THE SOLIDIFICATION OF HOT DIPPED GALVANIZED COATINGS
ON STEEL

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ABSTRACT

Galvanized sheet is produced commercially by hot dipping steel sheet in a galvanizing bath to produce a thin zinc rich protective coating on the steel. This investigation is concerned with the solidification of the galvanized layer with particular reference to the growth of large "spangles" in the galvanized layer. The manner in which the galvanized layer solidifies was found to be dependent on a number of factors including melt supercooling, nucleation rate, dendritic growth, bath composition, bath impurities, and cooling rate.

The present results show that the supercooling necessary to activate nucleating sites in a typical galvanizing bath is less than 1°C. The supercooling which occurs in the galvanized layer as it solidifies is also generally less than 1°C, contrary to results reported in the literature. This suggests that grains nucleate in the bulk of the galvanized layer, and not necessarily at the air or iron surfaces of the melt as has been reported. No clear evidence was obtained which shows that spangles, with large dendrite spikes, are associated with large melt supercooling. Accordingly, spangle formation cannot be attributed to higher dendritic velocities resulting from large thermal supercooling.

The surface topography of the galvanized layer is a property of major consideration in industrial applications of the galvanized product. Present measurements show that the surface topography is strongly dependent on the solidification structure of the galvanized layer. Large spangles solidify dendritically with large variations in the surface topography. The spangles have shiny and frosty sectors, which are relatively smooth and rough respectively, and inclined to the steel sheet surface. Large depressions are present at the boundaries between adjacent spangles, termed "pulldown", which can markedly
reduce the effective thickness of the galvanized layer, and cannot be removed by subsequent treatment of the galvanized sheet. Increasing the concentration of lead in the bath increased the pulldown. The mechanism of pulldown formation is not clear. Volume shrinkage during solidification cannot account for the large depressions observed.

The hot dipped galvanized samples prepared in this investigation used galvanized sheets as starting material. Observation of the distribution of bath alloy additions in the samples, using microprobe analysis and radioactive tracers, clearly showed that the original galvanized layer was replaced by the metal from the bath.

Solute segregation in a galvanized layer containing spangles is directly associated with the dendritic growth of the spangles. Solute is depleted in the dendrite spikes and concentrated between the spikes. No solute concentration was observed at the grain boundaries between adjacent spangles. Some preferential surface segregation, associated with shiny and frosty sectors of a spangle, was observed.

The growth of large spangles in the galvanized layer is directly related to the galvanizing bath composition. Large spangles are obtained with alloying additions which have very limited solid solubility in zinc and relatively low liquid surface tensions. The diameter of the spangles decrease as the surface tension of the alloy addition increases.

Spangle growth is associated with dendritic growth. Dendritic growth occurs as a result of constitutional supercooling at the dendrite tip due to solute segregation during growth at the solid/liquid interface. It is proposed that the presence of a thin layer of highly concentrated solute at the dendrite tip changes the curvature of the tip. The change is related to the liquid surface tension of the solute. Solutes with lower values of surface tension decrease the tip curvature which results in an increase in dendrite velocity and larger spangles.

The orientation of the spangles is shown to vary appreciably. The basal plane of a spangle is observed to be inclined to the surface of the steel sheet at angles between 8
and 80 degrees. This differs from reports which indicate that the basal plane is nearly parallel to the steel sheet.

The growth of a spangle is primarily associated with dendritic growth. Small (0001) platelets of solid form at heterogeneous nucleating sites in the melt from which $<10\bar{1}0>$ spikes grow. Each spangle forms from a single nucleating source which is randomly oriented with respect to the surface of the steel sheet. As the dendrite spikes grow they shortly encounter the melt/air interface or the melt/steel interface. The spikes will continue to grow along the surfaces at a high velocity in a direction defined by the initial $<10\bar{1}0>$ direction of the growing spikes. As the primary spike grows, secondary and tertiary spikes form, generally inclined to the melt surface and in $<10\bar{1}0>$ directions when possible. The secondary branches of a primary stalk which grow along the melt/air interface form shiny spangle segments. The secondary branches on the opposite side of the primary spike grow along the melt/steel surface and form frosty sectors. The difference is not due to an orientation difference between the spangles as reported in the literature.
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DEDICATION

Dedicated
To the Memory of My Father
Pa Daniel Fasoyinu Fasedemi
Who passed away peacefully
Chapter 1

INTRODUCTION

1.1 Hot Dipped Galvanized Coatings on Steel Sheet

Hot dipped galvanized coatings on steel sheet are easily recognizable because of their macroscopically discernible grain structure (spangles). Many studies [1]-[10] have shown that making solute additions at concentrations of a few hundredths of a percent to the galvanizing bath, and changing the cooling rate during solidification, can markedly change the spangle size and the mechanical properties of the galvanized steel sheet. There is no general agreement regarding the mechanism of spangle nucleation and growth during galvanized coating solidification.

The widespread use of hot dipped galvanized steel sheet in construction and light engineering industries arises from three basic factors:

1. the resistance of coated sheet to corrosive attack under a wide variety of atmospheric conditions,

2. the sacrificial property of zinc over iron or steel, giving full protection even when localized voids in a coating occurs, and

3. the relatively inexpensive nature of the coating process compared to other forms of metal coating (electrogalvanizing, metal spraying, etc.).

These factors have been instrumental in the continued growth of the galvanizing industry for over a century and the emphasis on quality and innovation is reflected in the regularity
at which international conferences are held over the last thirty-eight years.

In general, during batch galvanizing, an article to be galvanized is cleaned, pickled, and fluxed before it is dipped into a galvanizing bath. Alternatively, it can be given suitable heat treatment in a reducing atmosphere to remove surface oxide before it is dipped into the galvanizing bath during a continuous galvanizing process. Each stage in the process is crucial to the production of good quality coating on the articles being galvanized.

