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INTERMETALLIC PHASES FORMED DURING GALFANIZING

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Galfan (5 wt% Al-Zn plus 0.05 wt% mischmetal or 0.1 wt% Mg) is a coating which in recent years has undergone many industrial studies and trials. The aim with Galfan is to produce a coating which has no intermetallic phases in the coating but this condition is not always achieved. Though it is important, the nature of the intermetallic phases and the mechanisms of their formation and growth during Galfanizing are far from fully understood.

The overall objective of this investigation was to identify the intermetallic phases which form and grow during Galfanizing.

At 450°C, the formation of the intermetallic phases was in the form of a local outburst and the intermetallic phases then grew in a breakaway morphology. The previously reported structure and composition of the intermetallic phases were found to be either incorrect or incomplete. The intermetallic local outburst was determined to be mainly Fe₅Al₃-Znₐ with the outer part next to the eutectic being FeAl₃-Znₐ. The breakaway phase was FeAl₃-Znₐ and another phase next to the interface was Fe₅Al₃-Znₐ. The intermetallic growth is characterized by the growth of Fe₅Al₃-Znₐ towards the substrate with a <001> growth direction, following a reaction path of α (substrate) - Fe₅Al₃-Znₐ - FeAl₃-Znₐ - Galfan (melt).

When the dipping temperature was increased, the rates of intermetallic formation and growth were greatly increased. The intermetallic morphology was shown to change from predominantly breakaway at 450°C to predominantly layered at temperatures higher than 490°C resulting from a fast growth of Fe₅Al₃-Znₐ. The degree of the preferred orientation of Fe₅Al₃-Znₐ increased at higher dipping temperatures. It was shown that the lattice parameters and therefore the interplanar spacings of Fe₅Al₃-Znₐ formed during Galfanizing were dependent on the dipping temperatures. The same reaction path as that described for 450°C was also followed at higher temperatures. However, when the substrate is dipped at high temperatures and when the Fe₅Al₃-Znₐ grows to a considerably thickness, the limited diffusion rate of aluminium across a thick Fe₅Al₃-Znₐ layer resulted in the formation of FeZn₁₀-Alₐ.

When silicon was present in the substrate, the time for the intermetal-
lic formation was much lengthened and the growth of Fe₃Al₃-Znₓ and therefore the whole intermetallic layer became considerably slower. When silicon was present in the melt, the intermetallic phases did not grow to any noticeable extent at 450°C and 470°C. However, at 490°C and above though the nucleation time of the intermetallic was also delayed, once nucleated the growth was fast resulting in a highly localized growth.

It was found that the existing data on the interplanar spacings of Fe₃Al₃-Znₓ were incorrect. The two most intense peaks were shown to be due to diffraction from 221 and 311 rather than from 002 and 130. A new list of interplanar spacings was proposed. It was shown that the lattice parameters and therefore interplanar spacings of Fe₃Al₃-Znₓ formed during galvanizing were dependent on the aluminium content of the bath.

The compositions of intermetallic phases determined in this study were not consistent with those expected from previously published ternary phase diagrams. At 450°C, the solubility of zinc was found to be 5.3 wt% in FeAlₓ, 20.9 wt% in Fe₃Al₃, and 2.0 wt% in FeAl at 450°C. Based on these results, a new version of the Fe-Al-Zn ternary phase diagram at 450°C was proposed.
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CHAPTER 1 INTRODUCTION AND REVIEW OF THE LITERATURE

1.1 HOT DIP GALVANIZING - a General Comment

In the search for a solution to the problem of corrosion and oxidation of steel, various technological approaches have been developed. Coating of the steel is an important one and widely used.

Hot dipping is one of the many coating processes. During this a metal substrate is dipped into a molten metal bath the metal of which has a lower melting point than the substrate itself. A metallurgical reaction takes place during the hot dipping. Upon withdrawal of the substrate and subsequent solidifying of the remaining molten metal, the latter forms a coating which protects the substrate.

There are basically two main hot dipping processes, namely the traditional batch process and the more advanced continuous process. In the batch process, the articles being hot dipped are individually suspended in a molten bath. In the continuous hot dipping process, the coating is produced by passing a strip, sheet or wire continuously through a molten bath.

Traditionally, galvanizing, a hot dipping process which uses zinc, has been the major method for providing a coating for protection of steel from atmospheric corrosion. The lower corrosion potential of zinc compared to iron provides efficient sacrificial protection when used as a coating for steel. The low corrosion rate of zinc in various atmospheres offers an effective coating due to its corrosion products of basic zinc chloride and carbonate; the corrosion products significantly reduce the corrosion rate of the zinc coating. The aggressive atmospheres or the environments in which the steel can be protected by the galvanized coating include a marine atmosphere (high content of sodium chloride), the urban (containing sulfate), and the industrial (high content of sulfide and containing chloride).

Aluminizing, hot dipping in an aluminium bath, offers a high degree of corrosion resistance due to a thin and tenacious oxide film formed on the aluminium surface; the formation of this oxide film stifles further corrosion. Besides its use for the protection of steel from atmospheric corrosion and its decorative appearance, aluminized coatings have a par-
ticular application for protecting steel against high temperature oxidation.

In recent years, various Zn-Al alloy systems have been developed and examined. Galvalume, the most successful Zn-Al system for hot dipping, was introduced in 1976 and is nowadays in production worldwide on a large scale. The composition of Galvalume is 55 wt% Al, 43.4 wt% Zn, 1.6 wt% Si and the Galvalume coating was claimed to possess the best combination of the properties of zinc and aluminium coatings (1).

In 1978, several research groups in the world started to search for a new alloy system for steel coating. Among many criteria, the following were then of primary importance for the development of the new alloy coatings (2):

1. The corrosion resistance of the new alloy coating should be superior to that of the galvanized,
2. The cathodic protection of the new alloy coating should be as good as that of the galvanized,
3. The new alloy system should be able to be used in the existing galvanizing plant with minimal modification,
4. The new alloy coating should be free of intermetallic compounds.

A new alloy system was then chosen and called Galfan; the alloy is basically a Zn-Al system and the composition is of two types, according to a recent definition (3), as follows:

- Type 1. 5 wt% Al-Zn with up to 0.05 wt% mischmetal,
- Type 2. 5 wt% Al-Zn with 0.1 wt% Mg.

Since then, Galfan as a coating has undergone many industrial studies and trials; the coating is now beginning to be produced commercially worldwide.

The main object of the research reported in this thesis was to study the reaction taking place and the growth of the intermetallic compounds during hot dip Galfanizing (galvanizing using Galfan bath). As Galfanizing is a Zn-Al hot dip process and has similarities with both galvanizing and aluminizing, a general discussion and review of galvanizing, aluminizing and the Fe-Al-Zn system as it relates to Galfanizing is therefore given in the following sections.
1.2 PRETREATMENT OF SUBSTRATE

1.2.1 The Concept of Wetting

The substrate surface needs to be wetted by liquid metal before a solid-liquid reaction can take place. By definition, a solid is completely wetted by a liquid if the contact angle between them is zero (4) (see Fig. 1.1). Resolution of the interfacial forces shows that:

\[ S_{s/g} = S_{s/l} + S_{s/g} \cos \theta \]  

1.1

where \( S_{s/g} \) - surface tension between solid metal and gas
\( S_{s/l} \) - surface tension between solid and liquid metal
\( S_{l/g} \) - surface tension between liquid metal and gas
\( \theta \) - contact angle as shown in Fig.1

When a metallurgical reaction takes place, the \( S_{s/l} \) decreases and there will be greater force spreading the liquid metal over the surface. The angle \( \theta \) will then be caused to decrease in order to maintain the balance of the forces. With perfect spreading, the contact angle should approach zero corresponding to infinite spreading (5).

For better wetting, oxide films have to be removed as such films often have higher surface free energies than the metals from which they form; a surface with higher free energy is harder for liquid to wet.

![Diagram](Fig. 1.1) The balance of interfacial tensions acting around the periphery of a droplet of liquid at equilibrium.
1.2.2 Surface Treatment

The primary purpose of surface treatment is to remove any surface contaminants prior to the substrate-melt reaction. Basic steps of surface treatment involve:

1. **Degreasing**  Surface contaminants are always present as a result of, for example, production processes or some application of temporary protection. Alkaline or some organic solvents are used to detach contaminants such as oil, grease, dirt, etc.

2. **Pickling**  Superficial corrosion of the substrate occurs as a result of oxidation during processing or during storage while the environment is corrosive to some degree. Hydrochloric and/or sulphuric acids are used to remove the oxide films.

3. **Fluxing**  After acid treatments, oxide films begin to reform immediately on the surface during subsequent water washing and exposure to air. Such oxide films must also be removed before a molten metal can wet and react with the substrate. Flux, a chemical reagent, is used for this purpose. For zinc galvanizing, zinc chloride forms the base of most satisfactory fluxes because on hydrolysis it forms hydrochloric acid (6):

   \[
   \text{ZnCl}_2 + \text{H}_2\text{O} \rightarrow \text{Zn(OH)}\text{Cl} + \text{HCl}
   \]

   or

   \[
   \text{ZnCl}_2 + \text{H}_2\text{O} \rightarrow \text{Zn(OH)}_2 + \text{HCl}
   \]

   The acid then removes any oxide present. For example in the case of steel substrate, the reaction is:

   \[
   \text{FeO} + 2\text{HCl} \rightarrow \text{FeCl}_2 + 2\text{H}_2\text{O}
   \]

   In addition to ZnCl₂, NaCl and NH₄Cl may be present in the fluxes.

4. A reducing atmosphere may be used instead of a flux. For the continuous hot dip galvanizing process, the substrate is continuously annealed in-line in a reducing atmosphere, usually hydrogen, after pickling and rinsing. The substrate then passes
straight into the bath while protected by the reducing atmosphere.

1.3 GALVANIZING

1.3.1 The Fe-Zn System

The iron-zinc binary system is basic to the galvanizing process though the addition of approximately 0.2 wt% Al in the molten zinc bath is common practice commercially. Fig. 1.2 presents a recent version of the Fe-Zn phase diagram which, according to the authors (7), is based on an evaluation of all the data available up to 1976.

![Phase Diagram](image)

* a iron-zinc equilibrium phase diagram; b zinc-rich end of iron-zinc equilibrium phase diagram

Fig. 1.2 Fe-Zn phase diagram (7).

From the phase diagram, the reaction path between iron and zinc indicates that at the temperatures for normal galvanizing (around 450°C), it is thermodynamically possible for four intermetallic phases to be present. These are \( \Gamma, \Gamma_1, \delta, \) and \( \zeta, \) the properties of which are listed in Table 1.1. In a galvanized coating the \( \Gamma+\Gamma_1 \) layer is normally thin (<1 μm) and the \( \delta_1 \) consists of two distinct phases, \( \delta_{\text{h}} \) (compact) and \( \delta_{\text{p}} \) (palisade).

Since the publication of this phase diagram, the zinc-rich end of it has been studied critically by Gellings et al (9,11,12,13). The existence of the \( \Gamma_1 \) phase was confirmed by them but there was no indication of the existence of the high temperature \( \delta \) phase.
Table 1.1 Properties of Fe-Zn intermetallic compounds (7).

<table>
<thead>
<tr>
<th>Phase</th>
<th>Γ, Fe$<em>3$Zn$</em>{10}$</th>
<th>Γ$_1$, Fe$<em>3$Zn$</em>{21}$</th>
<th>δ$<em>1$, FeZn$</em>{10}$</th>
<th>ζ, FeZn$_{13}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crystal type</td>
<td>bcc</td>
<td>fcc</td>
<td>hcp</td>
<td>monoclinic</td>
</tr>
<tr>
<td>Lattice const.</td>
<td>a=8.97</td>
<td>a=17.96</td>
<td>a=12.8; c=57.7</td>
<td>a=13.4; c=5.1</td>
</tr>
<tr>
<td>Comp. (wt% Zn)</td>
<td>71.8-78.9</td>
<td>80.5-83.8</td>
<td>88.8-92.6</td>
<td>93.8-94.3</td>
</tr>
<tr>
<td>at 450°C</td>
<td>(8)</td>
<td>(8)</td>
<td>(9)</td>
<td>(9,10)</td>
</tr>
</tbody>
</table>

1.3.2 Reaction during Hot Dipping

The mechanisms of intermetallic formation and growth during the dipping of iron into molten zinc have been the subject of numerous researches for many years. They have been thoroughly reviewed by Mackowiak and Short (7).

Fig. 1.3 Microstructures of iron specimens galvanized for 20 min. at the indicated temperature (14).
The intermetallic phases present in hot dipping can be summarized as in Fig. 1.3 for four typical temperatures; the morphologies of the phases vary to a considerable extent with the change of dipping temperature. At 462°C the coating consists of a thin Γ layer, a δ₁₇ layer, a ω layer and finally a zinc layer. ζ phase, which according to the phase diagram should be stable up to 530°C, appears to be absent above 500°C.

Onishi et al (15) showed that in a solid iron and solid zinc diffusion couple at 410°C, the formation and growth kinetics can be represented by the characteristic processes in a numerical order as illustrated in Fig. 1.4. Mackowiak and Short (7,16) suggested that a similar sequence of the formation and growth as in the solid-solid couple may be followed in the case of solid iron and liquid zinc. However, it is apparent that when ζ phase becomes unstable as will be described in the following, the Onishi model of formation and growth can not be applied.

<table>
<thead>
<tr>
<th>Step</th>
<th>Reaction</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Fe → ζ Zn</td>
<td>Formation, Parabolical Growth</td>
</tr>
<tr>
<td>2</td>
<td>Fe → δ₁ δ₂ Zn</td>
<td>δ₁ Formation</td>
</tr>
<tr>
<td>3</td>
<td>Fe → Γ δ₂ δ₁ Zn</td>
<td>Γ Formation</td>
</tr>
<tr>
<td>4</td>
<td>Rapid Growth of δ₁</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>Fe → δ₁ δ₂ Zn</td>
<td>Formation of Thin Double Layer (Double Γ Layer)</td>
</tr>
<tr>
<td>6</td>
<td>Fe → c. δ₁ p. δ₂ δ₁ Zn</td>
<td>Formation of Compact δ₁</td>
</tr>
<tr>
<td>7</td>
<td>Rapid Growth of Palisade δ₁</td>
<td></td>
</tr>
</tbody>
</table>

Fig. 1.4 Modes of formation and growth of the phases in solid iron and solid zinc couple at 410°C. In the second to fifth processes the δ₁ phase can be regarded as the palisade δ₁ (15).

The rate of reaction between solid iron and liquid zinc as a function of temperature is shown in Fig. 1.5. This rate is expressed as iron loss and it takes into account all the iron which dissolves or breaks off during hot dipping.
At temperature up to 490°C, the coating consists of various intermetallic layers, i.e., \( \Gamma \), \( \delta_i \) and \( \zeta \). The compositions of the phases near the interfaces can be predicted closely from the phase diagram as the equilibrium is approached. In this case the diffusion is in steady state and the growth of the intermetallic composite is parabolic. The relative growth rates for individual layers are shown in Fig. 1.6.

It has been shown (7,18) that during the reaction, the \( \alpha/\Gamma \) and \( \Gamma/\delta_i \) interfaces shift towards the iron while the \( \delta_i/\zeta \) and \( \zeta/Zn \) interfaces shift towards the zinc. The \( \zeta \) is the only phase to form at the intermetallic-zinc interface; it converts to \( \delta_i \) at the \( \delta_i/\zeta \) interface.

