temperature at other decomposition fractions. The calculated temperatures are summarized in table 5.5. These show that an error is introduced by this calculation method, but it is less than 5 %. This means that this method can be used to deduce the start temperature of the reaction.

<table>
<thead>
<tr>
<th>α %</th>
<th>$T_e$(K)</th>
<th>$T_{α=20}$ (K)</th>
<th>$T_{α=30}$ (K)</th>
<th>$T_{α=40}$ (K)</th>
<th>$T_{α=50}$ (K)</th>
<th>$T_{α=60}$ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>1075</td>
<td>1058</td>
<td>1041</td>
<td>1085</td>
<td>1032</td>
<td>1061</td>
</tr>
<tr>
<td>20</td>
<td>1105</td>
<td>1095</td>
<td>1085</td>
<td>1092</td>
<td>1077</td>
<td>1112</td>
</tr>
<tr>
<td>30</td>
<td>1125</td>
<td>1117</td>
<td>1114</td>
<td>1122</td>
<td>1107</td>
<td>1120</td>
</tr>
<tr>
<td>40</td>
<td>1140</td>
<td>1134</td>
<td>1136</td>
<td>1146</td>
<td>1140</td>
<td>1144</td>
</tr>
<tr>
<td>50</td>
<td>1155</td>
<td>1156</td>
<td>1155</td>
<td>1165</td>
<td>1150</td>
<td>1169</td>
</tr>
<tr>
<td>60</td>
<td>1165</td>
<td>1174</td>
<td>1172</td>
<td>1183</td>
<td>1169</td>
<td>1178</td>
</tr>
<tr>
<td>70</td>
<td>1183</td>
<td>1185</td>
<td>1189</td>
<td>1202</td>
<td>1186</td>
<td>1204</td>
</tr>
<tr>
<td>80</td>
<td>1200</td>
<td>1200</td>
<td>1206</td>
<td>1217</td>
<td>1205</td>
<td>1218</td>
</tr>
<tr>
<td>90</td>
<td>1230</td>
<td>1217</td>
<td>1226</td>
<td>1221</td>
<td>1226</td>
<td>1242</td>
</tr>
<tr>
<td>95</td>
<td>1250</td>
<td>1228</td>
<td>1239</td>
<td>1254</td>
<td>1239</td>
<td>1247</td>
</tr>
</tbody>
</table>

It is interesting to note that the kinetics of the reaction dose not simply follow one reaction mechanism. In the literature, it is suggested that the reaction follows mechanism F1 [45]. While, it is found that below $α = 0.3$ and above $α = 0.6$ the
kinetics of this thermite reaction follow mechanism D3; the experimental data can better be described by mechanisms F1, D3 or D4 between $\alpha = 0.3$ and $\alpha = 0.6$. The calculated temperature shown in table 5.5 is based on mechanism D3.

In this work, the calculated mass of the Cr$_2$O$_3$–Al reactants (0.06 mg) is approximately 0.4 % of the 15 mg in the Ray’s and Ozawa’ work [62, 81]. The completely reacted mass of the reactants is 6 mg in the present work, and a calculated mass of 1 % of the total reaction mass defines the start of the reaction [79]. Therefore data from the Ray’s and Ozawa’ work at $\alpha = 0.4$ is taken to refer to the completely reacted mass and the start temperature of this thermite reaction is determined. A start temperature of 820 K is deduced from the calculation method discussed above as shown in the figure 5.8.

![Figure 5.8 Calculated initial temperature for the Cr$_2$O$_3$ thermite reaction.](image)

The start temperature of the thermite reaction in this work is calculated to be $820 \pm 25$ K ($547 \pm 25$ °C). As discussed before, the start temperature is the temperature at which the oxide layer is completely removed and interdiffusion between iron, chromium, nickel and aluminium begins. The start temperature should also be the start pointing for the growth of the intermetallic layer. A temperature of 820 K (547 °C) is probably a little high as the intermetallic layer has already been observed at 550 °C (figure 4.4). However the start temperature most likely lies within the lower bounds of the $\pm 25$ °C error bound.
5.1.3 Atomic diffusion

Once the oxide layer (Cr₂O₃) on the stainless steel surface is removed, pure aluminium is in contact with the stainless steel. Iron, chromium, nickel and aluminium atoms start to interdiffuse along dislocations, grain boundaries and phase boundaries. These defects are associated with a more open structure and it has been shown experimentally that the jump frequency for atoms migrating along these defects is higher than that for diffusion in the lattice [60]. The roughness on both contact faces of the base metals provides ideal locations for the atomic diffusion. The local atomic concentration at the interface of aluminium and stainless steel is built up by the diffusion of these atoms. The localized concentration increases with time and temperature until the saturation solubilities are reached (table 5.6).

<table>
<thead>
<tr>
<th>Element</th>
<th>Maximum solid solubility in aluminium Cₘₐₓ (at. %)</th>
<th>The maximum solubility of aluminium in austenitic stainless steel is 7.1 at. %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>0.025 at 928K</td>
<td></td>
</tr>
<tr>
<td>Cr</td>
<td>0.37 at 934K</td>
<td></td>
</tr>
<tr>
<td>Ni</td>
<td>0.023 at 913K</td>
<td></td>
</tr>
</tbody>
</table>

Because the local atomic concentration is affected by atomic mobility, which element reaches the limiting solubility firstly determines the initial intermetallic compounds formed. The mobility is employed to describe the atomic diffusion process. The mobility can be calculated with

\[
D_N = M_bRT \\
\log(M_b) = \log \left( \frac{D_N}{RT} \right) - \left( \frac{Q_0}{RT} \right) \log(e)^
\]

where \(N\) is the metal which the atoms diffuse into, \(D_N\) is the diffusion coefficient, \(M_b\) is the atomic mobility, \(Q_0\) is the atomic diffusion activation energy, \(R\) is gas constant and \(T\) is the absolute temperature. The diffusion coefficient \(D_N\) and diffusion activation energy in stainless steel and aluminium are shown in table 5.7.