In the past, the formation of large spangles was regarded as a trade mark of quality; but more recently, the automotive and appliance industries have increased their consumption of zinc coated sheets in highly visible and exposed parts (for increased corrosion protection) where large spangles are objectionable. The increased demand from these industries has catalysed many research efforts with a view to developing novel techniques capable of producing galvanized sheets that can be painted without objectionable surface finish.

1.2 Thermal Supercooling During Galvanized Coating Solidification

In previous investigations [7,9] it has been reported that the zinc galvanizing layer supercools during solidification. The extent of supercooling reported varies widely from 0 to a maximum of 23 °C. The grain size distribution and structure of the galvanized layer could be sensitive to the extent of supercooling during solidification.

The presence and amount of supercooling during solidification is determined from cooling curves in which the temperature is measured as a function of time during solidification. Typical cooling curves which are observed during the solidification of a pure metal are shown in Figure 1.1. If a metal cools slowly without any phase change the cooling curve would be continuous and non-linear as shown in Figure 1.1, curve A. With
solidification and no supercooling a flat plateau in the cooling curve would be observed as shown in curve B. The plateau would occur at the freezing temperature of the metal. If supercooling of the melt occurs then any of the cooling curves C, D, or E could be obtained. In curve C, with modestly rapid cooling, enough latent heat is evolved to raise the melt temperature to the freezing point producing a short plateau. In curve D, the rate of heat extraction is greater than the rate of latent heat generation and the liquid temperature never reaches the freezing temperature. In curve E, with the most rapid cooling rate, the latent heat generated only slows the cooling rate, producing a shallow sloped region well below the melt temperature. The extent of supercooling is determined from curve C as the temperature difference between the lowest temperature reached by the melt and the freezing temperature.

In alloy solidification with precise temperature measurements a horizontal plateau is not observed in the cooling curve since the liquidus temperature is a function of melt composition which changes during solidification. In this case the supercooling is estimated from the cooling curve by subtracting the minimum temperature observed before the temperature rise at the start of freezing from the equilibrium liquidus temperature of the initial melt obtained from the phase diagram.

In general, solidification is accompanied by a small amount of supercooling, the amount depending on the supercooling necessary to activate the heterogeneous nuclei present in the melt. Many experiments on the nucleation of solids from liquids have shown that small solid particles present in the liquid or at the mould wall are capable of acting as heterogeneous nuclei. Large supercooling is observed in small samples of high purity metal solidified in “clean” crucibles. Much less supercooling is observed in alloys under normal casting conditions.
1.3 Redipping of Galvanized Steel Sheet and Segregation Studies

In continuous and batch galvanizing processes several stages of surface preparation are normally required to remove any corrosion products, residual lubricants or other surface contaminants on the metal. The choice of surface treatment depends on the characteristics of the contaminants on the steel, the steel sheet being coated and the galvanizing bath composition.

Prior surface treatment of the steel to produce a clean, oxide free surface is critical to producing high quality galvanized coatings. This is because the coating adhesion and ductility is strongly dependent on strong metallurgical bonding between the steel sheet and the galvanizing coating. Surface impurities or oxides will inhibit good bonding.

In the present investigations galvanized sheets were used as the starting material in order that the normal stages of surface preparation could be bypassed. This procedure is acceptable if the original coating on the sheet remelts rapidly during redipping in the new bath, and is replaced by the new bath material. This also requires that the new bath composition is not significantly changed by the remelted galvanized material.

A series of experiments and observations were carried out to justify the use of galvanized steel sheets as starting material for the experimental programme. The experiments were primarily directed at establishing that all the galvanized layer was rapidly removed from the sheet upon immersion, and replaced by the galvanized bath material of a different composition when the sheet was withdrawn from the bath. Apart from assessing the distribution of the radioactive thallium ($^{204}$TI), in the doped galvanized layer, the concentration of lead and antimony across the galvanized layer thickness in the regular baths were measured using an electron probe X-ray microanalysis technique. The distribution of solute elements in the spangle boundaries and areas close to it was also assessed using EDX and other electron metallographic techniques.
1.4 Surface Topography of Hot Dipped Galvanized Steel Sheet

Visual examination of a galvanized sheet often shows that the surface is patterned in the form of spangles, with some areas of the spangles being highly reflective and smooth (shiny) and other areas non-reflective (frosty) with some surface structure. The galvanized sheet surface is clearly observed to be non-planar with depressions at the spangle boundaries, high ridges in the radial arms of the spangles, and smooth and rough components in the spangles.

The surface topography of galvanized sheets has been attributed to a number of factors. The primary factors are galvanizing bath composition and solidification shrinkage of the galvanized layer. The shiny and frosty sectors of spangles have been attributed to orientation differences between the spangle sectors.

Galvanized sheet is used in many different applications. In many cases the surface appearance is important, and therefore the surface smoothness, spangle appearance, and shiny and frosty spangle segments are significant. In addition the galvanized sheet is often painted. It has been reported that the surface roughness influences the adherence of the paint on the galvanized surface.

Since the surface roughness is a very important characteristic of galvanized sheet, measurements of surface roughness were made in this investigation, using a Talysurf 5 instrument. The general micro-roughness parameters of the galvanized sheets were obtained with typical surface roughness profile graphs. The approximate distance between spangle boundary depressions, the width and depth of spangle grooves were estimated. The coating thickness associated with measured parameters was determined, using an inductive coating thickness measuring device.
1.5 Objective and Scope of the Work

Large spangles are generally formed on galvanized sheets when the coating cools naturally in air during conventional hot dip galvanizing processes. Dendritic growth is a marked feature of the large spangles formed, with depressions at the spangle boundaries. The presence of large spangles, and depressions at spangle boundaries on a coated surface are objectionable, particularly in applications that require a highly smooth painted surface. The mechanism of spangle nucleation and growth, and the formation of depressions at spangle boundaries during galvanized coating solidification are not fully understood.