There exists a temperature range where the growth becomes linear. From Fig. 1.5 it can be seen that the reaction rate becomes much more rapid at around 480°C, reaching a maximum at around 510°C and becoming parabolic again above around 530°C.

In the linear range the microstructure of the coating differs remarkably from that obtained by galvanizing in the lower parabolic range. The \( \zeta \) phase, after becoming discontinuous at around 490°C, disappears when above 500°C though according to the phase diagram (Fig. 1.2) it should be stable up to 530°C.
Ghoniem and Lohberg (19) proposed that the $\zeta$ phase is stable only up to 495°C and that the peritectic temperature determined by Lichti and Niessen is 512°C (20, 21). However, it has been confirmed (22) that the $\zeta$ phase is thermodynamically stable in the linear temperature range (480°C–530°C) when it precipitates and grows in the melt. These observations are reconciled by Horstmen and Peters (23), who proposed that the $\delta_1$+Zn$\rightarrow\zeta$ peritectic reaction proceeds very slowly above 475°C and that between 500°C and 530°C the $\zeta$ is not nucleated on the $\delta_1$ but precipitates from the melt.

It is the non-continuity or the absence of the $\zeta$ layer at 490°C to 530°C that creates conditions for the linear reaction rate. In Habraken’s view (24), a metastable state is formed by $\delta_{ip}$ (the palisade $\delta_1$ as in Fig. 1.3) and Zn$_l$ (liquid zinc) with the composition of the phases fixed by the common tangent at the lower level of the free energy parabolas representing the phases (see Fig. 1.7). Because of the existence of internal stresses in $\delta_{ip}$, the parabola for this phase has a slightly higher energy level than that of stress-free $\delta_{ip}$. This in turn gives a further increase in the zinc content of $\delta_{ip}$ at least in the vicinity of Zn$_l$ which is itself rich in iron.

Fig. 1.7 A qualitative drawing of the $\Delta G/T$ curves for Fe-Zn system (24).
At temperatures of around 490°C, the non-continuity of \( \zeta \) allows liquid zinc to come directly into contact with \( \delta_{sp} \). As pointed out by Habraken stress corrosion occurs in the \( \delta_{sp} \) phase, the zinc penetrates the cracks, enlarges them and relaxes the stresses. As a result, the \( \delta_{sp} \) partially dissolves and becomes fragmented. When the temperature is above 500°C, the reaction is more vigorous as the \( \zeta \) is no longer present though the higher temperature weakens the residual stresses. The absence of \( \zeta \) causes more redissolution of \( \delta_{sp} \) at the interface because of the higher zinc content of the phase.

In contrast to Habraken’s view, Mackowiak and Short believes (7) that the increased attack is caused by an unstable situation when the \( \zeta \) is absent or porous. These stresses build up in the growing layer, owing to volume changes, at a rate which can no longer be accommodated. These stresses ultimately cause rupture probably at the \( \delta_{sl}/\delta_{sp} \) (\( \delta_{sl} \) is compact \( \delta \) as in Fig. 1.3) interface, causing the \( \delta_{sp} \) phase to buckle and cracks to appear in the phase. With porous \( \zeta \) or in the absence of that phase, the liquid zinc penetrates directly to the \( \delta_{sl} \) and reacts to form new \( \delta_{sp} \). Eventually the buckled \( \delta_{sp} \) breaks and more zinc attacks directly the \( \delta_{sl}/\delta_{sp} \) interface.

When the temperature is above 530°C, the \( \delta_{sp} \) can no longer be formed (25). As the \( \delta_{st}-\text{Zn} \) boundary is in a stable equilibrium, the thickness of \( \delta_{st} \) increases with time and the overall intermetallic growth is parabolic again.

### 1.3.3 The Effect of Silicon in the Substrate

Of all alloying elements in steel, silicon is the one that has the greatest practical influence on the reactions during hot dip galvanizing. With certain ranges of silicon contents in the steel substrates, the structures of the intermetallic layers are significantly different and the coatings are excessively thick. It is generally known that the excessive thickness of the coating is due to abnormal growth. This involves the breakdown of the continuous intermetallic layers, \( \zeta \) phase in particular, and consequently a linear growth region (7,24,26,27).

Fig. 1.8 shows schematically the behaviour of steel containing silicon when hot dip galvanized (24). Coating thickness varies at different temperatures and is a function of silicon content. Over the range of silicon content up to 0.6 wt% Si, the behaviour of silicon steels is
characterized by two peaks (Fig. 1.8). The first, called Sandelin’s peak, is associated with approximately 0.1 wt% Si; the second peak occurs at a silicon content of approximately 0.4 wt%. With further increase of silicon content to approximately 1.5 wt%, there is another peak where the coating reaches a maximum thickness; coating thickness decreases for higher silicon contents (28, 29).

![Graph showing variation of average coating thickness as a function of silicon content.](image)

**Fig. 1.8** Variation of average coating thickness as a function of silicon content (up to 0.6 wt%) of steel, hot dipping for 15 minutes (24).

Habraken (24) explained that the Sandelin peak observed at temperatures below 500°C is the result of the following reactions:

\[
\zeta_{\text{Si, satd}} + \text{Zn}_L \rightarrow \text{Zn}_{L(\text{Fe, satd})} + \text{FeSi}
\]

\[
\text{Zn}_{L(\text{Fe, satd})} \rightarrow \zeta + \text{Zn}_L \text{ or}
\]

\[
\delta_{(\text{Si, satd})} + \text{Zn}_L \rightarrow \text{Zn}_{L(\text{Fe, satd})} + \text{FeSi} \text{ (esp. at } \delta/\zeta)
\]

\[
\text{Zn}_{L(\text{Fe, satd})} \rightarrow \zeta_{\text{secondary}} + \text{Zn}_L
\]

The above reactions are due to the lower solubility of silicon in the intermetallic than in the liquid zinc and the reactions lead to the broken form of the \( \zeta \) layer. When the silicon content is increased, the reaction
rates are reduced since the silicon in the $\delta_i$ may form clusters. This process reduces the stress in the phase and therefore stabilises the $\delta_i$ phase and perhaps also the $\zeta$ phase.

Habraken (24) attributed the second peak to formation of a diffuse zone in the inner region. Some silicon surrounds the $\zeta'/\zeta$ and $\delta_i/\zeta$ interfaces and the phases are saturated with silicon causing the reaction:

$$\zeta_{Si, satd} \rightarrow FeSi + Zn_L \text{ and }$$

$$Zn_L(Fe, satd) \rightarrow \zeta_{(secondary)} + Zn_L$$

The liquid zinc reaches the $\delta_i$ and the secondary $\zeta$ forms at the $Zn_L/\delta_i$ interface with local dissolution or fragmentation of the $\delta_i$ phase. Habraken's explanation is that there is a small diffuse zone of $Zn + FeSi + \zeta_{(secondary)} + \delta_i$ (dispersed) found between the $\zeta$ and $\delta_{ip}$ or between $\zeta'/\zeta$ (without $\delta_{ip}$ in this case). As implied in the preceding section, the continuity of the intermetallic layer is important for parabolic growth. Since the intermetallic grows in a highly broken form with silicon present, the growth therefore follows the linear law instead of the parabolic.

1.3.4 The Addition of Aluminium into the Bath

In galvanizing practice, approximately 0.2 wt% Al is added into the zinc bath. The aluminium is added to inhibit the growth of the Fe-Zn intermetallic within an incubation period. After this period, growth of the Fe-Zn intermetallic occurs.

It is generally known that a continuous thin layer rich in aluminium forms prior to the formation of the Fe-Zn intermetallic. The exact nature of this thin aluminium rich layer and its formation as well as its inhibiting effect on the formation of the Fe-Zn intermetallic have been the subjects of many studies. Recently, Caceres et al (30) have summarized and listed the composition of the inhibiting layer given by previous workers (Table 1.2). The discrepancies in the structure and composition given for the inhibiting layer are possibly the result of differing aluminium concentrations in the baths and the difficulties in analyzing the layer where thickness was less than 1 $\mu$m. The composition determined by Caceres et al (Table 1.2) is not directly related to the mechanism of the inhibiting
effect of the 0.2 wt% Al in the zinc bath since their result was from hot dipping experiments in zinc baths containing 2.7 and 5.6 wt% Al.

Table 1.2 Reported phases of the inhibiting layer during galvanizing (30).

<table>
<thead>
<tr>
<th>Year</th>
<th>Inhibiting layer</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1950</td>
<td>FeAl,</td>
<td>Bablik (31)</td>
</tr>
<tr>
<td>1951</td>
<td>FeAl, containing 16-27 wt% Zn</td>
<td>Hughes (32)</td>
</tr>
<tr>
<td>1953</td>
<td>Fe₃Al₄</td>
<td>Haughton (33)</td>
</tr>
<tr>
<td>1969</td>
<td>Fe₃Al₄+Al containing Fe₂Zn₃</td>
<td>Borzillo &amp; Hahn (34)</td>
</tr>
<tr>
<td>1971</td>
<td>Double layer of Fe-Al-Zn phases</td>
<td>Ghuman &amp; Goldstein (35)</td>
</tr>
<tr>
<td>1973</td>
<td>Zn containing Fe₃Al₄ and FeAl,</td>
<td>Urednicek &amp; Kirkaldy (36)</td>
</tr>
<tr>
<td>1973</td>
<td>Fe₃Al₄₋ₓZnₓ, 0.5&lt;ₓ&lt;0.8</td>
<td>Harvey &amp; Mercer (37)</td>
</tr>
<tr>
<td>1986</td>
<td>Fe(AlₓZn₁₋ₓ)ₓ, 0.75&lt;ₓ&lt;0.95</td>
<td>Caceros et al (30)</td>
</tr>
</tbody>
</table>

Fig. 1.9 shows an example of the inhibiting effect of aluminium on the growth of the intermetallic layer during galvanizing. A thin layer forms and inhibits the iron-zinc intermetallic formation within the incubation time. Longer hot dipping times lead to the initiation of localized growth. With still longer dipping times, a normal thick iron-zinc intermetallic layer develops.

(a) Dipped for 3 second. The thin layer is indicated by an arrow.

(b) Dipped for 60 seconds. The localized growth is indicated by an arrow.

Fig. 1.9 Microstructures of coatings dipped in 0.25 wt% Al-Zn bath at 450°C (35).
1.4 ALUMINIZING

1.4.1 Fe-Al System

The iron-aluminium system is the base of aluminizing. In hot dip aluminizing, the bath is normally pure aluminium with approximately 2 wt% Si added to the bath. Fig. 1.10 presents the Fe-Al phase diagram. The phases $\alpha$ (FeAl), $\zeta$ (FeAl$_2$), $\eta$ (Fe$_2$Al$_4$), $\theta$ (FeAl$_3$) are thermodynamically possible when aluminizing at around 700°C. Table 1.3 lists the properties of the binary Fe-Al intermetallic phases.

![Fe-Al phase diagram](image)

Fig. 1.10 Fe-Al phase diagram (38,39,40).

Table 1.3 Properties of Fe-Al intermetallic compounds (42).

<table>
<thead>
<tr>
<th>Phase</th>
<th>$\alpha$, FeAl</th>
<th>$\zeta$, FeAl$_2$</th>
<th>$\eta$, Fe$_2$Al$_4$</th>
<th>$\theta$, FeAl$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lattice const. (Å)</td>
<td>a=2.912</td>
<td>a=6.326</td>
<td>a=7.675</td>
<td>a=15.489</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\alpha=87°24'28&quot;$</td>
<td>b=6.403</td>
<td>b=8.083</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>c=4.203</td>
<td>c=12.476</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>$\beta=107°43'$</td>
</tr>
<tr>
<td>Volume of cell (Å$^3$)</td>
<td>24.65</td>
<td>252.4</td>
<td>205.5</td>
<td>1487.9</td>
</tr>
<tr>
<td>Atoms in unit cell</td>
<td>2</td>
<td>18</td>
<td>14</td>
<td>100</td>
</tr>
<tr>
<td>Fe: Al</td>
<td>Fe:1</td>
<td>Fe:6</td>
<td>Fe:4</td>
<td>Fe:25</td>
</tr>
<tr>
<td></td>
<td>Al:1</td>
<td>Al:12</td>
<td>Al:10</td>
<td>Al:75</td>
</tr>
<tr>
<td>Comp. at 800°C (wt% Al)</td>
<td>32.5</td>
<td>47.7-49.8</td>
<td>53.0-56.2</td>
<td>58.2-62.7</td>
</tr>
<tr>
<td></td>
<td>(39)</td>
<td>(41)</td>
<td>(42,43)</td>
<td></td>
</tr>
</tbody>
</table>
1.4.2 Reaction during Hot Dipping

In hot dip aluminizing, as in galvanizing, an intermetallic layer is formed as a reaction product between the steel substrate and liquid aluminium. Fig. 1.11 is the microstructure of the aluminide layer formed in the hot dipping; it is notably serrated along the substrate-aluminide interface.

Fig. 1.11 Microstructure of the aluminized layer of pure iron dipped for 1 minute into a pure aluminium bath at 700°C (44).

The aluminide layer is known to be predominantly η phase and the growth of this layer has a preferred orientation of (002) (44). Heumann and Dittrich (45) explained that the serrated interface morphology was the result of an extremely high rate of diffusion in the direction of c-axis of the η phase; the c-axis corresponds to the preferred (002) orientation of the η layer formed in aluminizing. On the other hand, in Kwon and Lee’s view (44), the serrated interface is the consequence of the preferred nucleation of η crystallites on the crystallographic planes of the substrate.

A thin layer of θ phase can be detected between η and aluminium (46). However, there are no reports of ζ phase being observed between the η and the substrate; the existence of a narrow FeAl layer inside the tongue-like Fe₅Al₅ next to the substrate has been reported (47).

1.4.3 The Effect of Silicon

In aluminizing, around 2 wt% Si is added into the aluminium bath in order to slow the growth of the aluminide layer. The aluminide layer also grows more slowly when silicon-containing steel is used. Note that this is the reverse of its effect in galvanizing. Fig. 1.12 is an example of the
microstructure obtained from aluminizing (a) silicon-containing steel and (b) iron in a bath containing silicon; the presence of silicon in the iron also produces uniform nucleation rates of η phase resulting in a planar rather than a serrated interface.

![Microstructure of aluminized layer](image)

Fig. 1.12 Microstructure of the aluminized layer. (a) steel containing 1.58 wt% Si dipped into pure Al bath and (b) pure iron dipped bath containing 4 wt% Si for 1 min. at 700°C (44).

![Graph A](image)  
![Graph B](image)

Fig. 1.13 Relation between thickness of intermetallic compounds in alloy layers and the dipping time (a) in pure Al bath, 730°C, (b) in Al-2.5 wt% Si bath, 710°C (50).
To explain the effects of silicon, Nicholls (48) and Eggeler et al (49) proposed that the silicon atoms occupied the vacancies in the structure of the η phase resulting in slower solid state growth; without the presence of silicon the vacancies in the phase allowed faster diffusion of aluminium atoms. By contrast, Uchida et al (50) reported that when the steel was dipped in an aluminium bath containing 2.5 wt% Si, the alloy layer was composed of η phase, θ phase and (Al,Fe,Si) H phase and the growth was much slower than that in a pure aluminium bath (Fig. 1.13). With the increase of silicon content to 8 wt% (50), the alloy layer formed consisted only of (Al,Fe,Si) H phase and this did not grow at all for dipping times up to 30 seconds.