<table>
<thead>
<tr>
<th>Atom</th>
<th>Activation energy in γ- Fe (kJ mol⁻¹)</th>
<th>Activation energy in aluminium (kJ mol⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>284.1</td>
<td>193</td>
</tr>
<tr>
<td>Cr</td>
<td>335</td>
<td>257</td>
</tr>
<tr>
<td>Ni</td>
<td>282.5</td>
<td>Varies with temperature</td>
</tr>
<tr>
<td>Al</td>
<td>184</td>
<td>142</td>
</tr>
</tbody>
</table>

The mobility of the atoms calculated from the equation (5.5) is shown in figure 5.9, in which atomic mobility increases with temperature. The mobility of aluminium atoms
is not compared here because the solubility of aluminium atoms in austenitic stainless steel is much higher than that of iron, chromium and nickel atoms in aluminium. The mobility is affected by the atomic radii. The atomic radii of aluminium is larger than the radii of Fe, Cr and Ni atoms, which means that the appearance of intermetallic compounds formed on stainless steel side is slower than on the aluminium side (figure 4.4). This indicates that the growth of the intermetallic layer on the stainless side is slower than the intermetallic layer on the aluminium side (figure 4.6 (a)).

![Graph showing the relationship between atomic mobility and temperature in aluminium.](image)

**Figure 5.9** The relationship between atomic mobility and temperature in aluminium.

Comparing the mobility of iron, chromium and nickel in aluminium,

\[-\log(M_b)(Ni) < -\log(M_b)(Fe) < -\log(M_b)(Cr).\]  \hspace{1cm} (5.6)

thus, \( M_b(Cr) < M_b(Fe) < M_b(Ni) \). Nickel atoms therefore diffuse faster than the iron or chromium atoms in aluminium.

### 5.1.4 Formation of the mixed intermetallic compounds

Once the saturated solid solubility of the iron, chromium and nickel atoms in aluminium is reached, chemical reaction (2.4) occurs and an intermetallic compound will form at the interface of aluminium and stainless steel. Based on the binary diagrams of Fe–Al, Cr–Al, and Ni–Al [85], the chemical compounds FeAl₃, CrAl₇
and NiAl₃ will firstly appear on the aluminium side. But, the formation of intermetallic compounds is not only determined by the limited atomic solubility but also by the minimum Gibbs free energy. Both govern the first appearance of the intermetallic compounds [86]. It is even possible to form alloys with multi-elements, of which the Gibbs free energy is lower than the intermetallic compounds [65]. Table 5.8 provides the Gibbs free energy of different intermetallic compounds in the liquid state.

Table 5.8 Gibbs free energy of formation of intermetallic compounds [65].

<table>
<thead>
<tr>
<th>Intermetallic compound</th>
<th>ΔG° kJ mol⁻¹</th>
<th>Intermetallic compound</th>
<th>ΔG° kJ mol⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al₃Fe</td>
<td>-8.07</td>
<td>CrAl₁₁</td>
<td>-4.09</td>
</tr>
<tr>
<td>Al₃Fe₂</td>
<td>-8.89</td>
<td>Cr₂Al₁₁</td>
<td>-4.90</td>
</tr>
<tr>
<td>Al₂Fe</td>
<td>-9.66</td>
<td>Ni₂Cr</td>
<td>-5.90</td>
</tr>
<tr>
<td>AlFe</td>
<td>-11.10</td>
<td>Ni₃Al</td>
<td>-17.40</td>
</tr>
<tr>
<td>AlFe₃</td>
<td>-8.60</td>
<td>Ni₃Al₃</td>
<td>-21.40</td>
</tr>
<tr>
<td>Al₂Fe₉</td>
<td>-6.89</td>
<td>Ni₃Al₃</td>
<td>-21.40</td>
</tr>
<tr>
<td>Al₃Fe</td>
<td>-5.21</td>
<td>NiAl₃</td>
<td>-16.50</td>
</tr>
<tr>
<td>Cr₂Al</td>
<td>-9.01</td>
<td>Ni₃Fe</td>
<td>-1.16</td>
</tr>
<tr>
<td>Cr₃Al₈</td>
<td>-9.20</td>
<td>NiFe</td>
<td>-1.55</td>
</tr>
<tr>
<td>Cr₄Al₉</td>
<td>-8.19</td>
<td>NiFe₃</td>
<td>-1.16</td>
</tr>
<tr>
<td>CrAl₄</td>
<td>-6.05</td>
<td>CrFe</td>
<td>-1.45</td>
</tr>
</tbody>
</table>

Combining the atomic mobility (figure 5.9), the maximum solid solubility (Table 5.6) and the Gibbs free energy (Table 5.8) to analysis the first appearance of intermetallics formed at the interface. \( M_b (Ni) : M_b (Fe) : M_b (Cr) \approx 100 : 1 : 1 \), which indicates that, when the maximum solid solution of iron in aluminium is reached (\( C_{\text{max(Fe)}} = 0.025 \) at. %), the concentration of nickel \( C_{(Ni)} \) is already over the maximum solid solubility in aluminium (\( C_{\text{max(Ni)}} = 0.023 \) at. %) and the concentration of chromium \( C_{(Cr)} = C_{\text{max(Fe)}} = 0.025 \) at. % is far from the limiting solid solubility in aluminium. It shows that the nickel-aluminium intermetallic compounds will therefore appear before other intermetallic compounds. As the chemical composition of nickel is lower than iron and chromium, and the limiting solubility is reached only in localized positions, nickel-aluminium intermetallics cannot cover the whole interface. Once the saturated solubilities of iron and chromium are reached, other intermetallic compounds form, such as FeAl and Cr₅Al₈, which mix with the nickel-aluminium intermetallics at the interface.

**5.1.5 The formation of the first intermetallic layer**

As the thermite reaction removes the Cr₂O₃ oxide at the interface, atomic interdiffusion accelerates the formation of the first intermetallic layer; the formed layer is shown in figure 4.4 (b). The products of the thermite reaction and the
intermetallic compounds govern the composition of this layer. Mixed intermetallic compounds form locally at the interface of aluminium and stainless steel and grow with time and temperature. Due to the high concentration of iron, an excess of iron-aluminium intermetallics (mainly FeAl₃) form on top of the mixed intermetallic layer as shown in figure 4.5 (a).

During the first intermetallic layer formation process, different intermetallic compounds appear. This process can be schematically shown in figure 5.10. Based on binary diagrams between Al-Fe, Al-Ni and Al-Cr, FeAl or Fe₂Al tend to form on the stainless steel side as aluminium diffuses into the stainless steel. FeAl₃, NiAl₃ and CrAl₇ tend to form on the aluminium side as iron, chromium and nickel diffuse into the aluminium. These intermetallic compounds appear at localized positions where the saturated solubilities are reached (see figure 5.10 (a)).