The objective of this investigation is to determine the mechanisms of spangle nucleation and growth during the solidification of the galvanized layer. Experimentally the effect of the following factors influencing spangle formation are considered: galvanizing bath composition, degree of supercooling and cooling rate during solidification, surface tension, and segregation. The surface textures of spangles are examined by measuring the surface roughness as a function of spangle size, morphology, shiny/frosty segments and grain boundary pulldown.

1.6 Thesis Organization

The thesis is divided into six main chapters; a general introduction to the investigation is given in Chapter 1. A summary of literature relevant to this study is given in Chapter 2. A general description of the apparatus and experimental procedures common to all the experiments is given in Chapter 3. The results of the investigations are presented in Chapter 4, and discussed in Chapter 5. The summary and conclusions are presented in Chapter 6.
Figure 1.1: Schematic drawing of typical cooling curves during the freezing of a pure melt.
2.1 Galvanizing Bath Composition and Spangle Size

Spangle formation generally results from the dendritic mode of solidification exhibited in alloys that contain elements that are soluble in liquid zinc but have limited solubility in solid zinc. The classical spangle \([6,7]\) consists of a number of sectors of related orientation made up of alternate shiny and frosty sections which radiate from a single nucleating point. Cameron and Harvey \([7]\) reported that coatings containing lead and tin displayed a highly spangled surface with alternate shiny and frosty regions.

It has been established that additions of lead to the galvanizing bath lower the overall surface tension of the bath \([11]\). Decreasing the surface tension of the bath increases the wettability of the steel by molten zinc and eliminates bare spots from the galvanized sheet. Also, lead additions are closely related to the formation of spangles on the galvanized layer, and surface depressions or grooving at the spangle boundaries. Surface depressions at spangle boundaries are not desirable since the thickness of the coating is substantially reduced at the boundaries \([7]\). In addition, if solute is segregated to the thin regions during solidification this could lead to reduced strength and higher corrosion rates in the boundary region.

Sebisty and Palmer \([2]\) reported that in the absence of lead, coatings with less than either 0.15 % Sn, or 1.25 % Cd did not display spangles. When higher concentrations of tin were made very small dendritic spangles were formed. A wide range of Zn-Sn-Al
alloys for hot dip galvanizing was patented by Ohbu and Higuchi [8]. They claimed that a smooth surface is obtained for alloys containing 30% Sn with 0.005 to 0.50% Al; 20% Sn with 0.005 to 20% Al; and 0.30% Al with 5 to 60% Sn.

Aluminum is added to galvanizing baths principally to suppress the growth of the brittle Zn-Fe phases at the steel/zinc interface. Aluminum also enhances coating brightness. Sebisty and Edwards [1] reported that high aluminum coatings (in excess of about 0.2%) resulted in a generally unsatisfactory coating appearance.

Kim and Patil [9] reported that the addition of aluminum up to 0.20% to a zinc bath, without lead, slightly reduced the grain size, and that a small addition of lead (0.03%) did not change the spangle size. However, when larger concentrations of lead were made the spangle size increased substantially.

The conclusions drawn by Cameron and Harvey [7] in their extensive study are summarized below.

1. Spangles nucleate at, and grow from the steel/zinc interface.

2. The spangle structure is dendritic, with a hexagonal structure associated with the hexagonal close packed structure of zinc.

3. The most prominent spangles with the largest diameters are those in which the basal plane of the spangle is nearly parallel to the steel surface.

4. Lead or bismuth is a necessary addition to the galvanizing bath to produce spangles.

5. The added lead or bismuth suppresses the number of nuclei in the melt which can grow to produce grains. The remaining nuclei are much wider spaced, leading to the formation of coarser grains in the form of spangles.

The mechanism by which lead or bismuth reduces the number of effective growth
centres in the galvanizing layer is not known. No experimental evidence was presented to show that this suppression did occur.

Like lead, antimony has negligible solubility in solid zinc, and galvanized layers containing antimony tend to solidify dendritically, producing spangles. Radeker and Frihe [4] reported that small spangles, comparable to the grains observed with a pure zinc bath, were obtained when the antimony concentration in the galvanizing bath was 0.09%. Increasing the antimony concentration to 0.58% dramatically increased the spangle size (30 to 50 mm).

In a patent related to continuous galvanizing methods, Lee et al. [13] reported that additions of 0.02 to 0.15% Sb to a bath containing 0.20% Al and less than 0.02% Pb gave large, flat spangles. Furthermore, the rippling that occurs when using a Zn-5% Al bath with low lead concentrations was eliminated when the antimony level was in the range 0.02 to 0.15%. They reported that substituting antimony for lead in a galvanizing bath reduced pulldown at spangle boundaries. They also reported better corrosion characteristics are obtained with antimony additions in the galvanizing bath, as compared to lead additions.

There is a current trend in the galvanizing industry to lower the lead levels in galvanizing baths. Lower lead concentrations reduce the spangle size, reduce the depressions at spangle boundaries, and produce a galvanized surface which is better for painting. However, lowering the lead concentration also reduces the fluidity of the galvanizing bath, which can lead to bare spots on the galvanized sheet. This sets a lower limit on the lead content.
2.2 Other Factors That Influence Spangle Size

Apart from bath chemistry, other factors that influence the spangle size include available nucleation sites, dipping and cooling procedures, and the growth rate of the grains. Finer grains are produced with higher sheet cooling rates.