1.5 HOT DIPPING IN Zn-Al ALLOYS BATHS

In recent years, besides the application of almost pure zinc and almost pure aluminium in hot dipped coatings, different Zn-Al alloys systems have been used or are under study. As the compositions of the baths and the hot dipping conditions differ, the reaction products (the alloy layers) differ in composition, morphology and growth rate.

Hot dipping in zinc-aluminium alloy baths can be treated as a diffusion couple which consists of solid iron and liquid Zn-Al. During the dipping, a new phase which is thermodynamically possible will be nucleated at the interface provided that the nucleation barrier is not too high. On an empirical basis, for hot dipping in a zinc-aluminium bath with aluminium content greater than approximately 0.2 wt%, the initial phase nucleated is aluminium and iron rich. However the further growth of the phase formed initially is to a large extent determined by the aluminium content in the bath. For example, with 0.2 wt% aluminium in the bath, as in galvanizing, the initial formation of an aluminium rich phase results in a local depletion of aluminium in the liquid immediately next to the interface; this leads to the subsequent formation of the more stable iron and zinc rich intermetallic. On the other hand, in the Galvalume (55 wt% Al) process, there is a sufficient supply of aluminium in the melt to ensure that no local depletion of aluminium can occurs.
1.5.1 The Al-Zn and Fe-Al-Zn Systems

The Al-Zn and Fe-Al-Zn systems form the basis for understanding the formation and growth mechanisms of intermetallics during hot dipping in an Al-Zn bath. In practice, small amounts of one or more other alloying elements are often added into the melt.

Fig. 1.14 shows the Al-Zn phase diagram. At 5 wt% aluminium, which corresponds to the aluminium content of Galfan, there is a eutectic of η and β with a melting point of 382°C. The η phase is zinc with approximately 1 wt% of aluminium in the solid solution, and β is a phase which is only stable at high temperature and decomposes through a eutectoid reaction at a temperature of 275°C to γ and η (52,55,56).

In 1962, Cameron and Ormay (57) constructed a tentative section of the ternary Fe-Al-Zn phase diagram at 450°C as shown in Fig. 1.15a. In 1969, Koster and Godecke (54) carried out an investigation into the ternary Fe-Al-Zn system with emphasis on the zinc rich corner. Their isothermal sections at 700°C, 575°C and 500°C are shown in Fig. 1.15. Some time later, Urednicek and Kirkaldy (58) investigated the phase constitution of Fe-Al-Zn at 450°C. Their isothermal section at this temperature is also included in Fig. 1.15. (The Fe-Al-Zn ternary phase diagram at 450°C will be discussed in details in section 2.4).
Fig. 1.15 Ternary Fe-Al-Zn phase diagrams from:
A. Cameron and Ormay (57),
B, C and D. Koster and Godecke (54),
E. Urednicek Kirkaldy (58).
The isothermal sections other than the one given by Cameron and or may show that there is no ternary intermetallic compound in the system. All of the Fe-Al-Zn intermetallics have their isomorphous binary forms. This means that each intermetallic phase is an Fe-Al intermetallic containing dissolved zinc or an Fe-Zn intermetallic containing dissolved aluminium.

1.5.2 Hot Dipping Experiments in 45, 55 and 75 wt% Al-Zn Baths

Selverian et al (59) have recently investigated the reaction between iron sheet (0.65 mm) and three liquid aluminium-zinc baths; the bath compositions and hot dipping temperatures are as set out in Table 1.4.

The reactions between the iron substrate and the baths were found to be highly exothermic; specimens hot dipped for times of 4 and 9 seconds in all the baths glowed red a few seconds after being withdrawn from the baths and held in the air. The highly exothermic nature of the reaction was attributed to the high heat of formation of FeAl.

Table 1.4 Bath compositions and temperatures used by Selverian et al (59).

<table>
<thead>
<tr>
<th>Bath Composition, wt%</th>
<th>Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al 53.1 Zn 1.4 Fe 1.8</td>
<td>570, 590</td>
</tr>
<tr>
<td>54.1 Zn 1.5 Fe 1.8</td>
<td>590, 610</td>
</tr>
<tr>
<td>73.7 Zn 1.8</td>
<td>635, 655</td>
</tr>
</tbody>
</table>

The reaction was rapid and severe; hot dipping in the 45Al-55Zn bath at 590°C for 36 seconds produced a coated specimen which had swelled to 20 times its original thickness. The microstructures of the hot dip coatings are represented in Fig. 1.16. These specimens were water quenched after hot dipping. As described by Selverian et al, the coatings have the following characteristics:
(a) 45Al-55Zn bath, 36 seconds at 590°C. A consists of Fe₂Al₃+L, B is of FeAl₃+L, and C is the overlay (FeAl₃ crystals floating in the Al-Zn bath)

(b) 55Al-45Zn bath, 81 seconds at 610°C. Small arrows point to a discontinuity in the intermetallic layer, large arrows indicate the 'cored' particles. The center of these particles is Fe₂Al₃ surrounded by FeAl₃.

(c) 75Al-25Zn bath, 25 seconds at 655°C. Intermetallic layer similar to that dipped in 45Al-55Zn bath for 36 seconds. The overlay consists of a heavy concentration of diffuse FeAl₃ floating in the Al-Zn liquid.

Fig. 1.16 Microstructures of coatings dipped in Al-Zn baths (Back scattered electron image) (59).

45Al-55Zn bath: Coatings had an adherent intermetallic layer. For short dipping time (4 seconds at 570°C), the intermetallic layer consisted of two layers, i.e., FeAl₃ and Fe₂Al₃. Both layers contained small regions of liquid zinc. FeAl₃ was starting to flake off into the molten bath. The microstructure of the coating for longer dipping (Fig. 1.16a) was similar to that for a short dipping time.
55Al-45Zn bath: Hot dipping at 610°C for 81 seconds produced the intermetallic layer which was thin and not continuous (small arrows in Fig. 1.16b). The 'cored' particles (large arrows in Fig. 1.16b) consisted of Fe₅Al₃ in the core surrounded by FeAl, resulting from a peritectic reaction, i.e., Fe₅Al₃+liquid → FeAl,

75Al-25Zn bath: For short dipping time (4 seconds) at 635°C, there were localized regions of severe attack on the iron specimen which gave rise to 'blocks' or 'columns' of non-compact FeAl, floating into the melt. For longer dipping time (25 seconds) at 655°C, the attack was more severe and the continuous intermetallic layer was made up of Fe₅Al₃+FeAl₃+Zn (Fig. 1.16c), similar to that from 45Al-55Zn bath.

The reaction path given by Selverian et al for hot dipping of iron in 45, 55, 75 wt% Al-Zn baths is shown in Fig. 1.17. This applies only to coatings with a continuous intermetallic layer. In the temperature range studied, the zinc-rich phase closest to the diffusion path was liquid zinc. Thus the path passed through the Fe₅Al₃+FeAl₃+Zn(L) region, and then through the Fe₅Al₃+Zn(L) region, and finally ended in the α-Fe single phase region.

Fig. 1.17  Schematic diffusion path given by Selverian et al for hot dipping of iron in 45, 55 and 75 wt% Al-Zn baths in the temperature range of 570°C to 655°C (59).

1.5.3 Galvalume Hot Dipping

The Galvalume bath contains 55 wt% Al, 43.4 wt% Zn and 1.6 wt% Si. As described in the preceding section, without silicon the reaction between iron and the 55Al-45Zn bath is rapid and severe. Silicon is added to the bath with similar effects as in aluminizing; it prevents rapid intermetallic
layer growth during hot dipping. Bath temperature is held at approximately 610°C for normal Galvaluming. In an investigation by Selverian et al (60), the exothermic type of reaction was not reported in Galvalume hot dipping.

The thickness of the intermetallic layers and their compositions are functions of dipping time in Galvaluming. A short dipping time results in the development of a thin Fe-Al-Si intermetallic layer (Fig. 1.18a) which has up to 7 wt% zinc dissolved in it (60). A thick intermetallic layer consisting of a number of different phases is obtained when dipping for a long time as shown in Fig. 1.18b and 1.18c.

Tables 1.5 and 1.6 give the phases formed during Galvalume hot dipping and their compositions (60). Fig. 1.19 shows part of the Fe-Al-Si system as modified by Selverian et al. T₁ is basically an Fe-Al-Si intermetallic compound with dissolved zinc content of 0.19 wt%. T₅ is another Fe-Al-Si intermetallic compound. T₅₅ is the cubic form of T₅ with 6.96 wt% zinc and T₅₆ is the hexagonal form of T₅ with 1.71 wt% zinc.

![Microstructures of coatings dipped in 55 wt% Al, 43.3 wt% Zn and 1.7 wt% Si bath at 610°C (60).](image)

25μm 50μm

a. for 4 seconds b. for 900 seconds
c. for 1800 seconds
Fig. 1.19 Reaction path (dotted line) in the steel dipped for 1800 seconds in the Galvalume bath plotted in the modified Fe-Al-Si system at 610°C (60).

Table 1.5 Phases present in the alloy layers formed during hot dipping in Galvalume bath at 610°C as a function of time (60).

<table>
<thead>
<tr>
<th>Time, s</th>
<th>Phases in the intermetallic layer</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>$T_{sc}$</td>
</tr>
<tr>
<td>900</td>
<td>$Fe_2Al_5$, $T_1$, $FeAl_3$, $T_{sc}$</td>
</tr>
<tr>
<td>1800</td>
<td>$Fe_2Al_5$, $T_1$, $FeAl_3$, $T_{sc}$, $T_{sa}$</td>
</tr>
</tbody>
</table>

Table 1.6 Reported compositions of phases referred to Table 1.5 (60).

<table>
<thead>
<tr>
<th>Phase</th>
<th>Composition, wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Al</td>
</tr>
<tr>
<td>$Fe_2Al_5$</td>
<td>51.26</td>
</tr>
<tr>
<td>$FeAl_3$</td>
<td>57.94</td>
</tr>
<tr>
<td>$T_1$</td>
<td>25.14</td>
</tr>
<tr>
<td>$T_{sa}$</td>
<td>57.66</td>
</tr>
<tr>
<td>$T_{sc}$</td>
<td>58.21</td>
</tr>
</tbody>
</table>
The considerably slower growth of the intermetallic in Galvalume hot dipping as compared to that in a silicon-free bath seems to be the result of the formation of the continuous layer of $T_x$; the effect of the silicon in the bath here in Galvalume hot dipping is similar to that in aluminizing as explained by Uchida et al (50) and as described in section 1.4.3).

1.6 REACTION DURING GALFANIZING

As mentioned previously (section 1.1), Galfanizing is a galvanizing process using a Galfan bath. The composition of Galfan is basically 5 wt% Al-Zn with the addition either of La and Ce up to 0.05 wt% or 0.1 wt% Mg; the small addition of either mischmetal or magnesium is to increase the wettability of the Galfan melt. The 5 wt% Al-Zn is at the eutectic point of the binary Fe-Al phase diagram with a melting point of 382°C. The investigation of alternative coating compositions and the basis for the final choice of the Galfan composition have been thoroughly reviewed by Skenazi et al (2). One of the aims in producing the Galfan coating is to develop a coating structure without intermetallics at the interface with the steel substrate. Under favourable industrially continuous hot dip conditions (i.e., bath temperature being 450°C, low strip inlet temperature, dipping time of a few seconds and rapid cooling), a uniform eutectic coating with intermetallic phases can be obtained; such a coating is shown in Fig. 1.20.

![Fig. 1.20](image)

Fig. 1.20 Galfan coating produced by continuous hot dipping, x1200 (61).

The nature of the interface between the substrate and the melt is not well understood. An intermetallic-free interface is, however, not maintained under unfavourable conditions such as longer dipping time, higher
temperature of the bath or of the incoming strip. Intermetallics can develop with different compositions and morphologies. The formation and growth of such intermetallic compounds was, in fact, reported even in the early stage of the Galfan development (62). Apart from an early study of Ghuman and Goldstein (35) on hot dipping in a zinc bath containing 1 to 10 wt% Al, there have been in the past three years and concurrent with the present study investigations studying the nature of the interface and the formation and growth of intermetallics during hot dipping in zinc baths which contain around 5 wt% Al. The investigations as they relate to the coating-substrate interface and intermetallic compounds are summarized in Table 1.7.

MakimattillLa and Ristolainen (refer Table 1.7) revealed that under the scanning electron microscope the interfacial layer of the Galfanized coating is less than 0.5 μm thick and when dipping was carried out with a low strip input temperature it could not be clearly distinguished. In the specimen coated at a higher strip input temperature (750°C), the layer is visible. A fracture along the coating-steel interface was prepared to demonstrate the intermetallic layer and the layer composition as detected by Auger electron spectroscopy on the fracture surface was: 13.5 wt% Fe, 29.1 wt% Al, 47.8 wt% Zn, 6 wt% O, 3 wt% C, 0.4 wt% P and 0.2 wt% S.

Ichiyama et al (refer Table 1.7) also found that the aluminium has a tendency to concentrate in the coating-substrate interface. In their study a 5 wt% Al-Zn bath with a small addition of sodium was used. They concluded:

1. when the coating thickness is equal to 20 μm, the phases are as follows:

Substrate + Fe₂Al₃ + Zn-Al-Na (eutectic),

2. when the coating thickness is equal to 40 μm, the phases are as follows:

Substrate + (Fe₂Al₃+FeZn₁) + (Fe₂Al₃+FeZn₃) + Zn-Al-Na

(eutectic).
Table 1.7 Various studies on coating-substrate interface and intermetallic phases in the coating hot dipped in zinc baths containing around 5 wt% Al.

<table>
<thead>
<tr>
<th>Year</th>
<th>Bath</th>
<th>Substrate</th>
<th>Hot dip conditions</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1985</td>
<td>Zn-5%Al</td>
<td>0.08-0.3%C steel sheet</td>
<td>Coated in a laboratory scale continuous galvanizing line: Annealing (850°C); Cooling to 750 to 500°C; Galvanizing (420°C); Air cooling.</td>
<td>Makimat-tila (63)</td>
</tr>
<tr>
<td></td>
<td>Zn-5%Al</td>
<td>Steel sheet</td>
<td>Degreased-pickled-fluxed-dried-galvanized</td>
<td>Ichiyama (64)</td>
</tr>
<tr>
<td>1970</td>
<td>Zn-5 to 10%Al</td>
<td>Iron 50x25x 0.4 mm</td>
<td>Degreased-pickled-fluxed-heated (120°C)-galvanized at: a. 450°C for 3, 5, 10, 30, 60, 120, 320, 640, 1800, 3800 s b. 525, 560, 590, 600, 610, 620, 640, 660°C for 10, 40, 300 s</td>
<td>Ghuman (35)</td>
</tr>
<tr>
<td>1986</td>
<td>Zn-2.7% -5.6%Al</td>
<td>Iron 70x25x 1 mm</td>
<td>Pickled-fluxed-galvanized at 450°C for</td>
<td>Caceres (65)</td>
</tr>
</tbody>
</table>

27
Table 1.7 Cont.

<table>
<thead>
<tr>
<th>Year</th>
<th>Bath</th>
<th>Substrate</th>
<th>Hot dip conditions</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1986</td>
<td>Zn-5%Al</td>
<td>low C steel</td>
<td>a. Annealed at 850;</td>
<td>Makimat-</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>a. bath</td>
<td>tila (62)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>300x50x</td>
<td>C cooled to 650-700°C;</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.65mm</td>
<td>Zinc quenched and</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>b. cont.</td>
<td>galvanized at 420°C;</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1500x1.5</td>
<td>b. same as above but</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>and 2mm</td>
<td>continuously.</td>
</tr>
</tbody>
</table>

Fig. 1.21 Reaction paths in (5-10) wt% Al-Zn bath given by Ghuman and Goldstein: 450°C, Fe-A-Zn, 525°C, Fe-B-Zn, 560°C, Fe-C-Zn, and 590°C, Fe-D-Zn (35).