Based on the atomic mobility and the Gibbs free energy, NiAl₃ appears before the Fe₂Al, FeAl, FeAl₃ and CrAl₇; iron-aluminides appear before CrAl₇. The intermetallics grow as time and temperature increase. Due to the high concentration of iron, excessive iron-aluminium intermetallics (FeAl₃) will precipitate around the phase boundaries of the FeAl, NiAl₃ and CrAl₇ on the aluminium side (see figure 5.10 (b)). FeAl also can change into FeAl₃ as temperature increases [69]. The growth of NiAl₃ and CrAl₇ is restricted by the formation of FeAl₃, because the FeAl₃ becomes a barrier for the atomic diffusion of Ni, Cr and Al.

The FeAl₃ keeps growing while the growth of the other intermetallic compounds is restrained. When FeAl₃ grows to a certain point where grain boundaries contact each other, the first intermetallic layer appears which contains intermetallics FeAl₃, NiAl₃ and CrAl₇. Interdiffusion occurs between this layer and the base metals and also occurs between intermetallics FeAl₃, NiAl₃ and CrAl₇ [86], as a result FeAl₃ changes into Fe₂Al₅ (see figure 5.10 (c)). The first intermetallic layer therefore primarily contains Fe₂Al₅ with mixed intermetallic compounds.

![Figure 5.10 schematic formation process of the first intermetallic layer.](attachment:image.png)

The chemical distribution and crystal structure across the intermetallic layers were examined with EDS and XRD respectively. It is confirmed that Fe₂Al₅ is the main intermetallic compound in this layer mixed with NiAl₃ and CrAl₇.
5.1.6 The growth of the intermetallic layers

The phase diagram of pure aluminium and iron indicates that the Fe$_2$Al$_5$ forms after FeAl$_3$ (figure 5.11) as iron atoms diffuse into the aluminium side [87].

![Fe-Al equilibrium phase diagram](image)

**Figure 5.11 Fe-Al equilibrium phase diagram [87].**

At the interface of aluminium and stainless steel, due to the first intermetallic layer acting as a barrier for the diffusion of Ni and Cr atoms and the low chemical concentration of these atoms compared to iron, the second intermetallic layer grows on the top of the first layer. Both layers grow as time progresses and temperature increases. In addition to the chemical concentration difference between these two layers, there is a limitation for the growth of the first layer because this layer becomes a barrier for aluminium atoms, which can no longer diffuse into the stainless steel.

5.1.6.1 The growth of intermetallic layers (the Lorier system)

Based on the Lorier system (see section 2.2.1), the growth of the initial (first) intermetallic layer is limited by equation (2.3). As Dybkov [4, 8, 88] reported, the initial layer is porous, the reasons are not reported but this may be primarily caused by the remaining Al$_2$O$_3$ produced by the thermite reaction (2.4) at the interface; the mixed intermetallic compound may also be responsible.

The thickness of the first layer observed (figure 4.6) in this work is in the order of $10^{-5}$ m. Thus, with equation (2.3), parameter $k_1$ is calculated and is approximately in the order of $10^{-13}$ m$^2$ s$^{-1}$.

The secondary intermetallic layer grows on top of the first layer. At the interface of
the first layer and the second layer, there is a transition zone with mixed intermetallic compounds formed from both layers. As a result, it is hard to indentify the thickness of this transition zone, the thickness of the second layer was measured as the whole thickness of the intermetallic layer less the maximum thickness \(10^{-5}\ m\) of the first intermetallic layer. The relationship between thickness of the second intermetallic layer and time can be established based on equation (2.3) and is shown in figure 5.12.

![Figure 5.12 Relationship between the secondary intermetallic layer and time.](image)

\[
y = K_0(t - t_0) + y_0 \ [10^{-6} \ m]
\]

\[K_0 = 0.00478 \pm 2.75549E - 4\]

\[y_0 = -8.66596 \pm 0.8986\]

\[t_0 = 1813 \ (s)\]

Compared to Dybkov’s work [4, 8, 88], the relationship between the thickness of the second intermetallic layer and time is similar, which can be described by

\[
y = 0.00478t + 1.344, \quad (5.7)
\]

where \(y \ [10^{-6} \ m]\) is the thickness and \(t\) is the time for the growth of the second layer.

The diffusion parameter \(k_0\) has the same order as in Dybkov’s work \((1 \times 10^{-8})\) [8], but the value of \(k_0\) is smaller in this work, because the experimental holding temperature is different. The relationship between the intermetallic layer thickness and time established in Dybkov’s work was from experimental data obtained from stainless steel reacted with molten aluminium at 700 °C. In this work the experiments were carried out in the temperature range between 500 °C and 640 °C; i.e., lower than 700 °C.

### 5.1.6.2 Average thickness approach

To establish the relationship between the thickness of the intermetallic layer and temperature, the average thickness of the intermetallic layers at different temperatures were measured. An Arrhenius empirical relationship is applied, instead of dividing
them into two layers.

\[
\begin{align*}
X_{\text{int}}^2 &= Kt \\
K &= k_{\text{int}} \exp \left( -\frac{Q_{\text{av}}}{RT} \right),
\end{align*}
\]  
(5.8)

which can be expressed as

\[
\begin{align*}
\ln X_{\text{int}} &= \ln \left( \frac{\ln(k_{\text{int}} t)}{2} \right) + \frac{-Q_{\text{av}}}{2RT} = A + \frac{B}{T} \\
A &= \frac{\ln(k_{\text{int}} t)}{2} \\
B &= \frac{-Q_{\text{av}}}{2R}
\end{align*}
\]  
(5.9)

where \( X_{\text{int}} \) is the average thickness of the intermetallic layers, \( k_{\text{int}} \) is the temperature-dependent constant proportional to the interdiffusion coefficient \( D \), \( Q_{\text{av}} \) is the average activation energy for the growth of the intermetallic layers and \( t \) is the atomic diffusion time, which is related to the start temperature calculated in section 5.1.2.2. Figure 5.13 shows the experimental results between the thickness of the intermetallic layer and temperature. The average thickness of the intermetallic layer is measured from the solid-state diffusion bonds.