Cameron et al. [6] varied the cooling rate during solidification of the galvanized layer by changing the thickness or shape of the steel sheet being galvanized. They observed that reduced cooling rates increased the size of the spangles and decreased the groove depth at the spangle boundaries. Kim and Patil [9], using different cooling procedures (natural convection, forced convection, and contact cooling), observed that smaller grains formed at higher cooling rates, as expected. The specific cooling procedure did not appear to affect the grain size. They also investigated the effect of nucleating agents on spangle size by blowing zinc dust and atomized water on the surface of the hot dipped sheets. They observed that both processes were very effective in reducing the grain size of the coating. However, it is difficult to separate the effects of the nucleating agents from the change in the cooling rate. Both reports of Cameron and Harvey [7] and Kim and Patil [9] indicated that the coatings started to freeze from the steel/zinc interface. They suggested that this was due to the abundance of potential heterogeneous nucleating sites on the sheet surface.

2.2.1 Industrial Practice of Spangle Size Control

Three techniques are currently being used to control spangle size and surface roughness aside from lowering the lead concentration in the galvanizing bath.

One technique is to blow high pressure steam on the solidifying coating. A second technique is to blow zinc dust particles on the galvanized steel surface before the zinc solidifies. The third technique is to temper roll the galvanized sheet to produce a smooth
Chapter 2. LITERATURE REVIEW

2.2.1.1 Atomized Steam Process

In this technique high pressure steam is blown on the surface of the solidifying coating to accelerate the cooling rate of the coating. Typical spangle sizes produced using this process vary between 0.1 to 2.5 mm. The reduction in spangle size is associated with the high cooling rates and the possible activation of more nucleation sites as a result of the steam impingement. This technique is not being widely used currently, because of the large variation in spangle size across a given sheet, the high cost of the process, and the difficulty in controlling the high pressure steam.

2.2.1.2 The Heurtey Process

In this process, zinc powder of approximately 5 \( \mu \)m diameter, contained in a special "minispangle" unit is blown against a galvanized sheet. This both cools the liquid layer and adds nucleating sites to the layer. The process is widely used because it gives good control of spangle size. With this process fine spangles of 0.1 to 1.5 mm diameter are obtained, appreciably finer than that obtained with steam impingement. The process is expensive, as it uses zinc powder, and is difficult to control. In addition, a range of spangle sizes can be present across a galvanized sheet.

2.2.1.3 Temper Rolling of Galvanized Sheet

The rough patterned surface on hot dipped galvanized sheet, which is associated with spangles, can be smoothed by temper rolling. However, this tends to flatten the projections on the surface, but does not remove the depressions, particularly the large depressions at the spangle boundaries. If the galvanized sheet is rolled further, in an
attempt to remove the depressions, the sheet becomes highly deformed, which is undesirable. Therefore, temper rolling with an appreciable reduction in thickness is not a satisfactory means of obtaining an acceptable smooth surface on a galvanized sheet, if the ductility of the base steel is to be preserved.

2.3 Coating Solidification and Spangle Morphology

2.3.1 Spangle Classification

Previous attempts at describing the appearance and solidification of zinc coatings have resorted to classifying the different surface topographies. On the basis of surface appearance, Cameron et al. [6] proposed three classifications of spangles: shiny, frosty, and snowflake. They also referred to specular, specular ridged, triangular and flowery types of spangles. They reported a possible orientation difference between the different sectors of a given spangle.

With respect to the ease with which the various topographies can be recognized, the best classification is probably given by Jaffrey et al. [14], who distinguished between four types of regions: mirror-like, feathery, dimpled, and ridged. The first two can be recognized without magnification; the mirror-like corresponds to a flat, featureless surface with high reflectivity, and the feathery type corresponds to high reflectivity with an underlying dendritic pattern. Dimpled and ridged describe surfaces with relatively low reflectivity; small scale regular hills without preferred direction and low reflectivity, and small scale hills and valleys arranged in one or occasionally two systems of ridges, respectively. The dimpled and ridged regions seem to represent the general microscopic characteristics of the frosty sectors.

Wall et al. [15] reported four classifications of spangles, similar to that previously reported by Jaffrey et al. [14]. They reported that the parallel laths which give rise to
the feather structures lie most often at 60 degrees, but occasionally at 90 degrees, to the dendrite arms from which they emanate.

2.3.2 Spangle Orientation

The orientation of spangles with respect to the surface of galvanized sheet has been reported in the literature and the results are not consistent. Measurements have been reported for the relative orientation of shiny and frosty segments of a given spangle, as well as the overall spangle orientations.

The orientation of a series of consecutive segments of one spangle, measured by Cameron et al. [6] by X-ray transmission, is listed in Table 2.1. Their results show that the orientation in a given spangle varies between segments, and that the overall spangle orientation in this case, with respect to the steel surface, averages 45 degrees. The angle between the shiny segments and the steel sheet is larger than the frosty segments. As a result, there is a small decrease in angle in going from a shiny to a frosty segment. They also reported that the primary growth direction of the dendrite arms forming the spangle is \(<10\bar{1}0>\).

Jaffrey et al. [14] reported that the orientation of the spangles was dependent on their appearance. Mirror-like, feathery, or dimpled spangles were oriented with the basal plane parallel to the sheet surface. Spangles with ridges had their basal plane oriented at about 60 degrees to the steel surface. They did not report orientation data results to indicate how close the parallel orientation was or how much deviation from 60 degrees was observed.

Wall et al. [15] examined the orientation of spangles on commercially produced galvanized mild steel sheet. They reported that the maximum inclination of the basal plane was 10 degrees, and that segments of a spangle had similar orientations. As spangles became smaller, the percentage of grains with basal planes almost parallel to the sheet
Accordingly, it is not clear whether the basal plane in spangles is inclined at a large or small angle with respect to the steel surface and to what extent the orientation between adjacent shiny and frosty sections differs.