In Ghuman and Goldstein’s study (refer Table 1.7), it was found that for hot dipping in 5 to 10 wt% Al-Zn baths at 450°C, no reaction was observed between iron and the melts when the dipping times were short. Longer dipping (>640 s) resulted in the growth of a dark grey phase. This phase started to grow at localized sites on the surface and finally covered the entire surface. Their X-ray diffraction results showed that the intermetallic compound formed during hot dipping at temperatures between 450°C
and 590°C had a structure isomorphous with FeAl₁. The compositions of the intermetallics were:

1. when dipped at 450°C:
   (31-35) wt% Fe, (44-45) wt% Al and (20-25) wt% Zn,
2. when dipped at 525°C:
   (36-38) wt% Fe, (45-48) wt% Al and (17-20) wt% Zn.

For dipping at temperatures between 525°C and 590°C, the composition of the intermetallic was about the same as that obtained at 525°C. Fig. 1.21 shows the paths of reaction following hot dipping in 5 to 10 wt% Al-Zn baths as proposed by Ghuman and Goldstein.

Ghuman and Goldstein (35) reported that a very rapid reaction was observed when iron specimens were dipped in 1 to 10 wt% Al-Zn baths at temperatures higher than 600°C. The reaction was exothermic in nature. (This is a similar observation to that of Selverian et al (55) when iron was hot dipped in 45 to 75 wt% Al-Zn baths with free silicon at temperatures between 570°C and 655°C (section 1.5.2)). The coating consisted of Fe-Zn intermetallics with dissolved aluminium and an Fe-Al intermetallic with dissolved zinc. The reaction path can be shown as in Fig. 1.22 and the reactions can be summarized as:

![Diagram](image-url)

Fig. 1.22 The reaction path followed when hot dipping iron in 1 to 10 wt% Al-Zn bath at temperature > 600°C as suggested by Ghuman and Goldstein (35).
1. Fe+(Al-Zn) alloy bath $\rightarrow$ Fe$_2$Zn$_{15}$+FeZn$_7$.
2. FeZn, (+ Al) $\rightarrow$ FeZn, with dissolved Al less than 4 wt%.
3. FeZn$_4$-Al, (+ Al) $\rightarrow$ Fe-Al-Zn ternary (+ Al) $\rightarrow$ Fe(AlZn)$_3$.

Ghuman and Goldstein also suggested that the exothermic nature of the reaction was attributed to the high heat of formation of the Fe(AlZn)$_3$ intermetallic in reaction 3 above.

By contrast with Ghuman and Goldstein, Caceres et al (refer Table 1.7) detected the formation of the intermetallic outburst for dipping times as short as 8 seconds in their 2.7 wt% Al-Zn bath and 4 seconds in their 5.6 wt% Al-Zn bath, both baths being held at 450°C. The abnormal growth (breakaway) of the outburst was accompanied by extensive irregularities. On increasing the immersion time to 128 seconds for the 5.6 wt% Al-Zn bath and 64 seconds for the 2.7 wt% Al-Zn bath, the growth of the intermetallic layer tended to become more regular and uniform in thickness. However the presence of the extensive but irregular zinc-rich layers within the intermetallic layer was clearly detected.

According to Caceres et al, there is a radical change in the growth morphology of the intermetallic layer in prolonged dipping times such as 512 seconds. An irregular breakaway growth changes to a columnar fibre-like morphology. The columnar layer is accompanied by a very well marked-intercolumnar region, rich in zinc. X-ray diffraction showed that the intermetallic had a structure isomorphous with FeAl$_3$.

In Caceres et al’s analysis, the compositions of the intermetallics were:

1. (26-28) wt% Fe, (24-33) wt% Al and (34-53) wt% Zn for the early outburst,
2. 37 wt% Fe, 44 wt% Al and 19 wt% Zn for both breakaway and columnar.

Caceres et al argued that the early irregular growth of intermetallic took the form of Zn-rich 'waves' within the intermetallic and the 'waves' might have distorted the compositional analysis obtained. They also pointed out that the columnar 'breakaway' layer and the initial inhibiting layer seemed to represent different morphologies of the same phase; the composition corresponds to a stoichiometry of the Fe(Al$_x$Zn$_{1-x}$)$_3$, type where x=0.85.
In Makimattila’s more recent work (refer Table 1.7), it was shown that when the steel sheet had a thickness greater than 1.5 mm a continuous intermetallic alloy layer (porous) was found to cover the interface. In thinner strips, however, the intermetallic phase was either local or not thick enough to be detectable. Formation of a relatively thick intermetallic layer was asymmetric so that the strip side which was more effectively cooled by the liquid metal stream had practically no intermetallic particles.

Fig. 1.23 Makimattila’s compositional fields of intermetallics (65).

As reported by Makimattila, it seemed clear that there existed two Fe-Al-Zn phases. The phases have nearly the same Fe/Al ratio but different zinc content (Fig. 1.23). When the intermetallic layer was relatively thick (3 to 5 μm), the division of the phases into two separate compositions was more pronounced.

The intermetallic phase growing during industrially continuous Galvanizing has also been reported more recently (3). For a gauge thickness of greater than 1.5 mm, the heat input for a slow moving strip was higher and the immersion time was longer. This caused the bath temperature to rise which in turn induced an irregular intermetallic compound growth, capable of reaching the surface of the coating. In order to prevent this phenomenon, it is necessary to reduce the inlet temperature depending on the strip thickness. However, such a reduction in temperature may cause wettability problems. It was also reported in the same study (3) that with the addition of silicon up to 0.015 wt% a significant inhibition of the intermetallic growth was found.
In summary, it seems to be agreed that the substrate-melt interface, before apparent intermetallic growth takes place, is rich in aluminium. However, despite Makimattila’s Auger electron spectroscopy analysis, the composition and the structure of the interface are far from clear.

Not only is the interface unidentified, there are also variations in the reported compositions and structures of the intermetallic phases which develop during hot dipping in melts containing around 5 wt% Al. Ghumen and Goldstein and Caceres et al reported that the intermetallic was structurally isomorphous with FeAl, when dipping at 450°C, and Ghumen and Goldstein reported the same intermetallic when dipping at temperatures within the range of 450°C to 590°C. However, Makimattila assumed that there exist two separate Fe-Al-Zn phases (Fig. 1.23).

It has been reported that the addition of silicon into the Galfan bath has the effect of inhibiting the growth of intermetallic.

1.7 THE SCOPE OF THE PRESENT RESEARCH

Systematic investigation into Galfan hot dipping, i.e., covering a wide range of temperatures and dipping times, is clearly required and this was carried out in the present study.

Specifically, low carbon steel sheets were Galfanized in the temperature range of 450°C to 575°C with dipping times from 3 seconds to 4096 seconds; lower temperatures required longer times for the intermetallics to fully develop. The studies of the intermetallic phases present in Galfanized coatings were then carried out in three aspects:

1. The growth morphology of the intermetallic phases was studied by using scanning electron microscopy;

2. An X-ray diffraction technique was used to identify the structures of the intermetallic phases;

3. Compositional analysis was carried out using the Scanning Electron Microscope with an X-ray energy dispersive system.

In order to study the structural and compositional characteristics of the intermetallic phases in the coatings, a full understanding of the interplanar spacings of Fe₃Al₃-Zn, and more knowledge of the Fe-Al-Zn ternary
section, particularly on the Fe-Al rich side are important. Two preliminary studies were therefore carried out:

1. Interplanar spacings and lattice parameters of Fe$_2$Al$_3$ and Fe$_3$Al$_5$-Zn$_x$.

2. The Fe-Al-Zn ternary phase diagram at 450°C.

From the studies described above, the growth morphology, structure and composition of the intermetallic phases were deduced. The mechanisms of formation and growth of intermetallics during Galfanizing can then be suggested.

Following the Galfanizing of low carbon steel, the effect of silicon on the reaction between the steel substrate and the Galfan bath was investigated. Firstly, three steels with different silicon compositions, namely, Si wt% = 0.1, 0.5 and 1.58 were used as substrates for Galfanizing. Secondly, silicon was added into the Galfan bath while low carbon steel was used as a substrate.
In this investigation a brief series of experiments on the substrate pretreatment was first carried out and then a systematic in-depth study on Galfanizing was completed. In the latter study, morphological observations, studies of structure and compositional analyses were carried out. The details of the procedures and methods of the investigation are described in this chapter. Two preliminary studies, first the study of the interplanar spacings of Fe,Al, and Fe,Al-Zn, and second the study of the Fe-Al-Zn ternary phase diagram at 450°C, are also described in this chapter.

2.1 PRETREATMENT PROBLEM

A reducing atmosphere was not introduced in any of this work. An alternative surface treatment (i.e., a fluxing type treatment) was used instead.

With the development of Galfan, it has become apparent that the conventional NH₄Cl-ZnCl₂ fluxes normally used for hot dip galvanizing are not compatible with Galfan. The chemical reaction between the aluminium and the fluxes lead to the formation of AlCl₃ during Galfanizing and the appearance of black spots and uncoated areas in the coating (66).

In recent years, a number of investigations have been carried out in an attempt to develop fluxes that are compatible with the Galfan bath (66,67). Some of the fluxes developed gave good results which showed that flux residues and barespots can be eliminated. However all these fluxes have compositions which are proprietary. One can only guess that the successful fluxes might contain, in addition to the conventional flux, one or more of the following: NaCl, NaF, NaBF₄. In a recent patent, it was claimed that a flux combining SnCl₂, NH₄HF₂, NaHF₂, KHF₂, NaCl, KCl and ZnCl₂ enables a superb coating to be produced in (3.5-5) wt% Al-Zn baths (68).

As the primary aim of this study was not to investigate and search for a successful flux, a thorough study on this topic was not carried out. The choice of the surface treatment was based on a preliminary study as described below.
2.1.1 Preliminary Experiment

In this preliminary experiment low carbon steel with dimensions 0.45 x35x35 mm was used for hot dip Galfanizing. The compositions of the steel and Galfan bath will be given later (section 2.2.1). The Galfanizing involved the following steps:

1. degreasing,
2. pickling,
3. fluxing, (this step sometimes omitted)
4. hot dipping,
5. air cooling.

Specimens were degreased by immersing them in 8% NaOH solution for 50 seconds in an ultrasonic cleaning bath. Each specimen was then pickled by immersion in 11% HCl for 70 seconds in the ultrasonic cleaner. The pickling treatment was done in two baths. After 60 seconds pickling in the first bath, there was probably no rust left (no rust was visible). The specimen was then immersed in the second bath for another 10 seconds. Between the degreasing and pickling treatments, each specimen was water washed using the ultrasonic cleaning bath. After pickling, the specimen was then further treated by one of the methods listed in Table 2.1.

Table 2.1a Types of substrate surface treatments (no flux).

<table>
<thead>
<tr>
<th>No. and type</th>
<th>Treatment</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. HCl-Wtr-Alc</td>
<td>After pickling, specimen was rinsed in water and ethanol for 10 seconds in an ultrasonic cleaning bath, then dried in a stream of oxygen free nitrogen</td>
</tr>
<tr>
<td>2. HCl-Alc</td>
<td>Similar to No. 1 but no water rinsing</td>
</tr>
<tr>
<td>3. HCl-Wtr</td>
<td>Similar to No. 1 but no ethanol rinsing</td>
</tr>
<tr>
<td>4. HCl</td>
<td>Similar to No. 1 but no water &amp; ethanol rinsing</td>
</tr>
</tbody>
</table>
Table 2.1b Types of substrate surface treatments (fluxing).

<table>
<thead>
<tr>
<th>No. and type</th>
<th>Treatment</th>
</tr>
</thead>
<tbody>
<tr>
<td>5. ZnCl₂ (fluxing)</td>
<td>Fluxed: 450 g/l ZnCl₂, pH 1.7 adjusted by adding HCl. Specimen was fluxed at 70°C for 60 seconds, then dried in a stream of oxygen-free nitrogen.</td>
</tr>
<tr>
<td>6. ZnCl₂, NaCl, and NaF (fluxing)</td>
<td>Fluxed: (450 g ZnCl₂ + 100 g NaCl + 50 g NaF)/l, pH 1.3-1.8 adjusted by adding HCl. Specimen was fluxed at 70°C for 60 seconds, then dried in a stream of oxygen-free nitrogen</td>
</tr>
</tbody>
</table>

The conditions for hot dipping are summarized in Table 2.2 and the operation of the hot dipping will be described in a later section (section 2.2.3).

2.1.2 Observations

The coatings produced by different surface pretreatments are shown in Figures 2.1, 2.2, 2.3, 2.7, 2.8 and 2.10. Cross sections of the coatings were observed under the scanning electron microscope and scanning electron micrographs were taken to show the coating characteristics; these micrographs are included in Figures 2.4, 2.5, 2.6 and 2.9. In this section, the characteristics of the coatings are discussed only in terms of the pretreatment.

Pickling

Pretreatment 1 HCl-Wtr-Alc:

T=420°C: For immersion of specimens up to 900 seconds in the hot dipping bath, the steel substrate did not react at all with the liquid Galfan. Evidence for this is that a large area of the sample remained uncoated after the hot dipping; the coating itself could simply be peeled
Table 2.2 Conditions of hot dipping in the pre-treatment experiment.

<table>
<thead>
<tr>
<th>Temp., °C</th>
<th>420</th>
<th>440</th>
<th>460</th>
<th>480</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pickl.¹</td>
<td>1</td>
<td>1</td>
<td>4</td>
<td>3</td>
</tr>
<tr>
<td>t, s</td>
<td>0³</td>
<td>0</td>
<td>0</td>
<td>5</td>
</tr>
<tr>
<td>Flux.²</td>
<td>6</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

| 30        | -   | -   | +   | -   |
| 45        | +   | -   | -   | -   |
| 60        | +   | +   | +   | +   |
| 80        | +   | -   | -   | -   |
| 100       | -   | +   | +   | -   |
| 120       | +   | -   | -   | -   |
| 160       | -   | +   | -   | -   |
| 180       | +   | -   | -   | -   |
| 260       | +   | +   | -   | -   |
| 360       | +   | -   | -   | -   |
| 400       | -   | +   | -   | -   |
| 480       | +   | -   | -   | -   |
| 600       | -   | +   | -   | -   |
| 660       | +   | -   | -   | -   |
| 900       | +   | +   | -   | -   |
| 1300      | -   | +   | -   | -   |

1. number of treatment type after pickling (refer to Table 2.1).
2. number of fluxing type (refer to Table 2.1).
3. 0 - no fluxing.
+ hot dip Galfanizing.
- no hot dip Galfanizing, *not attempted*.

off indicating that the coated area was only molten Galfan frozen on to the substrate without any metallurgical reactions having taken place between the two. The peeled area was visibly clean and shiny as opposed to the black colour of the uncoated area.
T=440°C: (Fig. 2.1) No reaction occurred up to 600 seconds in the hot dipping bath. Longer dipping times resulted in a reaction progressing from the edges of the samples. The peeled coating, clean peeled area in the substrate and the uncoated black area can be seen in Fig.2.1.