The average thickness of the intermetallic layers is measured from optical microscopy. The thickness produced at different holding temperatures is subject to a least squares fit to acquire the value \( A \) \([10^6 \text{ m}] \) and \( B \) \([\text{K}] \) in equation (5.8). The calculated relationship between the intermetallic layer thickness and the temperature is shown in figure 5.14. The average activation energy for the growth of the intermetallic layer is 250 kJ mol\(^{-1}\), which lies within the range of 166-276 kJ mol\(^{-1}\) consistent with the results found in the literature [8, 63, 64, 88].

![Figure 5.13 Thickness of the intermetallic layer form experiments above 600 °C.](image-url)
Figure 5.14 Calculated results of parameter A and B from equation 5.9.

It was reported that diffusion parameter $k_{int}$ is proportional the interdiffusion coefficient of the stainless steel and aluminium [45, 63], but the specific relationship between $k_{int}$ and interdiffusion coefficient has not been reported. The relationship can be established if the interdiffusion coefficient is known. The interdiffusion coefficient is calculated to predict the thickness of the intermetallic layer in the next section.

5.1.7 Interdiffusion coefficient

Based on the deduction in section 2.3, the interdiffusion coefficient can be calculated with equation (2.29). The atomic diffusion coefficients of iron, chromium and nickel in aluminium and aluminium in austenitic stainless steel were reported by Minamino et al. [89] and Hirano et al. [90]. The diffusion coefficients were generalized by these authors and expressed as

$$
\begin{align*}
D_a &= 1350 \times 10^{-5} \exp\left(\frac{-193000}{RT}\right) \\
D_b &= 29000 \times 10^{-5} \exp\left(\frac{-257000}{RT}\right) \\
D_c &= 2.9 \times 10^{-12} \exp\left(\frac{-157000}{RT}\right) \\
D_d &= 17.1 \times 10^{-5} \exp\left(\frac{-184000}{RT}\right)
\end{align*}
$$

(5.10)

where the numerical values of the pre-factors were directly taken from the literature[89, 90]. The chemical concentrations of iron, chromium, nickel and aluminium at the interface of the solid state diffusion bonds were acquired from the results of the EDS examination. The average atomic chemical concentrations of these atoms at 500 and 640 °C are summarized in table 5.9.
Table 5.9 Chemical concentration (at. %) at the interface of Al 1050/AISI 326L.

<table>
<thead>
<tr>
<th>T (K)</th>
<th>Fe (C₀)</th>
<th>Cr (C₀)</th>
<th>Ni (C₀)</th>
<th>Al (C₀)</th>
<th>Comment</th>
</tr>
</thead>
<tbody>
<tr>
<td>823</td>
<td>18.78</td>
<td>5.14</td>
<td>2.54</td>
<td>73.54</td>
<td>Intermetallic layer</td>
</tr>
<tr>
<td>913</td>
<td>25.23</td>
<td>7.07</td>
<td>2.16</td>
<td>65.54</td>
<td>First intermetallic layer</td>
</tr>
<tr>
<td></td>
<td>14</td>
<td>4.68</td>
<td>1.32</td>
<td>80</td>
<td>Second intermetallic layer</td>
</tr>
</tbody>
</table>

\[ X_a = C_a / C_0, \quad X_b = C_b / C_0, \quad X_c = C_c / C_0, \quad \text{and} \quad X_d = C_d / C_0 \]

\[ X_a, X_b, X_c, \text{and} \quad X_d \] are concentration fractions. \( C_0 \) is the summation of the atomic concentration of all the elements which is equal to 1. Thus, \( X_a = C_a, \quad X_b = C_b, \quad X_c = C_c, \text{and} \quad X_d = C_d \). With equation (2.25), the ratios of \( \beta / \varepsilon, \gamma / \varepsilon \text{and} \lambda / \varepsilon \) can be determined and are summarized in table 5.10.

Table 5.10 The calculation parameters for equation (2.29).

<table>
<thead>
<tr>
<th>T (K)</th>
<th>( \beta / \varepsilon )</th>
<th>( \gamma / \varepsilon )</th>
<th>( \lambda / \varepsilon )</th>
<th>Comment</th>
</tr>
</thead>
<tbody>
<tr>
<td>823</td>
<td>0.255</td>
<td>0.073</td>
<td>0.064</td>
<td>Intermetallic layer</td>
</tr>
<tr>
<td>913</td>
<td>0.385</td>
<td>0.108</td>
<td>0.033</td>
<td>First intermetallic layer</td>
</tr>
<tr>
<td></td>
<td>0.175</td>
<td>0.058</td>
<td>0.017</td>
<td>Second intermetallic layer</td>
</tr>
</tbody>
</table>

Taking data from Table 5.9 into equation (5.10), the diffusion coefficients of iron, chromium and nickel in aluminium and aluminium in the austenitic stainless steel can be calculated. Taking data from table 5.10 into equation (2.29), the interdiffusion coefficient between the aluminium and the stainless steel can be calculated. The calculated diffusion and interdiffusion coefficients are summarized in table 5.11.

Table 5.11 Calculated diffusion and interdiffusion coefficients (m² s⁻¹).

<table>
<thead>
<tr>
<th>T (K)</th>
<th>Fe ( (D_a) )</th>
<th>Cr ( (D_d) )</th>
<th>Ni ( (D_d) )</th>
<th>Al ( (D_d) )</th>
<th>( \bar{D} )</th>
<th>Comment</th>
</tr>
</thead>
<tbody>
<tr>
<td>823</td>
<td>7.49×10⁻¹³</td>
<td>1.39×10⁻¹⁷</td>
<td>2.9×10⁻¹³</td>
<td>3.53×10⁻¹⁶</td>
<td>1.33×10⁻¹⁴</td>
<td>Intermetallic layer</td>
</tr>
<tr>
<td>913</td>
<td>1.21×10⁻¹³</td>
<td>5.64×10⁻¹⁶</td>
<td>3.65×10⁻¹³</td>
<td>5.02×10⁻¹⁵</td>
<td>3.17×10⁻¹⁴</td>
<td>First intermetallic layer</td>
</tr>
<tr>
<td></td>
<td>1.21×10⁻¹³</td>
<td>5.64×10⁻¹⁶</td>
<td>3.65×10⁻¹³</td>
<td>5.02×10⁻¹⁵</td>
<td>1.59×10⁻¹⁴</td>
<td>Second intermetallic layer</td>
</tr>
</tbody>
</table>

As the intermetallic layer grows into the aluminium, the relationship with the interdiffusion coefficient can be expressed as

\[
\begin{align*}
\left\{ \begin{array}{l}
X_{\text{int}} \approx \sqrt{\bar{D}t} \\
t = t_1 + t_2 + t_3,
\end{array} \right.
\end{align*}
\] (5.11)

where \( t_1, t_2, \text{and} t_3 \) are the time of heating, holding and cooling during solid state diffusion bonding experiments (Table 5.12). A start temperature of 798 K close to the lower bound of the range calculated in section 5.1.2, is used to determine the growth time of the intermetallic layer. The heating time \( t_1 \) is taken from 798 K to the maximum experimental temperature. Holding time \( t_2 \) is 45 min (2700 s). Cooling time \( t_3 \) is taken from the maximum experimental temperature to 798 K, below which intermetallics cannot readily form [63]. This means that the interdiffusion virtually
stops below this temperature.