2.4 Coating Thickness and Alloy Layer Formation

2.4.1 Steel Composition, Dipping Time, and Bath Temperatures

Many workers [16]-[30] have studied the effects of steel composition, bath chemistry, bath temperature, and dipping time on coating thickness and alloy layer formation. Pavlidis [17] studied the effect of steel composition on both the structure and thickness of the coating. He reported that the galvanized coating on steel with silicon content in the range 0.05 to 0.15 % tended to be thicker than on steel without silicon additions. The galvanized layer consisted almost entirely of Zn-Fe alloys. Similar coatings were produced with steels having a combination of high phosphorus and carbon level. For this reason, sheet steels used for galvanizing are rimmed low carbon steels with low phosphorus and aluminum killed. Horstmann [18] reported that some alloying elements and impurities in steel, such as carbon, manganese, silicon, and phosphorus, increase the rate of alloy formation, and thus the alloy thickness in the temperature range 475 to 495 °C.

Gerber et al. [19] reported that coating thickness increased with increases in the silicon content of the steel. They also observed that the coating thickness increased with increasing immersion time for hot dipping at bath temperatures of 450 °C. This effect became more pronounced with higher Si levels in the steel sheet.
2.4.2 Galvanizing Bath Composition

The effect of aluminum additions to the galvanizing bath on the alloy layer has been investigated extensively [20]-[24]. It is reported that the thickness of the Zn-Fe alloy layer can be markedly reduced with additions of 0.1 to 0.3 Al % to the bath at normal bath temperatures. It is believed that the reduction of alloy layer thickness is due to the formation of a thin aluminum-rich layer on the surface of the steel. It is not clear whether the aluminum-rich layer is an Fe-Al binary alloy [21,23], an Fe-Al-Zn ternary alloy [20,22], or a combination of both [24,29].

Bablik [21] proposed that aluminum initially delayed the reaction for a short time between the liquid zinc and solid iron at immersion. Once the reaction began, the rate of the reaction increased, surpassing the rate achieved in aluminum-free baths. He proposed that a binary alloy of Fe-Al (Fe$_3$Al) inhibited the growth of the Fe-Zn alloy layer.

Hughes [22,30] proposed that a ternary alloy of Fe-Al-Zn is responsible for the suppression of the Fe-Zn alloy growth, and that the aluminum level needed to suppress the growth is dependent on the galvanizing bath temperature, and the dipping time. Haughton [23] reported finding a film of Fe$_2$Al$_5$ on the surface of a steel sheet after removing the galvanized layer containing aluminum. Based on this finding he proposed that the Zn-Fe reaction was inhibited by the Fe$_2$Al$_5$ layer rather than the Fe-Al-Zn alloy layer suggested by Hughes [22,30]. Cameron and Ormay [29] reported the presence of Fe$_2$Al$_5$, and aluminum-bearing FeZn$_7$, aluminum-bearing FeZn$_{13}$, FeAl$_3$, and an unidentified ternary compound.

An extensive study was conducted by Ghuman and Goldstein [20] on the reaction mechanism and phases formed during hot dipping in 0.0 to 10.0 % Al-Zn galvanizing baths at 450 to 700 °C using electron microprobe and X-ray techniques. They reported that below 600 °C the suppression of the Fe-Zn reaction is caused by the formation of a
thin Fe-Al-Zn ternary alloy layer. They proposed that as the ternary alloy becomes richer in aluminum it transforms into a more stable structure, isomorphous with Fe$_2$Al$_5$, and that the diffusing zinc atoms react with the iron to form the conventional Fe-Zn phases. Above 600 °C a very violent and highly exothermic reaction occurs and continues even when the sample has been removed from the bath. They proposed that particles of aluminum-bearing FeZn$_7$ (δ-phase), which had formed initially, transformed to a very stable Fe$_2$(AlZn)$_5$ structure.

The observations reported above are for small samples dipped in laboratory experiments. Immersion times in these cases are generally appreciably longer than dipping times in commercial hot dip galvanizing.

Rowland [16] in an extensive metallographic study of both laboratory and commercially produced hot dipped galvanized coatings at 450 °C showed that each of the phases present in the Fe-Zn phase diagram could be detected with clearly defined interfaces. Referring to an earlier investigation on diffusion rates, he reported that the rate of Fe diffusion in the alloy layer was greater than that of Zn. The layers therefore tend to grow outward from the steel to form the alloy layers. Experimental observations indicate that the alloy layer forms rapidly, within several seconds after immersion. Further thickening of the layer depends on the galvanizing bath temperature and the dipping time.

At present, it is not clear whether the presence and size of spangles in the galvanized layer is related to the galvanized layer thickness or the alloy layer. It is possible that spangles may be nucleated near or at the alloy layer and therefore may be influenced by the layer. However, there is no clear evidence that this is the case.
2.5 Galvanized Steel Sheet Forming and Paint Adhesion

The mechanical behavior of hot dipped galvanized sheet as it is formed into a product is strongly dependent on the orientation of the zinc grains in the galvanized layer [14], [31]-[33]. The adhesion of paint to the galvanized layer is also related to the orientation of the zinc grains. Leidheiser and Kim [31]-[33] showed that the best adherence of paint to the surface was obtained when a high percentage of the zinc grains had their basal plane (0001) parallel to the surface of the steel.

Other workers [14,34] have studied the deformation characteristics of galvanized sheets with particular attention being paid to the topography of the coated sheet. Wall et al. [34] reported that in all the galvanized sheets they examined, cracks originated at the spangle boundaries. The galvanized sheets with larger spangles developed cracks at spangle segment boundaries, which varied between spangles, depending on the spangle orientation. Jaffrey et al. [14] reported that ridged spangles fractured at low tensile strains. With higher tensile strains, cracking increased in the ridged spangles followed by cracking of other types of spangles. They associated the observed cracking pattern with the relative orientation of the spangle and the tensile stress; specifically grains that have their basal plane inclined to the plane of stress cracked more readily.