T=460°C: (Fig. 2.2) A reaction was observed locally for 260 seconds hot dipping. The density and the size of such local spots increased with longer dipping time; the spots appear like "pimples" in the photograph. While the coating again could be peeled off in the unpimpled areas, the pimples stuck firmly to the substrate indicating that a metallurgical reaction had taken place there.

T=480°C: (Fig. 2.3) Reaction was similar to that when hot dipped at 460°C but with denser and larger pimples. In a sample dipped for 600 seconds, the substrate was coated completely with a thick alloy layer; the pimples were so dense and so large with longer dipping times that they met and grew together to become a thick layer.

Scanning electron micrographs (Fig. 2.4, 2.5 and 2.6) show that the interface between the pimples and the substrate is mainly a well-developed intermetallic layer. In the unpimpled areas, however, the steel substrate generally remained bare.

A similar result was obtained with the slightly different pretreatments 2 and 3 (HCl-A1c and HCl-Wtr); photographs are presented in Fig. 2.7.

The conclusion from these results seems to be that surface treatment of this kind sets up a physical barrier which prevents the reaction between the substrate and the molten Galfan taking place. The barrier is probably a film of oxide formed during the rinsing after pickling. Though it is not clear how the metallurgical reaction starts locally, local breakdown of the oxide film might be an important factor. Higher temperatures enhance the metallurgical reaction. We therefore conclude that pretreatments 1, 2 and 3 do not allow molten Galfan to wet the steel substrate.
Fig. 2.1 Appearance of Galfanized coatings. Pickling: HCl-Water-Ethanol, no Fluxing, Hot dipping: T=440°C, t as indicated.
Fig. 2.1 Cont.
Fig. 2.2 Appearance of Galfanized coatings. Pickling: HCl-Water-Ethanol, no Fluxing, Hot dipping: T=460°C, t as indicated.
Fig. 2.3 Appearance of Galfanized coatings, Pickling: HCl-Water-Ethanol, no Fluxing, Hot dipping: T=480°C, t as indicated.
Fig. 2.4 Microstructures of a Galvanized coating. Pickling: HCl-Water-Ethanol, no fluxing, Hot dipping: T=460°C, t=900 s.
A. low magnification;
B. high magnification of substrate-coating interface.

Fig. 2.5 Microstructures of two Galvanized coating. Pickling: HCl-Water-Ethanol, no fluxing, Hot dipping: T=480°C, t: A=400 s, B=600 s.

Fig. 2.6 Microstructures of a Galvanized coating at high magnification of substrate-coating interface. Pickling: HCl-Water-Ethanol, no fluxing, Hot dipping: T=480°C, t=600 s.
Fig. 2.7  Appearances of Galfanizied coatings. Pickling as indicated, no fluxing, Hot dipping: T=460°C, t=160 s.
Pretreatment 4  HCl:

T=440°C: (Fig. 2.8) Using this pretreatment the substrate had a fixed coating of Galfan for a dipping time as short as 30 seconds but some areas remain bare. The surface is reasonably smooth for short dipping time (<60 s). Longer dipping leads to a reduction in the bare area, the surface becoming rougher and the coating thicker. Metallurgical examination under the scanning electron microscope reveals that the alloying reaction between molten Galfan and the steel substrate at the early stage is basically uniform. Micrographs A, B and C in Fig. 2.9 show how the coating is uniform rather than pimpled. Molten metal has solidified in the classic Galfanizing manner for dipping times less than 60 seconds; a considerable amount of proeutectic appears near the interface. A local outburst of the intermetallic phase is apparent in Fig. 2.9a and 2.9b while longer dipping (100 seconds) results in further growth of the intermetallic as shown in Fig. 2.9c.

![30 s](image1)
![60 s](image2)
![100 s](image3)

Fig. 2.8 Appearances of Galfanized coatings, Pickling: HCl, no fluxing, Hot dipping: T=440°C, t as indicated.
Note: Coatings can not be peeled off.

T=460°C: (the third photograph in Fig. 2.7) Higher bath temperatures produce a rougher and thicker coating; this indicates more growth of the irregular intermetallic compound.

The pretreatment of this type (pretreatment 4) differs from that of HCl-Wtr-Alc only slightly, i.e., no rinsing after pickling. It is assumed that the substrate surface remains covered by a type of acidic layer such as FeCl3(H2O), or simply a residual acid layer instead of an oxide film. This layer, unlike the reformed oxide film, makes the wetting possible.
Fig. 2.9 Microstructures of Galfanized coatings. Pickling: HCl, no fluxing, Hot dipping: $T=440^\circ C$, $t$: $A - 30$ s, $B - 60$ s and $C - 100$ s. $A'$, $B'$ and $C'$ are higher magnifications of $A$, $B$ and $C$. 
Fluxing

Pretreatment 5  ZnCl₂:

As shown in Fig. 2.10c, on hot dipping at 440°C for 60 seconds, the substrate has a fixed coating. However, the surface of the coating is rough and many small and discrete areas remain uncoated.

Pretreatment 6  ZnCl₂, NaCl, NaF:

Fig. 2.10d indicates that when the flux contains NaCl and NaF in addition to ZnCl₂, the quality of the coating is improved with respect to surface smoothness and bare areas.

Fig. 2.10 Appearance of Galfanized coatings. Pickling: a. HCl-Water-Ethanol, b. HCl, c & d. HCl-Water, Fluxing as indicated, Hot dipping: T=440°C, t=60 s. Note: except coating A, all coatings can not be peeled off.
2.1.3 Conclusion

It seems from Fig. 2.10 that HCl pickling without rinsing and fluxing is the most satisfactory method in the production of the best coating. For a flux to reach its optimum, the following parameters are important: flux concentration, flux pH, fluxing temperature, fluxing time, etc.. A thorough investigation into these variations has not been carried out in this study.

From Fig. 2.9 it can be seen that the intermetallic formation and growth, at least at the early stage, is highly localized at 440°C; this is similar to those results observed in other laboratory and industrial studies in which different fluxes or a reducing atmosphere were used (3,30,35,62-63, 65).

The outcome of this pretreatment experiment was, therefore, that the simple form of HCl pickling without further rinsing and fluxing was adopted as the surface treatment for later studies of intermetallic formation and growth.

2.2 GALFANIZING

2.2.1 Materials

Low carbon steel sheet with a thickness of 0.45 mm was used as substrate for the major part of this investigation. Three other types of steel sheets with different silicon contents were also included and they were 0.5 mm thick. All the steels were cold rolled. The three different steels containing different silicon contents were not-specifically-oriented transformer steel. Specimens of 35 mm square were cut from the steel sheets. The transformer steel specimens were surface polished on 1200 grade SiC paper before hot dipping as they were chemically treated in the as-received condition. The microstructures of the steels are shown in Fig. 2.11. The edge of each specimen is shown because the edge is most important when hot dipping is being considered.

The chemical compositions for the steels are listed in Table 2.3. Except for the marked differences in silicon contents, low carbon steel has a composition similar to the 1.58 wt% Si steel and the compositions of 0.1
and 0.5 wt% Si steels are essentially the same.

The hot dipping bath contained approximately 3 kg Galfan, the chemical composition of which was: 5 wt% Al, 0.02 wt% Ce, 0.031 wt% La, 0.0006 wt% Mg, <0.005 wt% Pb, iron saturated and the balance zinc (analysis by N.Z. Steel).

![Microstructures of the steel substrates.](image)

Fig. 2.11 Microstructures of the steel substrates.

The iron content of the as-received Galfan ingot was 0.013 wt% according to the N.Z. Steel analysis. To saturate the melt with the iron, iron was allowed to dissolve into the melt. Several small pieces of Armco iron were put in each bath and left for at least a few hours before hot dipping. Simigliano reported that the Galfan bath analysis of iron was 0.075 wt% causing precipitation which appeared as top dross (3). For a bath containing 3 kg Galfan, approximately 1.8 g iron was therefore required.
Table 2.3 Chemical compositions for four different Steel substrates (wt%).

<table>
<thead>
<tr>
<th>Element</th>
<th>Low carbon</th>
<th>0.1 wt% Si</th>
<th>0.5 wt% Si</th>
<th>1.58 wt% Si</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si</td>
<td>&lt;0.005</td>
<td>0.1</td>
<td>0.5</td>
<td>1.58</td>
</tr>
<tr>
<td>C</td>
<td>0.05</td>
<td>0.02</td>
<td>0.02</td>
<td>0.015</td>
</tr>
<tr>
<td>Mn</td>
<td>0.25</td>
<td>0.40</td>
<td>0.40</td>
<td>0.28</td>
</tr>
<tr>
<td>P</td>
<td>0.016</td>
<td>0.04</td>
<td>0.04</td>
<td>0.033</td>
</tr>
<tr>
<td>S</td>
<td>0.02</td>
<td>0.03</td>
<td>0.03</td>
<td>0.006</td>
</tr>
<tr>
<td>Al</td>
<td>0.5</td>
<td>0.5</td>
<td></td>
<td>0.46</td>
</tr>
<tr>
<td>Ni</td>
<td>0.1</td>
<td>0.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cr</td>
<td>0.05</td>
<td>0.05</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu</td>
<td>0.05</td>
<td>0.05</td>
<td></td>
<td></td>
</tr>
<tr>
<td>N</td>
<td></td>
<td></td>
<td></td>
<td>0.0039</td>
</tr>
</tbody>
</table>

1. analysis by N.Z. Steel,  
2. analysis given by Kawasaki steel.

When the bath contained silicon, the mixture was prepared as 0.1 wt% Si-Galfan. However the maximum level of silicon which will dissolve in Galfan at 450°C is 0.015 wt% (3). The final silicon content in the Galfan bath was therefore expected to be 0.015 wt%.

The Si-Galfan bath was made by mixing: 2700 g Galfan, 14.6 g 20 wt% Si-Al, 220 g pure zinc; this was based on the following:

Assuming 1 part (in weight) Galfan then:

\[ X = ZY/(1+Z+S) \]
\[ R = 5\% = [0.05+Z(1-Y)]/(1+Z+S) \]
\[ S = (0.95Z-ZY)/0.05 \]
\[ X(1+Z+S) = ZY \]
\[ X[1+Z+(0.95Z-ZY)/0.05] = ZY \]
\[ Z = X/[Y-(1-Y)X/0.05] \]

where \( X = \% \text{ Si in the Si-Galfan} \),  
\( Y = \% \text{ Si in the Si-Al alloy} \),  
\( Z = \text{parts of Si-Al alloy needed} \),  
\( X = \) parts of Si-Al alloy needed,
R = % Al in the Si-Galfan,
S = parts of pure zinc needed.
The Galfan and pure zinc were first melted together at 700°C, and then
enough 20 wt% Si-Al was introduced and pushed down to the bottom of the bath
with a stainless steel holder. The bath was held at 700°C for 5 hours
before the temperature was turned down to the required value.

2.2.2 Apparatus

Fig. 2.12 shows the apparatus used in this investigation for hot dip
Galfanizing. For the substrate surface pretreatment, there was a gas
cylinder of oxygen free nitrogen for drying specimens and an ultrasonic
cleaner with four containers in it: of these four containers, one contained
NaOH for degreasing, one contained rinsing water and the other two contained
HCl for pickling.

![Apparatus for hot dip Galfanizing.](image)

Fig. 2.12 Apparatus for hot dip Galfanizing.

Fig. 2.13 is a schematic drawing of the furnace and melt pot used for
hot dip Galfanizing. Galfan in a graphite crucible was melted in the elect-
ric furnace; the furnace temperature was controlled by an auto-setting PID
in a microprocessor-based temperature controller. Two R type thermocouples
were used for the temperature control; one measured the furnace temperature and controlled it through the temperature controller and the other measured the temperature of the melt in the crucible. Temperature of the melt fluctuated slightly under the disturbance of dipping. The melt thermocouples indicated that the temperature was controlled to ±2°C or better.

Fig. 2.13 Schematic drawing of the furnace and bath used in hot dipping Galfanizing.
2.2.3 Hot Dipping Procedure

Specimens were first surface pretreated. As discussed previously (section 2.1.3), the pretreatment was done without using a flux. The details of the pretreatment were:

1. degreasing in 8% NaOH for 70 seconds in an ultrasonic cleaner,
2. rinsing in water for 10 seconds in an ultrasonic cleaner,
3. pickling in 9% HCl for 60 seconds in the first bath and 10 seconds in the second bath in an ultrasonic cleaner,
4. drying by blowing oxygen free nitrogen through a nozzle.

Immediately after drying, the surface of the melt was skimmed off and the specimen was then hot dipped. During the hot dipping, the specimen and the bath were not agitated. Immediately before the withdrawal of the specimen, the surface of the bath was skimmed off again. After withdrawal, the specimens were air cooled in most cases. To study post-cooling effects, a set of low carbon steel specimens were quenched in ice water within 1 second after their withdrawal from the melt. The bath temperatures and the hot dipping times for four types of steel substrates are detailed in Table 2.4.

Table 2.4 Temperatures and hot dipping times for four steel substrates.

A. Low carbon steel, air cooled.

<table>
<thead>
<tr>
<th>Temp., °C</th>
<th>Dipping time, sec.</th>
</tr>
</thead>
<tbody>
<tr>
<td>450</td>
<td>16  32  64  128  256  512  1024  4096</td>
</tr>
<tr>
<td>460</td>
<td>20  80  110  145  185  230</td>
</tr>
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<td>470</td>
<td></td>
</tr>
<tr>
<td>480</td>
<td>5  10  20  35  55</td>
</tr>
<tr>
<td>490</td>
<td>5  10  20  35  55</td>
</tr>
<tr>
<td>500</td>
<td>5  10  20  35  55</td>
</tr>
<tr>
<td>510</td>
<td>5  10  20  35  55</td>
</tr>
<tr>
<td>520</td>
<td>5  10  15  20  40  60  80</td>
</tr>
<tr>
<td>575</td>
<td>3  7  10  20  40</td>
</tr>
</tbody>
</table>

53
Table 2.4 Cont. 1

B. Low carbon steel, ice water quenched

<table>
<thead>
<tr>
<th>Temp., °C</th>
<th>Dipping time, sec.</th>
</tr>
</thead>
<tbody>
<tr>
<td>450</td>
<td>128 256 512</td>
</tr>
<tr>
<td>490</td>
<td>20 55</td>
</tr>
<tr>
<td>520</td>
<td>10 40</td>
</tr>
<tr>
<td>575</td>
<td>7 20</td>
</tr>
</tbody>
</table>

C. Dipping times for 0.1 wt% Si, 0.5 wt% Si, 1.58 wt% Si steel substrates (seconds).

<table>
<thead>
<tr>
<th>Steel sub.</th>
<th>0.1 wt% Si</th>
<th>0.5 wt% Si</th>
<th>1.58 wt% Si</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temp., °C</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>450</td>
<td>600</td>
<td>1020</td>
<td>300</td>
</tr>
<tr>
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<td>1560</td>
<td>600</td>
<td></td>
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<td>2100</td>
<td>1020</td>
<td></td>
</tr>
<tr>
<td>2100</td>
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<td>300</td>
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<tr>
<td>180</td>
<td>600</td>
<td>180</td>
<td></td>
</tr>
<tr>
<td>300</td>
<td>840</td>
<td>300</td>
<td></td>
</tr>
<tr>
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<td>840</td>
<td></td>
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</tr>
<tr>
<td>1020</td>
<td>1080</td>
<td></td>
<td></td>
</tr>
<tr>
<td>520</td>
<td>9</td>
<td>60</td>
<td>120</td>
</tr>
<tr>
<td>14</td>
<td>120</td>
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<td>270</td>
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<td>270</td>
<td>390</td>
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</tr>
<tr>
<td>50</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table 2.4 Cont. 2

D. Si-Galfan bath, air cooled.

<table>
<thead>
<tr>
<th>Temp., °C</th>
<th>Dipping time, sec.</th>
</tr>
</thead>
<tbody>
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<td>128 256 512 1024</td>
</tr>
<tr>
<td>470</td>
<td>55 110 220 440</td>
</tr>
<tr>
<td>490</td>
<td>20 40 80 160</td>
</tr>
<tr>
<td>520</td>
<td>10 20 40</td>
</tr>
<tr>
<td>575</td>
<td>5 10 20</td>
</tr>
</tbody>
</table>

2.3 METALLOGraphy

For microstructural examination, a cross section of each sample was cut and mounted in bakelite. Specimens were then polished, through SiC papers of 80, 220, 600, 1200 grade and then diamond cloths of 8, 3 and finally down to 1 µm.