<table>
<thead>
<tr>
<th>$T$ (K)</th>
<th>$t_1$ (s)</th>
<th>$t_2$ (s)</th>
<th>$t_3$ (s)</th>
<th>Comment</th>
</tr>
</thead>
<tbody>
<tr>
<td>823</td>
<td>300</td>
<td>2700</td>
<td>1800</td>
<td>Intermetallic layer</td>
</tr>
<tr>
<td>913</td>
<td>1380</td>
<td>2700</td>
<td>1800</td>
<td>First intermetallic layer</td>
</tr>
<tr>
<td></td>
<td>480</td>
<td>2700</td>
<td>1800</td>
<td>Second intermetallic layer</td>
</tr>
</tbody>
</table>

The calculated value of $\sqrt{Dt}$ at 823 K is approximately 7.99 μm and at 913 K is approximately 22.55μm. While the average thickness of the intermetallic layer measured from the experiments at 823 K and 913 K were 7.89 μm and 22.67 μm, respectively. The calculated thicknesses of the intermetallic layer match the experimental results.

The interdiffusion coefficient can also be calculated from Fick’s second law. Based on Fick’s second law, the interdiffusion coefficient can be calculated from the error function

$$X_{AI} = X_{AI1} + \left(\frac{X_{AI2} - X_{AI1}}{2}\right) \left[1 + erf\left(\frac{d}{\sqrt{Dt}}\right)\right]$$

(5.12)

where $X_{AI}$ is the composition fraction of aluminium at distance $d$ ($-\infty < d < +\infty$) from weld interface which can be determined from EDS results; $X_{AI1}$ is the composition fraction of aluminium in one component and $X_{AI2}$ is the composition fraction of aluminium in another component. At 823 K, because the intermetallic layer formed between the AISI 316L and Al 1050, $X_{AI}$ represents the aluminium fraction in stainless steel which is zero. $X_{AI2}$ is the fraction of aluminium in aluminium which is one. At 913 K, the second intermetallic layer formed between the first intermetallic layer and Al 1050, therefore the $X_{AI}$ represents the aluminium fraction in the first intermetallic layer which is 0.7 and $X_{AI2}$ is aluminium fraction in aluminium which is one. Putting the data into the error function (5.12), the interdiffusion coefficients are calculated and shown in table 5.13. These calculated interdiffusion coefficients are close to the results calculated from interdiffusion theory (see table 5.11).

<table>
<thead>
<tr>
<th>$T$ (K)</th>
<th>$d$ (m)</th>
<th>$X_{AI}$</th>
<th>$X_{AI1}$</th>
<th>$X_{AI2}$</th>
<th>Comment</th>
<th>$D$</th>
</tr>
</thead>
<tbody>
<tr>
<td>823</td>
<td>$7.89 \times 10^{-6}$</td>
<td>0.73</td>
<td>0</td>
<td>1</td>
<td>Intermetallic layer</td>
<td>$1.43 \times 10^{-14}$</td>
</tr>
<tr>
<td>913</td>
<td>$10.68 \times 10^{-6}$</td>
<td>0.70</td>
<td>0</td>
<td>1</td>
<td>First intermetallic layer</td>
<td>$3.02 \times 10^{-14}$</td>
</tr>
<tr>
<td></td>
<td>$11.51 \times 10^{-6}$</td>
<td>0.94</td>
<td>0.70</td>
<td>1</td>
<td>Second intermetallic layer</td>
<td>$1.84 \times 10^{-14}$</td>
</tr>
</tbody>
</table>
5.2 Laser welding

There are many interesting physical phenomena occurring in the bead-on-plate laser welding experiments. The main interest in this work is to study the behaviour of intermetallic compounds and intermetallic layers at the fusion line and in the weld pool.

5.2.1 Fusion line and weld pool of the laser weld

At the fusion line of the laser weld made at a power of 1.2 kW, a crack appears in the brittle intermetallic next to fusion line between aluminium and stainless steel (figure 4.7). The hardness of the dark phases in figure 4.7 (b) is over 700 HV, while the hardness of the light phase is around 50 HV. Due to the low heat input and the fast cooling after laser welding, there is not enough time for the interdiffusion between the dark and light phases around the fusion boundary and in the weld pool. Due to the low solubility of iron in molten aluminium, the intermetallic compounds form and solidify along the maximum temperature gradient, and a bamboo-leaf like microstructure forms in the weld.

![Weld Pool Image](image)

*Figure 5.15 the intermetallic compound flowing into weld (1.5 kW laser power).*

By increasing the laser power to 1.5 kW, a completely different microstructure appears in the weld pool (figure 4.8). The crack moves away from the fusion line and islands-like phases form in the weld pool. A continuous metallic bond forms at the fusion line and the hardness at the fusion line within the red line in figure 4.8 is around 350-450 HV. This indicates that the metallic bond does not contain brittle intermetallics. In the weld pool, intermetallic compounds should appear where the saturated solubilities of iron, chromium and nickel are initially obtained. In figure 4.8, the hardness of the dark phase reduced to around 550 HV and the hardness of the light phase increases to around 600 HV, which indicates that there is interdiffusion between
these phases at the higher laser power. The interdiffusion changes the chemical compositions and results in the formation of new phases. Due to diffusion between the dark and light phases, the intermetallic compound changes from a bamboo-leaf shape to an island shape microstructure (figure 5.15). Because the density of the aluminium is lighter than stainless steel, the dark phases observed by optical microscopy appear light in the SEM image figure 5.15, and the light phases appear dark.

In order to observe the localized reaction between molten aluminium and molten stainless steel, 1.7, 1.9 and 2.0 kW laser powers were also employed. The welds produced under these powers are shown in figures 4.9 to 4.12.