2.6 Theories and Models of Spangle Formation

Cameron and Harvey [7] have proposed the presence of presolidification centers on the galvanized sheet surface based on experimental observations. They reported that a few seconds after removal of the steel sheet from the galvanizing bath, an outline appears on the still liquid surface which later developed into the spangle boundaries. The liquid surface within these boundaries starts to "hump up" slightly over a further few seconds, and near the center of the hump a solidification spot then appears, and grows rapidly.
outwards, appearing almost to accelerate as the boundary is reached.

Based on these observations, they postulated that the early appearance of an outline on the liquid surface of the coating, which eventually coincided with the spangle boundary, could occur only if a thin layer of solidified zinc of full spangle size formed on the steel base. As solidification proceeds, they postulate that the centre of the spangle thickens from the base and then spreads laterally. The resultant shape of the top surface of the spangle is conical with the thickest region at the centre and thinnest at the edge due to unspecified surface tension effects. As part of the mechanism they postulate nucleation of the spangle occurs at the steel/zinc interface.

2.7 Theories and Models of Dendrite Formation

In practice many crystals grow as dendrites (a tree-like structure) at high growth rates. Growth starts with a primary dendrite branch, followed by secondary and tertiary branches. The leading tip of a dendrite branch has a shape close to a paraboloid of revolution.

The study of dendritic growth during crystallization has remained an active subject for experimental and theoretical investigations over many years. The early studies of Weinberg and Chalmers [35,36], and Bolling and Tiller [37] have shown that dendrites represent the most advanced stage of interfacial instability in a wide class of material, and that the dendrite growth direction is defined by the crystallographic orientation of the dendrite. Specifically, Weinberg and Chalmers [35] reported that zinc dendrite branches grow in pure supercooled zinc in the [1010] direction and equivalent directions with slight growth in the [0001] direction.

In another study, Edmunds [38,39] has reported that there is a natural tendency for zinc crystals near a chill to align their basal (0001) planes parallel to the chill plane.
This tendency was attributed to the marked growth anisotropy of zinc, the growth in the basal plane being much faster than growth perpendicular to it. This same growth pattern has been reported by various investigators during the solidification of the zinc layer on continuously galvanized steel sheets [15], [31]-[33].

A number of theoretical models [37], [40]-[48] have been advanced to account for dendritic growth during solidification. The majority of these models assume steady state dendritic growth in a supercooled pure melt, and confine the model to the dendrite tip, without considering side branching. Nash and Glicksman [45] reported that the growth velocity \( V \) is related to the supercooling \( \Delta T \) by the following expression:

\[
V = \beta G \Delta \theta^n
\]  

(2.1)

where \( \beta \) and \( n \) are numerical constants, \( G \) is a materials parameter, and \( \Delta \theta \) is the normalized supercooling. This is for nonisothermal, steady state dendritic growth.

The materials parameter \( G \) is defined as:

\[
G = \frac{\alpha_l \Delta S_f L}{\gamma_{sl} C_l}
\]  

(2.2)

where

- \( \alpha_l \) = Thermal diffusivity of the liquid
- \( \Delta S_f \) = Entropy of fusion per unit volume
- \( L \) = Latent heat of fusion
- \( \gamma_{sl} \) = Solid-liquid interfacial energy
- \( C_l \) = Heat capacity of the liquid

The normalized supercooling \( \Delta \theta \) is defined as:

\[
\Delta \theta = \frac{\Delta T C_l}{L}
\]  

(2.3)
where $\Delta T$ is the thermal supercooling of the melt.

Glicksman et al. [48] investigated dendritic growth during the solidification of succinonitrile. Succinonitrile is a transparent material which solidifies in a non-faceted manner, similar to metals. They found that the growth velocity defined by Equation 2.1 is in good agreement with the theoretical models over the range of normalized supercooling $0 < \Delta \theta < 0.2$. It was noted that for cases where the normalized supercooling is greater than 0.2, the theoretical values of $\beta$ and $n$ will depend on $\Delta \theta$, generally increasing with increasing $\Delta \theta$. The numerical constants $\beta$ and $n$ were taken to be 0.114 and 2.65 respectively. Using the above equations for succinonitrile, they concluded that dendritic growth kinetics can be compared with steady state theoretical predictions only when conditions for growth without the influence of substrate or container walls are fully met.

### 2.8 Supercooling of the Hot Dip Galvanizing Bath

There is limited information in the literature regarding the supercooling associated with the solidification of galvanized coatings on steel sheet. Cameron and Harvey [7] reported that for a zinc melt containing 0.5 % Pb and 0.2 % Al, the supercooling associated with the solidification of the galvanized coating was between 6 and 10 °C. Details of the experimental procedure for the measurements were not given. White [53] reported a supercooling of less than 1 °C during the solidification of high purity zinc droplets.

Kim and Patil [9] reported a supercooling of 23 °C during the solidification of the coating layer on steel sheet using a non-contact infrared (Ircon 6000 series) temperature sensing device. They calibrated their infrared detector by attaching a thermocouple to the back surface of the steel sheet behind the spot imaged by the infrared detector. The temperature readings from the two detectors were recorded simultaneously. The infrared detector temperature was made coincidental with the thermocouple temperature by using
a surface emissivity setting of 0.14. They concluded that because of the high supercooling of 23 °C observed, the zinc crystals grew from the steel/zinc interface instead of the colder interface between the zinc and the atmosphere.

The use of optical pyrometers to measure the temperature of steel sheet in continuous processing lines (annealing, rolling, galvanizing, etc.) is a common industrial practice. The accuracy and reliability of this technique depends very strongly on how well the surface emissivity of the sheet is known as it oxidizes or moves on the continuous line.

The interest in studying the extent of supercooling during coating solidification is related to the usually large and highly dendritic grains (spangles) observed on conventional galvanized sheets. It is not certain why large spangles form during coating solidification, but it has been reported [49] that as the supercooling of a melt increases, dendrite formation and growth are favoured. The extent to which this is true during zinc coating solidification is not clear.