Specimens were then etched. Etching was generally done in two different ways:

- light etching: 2% nital 3 seconds,
- heavy etching: 5% nital for 1 to 2 minutes and then 4% HF (in water) for 20 seconds.

Fig. 2.14 shows the features obtained by the two different etching methods. By using the light etching the pro-eutectic zinc and eutectic in the Gal-fanized coating can be observed clearly; heavy etching emphasizes the intermetallic phases as well as the substrate. In some cases, specimens were etched only by 4% HF.

A Philips scanning electron microscope 505 with 20 kV accelerating voltage was used to study features of the microstructures, in particular the coating-substrate interface and the growth of the intermetallic phases; scanning electron micrographs were taken to show such coating morphologies.
2.4 X-RAY DIFFRACTION

2.4.1 Specimen and Diffractometer

An X-ray diffraction technique (69) which used a diffractometer was used to identify the phases present in the Galfanized coatings.

Specimen

Samples for X-ray diffraction analysis were cut in disk form (18 mm diameter) from the hot dipped Galfanized coatings and mounted in a flat rotating sample holder by using an epoxy resin. Diffraction patterns were obtained from the coating surface through to the steel substrate by successive determinations with intermediate grinding and polishing. After X-ray diffraction investigation of the sample surface, the surface was polished off on 600 mesh SiC paper and the second X-ray diffraction analysis was run again on the sample. The sample was then polished for the third X-ray diffraction and this process was repeated until the steel substrate was reached.

Diffractometer

Diffraction experiments were performed using a Philips X-ray diffrac-
tometer system. This system consists of a PW 1729 X-ray generator, a PW 1050 vertical goniometer, a PW 1771 diffractometer, a PW 1133 sample spinner (120 rpm), a PW 1752 curved graphite monochromator and a xenon sealed proportional detector, a PW 1710 diffractometer control unit and a PM 8203A online recorder. The system is shown in Fig. 2.15.

Two different X-ray tubes and two scanning ranges (2θ, where θ is the Bragg angle) were used as follows:

1. Cr Kα radiation, no filter, 30 kV and 30 mA, 2θ=25° to 140°, 1/4° slit.

2. Co Kα radiation, Fe filter, 35 kV and 35 mA, 2θ=20° to 100°, 1/2° slit.

During X-ray diffraction analysis, the X-ray beam from the line source with or without filtering passed through a Soller slit and a divergence slit of 1/4° or 1/2° angular aperture, fell on the spinning sample and was diffracted. The diffracted beams then passed through a receiving slit and another Soller slit, into the monochromator and finally into the detector.

Fig. 2.15 The system of the diffractometer measurement.
The following parameters were used for the X-ray diffraction analysis:

1. scanning speed: 2θ/t =0.025 deg./s,
2. scanning step: 2θ/step = 0.005 deg./step,
3. recorder time constant: 1 s,
4. recorder paper speed: 12 mm/deg. (2θ) = 0.3 mm/s.

These parameters were controlled by the control unit.

Penetration depth

The penetration depth of X-rays into a specimen can be considered as follows. The intensity of an X-ray beam after passing through a specimen is:

\[ I_x = I_o \exp(-\mu/\rho \, pX) \]  \hspace{1cm} (2.1)

where \( I_x \) = intensity of the beam after passing through thickness \( X \),
\( I_o \) = intensity of the incident beam,
\( \mu/\rho \) = mass absorption coefficient,
\( \rho \) = density.

Table 2.5 lists the mass absorption coefficients (\( \mu/\rho \)) of Fe, Al and Zn for Cr and Co Kα radiation. For a mixture of these three elements:

\[ \mu/\rho = W_{f} (\mu/\rho)_{Fe} + W_{Al} (\mu/\rho)_{Al} + W_{Zn} (\mu/\rho)_{Zn} \]  \hspace{1cm} (2.2)

where \( W_A \) is the weight fraction of element A.

For two typical examples:

1. 45.4 wt% Fe-Al (composition of Fe,Al), \( \rho \)=3.99 g/cm³, for Cr Kα radiation, \( \mu/\rho \)=133.6 cm²/g, therefore:

\[ I_x/I_o = \exp(-533.1X) \]

for Co Kα radiation, \( \mu/\rho \)=67.1 cm²/g, therefore:

\[ I_x/I_o = \exp(-267.7X) \]
2. 5 wt% Al-Zn (composition of Galfan), $\rho$=6.59 g/cm$^3$, for Cr K\(\alpha\) radiation, \(\mu/\rho=150.0\) cm$^2$/g, therefore:

\[
I_r/I_o = \exp(-988.5x)
\]

for Co K\(\alpha\) radiation, \(\mu/\rho=74.2\) cm$^2$/g, therefore:

\[
I_r/I_o = \exp(-489.0x)
\]

Table 2.5 The mass absorption coefficients of Fe, Al and Zn (69).

<table>
<thead>
<tr>
<th>Sample</th>
<th>(\mu/\rho,) cm$^2$/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>115</td>
</tr>
<tr>
<td>Al</td>
<td>149</td>
</tr>
<tr>
<td>Zn</td>
<td>169</td>
</tr>
</tbody>
</table>

Fig. 2.16a illustrates the X-ray penetration depth in the diffraction experiment; the penetration depth \(S\) and \(X\) are simply related by equation:

\[
S = X/2 \sin \theta
\]

where \(\theta\) is the Bragg angle as in Fig. 2.16a and \(X\) is the thickness as defined in equation 2.1.

In Fig. 2.16b and 2.16c which are for examples 1 and 2 above respectively, the values of \(I_r/I_o\) is plotted against the penetration depth \(S\) for the lowest and the highest Bragg angles in a X-ray scanning diffraction experiment. The penetration depth for any angle must lie between these two curves and the penetration depth is greater for higher Bragg angles. The figures show that when the penetration depth is much larger than about 10 \(\mu\)m the attenuation becomes quite large. This means that the diffracted X-ray is mostly contributed by the layers 10 \(\mu\)m deep at the sample surface. Fig. 2.16 also shows that the penetration depth is greater when using Co K\(\alpha\) rather than Cr K\(\alpha\) radiation. The Co target and a higher aperture divergence slit were used in the later part of this investigation in order to increase the intensity of the diffracted beam.
(a) A sketch of the X-ray penetration depth

(b) The penetration depth in Fe₃Al, (example 1)

(c) The penetration depth in Galfan (example 2)

Fig. 2.16 The penetration depth of X-ray in X-ray diffraction experiment.
2.4.2 Error Estimation

Errors in the interplanar spacing measurement were estimated by using three kinds of powder samples, viz, iron, aluminium, and zinc as pure metal standards. Values of two theta covered the range from approximately 42° to 100°. The tests were carried out using Co Kα radiation, and an Fe filter with voltage and current set at 40 kV and 35 mA. Tests were run twice for each powder sample and the two theta value for each peak was determined by taking the average of three independent measurements.

Systematic error

The error is defined by:

\[ \Delta \theta = \theta_1 - \theta_2 \]

where \( \theta_1 \) -- \( \theta \) derived from the published standard interplanar spacing, (see appendix 1)

\( \theta_2 \) -- \( \theta \) measured from the powder diffraction.

Fig. 2.17a shows \( \Delta \theta \) plotted against \( \theta \) (data are in Appendix 2); the straight line is the overall linear regression line and has been extrapolated to \( \theta = 30^\circ \). The figure suggests that there is a systematic error in the measured two theta; to a first approximation, the error seems to have a positive linear relationship with two theta. The equation of the linear regression line is:

\[ \Delta \theta = [0.00229(\theta) - 0.0376] \text{ deg.} \]

This can be converted to an error in interplanar spacing by considering the following. From Braggs law:

\[ \lambda = 2d \sin \theta \text{ or } d = \frac{\lambda}{2 \sin \theta} \]

therefore, for an error in \( d \) of \( \Delta d \)

\[ d + \Delta d = \frac{(\lambda/2)}{\sin(\theta + \Delta \theta)} = \frac{(\lambda/2)}{(\sin \theta \cos \Delta \theta + \cos \theta \sin \Delta \theta)} \]
(a) $\Delta 2\theta$ plotted against $2\theta$, Fe1 and Fe2 are different diffraction runs on the same Fe powder sample, Al1 and Al2 for Al and Zn1 and Zn2 for Zn samples.

(b) Systematic error of d-spacing versus $2\theta$.

(c) Systematic error of d-spacing versus $d$.

Fig. 2.17 Systematic error in the X-ray diffraction experiment (data are in Appendix 2).

for a small $\Delta \theta$, $\cos \Delta \theta = 1$ and $\sin \Delta \theta = \Delta \theta$, Then:

$$\Delta d = (\lambda/2)/(\sin \theta + \cos \theta \Delta \theta) - d$$

$$= (\lambda/2)/(\sin \theta + \cos \theta \Delta \theta) - \lambda/(2\sin \theta)$$
Rearranging gives

\[ \Delta d = \frac{(\lambda/2) (\sin\theta - \sin\theta - \Delta\theta\cos\theta)}{\sin^2\theta - \Delta\theta\cos\theta \sin\theta} \]

\[ = \frac{(\lambda/2) (-\Delta\theta \cos \theta)}{\sin^2\theta} \]

\[ \Delta d = -\Delta\theta (\lambda/2) / (\sin\theta \tan\theta) \]  

2.7

where \( \Delta d = d - d' \) is the estimated error of interplanar spacing,

\( d \) -- interplanar spacing from the standard (Appendix 1),

\( d' \) -- interplanar spacing derived from the measured \( 2\theta \) in this experiment,

Fig. 2.17b and c show the error of interplanar spacing as a function of two theta and as a function of interplanar spacing respectively. The interplanar spacings obtained in this experiment are slightly larger than those published in the JCPDS standard (Appendix 1), by an amount which varies, depending on Bragg angle, from 0.0022 Å (when \( 2\theta = 100^\circ \), \( d = 1.1685 \) Å) to 0.0056 Å (when \( 2\theta = 20^\circ \), \( d = 3.4584 \) Å).

The very small systematic error described above is probably the result of a slight misalignment in setting the X-ray equipment used in this experiment. The error can easily be compensated for by using the linear regression equation 2.5.

Random error

Besides the systematic error, there is also a random error from the uncertainties arising during the X-ray analysis. The random error can be estimated from data in Fig. 2.17a; Appendix 2 details a statistical analysis of these data. The random error is calculated using a 90% confidence limit. Random errors (\( \Delta d \)) are plotted in Fig. 2.18 as a function of (a) \( 2\theta \) and (b) \( d \). These graphs parallel the graphs of Fig. 2.17 (b) and (c) which relate to the systematic error.

The random error can come from two sources. First, there is an uncertainty from the measurement of two theta on the chart paper. The uncertainty of the measurement \( \Delta x \) in this case is approximately 0.4 mm. As detailed previously (section 2.4.1), twelve millimeters of chart paper represents one degree of \( 2\theta \).
Then: \[ \Delta \theta = 0.0833 \Delta x \text{ deg.} = 0.033 \text{ deg.} \]

There is also an error between experimental runs taken as a whole. For example, \( \Delta \theta \) in the second zinc test (Zn2 in Fig. 2.17a) is slightly higher than that measured in first test (Zn1 in Fig. 2.17a).

![Graph](image1)

(a) Error of d-spacing versus \( \theta \) 
(b) Error of d-spacing versus \( d \)

Fig. 2.18 Random error of the X-ray diffraction experiment (data are in Appendix 2).

For X-ray diffraction experiments using a chromium target, similar errors are expected.

2.4.3 Standards and the Study of the Fe\_Al\_ File

**Standard file**

In the X-ray diffraction experiment of this investigation, the general principle of the identification of a substance by X-ray diffraction is followed. Specifically, the JCPDS (ASTM) X-Ray Powder Diffraction Data were normally used as standards for identification. Appendix 1 lists the JCPDS data cards for Fe-Al, Fe-Zn and Al-Zn compounds as well as some related data which are not in the JCPDS Powder Diffraction File. The standards for Fe\_Al\_, and FeAl, and their ternary forms are most important in identification of the intermetallic phases present in the Galfanized coatings. However, the JCPDS standard for Fe\_Al\_, as is shown below, is misleading. The use of the standard for Fe\_Al\_, and its ternary form will now be considered.
Harvey and Mercer (37) and Urednicek and Kirkaldy (36) have published data on interplanar spacings in Fe₄Al₅ (Appendix 1). Comparing Harvey and Mercer’s data and that from JCPDS (see Appendix 1), the following differences are apparent:

1. \( d=2.123 \, \text{Å}, \frac{I}{I_0}=100 \) and \( d=2.114 \, \text{Å}, \frac{I}{I_0}=12 \) in Harvey’s data, while \( d=2.11 \, \text{Å}, \frac{I}{I_0}=100, \) hkl=002 in JCPDS.

2. \( d=2.066 \, \text{Å}, \frac{I}{I_0}=98 \) and \( d=2.059 \, \text{Å}, \frac{I}{I_0}=27 \) in Harvey’s data, while \( d=2.05 \, \text{Å}, \frac{I}{I_0}=100, \) hkl=130 in JCPDS.

In Urednicek and Kirkaldy’s data, it was reported that there are two interplanar spacings, viz., \( d=2.116 \, \text{Å}, \frac{I}{I_0}=100 \) and \( d=2.100 \, \text{Å}, \frac{I}{I_0}=75 \) as opposed to \( d=2.11 \, \text{Å}, \frac{I}{I_0}=100 \) in JCPDS.