As the laser power increase, more stainless steel substrate has been melt and mixed with the filler metal. To describe the mixing of a weld, the mixing ratio between $M_r$ [89] is defined as

$$M_r = \frac{\text{weight of molten parent material}}{\text{total weight of molten material}} \times 100\%.$$  \hfill (5.13)

By measuring the cross sectional areas of the weld, the mixing ratio can be calculated. $M_{1.7}$ and $M_{2.0}$ are 74.7 % and 89.9 % respectively; the subscript 1.7 and 2.0 indicates the laser power applied. The measuring method is based on the position of the original stainless steel surface as a reference line; the area above this line is aluminium and below is stainless steel.

In figures 4.9 (d) and 4.12 (d), no obvious intermetallic compound formation occurs at the fusion line. But it is possible that an intermetallic layer can be formed at the edge of the weld (figure 4.10), because the power density of the laser is lower at the edge. Intermetallic layers appear at lower laser power shown in the 1.2 kW and 1.5 kW laser welds. It is interesting to note that during solidification new grains grow perpendicularly to the surface of the fusion line and into the weld pool (figure 4.12 (d)).

In the weld pool of the 2.0 kW laser weld, the oxides on the stainless steel may be driven by the fluid flow into the weld pool as can be seen in figure 4.12 (c). It is possible that some of the dark regions in figure 4.12 (c) are pores formed by gas trapped inside the weld or are cracks introduced during cooling. The aluminium diffusion along molten grain boundaries of stainless steel and inside the stainless steel is shown in figure 4.13. This is expected because during solidification, grains of the stainless steel will solidify before the low melting point aluminium.

The new grains, which are either intermetallics or an FeAlCrNi alloy can be observed in the 1.9 and 2.0 kW laser welds, but cannot be easily distinguished experimentally (see figure 4.12(d)). However, a theoretical analysis may be able to provide some explanation, although more experimental evidence is needed to support the theory.
5.2.2 Thermodynamic analysis

The alloy world can be divided into three fields based on the effect of the entropy of mixing (figure 5.16). Low-entropy alloys are traditional alloys; medium-entropy alloys are the alloys with 2-4 major elements; and high-entropy alloys are the alloys with at least five major elements. The high entropy effect of promoting the occurrence of the disordered solution phase is essentially found in the high-entropy alloy field and should be less prevalent in the medium-entropy alloys. This means that medium-entropy is a transition stage which can contain both intermetallics and high-entropy alloys. The stabilization of a simple solid solution phase is very significant in terms of the microstructure and properties which can be obtained in these materials [91].

![Figure 5.16 The alloy world divided by the entropy of mixing [91].](image)

High-entropy alloys are defined to have at least 5 principal metallic elements, each of which has an atomic percentage between 5 % and 35 %. These alloys form simple solid solutions due to the large configurationally entropy. It is reported that a high-entropy alloy or high-entropy alloys with multiple principal elements and multi-component alloys with high entropy of mixing can be produced [92-96]. These alloys have either simple crystal structures; i.e., FCC or BCC, which can precipitate easily at a nano-level, or an amorphous structure with high hardness and compressive strength, superior resistance to temperature softening, wear, oxidization and corrosion [97-101].

A theory has been developed from Miedema’s model [102] to calculate the enthalpy of intermetallic compounds, which has been modified by Ding et al. [103] and can be expressed as

$$\Delta H_{ij} = F(x_i, V) q(x_i, n_{ws}) \frac{q}{p(\Delta n_{ws}^{1/3})} - (\Delta \Phi)^2 - \alpha \left( \frac{r}{p} \right).$$  \hspace{1cm} (5.14)

The functions in equation (5.13) can be described as
\[ F(x_i, V) = x_i^2 x_j^2, \]  
\[ x_i^2 = x_i V_{ia}^{2/3} / (x_i V_{ia}^{2/3} + x_j V_{ja}^{2/3}), \]  
\[ x_j^2 = x_j V_{ja}^{2/3} / (x_i V_{ia}^{2/3} + x_j V_{ja}^{2/3}), \]  
\[ V_{ia}^{2/3} = V_i^{2/3} [1 + \mu_i x_j (\phi_i - \phi_j)], \]  
\[ V_{ja}^{2/3} = V_j^{2/3} [1 + \mu_j x_i (\phi_j - \phi_i)], \]  
\[ g(x_i, n_{ws}) = \frac{2x_i V_{ia}^{2/3} + 2x_j V_{ja}^{2/3}}{(n_{ws}^{1/3})_i^{-1} + (n_{ws}^{1/3})_j^{-1}}, \]

where \( \phi_i \) and \( \phi_j \) are electronegativities, \( n_{ws} \) and \( n_{ws} \) are the electron densities, and \( V_i \) and \( V_j \) are the molar volumes of \( i \) and \( j \) elements respectively; \( p, q, r, a, \) and \( \mu \) are the empirical parameters determined by Miedema et al. [102-104]. By choosing the parameters appropriately, the enthalpy of the intermetallic compounds can be calculated. The calculated enthalpy by Li and Zhang [65] is shown in table 5.8. Due to the absence of the elastic and structural contributions in liquids, the mixing entropy changes very little, the calculated enthalpy can be applied as the Gibbs free energy of the compounds.

In the solid solution, the Gibbs free energy is determined by the mixing enthalpy and entropy. The enthalpy can be described by a regular melt model [105-106] as

\[ \Delta H_{\text{mix}} = \sum_{i=1}^{n} \sum_{i \neq j}^{n} \Omega_{ij} c_i c_j, \]  

where \( \Omega_{ij} \) (\( = 4 \Delta H_{\text{mix}}^{AB} \)) is the regular melt model interaction parameter between different elements, \( c_i \) and \( c_j \) are the atomic percentages of the \( i \)th and \( j \)th elements respectively and \( \Delta H_{\text{mix}}^{AB} \) is the mixing enthalpy of the binary liquid alloy.

The mixing entropy follows Boltzmann’s hypothesis [107] in n-element regular solution alloys, which can be described as

\[ \Delta S_{\text{mix}} = -R \sum_{i=1}^{n} C_i' \ln C_i', \]
where $\sum_{i=1}^{l} c_i' = 1$, $c_i'$ is the mole percentage of a component, and $R$ is the gas constant.