2.9 Summary of the Literature Review

It is evident from the literature reviewed that galvanizing bath composition plays a significant role in spangle formation during coating solidification. Increasing the lead, antimony, or bismuth concentrations in a galvanizing bath increases the spangle size for a given cooling condition. The solute concentration required for spangle formation is commonly less than 0.1 %. The spangle size can be reduced by lowering the concentration of lead in the galvanizing bath and by increasing the cooling rate of the hot dipped sheet. Other methods of spangle size control, such as steam impingement, and zinc powder blowing, are partially successful. Extensive temper rolling to control galvanized sheet smoothness cannot be used if the formability of the sheet is to be preserved.

Dendrites form a marked component of the spangle structure observed on conventional
galvanized sheet steels. The possible relationship between dendritic growth and spangle formation during galvanizing layer solidification has not been addressed.

In basic terms the factors which influence spangle size, for a given bath composition, are nucleation rate, growth rate, and cooling arrangements during solidification. At present the dependence of spangle size on these factors is not clearly understood.

Widely varying supercooling values were reported during galvanized coating solidification. Temperature measurements on thin layers of melt on dipped steel sheets are difficult to make. The supercooling values reported for these layers are much larger than for bulk melts. Accordingly the extent of supercooling of the galvanizing melt before solidification commences is unclear.

Many workers have studied the effects of steel composition, bath chemistry, bath temperature, and dipping time on coating thickness and alloy layer formation. The dipping time used in majority of these investigations are longer than used during a continuous hot dip galvanizing process. However, the general effect of these variables appear to have been established.

The inhibition mechanism of the alloy layer growth, as influenced by the presence of aluminum in the galvanizing bath, appear to be clear. However, there is a controversy as to whether the aluminum-rich layer is an Fe-Al binary alloy, an Fe-Al-Zn ternary alloy, or a combination of both. The possible influence of alloy layer formation and coating thickness on the observed solidification structure in galvanized coating has not been addressed.

There is limited information in the literature regarding heat transfer measurements during hot dipped galvanizing process, except for bath temperature measurement and control. There is very little information about the temperature changes that occur in the steel strip and the molten zinc layer on the surface before freezing. For example, the temperature of the strip as it moves through the galvanizing bath, during wiping,
and cooling to solidification temperature in a continuous galvanizing line, has not been addressed. Since minispangle coatings are produced with fast cooling rates, it should be possible to relate spangle size to the prevailing thermal conditions during the continuous hot dip galvanizing process.
Table 2.1: Angle Between the Basal Plane and Sheet Surface Adjacent Sectors of One Spangle

<table>
<thead>
<tr>
<th>Frosty sector</th>
<th>Shiny sector</th>
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<tbody>
<tr>
<td>30</td>
<td>37</td>
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<tr>
<td>37</td>
<td>39</td>
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<td>61</td>
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<td>70</td>
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</table>
Chapter 3

EXPERIMENTAL PROCEDURES

3.1 Materials and Methods

3.1.1 Thermal Analysis of Bulk Melt

Cooling curves of bulk samples were obtained using the furnace (A) and crucible (B) arrangement shown in Figure 3.1. The electric resistance furnace has a total heating capacity of 1160 watts provided by two semicircular heating elements. Temperature measurements were made using chromel/alumel thermocouple sensors that had wires of 0.127 mm diameter sheathed in a sealed thin-wall copper tube. These wires were positioned along the vertical central axis (C) of the copper crucible with the thermocouple tip at approximately 20 mm from the crucible bottom. The thermocouple output during melt solidification was recorded on a Kipp & Zonen recorder Model BD 41, using an ice/water bath cold junction.

The galvanizing bath was contained in a copper crucible of 20 mm inside diameter, and 80 mm in height which holds approximately 145 grams of melt. The crucibles were coated with graphite (aquadag) to prevent the zinc from reacting with the crucible walls. The zinc ingots used in all the measurements were provided by Cominco Ltd. The nominal chemical composition range of the galvanizing baths (Baths 1 and 2) are shown in Table 3.1. These measurements were made to determine the level of supercooling necessary to activate the nucleating sites present in the melt.

The thermocouple system used in the thermal analysis was calibrated using a high
purity zinc melt (99.99 % Zn). The rate of cooling of the melt was varied by changing the environment of the crucible. This was done by replacing the furnace with an oil bath into which the sample was quenched.

3.1.2 Thermal Analysis of Galvanized Layer Melt

Temperature measurements with thermocouples and optical pyrometers were made of the liquid galvanized layer as it solidified on a steel sheet after immersion in different galvanizing baths (Table 3.1). The cooling curves associated with the freezing of the liquid layer on hot dipped galvanized steel sheets were obtained using the apparatus shown in Figure 3.2. The furnace consisted of four 850 watt shell heating elements surrounding an inconel shell, B, of 152 mm diameter, into which the assay crucible was placed. The galvanizing bath, A, was contained in the assay crucible (No.40), which held approximately 12,500 grams of melt. The furnace and bath temperatures were controlled and measured to within \( \pm 2 ^\circ C \), using one chromel/alumel thermocouple adjacent to a heating element and a second thermocouple immersed in the bath. Accurate control was maintained by a Thermo Electric Tempstar I, Model 3240100100, temperature controller, with full power on/off cycles. Thermocouples were prepared from chromel and alumel wire of 0.127 mm diameter. The wires were joined by beading the ends with a torch. The thermocouples were then spot welded to the center of a galvanized sheet and the temperature monitored as the sheet was dipped into the galvanizing bath, withdrawn, and cooled in air or other environments.

Using this procedure to measure the temperature of a thin layer of liquid metal (30-50 \( \mu m \) thick) can introduce errors. Heat conduction along the thermocouple wires from the welded joint, as the sheet cools in air, can reduce the measured temperature, and introduce temperature gradients in the sample below the bead. Chapman [50] has shown that for cases where the surface to which the thermocouple is attached has a
high thermal conductivity, similar to that of the thermocouple, the error in measured temperature would be less than 2 °C. In appendix A is shown that there would be no significant temperature gradient across the galvanized sheet during cooling in the present case.