To resolve these discrepancies, a detailed investigation of Fe₄Al₅ was carried out as followed:

1. **Possible diffracting planes in Fe₄Al₅**
   
   Possible planes of Fe₄Al₅ (from \( d=1.000 \, \text{Å} \) to \( d=5.000 \, \text{Å} \)) were searched and listed using a simple computer program (see Appendix 3). The calculation was based on the relationship amongst interplanar spacing, plane (hkl), and lattice parameters \( a, b, c \) for Fe₄Al₅: viz

   \[
   \frac{1}{d^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}
   \]

   where \( a=7.675 \, \text{Å}, b=6.403 \, \text{Å}, c=4.203 \, \text{Å} \) as from JCPDS.

2. **Calculation of intensities**

   The calculation of the relative intensity of the powder pattern lines is based on the following equation (69):

   \[
   I = F^2p\left[\frac{(1+\cos^2\theta)}{(\sin^2\theta\cos\theta)}\right]
   \]

   where \( F=\text{structure factor}, \)
   
   \( p=\text{multiplicity factor}, \)
   
   \( \theta=\text{Bragg angle}, \)
   
   \( (1+\cos^2\theta)/(\sin^2\theta\cos\theta) = \text{lorentz-polarization factor}. \)
The equation 2.9 needs only the insertion of a temperature factor to make it precise \((69,75)\), i.e.:

\[ I_s = I_0 e^{-2M} \]

2.10

where \( M = 8\pi^2 U_s^2 \sin^2 \theta / \lambda^2 \)

\( U_s \) is the mean-square displacement of a atom,

\( \theta \) is the Bragg angle,

\( \lambda \) is the wavelength

Table A3.3 (in Appendix 3) lists the results of the calculation by using equation 2.9 (for details of calculation see Appendix 3). These are compared with JCPDS, Harvey and Mercer’s, and Urednicek and Kirkaldy’s data. The omission of the temperature factor in equation 2.9 results in higher calculated intensities for the higher angle lines. However it is still reasonable to compare the calculated relative intensities of two adjacent lines \((75)\).

Table A3.3 clearly shows that:

1. The peak of \( d=2.11 \) Å is the combination of two peaks, from 221 and 002, rather than only from 002 as listed in JCPDS. The intensity of that from 221 is the higher of two.

2. The peak of \( d=2.05 \) Å is also the combination of two peaks, from 311 and 130, rather than only from 130 as listed in JCPDS. The intensity of that from 311 is the higher of two.

3. It is very likely that the diffraction peak at \( d=1.52 \) Å listed in the JCPDS file is from 421 rather than 331, while the tiny peak at \( d=1.55 \) Å should be attributed to 312.

4. There are several small peaks which are not listed in the JCPDS file. These include, in particular, the interplanar spacings of 1.223, 1.106, 1.057, 1.044, 1.007 Å.

These results point to the necessity for corrections and additions to the JCPDS file for Fe₃Al₄; the proposed file is listed in Table A3.4. Fe₃Al₄ can have a range of compositions between 53 and 56.2 wt% aluminium \((41)\). The lattice parameters, and therefore the interplanar spacings listed in Table A3.4 may vary slightly when the composition of the phase varies.
As the intermetallic phase present in the Galfanized coating is inevitably ternary, it is necessary to consider the ternary form of Fe₃Al, i.e., Fe₃Al₃ with zinc. Therefore, Harvey and Mercer’s diffraction data for the ternary phase, i.e., Fe₃Al₃-Zn, is used here as a standard rather than the JCPDS data. However, allowance must be made for the fact that the composition of Fe₃Al₃-Zn, formed during Galfanizing may differ slightly from that formed during galvanizing in a 0.2 wt% Al-Zn bath. Table 2.6 lists Harvey and Mercer’s data for the ternary alloy together with (hkl) values indexed according to the calculation for the binary form of Fe₃Al₃. The lattice parameters used for calculating the interplanar spacings were derived using the procedure outlined in Appendix 3. It is noted that, by comparing the list for Fe₃Al₃ and that for Fe₃Al₃-Zn, two peaks (311 and 130) change positions in the lists as a result of change in lattice parameters:

1. for (311) d=2.068 Å for binary and d=2.066 Å for ternary,
2. for (130) d=2.058 Å for binary and d=2.075 Å for ternary.

Three additional interplanar spacings of (223), (512), (313) are also listed in Table 2.6 since their peaks appeared in the present investigation; the intensities of their peaks in the binary form are used here for approximation. Two interplanar spacings, i.e., d=2.778 Å and d=2.015 Å in Harvey and Mercer’s original data have been omitted as according to this calculation there are no corresponding (hkl) values. The angle of (hkl) to (002) is also listed in Table 2.6 and this was calculated from the following equation:

\[
\phi = \cos^{-1}\left\{ \frac{1}{(c)} \left\{ \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2} \right\}^{-1/2} \right\}
\]

2.4.4 Method of Data Analysis

Diffraction pattern

Fig. 2.19 schematically illustrates an X-ray diffraction measurement on a Galfanized coating. The coating consists of the eutectic of zinc and aluminium on the surface layer. Going towards the substrate, there is then a section of pro-eutectic zinc followed by a mixture of zinc and intermetallic compounds and finally intermetallic completely. Though minor phases may not be picked up because of insufficient X-ray intensity, the major phases
present in the coating can be identified as explained below.

Table 2.6 Standard file of Fe₅Al₃-Zn₅ based on Harvey and Mercer's data.

<table>
<thead>
<tr>
<th>hkl</th>
<th>d', Å</th>
<th>φ</th>
<th>I/I₀</th>
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<td>4.936</td>
<td>90°</td>
<td>1</td>
</tr>
<tr>
<td>200</td>
<td>3.817</td>
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</tr>
<tr>
<td>020</td>
<td>3.235</td>
<td>90</td>
<td>11'</td>
</tr>
<tr>
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<td>3.211</td>
<td>40.6</td>
<td>44'</td>
</tr>
<tr>
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<td>2.368</td>
<td>90</td>
<td>9</td>
</tr>
<tr>
<td>221</td>
<td>2.131</td>
<td>59.8</td>
<td>66</td>
</tr>
<tr>
<td>002</td>
<td>2.115</td>
<td>0</td>
<td>55</td>
</tr>
<tr>
<td>130</td>
<td>2.075</td>
<td>90</td>
<td>30</td>
</tr>
<tr>
<td>311</td>
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<td>222</td>
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<td>241</td>
<td>1.405</td>
<td>70.8</td>
<td>8</td>
</tr>
<tr>
<td>113</td>
<td>1.355</td>
<td>16.1</td>
<td>4</td>
</tr>
<tr>
<td>223</td>
<td>1.224</td>
<td>29.8</td>
<td>13'</td>
</tr>
<tr>
<td>512</td>
<td>1.216</td>
<td>54.9</td>
<td>10'</td>
</tr>
<tr>
<td>313</td>
<td>1.211</td>
<td>30.8</td>
<td>16'</td>
</tr>
</tbody>
</table>

#. lattice parameters derived from Harvey and Mercer's data, i.e.:
   a=7.633 Å; b=6.470 Å; c=4.229 Å.

*. for approximation, I₁₁₀/I₁₁₁=8/41 from the calculation for binary form,
  ^. intensities are from that calculated for binary form.
Fig. 2.19 Schematic diffraction patterns for a Galfanized coating produced when a low carbon steel substrate is hot dipped for 35 seconds in a bath held at 490°C (Only selected peaks for zinc and steel substrate are shown here).
In Fig. 2.19 the diffraction patterns indirectly show the resultant changes of the microstructure from the coating surface through the coating to the steel substrate. For the coating surface the only peaks present have interplanar spacings which identify them as zinc. The two peaks at d=2.475 Å and d=2.092 Å (Fig. 2.19a) are the two major peaks for zinc (Appendix 1, 4-0831). The peak at d=2.092 Å is also a peak for FeAl, (Appendix 1, 29-42); because of being a common peak, it does not conclusively indicate the existence of FeAl, in this case where zinc is also present. The peaks attributed to zinc become weaker and weaker as the diffraction pattern comes from further down the coating (Fig. 2.18b, c and d).

In the second pattern (Fig. 2.19b), there are two small peaks with d=3.542 Å and d=2.013 Å. These two interplanar spacings belong to a structure isomorphous with FeAl, (Appendix 1, 29-42); peaks arising from this phase with interplanar spacings other than these two are not seen in the X-ray diffraction of the Galfanized coating as there is not sufficient intensity from the coating sample. The appearance of the two peaks in this second pattern indicates that the phase is present in the mid-portion of the coating.

From the third and fourth patterns (Fig. 2.19c and d), it is clear that the peak due to the steel substrate (d=2.027 Å, Appendix 1, 6-0696) becomes stronger as the diffracting layer approaches the substrate.

Fig. 2.19c shows nine peaks; the peaks increase in intensity as one moves further into the coating. The intensities of all nine peaks decrease however when the steel substrate is approached, indicating that the phase with the nine interplanar spacings is present in the coating next to the coating-substrate interface. Table 2.7 list the nine interplanar spacings and their peak intensities. A comparison of interplanar spacings with standard files shows that the phase with the nine interplanar spacings is Fe$_3$Al$_2$-Zn,; the corresponding interplanar spacings in the standard based on Harvey and Mercer’s lattice parameters are also listed in Table 2.7 for comparison. Four of the nine interplanar spacings measured here appear to be a combination of two in the standard file as detailed in Table 2.7. Not all the interplanar spacings listed in the standard file can be seen in the X-ray diffraction of the Galfanized coating; this can be explained by assuming that there is a preferred orientation present. (This preferred orientation will be discussed in a chapter 4.)

70
Table 2.7 The nine d-spacings of Fe₃Al₂-Zn₂ and their intensities from the standard file (Table 2.6) compared to the nine d-spacings and their intensities from the X-ray diffraction of the Galfanized coating as shown in Fig. 2.19.

<table>
<thead>
<tr>
<th>hkl</th>
<th>Standard d, Å</th>
<th>I/I₁</th>
<th>Galfanized coating d, Å</th>
<th>I, counts/second</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>NG' G¹ G² G³</td>
<td></td>
</tr>
<tr>
<td>200</td>
<td>3.817</td>
<td>38</td>
<td>3.831</td>
<td>0 0 2 2</td>
</tr>
<tr>
<td>020</td>
<td>3.235</td>
<td>11</td>
<td>3.213</td>
<td>0 6 7 5</td>
</tr>
<tr>
<td>111</td>
<td>3.211</td>
<td>44</td>
<td>2.118</td>
<td>0 100 170 94</td>
</tr>
<tr>
<td>221</td>
<td>2.131</td>
<td>66</td>
<td>2.066</td>
<td>0 15 8</td>
</tr>
<tr>
<td>002</td>
<td>2.115</td>
<td>55</td>
<td></td>
<td></td>
</tr>
<tr>
<td>130</td>
<td>2.075</td>
<td>30</td>
<td></td>
<td></td>
</tr>
<tr>
<td>311</td>
<td>2.066</td>
<td>100</td>
<td></td>
<td></td>
</tr>
<tr>
<td>112</td>
<td>1.944</td>
<td>36</td>
<td>1.944</td>
<td>0 11 13 6</td>
</tr>
<tr>
<td>022</td>
<td>1.770</td>
<td>20</td>
<td>1.768</td>
<td>0 2 4 0</td>
</tr>
<tr>
<td>132</td>
<td>1.481</td>
<td>20</td>
<td>1.477</td>
<td>0 0 2 0</td>
</tr>
<tr>
<td>223</td>
<td>1.224</td>
<td>13</td>
<td>1.225</td>
<td>0 3 4 0</td>
</tr>
<tr>
<td>512</td>
<td>1.216</td>
<td>10</td>
<td></td>
<td></td>
</tr>
<tr>
<td>313</td>
<td>1.211</td>
<td>16</td>
<td>1.212</td>
<td>0 5 5 0</td>
</tr>
</tbody>
</table>

# NG - coating surface,  
* G¹ - first grinding, etc.,  
^ peak is not clear as it interferes with d=2.092 Å.

2.5 EDS COMPOSITIONAL ANALYSIS

For compositional determination of the intermetallic phases present in Galfanized coating, a SEM/EDS (scanning electron microscope/energy dispersive X-ray analysis system) technique was used. A preliminary experiment was carried out to examine previously published data and to expand the knowledge of the Fe-Al-Zn ternary system at 450°C with the emphasis on Fe-Al sides. In the following the EDS analysis and then the preliminary
experiment are described.

2.5.1 Method of EDS Analysis

Composition of intermetallic phases was determined with a Philips 505 scanning electron microscope coupled to an EDAX 9100 energy-dispersive X-ray spectrometer system. Pure Fe, Al and Zn were analyzed to obtain the pure element spectra for a standard file. A total count of 10,000 was chosen. The parameters for the analyses of the pure elements are listed below:

Microscope condition
Voltage = 20.0 keV,
Tilt angle = 14.79°,
Beam current = 7.1x10^{-10} A;

Detector condition
Resolution at Mn-K = 149.0 eV,
Be window thickness = 6 (µm),
Si dead layer = 0.1 (µm).

The same parameters were used for the analysis of the intermetallic phases in Galfanized coatings in which a counting time of 300 live seconds was used for each spot analysis. During the analysis the spectrum was accumulated and then stored in files for later processing and ZAF correction. In the quantitative mode, the EDAX 9100 system subtracts the escape peaks and removes the Bremsstrahlung background. The system uses the standard file to calculate the background under the peak and ZAF correction using an iterative process.

By using a nomogram for calculating the X-ray resolution (76), the X-ray excitation volume of Fe₅Al₃-Zn, when excitation voltage is 20 kV is estimated to be a sub-surface hemisphere with diameter approximately 3-4 µm. Therefore, if a phase is less than approximately 4 µm in diameter, the compositional analysis by EDS is affected by interference from neighboring phases. For EDS analysis, the intermetallic phases were made stand proud of the surface. This was done by heavy etching which preferentially removes the zinc and eutectic.

The results of the EDS analysis were plotted in the Fe-Al-Zn ternary phase diagram which was used as a standard for identifying phases from the determined compositions. However, as will be described below, the solubi-
lity of zinc in various FeAl phases is somewhat uncertain. An accurate knowledge of the solubility in each phase is necessary for the identification of the phases in the Galfanized coatings. Therefore, a review of the previously published data and a investigation on the Fe-Al-Zn ternary phase diagram at 450°C were conducted as described in the following.

2.5.2 Existing Data for the Fe-Al-Zn Phase Diagram

Cameron and Ormay's work

Cameron and Ormay (57) constructed a tentative section of the ternary Fe-Al-Zn diagram at 450°C based on the following data:

1. Binary sides taken from Hansen (10,38,51),

2. Results given by Hughes (32) for defining the ternary areas. In Hughes's experiment, iron was dipped in a zinc bath which contained 1.5 wt% Al. The alloy layer was isolated by anodic attack on the outer layer of the coating. The inner layer was then removed and analyzed by chemical analysis (Table 2.8)

Table 2.8 Hughes's Composition of alloy layer formed during galvanizing in Zn bath containing 1.5 wt% Al at 460°C.

<table>
<thead>
<tr>
<th></th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>Average</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>43.9</td>
<td>40.7</td>
<td>40.6</td>
<td>43.1</td>
<td>40.0</td>
<td>41.7</td>
</tr>
<tr>
<td>Al</td>
<td>39.4</td>
<td>38.2</td>
<td>33.0</td>
<td>37.3</td>
<td>38.5</td>
<td>37.3</td>
</tr>
<tr>
<td>Zn</td>
<td>16.7</td>
<td>21.1</td>
<td>26.4</td>
<td>19.6</td>
<td>21.5</td>
<td>21.0</td>
</tr>
</tbody>
</table>

3. Results given by Raynor et al (77) for constructing the Al-Zn-FeAl, triangle. In Raynor et al's investigation, alloys were held at temperatures 25°C above the liquidus for 7 days and then cooled at 3/4°C/min. Crystals of FeAl, were separated from the alloys and analyzed chemically. The composition of the crystals is listed in Table 2.9.
Table 2.9 Raynor et al’s composition (wt%) of FeAl.