Thus, the Gibbs free energy for the multi-element alloys can be expressed as

$$\Delta G = \Delta H_{\text{mix}} - T \Delta S_{\text{mix}},$$  \hspace{1cm} (5.23)

where $T$ is the temperature.

The calculated interaction parameter $\Delta H_{\text{AB}}^{\text{mix}}$ of Miedema’s model for the atomic pairs between Al, Cr, Fe and Ni [108], applied in this work are shown in table 5.14.

<table>
<thead>
<tr>
<th>Element</th>
<th>Cr</th>
<th>Fe</th>
<th>Ni</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>-10</td>
<td>-11</td>
<td>-22</td>
</tr>
<tr>
<td>Cr</td>
<td>-1</td>
<td>-7</td>
<td></td>
</tr>
<tr>
<td>Fe</td>
<td></td>
<td>-2</td>
<td></td>
</tr>
</tbody>
</table>

The average chemical compositions at the fusion line and in the weld pool from EDS results are summarized in tables 5.15 and 5.16, indicating that iron, chromium, nickel and aluminium are the principal elements in laser weld. The mixing enthalpy and entropy can be calculated from equations (5.21) and (5.22), and the results are shown in table 5.17.

<table>
<thead>
<tr>
<th>Laser power</th>
<th>Fe</th>
<th>Cr</th>
<th>Ni</th>
<th>Al</th>
<th>Mo</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.2 kW</td>
<td>50.64</td>
<td>14.93</td>
<td>5.62</td>
<td>26.53</td>
<td>0.88</td>
</tr>
<tr>
<td>1.5 kW</td>
<td>46.56</td>
<td>11.65</td>
<td>6.85</td>
<td>28.41</td>
<td>0.57</td>
</tr>
<tr>
<td>1.7 kW</td>
<td>55.34</td>
<td>14.87</td>
<td>7.26</td>
<td>21.48</td>
<td>0.92</td>
</tr>
<tr>
<td>1.9 kW</td>
<td>54.68</td>
<td>14.16</td>
<td>7.26</td>
<td>23.46</td>
<td>0.44</td>
</tr>
<tr>
<td>2.0 kW</td>
<td>63.03</td>
<td>17.04</td>
<td>7.98</td>
<td>11.03</td>
<td>0.93</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Laser power</th>
<th>Fe</th>
<th>Cr</th>
<th>Ni</th>
<th>Al</th>
<th>Mo</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.2 kW</td>
<td>32.73</td>
<td>8.25</td>
<td>5.32</td>
<td>52.47</td>
<td>0.32</td>
</tr>
<tr>
<td>1.5 kW</td>
<td>39.66</td>
<td>10.11</td>
<td>5.66</td>
<td>35.55</td>
<td>0.49</td>
</tr>
<tr>
<td>1.7 kW</td>
<td>42.67</td>
<td>10.85</td>
<td>7.11</td>
<td>38.83</td>
<td>0.54</td>
</tr>
<tr>
<td>1.9 kW</td>
<td>46.36</td>
<td>11.49</td>
<td>7.30</td>
<td>34.37</td>
<td>0.48</td>
</tr>
<tr>
<td>2.0 kW</td>
<td>55.21</td>
<td>14.72</td>
<td>8.87</td>
<td>20.42</td>
<td>0.78</td>
</tr>
</tbody>
</table>

Entropy expresses the disorder or randomness of the constituents of a thermodynamic system and almost remains constant at the fusion line (table 5.17). The enthalpy of mixing of the stainless steel and aluminium system in the weld pool is lower than at the fusion line. This indicates that around the fusion line, physical and chemical
reactions are more aggressive than in the weld pool. The internal energy of the system is reduced by increasing the bonds formed by atoms when $\Delta H^{mix}_{AB} < 0$ [60]. As a result, an ordered substitutional solution forms in the weld pool.

### Table 5.17 The calculated mixing enthalpy and entropy ($\Delta H_{mix}$ kJ mol$^{-1}$, $\Delta S_{mix}$ J mol$^{-1}$ K$^{-1}$).

<table>
<thead>
<tr>
<th>Laser power</th>
<th>At the fusion line</th>
<th>In the weld pool</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\Delta H_{mix}$</td>
<td>$\Delta S_{mix}$</td>
</tr>
<tr>
<td>1.2 kW</td>
<td>-9.57</td>
<td>9.49</td>
</tr>
<tr>
<td>1.5 kW</td>
<td>-8.97</td>
<td>9.53</td>
</tr>
<tr>
<td>1.7 kW</td>
<td>-8.83</td>
<td>9.39</td>
</tr>
<tr>
<td>1.9 kW</td>
<td>-9.39</td>
<td>9.46</td>
</tr>
<tr>
<td>2.0 kW</td>
<td>-9.42</td>
<td>9.46</td>
</tr>
</tbody>
</table>

The appearance of a high-entropy alloy is determined by the Gibbs free energy. If the Gibbs free energy of the high-entropy alloy is lower than the intermetallic compounds, the alloy forms before the intermetallics. The lowest Gibbs free energy of the intermetallics that can be produced for the material under consideration is a nickel-aluminide, of which the Gibbs free energy is -21.4 kJ mol$^{-1}$ (see table 5.8). To determine whether intermetallic or alloy will be produced, -21.4 kJ mol$^{-1}$ is a threshold value, below which the high-entropy alloy will appear. This can be expressed as

$$\begin{align*}
\begin{cases}
\Delta G = \Delta H_{mix} - T\Delta S_{mix} \\
\Delta G < -21.4 \text{ kJ mol}^{-1}
\end{cases}
\end{align*}$$

(5.24)

Hence

$$T > \frac{-21400 + \Delta H_{mix}}{\Delta S_{mix}}$$

(5.25)

is used to determine the formation temperature of the high-entropy alloy.

Applying the data from table 5.17 into equation (5.25), the calculated temperatures $T_f$ and $T_w$ for the formation of the high-entropy alloy is summarized in table 5.18.

### Table 5.18 The calculated temperatures for the high-entropy alloy formation (K).

<table>
<thead>
<tr>
<th>Laser power</th>
<th>At fusion line $T_f$</th>
<th>In the weld pool $T_w$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.2 kW</td>
<td>1247</td>
<td>1046</td>
</tr>
<tr>
<td>1.5 kW</td>
<td>1304</td>
<td>1225</td>
</tr>
<tr>
<td>1.7 kW</td>
<td>1339</td>
<td>980</td>
</tr>
<tr>
<td>1.9 kW</td>
<td>1270</td>
<td>1023</td>
</tr>
<tr>
<td>2.0 kW</td>
<td>1266</td>
<td>1445</td>
</tr>
</tbody>
</table>
$T_f$ is the temperature required to form the high-entropy alloys at the fusion line and $T_w$ is the temperature required to form the high-entropy alloy in weld pool. Below these temperatures, the Gibbs free energy of the intermetallic compound is lower than that of the high-entropy alloys and intermetallics will form preferentially.