<table>
<thead>
<tr>
<th>Alloy composition</th>
<th>Fe</th>
<th>Al</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>3</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td>1.5</td>
<td>1.3</td>
<td>0.9</td>
</tr>
<tr>
<td></td>
<td>0.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>FeAl-Zn composition</td>
<td>38.3</td>
<td>61.4</td>
<td>0.3</td>
</tr>
<tr>
<td></td>
<td>38.5</td>
<td>61.2</td>
<td>0.3</td>
</tr>
<tr>
<td></td>
<td>37.8</td>
<td>61.3</td>
<td>0.9</td>
</tr>
<tr>
<td></td>
<td>38.4</td>
<td>60.5</td>
<td>1.1</td>
</tr>
<tr>
<td></td>
<td>38.4</td>
<td>59.2</td>
<td>2.4</td>
</tr>
<tr>
<td></td>
<td>39.8</td>
<td>59.0</td>
<td>1.2</td>
</tr>
<tr>
<td></td>
<td>38.8</td>
<td>60.5</td>
<td>0.7</td>
</tr>
<tr>
<td></td>
<td>38.1</td>
<td>60.5</td>
<td>1.4</td>
</tr>
</tbody>
</table>

Cameron and Ormay believed that the extent to which any of the binary phases could dissolve the third component was probably unlikely to exceed a few percent. The tentative ternary section at 450°C by Cameron and Ormay is given in Fig. 1.15a.

Koster and Godecke’s work

In Koster and Godecke’s (54) investigation, zinc-rich alloys containing up to 10 wt% Fe were mixed with 50Fe-50Al alloy and Fe, Al, Zn fillings. The mixtures were then compacted and pre-sintered at 450°C. They were then pulverized and again compacted by compressing under a pressure of 3 tonnes for 20 minutes into cylindrical compacts 6 mm in diameter. The compacts were melted in a small alumina crucible which embedded in a quartz ampoule. X-ray Guiner photographs were taken for phase identification (78). The ternary sections given by Koster and Godecke are shown in Fig. 1.15b, c and d; no ternary compound was detected.

Urednicek and Kirkaldy’s work

Equilibration experiments between Fe-Al compounds (FeAl, FeAl2, Fe2Al5 and FeAl3) and liquid zinc, and between the Fe-Al compounds and 1.7 wt% Al-Zn melt were carried out by Urednicek and Kirkaldy (58). For each test a small piece (5 g) of compounds (FeAl, FeAl2, Fe2Al5, FeAl3) was immersed in
a small (20 g) melts. The samples was then cooled in water, transferred to a pyrex tube (10 mm in diameter) and then evacuated 5 times and purged with argon and finally sealed under vacuum. The prepared capsules were then heated to 450°C and held at this temperature for 800 hours before being quenched in iced water. Electron microscope analysis was carried out. Fig. 1.15e is the ternary phase diagram at 450°C determined by Urednicek and Kirkaldy; again no ternary compound was detected.

The solubility of Zn in Fe,Al,

According to Urednicek and Kirkaldy's diagram, the limit of solid solubility of zinc in Fe,Al, is 14 wt%. However, there have been reports, which are summarised below, that the solubility is much higher than this:

1. The composition of Fe,Al,–Zn, present in coatings hot dipped in zinc baths containing 1-3 wt% Al at 450°C was determined by Ghuman and Goldstein (55) using electron microprobes analysis to be:

   34-39 wt% Fe, 42-44 wt% Al, 20-22 wt% Zn.

2. In Harvey and Mercer's (37) work, ternary crystals from dross of a zinc bath which contained 0.16 wt% Al were treated with fuming nitric acid and carefully freed from any impurities. The crystals were identified as Fe,Al,–Zn, of composition:

   39 wt% Fe, 43 wt% Al, 18 wt% Zn.

3. A columnar fibre-like intermetallic phase is found in coatings produced by hot dipping a steel substrate for more than 512 seconds in zinc baths which contains 3 and 6 wt% Al. In Caceres et al' (30) view, this phase is FeAl,–Zn, though it will be argued (section 5.1.3) that it is more likely to be Fe,Al,–Zn,. The composition of the phase was determined using a quantitative energy dispersive analysis technique to be:

   37 wt% Fe, 44 wt% Al, 19 wt% Zn.

**Present work**

In the present investigation a technique similar to Koster and Godecke (54) was used to produce Fe-Al-Zn alloys. Structural identification by X-
ray diffraction and fully quantitative compositional analysis by EDS were combined to investigate the Fe-Al-Zn phase diagram at 450°C. The emphasis is on the Fe-Al side and on the phase Fe₅Al₃-Zn. The details of this preliminary study are described in the following.

2.5.3 Preliminary Experiment

Materials

Fine powders of pure Fe, Al, Zn were combined to make mixtures of five different compositions as listed in Table 2.10. The mixtures were then compacted (35 kN for 20 min.) into cylinders whose diameter was 7 mm. The compacted specimens were placed in a small alumina crucible (8 mm diameter). The crucible was then embedded in a quartz glass tube which was then evacuated (<10⁻⁸ torr for 4 hours) and finally sealed under vacuum.

Table 2.10 Compositions of powder mixtures.

<table>
<thead>
<tr>
<th>Sp. No.</th>
<th>wt% Fe</th>
<th>wt% Al</th>
<th>wt% Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>49</td>
<td>51</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>10</td>
<td>90</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>15</td>
<td>40</td>
<td>45</td>
</tr>
<tr>
<td>4</td>
<td>40</td>
<td>35</td>
<td>25</td>
</tr>
<tr>
<td>5</td>
<td>25</td>
<td>15</td>
<td>60</td>
</tr>
</tbody>
</table>

Melting and annealing

The prepared capsules were heated initially at low temperatures for a few days; this initial sintering was carried out to minimize the vaporization of zinc in subsequent melting. The sintered specimens were then melted at high temperature. Fig. 2.20a shows the heating curves. After the melting the capsules were broken. Specimens were then annealed under argon atmosphere (1 atm) as shown in Fig. 2.20b. After the annealing treatment, the specimens were quenched in iced water from 450°C.
Fig. 2.20 Temperature-time history for vacuum heating, melting, and annealing of the five alloys.

**X-ray diffraction**

X-ray diffraction was used for phase identification. Specimens were mounted in bakelite, polished and placed into the X-ray diffraction specimen holder for X-ray diffraction. X-ray radiation and scanning range are:

Co Kα radiation, Fe filter, 35 kV, 35 mA, 2θ=(20-100)°.

**EDS quantitative analysis**

The same EDS fully quantitative analysis technique as described in 2.5.1 was followed to analyse the composition of the phases present in the five alloys.

**2.5.4 Results and Discussion**

**Results**

Results of the X-ray diffraction experiment on the five alloys are summarised in the tables given in Appendix 4. JCPDS data as given in Appendix 1 was used to allocate interplanar spacings to phases except for Fe₅Al₃ and Fe₂Zn₁₀. The proposed corrected file (Table A3.4) and Table 2.6 were used for Fe₅Al₃ and Fe₅Al₃-Zn₁. Since the file for Fe₂Zn₁₀ is not
available in JCPDS, data from Gelling et al (11) (see Appendix 1) were used. The phases identified in each specimen are listed in Table 2.11.

Table 2.11 Phases and their compositions in the five alloys.

<table>
<thead>
<tr>
<th>Specimen No.</th>
<th>Phase (By X-ray diffraction)</th>
<th>Composition, wt% (By EDS)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$\zeta$ - FeAl$_2$</td>
<td>49.6</td>
</tr>
<tr>
<td></td>
<td>$\eta$ - Fe$_2$Al$_5$</td>
<td>45.7</td>
</tr>
<tr>
<td>2</td>
<td>$\theta$ - FeAl$_3$</td>
<td>38.4</td>
</tr>
<tr>
<td></td>
<td>$\gamma$ - Al</td>
<td>0.2</td>
</tr>
<tr>
<td>3</td>
<td>$\theta$ - FeAl$_3$-Zn$_x$</td>
<td>36.6</td>
</tr>
<tr>
<td></td>
<td>$\gamma$ - Al(Zn)</td>
<td>0.0</td>
</tr>
<tr>
<td></td>
<td>$\beta$ - Al$_3$Zn$_x$</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>$\eta$ - Zn</td>
<td>-</td>
</tr>
<tr>
<td>4</td>
<td>$\eta$ - Fe$_2$Al$_5$-Zn$_x$</td>
<td>37.0</td>
</tr>
<tr>
<td></td>
<td>$\alpha$ - FeAl-Zn$_x$</td>
<td>64.4</td>
</tr>
<tr>
<td>5</td>
<td>$\eta$ - Fe$_2$Al$_5$-Zn$_x$</td>
<td>36.0</td>
</tr>
<tr>
<td></td>
<td>$\alpha$ - FeAl-Zn$_x$</td>
<td>63.7</td>
</tr>
<tr>
<td></td>
<td>$\delta$ - FeZn$_{10}$-Zn$_x$</td>
<td>9.0</td>
</tr>
</tbody>
</table>

Fig. 2.21 shows SEM micrographs of the five specimens; the results of the EDS fully quantitative analysis are listed in Table 2.11. For all the Fe$_2$Al$_5$-Zn$_x$ and FeZn$_{10}$-Al, phases, three separate spots were analysed. The errors listed in Table A4.6 (Appendix 4) represent 90% confidence intervals. The results are also superimposed on Urednicek and Kirkaldy's Fe-Al-Zn ternary section at 450°C as Fig. 2.22.
Fig. 2.21 Microstructures of specimen showing the phases identified.
Compositions of phases present in a specimen

Starting composition of a specimen (powder mixture)

Fig. 2.22 Results of EDS analysis plotted in Urednicek and Kirkaldy's Fe-Al-Zn ternary section at 450°C.

Discussion of Fe-Al binary

Scanning electron micrographs of specimen 1 and 2 show that two phases are present in each of these binary alloys (Fig. 2.21). X-ray diffraction clearly shows that the two phases in specimen 1 are ζ-FeAl₃ and η-Fe₂Al₅ (Table A4.1) and that the two phases in specimen 2 are θ-FeAl, and γ-Al (Table A4.2). The compositions determined in this investigation agree reasonably well with data from other investigations as can be seen by the comparisons made in Table 2.12.
Table 2.12 Composition (wt% Al) of three binary Fe-Al phases compared with previously published analyses.

<table>
<thead>
<tr>
<th></th>
<th>FeAl₂</th>
<th>Fe₅Al₃</th>
<th>FeAl₅</th>
</tr>
</thead>
<tbody>
<tr>
<td>Literature</td>
<td>(47.7)-49.8</td>
<td>53.0-(56.2)</td>
<td>(58.2)-62.7</td>
</tr>
<tr>
<td>This exp.</td>
<td>50.4</td>
<td>54.3</td>
<td>61.6 (Table 2.11)</td>
</tr>
</tbody>
</table>

Discussion of Fe-Al-Zn ternary

In specimen 3, there are four phases; compositions of these are listed in Table 2.11. The composition of the θ phase, which is the apex of the triangle θ-γ-L, can be seen in Fig. 2.22 to agree approximately with that suggested by Urednicek and Kirkaldy. However, it should be noted that the analysis of the θ phase (point D in Fig. 2.22) in Urednicek and Kirkaldy's experiment did not yield conclusive results because of a heavily damaged interface between the θ phase and the zinc (58).

Although the starting composition of the powder mixture of specimen 4 was apparently in a three phase region of the phase diagram, only two phases (η and α) were identified as being present. A small vaporization of zinc during melting shifts the final composition of the alloy slightly towards the Fe-Al side of the diagram.

The starting composition of specimen 5 was in the same three phase region as specimen 4 but it contained more zinc. In this specimen the additional phase δ₁ was therefore present. The corners of the three phase region determined by using specimen 5 agree qualitatively with those determined by Koster and Godecke (54) and Urednicek and Kirkaldy (58). Quantitative comparison of data with those of Koster and Godecke can not be made since there was no quantitative analysis in that investigation. However the results can be compared with data from Urednicek and Kirkaldy (Table 2.13) and show significant differences in α and η phases.
Table 2.13 Composition of the corners of the three phase region compared with the results of Urednicek and Kirkaldy.

<table>
<thead>
<tr>
<th>Phase</th>
<th>Analysis</th>
<th>Previous data</th>
</tr>
</thead>
<tbody>
<tr>
<td>α - FeAl-Zn₉</td>
<td>63.7 wt% Fe</td>
<td>69.1 wt% Fe</td>
</tr>
<tr>
<td></td>
<td>34.3 wt% Al</td>
<td>18.9 wt% Al</td>
</tr>
<tr>
<td></td>
<td>2.0 wt% Zn</td>
<td>12.0 wt% Zn</td>
</tr>
<tr>
<td>η - Fe₂Al₅-Zn₉</td>
<td>36.0 wt% Fe</td>
<td>42.9 wt% Fe</td>
</tr>
<tr>
<td></td>
<td>43.1 wt% Al</td>
<td>43.7 wt% Al</td>
</tr>
<tr>
<td></td>
<td>20.9 wt% Zn</td>
<td>13.4 wt% Zn</td>
</tr>
<tr>
<td>δ₁ - Fe₀.₈₉Al₋₅Zn₉</td>
<td>9.0 wt% Fe</td>
<td>8.2 wt% Fe</td>
</tr>
<tr>
<td></td>
<td>2.8 wt% Al</td>
<td>3.6 wt% Al</td>
</tr>
<tr>
<td></td>
<td>88.2 wt% Zn</td>
<td>88.2 wt% Zn</td>
</tr>
</tbody>
</table>

The reason for the discrepancy in the analysis of α may be explained by the fact that in Urednicek and Kirkaldy's (58) analysis, the composition was determined at the interface of α and η and the triple point of α-η-δ₁. Such an analysis may be easily distorted by the influence of the adjacent phases, δ₁ phase in particular, resulting in an overestimate of the zinc content.

The solubility of zinc in Fe₂Al₅ (point A in Fig. 2.22) determined in this investigation (approximately 21 wt%):

1. agrees well with that determined by Ghuman and Goldsten (20-22 wt%);

2. is slightly higher than that determined by Harvey and Mercer (18 wt%);

3. is slightly higher than that determined by Caceres et al (19 wt%). The columnar phase which was taken by Caceres et al to be FeAl₅-Zn₉ is here assumed to be Fe₂Al₅-Zn₉;

4. is much higher than that determined by Urednicek and Kirkaldy (14 wt%).
Based on the results, the ternary section at 450°C given by Urednicek and Kirkaldy has been modified and is presented in Fig. 2.23. A further error in Urednicek and Kirkaldy's diagram has also been corrected. In their diagram the solubility of zinc in iron on the binary Fe-Zn line is approximately 10 wt%; the value should be about 4 wt% (Fig. 1.2) and this has been used in constructing Fig. 2.23.

Fig. 2.23 The modified Fe-Al-Zn ternary phase diagram at 450°C.