From tables 5.15 and 5.16, it is clear that atomic concentrations of iron, chromium and nickel at the fusion line are higher than in the weld pool. Conversely, the atomic concentration of aluminium is lower. This is because the fusion line is a transition zone formed between solid base metal (AISI 316L) and liquid filler metal (Al 1050). On the one hand, more stainless steel substrate has been melted and the size of the weld pool increases as the laser power increases, indicating that the atomic concentration of iron, chromium and nickel increases in the weld pool. On the other hand, aluminium dilutes the weld pool.

At the fusion line of the laser weld, interdiffusion occurs between molten aluminium and solid stainless steel because the laser power mainly melts the filler wire and partially heats the stainless steel substrate. A smaller weld pool forms on stainless steel at lower laser powers. Above 1.7 kW, more energy is absorbed by the stainless steel and a larger weld pool is formed (compare figures 4.9 (a) and 4.12 (a)), leading to the more dilution of the aluminium in the stainless steel substrate, which causes the aluminium concentration in the weld pool to drop. This is reflected in the table 5.18, where the temperature $T_w$ required to form high-entropy alloys decreases from 1.5 kW to 1.7 kW laser power and increase again at 1.9 kW. This process is reflected in the EDS results from figure 4.17 (b) to 4.22 (b).

![Temperature distribution of bead on plate laser welding (1.9 kW laser power).](image-url)
The temperature field was measured experimentally to verify this theory. It turns out that the below 1.5 kW laser power, the measured temperature is below the calculated temperatures $T_f$ and $T_w$ (see table 5.18). Above 1.7 kW, the measured temperature can exceed the calculated temperatures $T_f$ and $T_w$ at the fusion line and in the weld pool, which means that high-entropy alloys can form at the fusion line and in the weld pool. The temperature distribution for the 1.9 kW laser weld is shown in figure 5.17.

The XRD results (figure 4.24) indicate that a simple B2 crystal structure (BCC based) appears in this laser weld pool, which is possibly, the crystal structure of the high-entropy alloys as indicated in the literature [90-108]. However, such FeAlCrNi alloys with the atomic concentration in this work have not been reported in the literature, although similar alloys with different atomic concentrations have been reported [65]. A Fe$_{1.3}$Al$_{0.7}$ iron-aluminium compound structure has been confirmed from XRD examination. The microhardness 400 to 500 HV results are higher than expected for iron-aluminium intermetallics (250 to 400 HV) [109]. Thus it is not certain whether the structure is an intermetallic or a high-entropy alloy.
Chapter 6

Conclusions and recommendations

6.1 General conclusions

Solid-state diffusion bonding and bead-on-plate laser welding experiments were carried out to investigate the evolution of intermetallic compounds and intermetallic layers at the interface of aluminium and stainless steel joints, and the following conclusions were derived:

1. A controllable and reproducible clamping device was designed to control the compressive force in solid-state diffusion bonding experiments. By applying difference in the thermal coefficients of materials, compressive force is controlled in the axial direction. A steel ring was also included to prevent extrusion of the aluminium component during high temperature compression.

2. Intermetallic compound formation is determined by the atomic solubility and the Gibbs free energy. Both criteria determine the type of intermetallic compound to first appear. Mixed intermetallic compounds have been observed.

3. Two different intermetallic layers appear at the interface of aluminium and stainless steel above 600 °C. The first layer comprises mixed intermetallic compounds and the second layer grows on top of the first layer. Thickness of first layer is limited to about 10 μm. The thickness-time relationship of the second intermetallic layer can be expressed as

\[ y = 0.00478t + 1.344 \ [10^{-6} \text{ m}]. \]  
(6.1)

4. The relation between the average thickness of intermetallic layers and temperature is established as

\[ \ln X = 15.606 - 15080.445T^{-1} \ [10^{-6} \text{ m}]. \]  
(6.2)

5. The intermetallic compound constructed in the first layer is mainly Fe\(_2\)Al\(_5\) and in the second layer is mainly FeAl\(_3\).

6. A model was developed to predict the start temperature for the intermetallic layer growth. 820 ± 25 K was calculated as a start temperature for the thermite reaction but the actual start temperature most likely lies within the lower error bounds.
7. Intermetallic compounds and layers appear in the weld of low laser powers (below 1.7 kW). The intermetallic compound can migrate from the fusion line into weld pool as a result of fluid flow.

8. By adjusting the laser welding parameters, it may be possible to prevent intermetallic compounds and intermetallic layer formation in stainless steel-aluminium joints.

9. It is possible to produce the high-entropy alloys with laser heating and casting by adjusting the chemical composition of the principle elements with similar atomic size and by choosing an optimal thermal cycle. Simple BCC based B2 crystal structure alloy(s) form in the laser weld. Whether there are intermetallics or high-entropy alloys can be determined by the Gibbs free energy of mixing of the component parts.

10. FeCrNiAl alloys may be produced with laser powers of 1.9~2.0 kW. If this does occur, then it is unnecessary to have at least five different elements to produce a high-entropy alloy.

6.2 Recommendations

The interesting experimental results show that there are many possible aspects waiting to be explored.

(a) More experiments need to be carried out to find the exact start temperature of intermetallic layer growth. Numerical models need to be developed to improve the accuracy of the approximation model. Mechanical tests on the solid-state diffusion bond should also be performed.

(b) Instead of furnace heating, an electromagnetic heating source such as induction coil can be applied to observe the localized behaviour of intermetallic compounds.

(c) Laser cladding of aluminium on the stainless steel may provide more information on intermetallic compound or layer formation to check if there are high-entropy alloys formed on the surface of the stainless steel.

(d) This study could be extended to use laser power to heat powders with different composition of iron, chromium, nickel and aluminium. The right chemical composition may introduce the formation of high-entropy alloys.

(e) Butt laser welding of AISI 316L to Al 1050 with Al-Cu filler metal would be an interesting start to investigate the microstructures of the laser weld.
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