These efforts are attempts to measure the supercooling of a 30 to 50 μm thick layer of liquid zinc on a steel sheet substrate using a thermocouple bead thicker than the liquid layer. This could make the measurement uncertain as it relates to the liquid metal. To ascertain the reliability of the measured temperatures, a different thermocouple system was developed, as shown in Figure 3.3. Two fine (0.102 mm diameter) thermocouple wires were threaded through a double-hole ceramic sleeve, and passed through a hole in the steel sheet. The end of the ceramic sleeve was positioned to coincide with the surface of the steel sheet. The galvanized layer then formed the thermocouple junction during the solidification of the coating.

In these experiments, the galvanized steel sheets were provided by Stelco Ltd. The steel sheets were standard low carbon (AISI 1008) aluminum killed, which is excellent for hot dip galvanizing. Steel sheet samples of 76.2 mm by 203.2 mm and 0.475 mm in thickness were cut from the bigger sheets and dipped into the galvanizing bath at a controlled rate. The as-received sheet sample was fastened to a vertical lift rod C, Figure 3.2. When the required bath temperature was reached the sheet was immersed in the bath at 10 cm/s by a hydraulic drive system controlling the vertical movement of the rod. The sheet was left in the bath for 10 seconds, then vertically lifted from the melt at the same rate and allowed to cool in air.

For water or oil bath cooling, the sample was lifted to well above the furnace and a large beaker containing the cooling bath was immediately placed between the furnace and the sample and lifted up to surround the sample as it cooled.
3.2 Temperature Measurements with Optical Pyrometer

The temperature of the solidifying galvanized layer melt on the steel sheet and that of the solidifying bulk melt were also measured using an Ircon infrared optical pyrometer (Model 300 TS) similar to that reported in the literature [9].

The accuracy and reliability of optical pyrometry are critically related to the emissivity of the sample surface, the emissivity setting at which the instrument is set, and the stability of the emissivity as the surface oxidizes or the sample moves. Uncertainty of the measurement increases if a liquid layer is observed while it solidifies, since the liquid and solid have different emissivities, and the surface topography changes upon freezing.

In the present investigation, the emissivity setting on the optical pyrometer was established for the liquid metal by sighting the top surface of the galvanizing bath, ensuring the area observed was free of oxide and clean. The bath temperature was established by a thermocouple immersed in the bath, 25.4 mm below the bath surface. After thermal stability was established the emissivity control on the optical pyrometer was adjusted to match the measured melt temperature. The emissivity setting in which the optical pyrometer measurement coincided with the thermocouple measurement was 0.46.

3.3 Hand Dipping Experiments

The furnace and crucible arrangement are as described in section 3.1 and shown in Figure 3.1. However, the galvanizing bath (approximately 1000 grams) was contained in a graphite crucible of 76.2 mm inside diameter and 127 mm in height. The starting bath was of special high grade zinc (SHG Zn) of nominal 99.95 % purity supplied by Cominco Ltd. All of the solute additions were of commercial purity (99.95 %) or better. For the single alloy additions, a weighed amount of the solute was added to the pure zinc bath and the bath thoroughly stirred with a graphite plunger. The alloy composition was
determined from the weights of the bath and solute addition. Aluminum was introduced into the bath by adding weighed amounts of a Zn - 10 % Al master alloy. The chemical analysis of the galvanizing baths (up to 0.2 % Pb) was carried out by Cominco Ltd. and found to be in good agreement with the composition determined from the weights of the bath and solute additions to within 5 percent.

The bath temperature for all the dipping experiments was controlled at 475 ± 3 °C. Melt temperatures were measured with chromel/alumel thermocouples of 0.254 mm diameter immersed in the melt and connected to a Kipp & Zonen chart recorder Model Bd 41, using an ice/water cold junction.

Different solute elements were added to the galvanizing bath to determine their effect on the galvanized layer structure. The effects of single element addition were determined using either lead or antimony. Twelve tests were carried out with lead additions from 0.0 to 2.09 %, and seven tests with antimony from 0.0 to 2.0 %. Multiple element additions to the bath were made in fifteen tests adding bismuth, cadmium, tin, aluminum, magnesium, as well as lead and antimony.

Test samples consisted of galvanized steel sheets 101.6 mm long, 38.1 mm wide and 0.475 mm thick. The samples were each dipped in the bath for 10 seconds, then pulled out vertically, by hand, at approximately 10 cm/s and cooled in air at room temperature. At least three individual samples were dipped into each bath and examined.

After the dipping and cooling procedure was completed, the samples were examined visually to assess the spangle size, surface roughness, and spangle boundary pulldown. The grain or spangle size on selected samples was measured by counting the number of grains on linear traces across the samples and averaging the results. The surface structure of the samples was examined at higher magnification using optical microscopy. The structures were photographed at low and high magnification.
3.4 Determination of Spangle Orientation

Spangle orientation was determined by the X-ray back reflection Laue technique using a standard apparatus. A copper target was used as an X-ray source, and operated at 35 kV and 15 mA. The collimator had a pinhole of approximately 0.5 mm diameter. Double-sided Kodak No Screen X-ray film was used, positioned 3 cm from the galvanized sheet sample. To locate a particular position on the sample, a small dot of fluorescent powder was placed at the position, and the sample translated until the spot fluoresced in the X-ray beam. The powder was removed prior to obtaining the back reflection Laue photograph at that point.

The orientation of the basal plane of the zinc at the point considered in the sample was determined from the spot pattern on the Laue figure. This was done by measuring the zone and point positions using a Greninger chart, and plotting the positions on a Wulff net. Further details about the procedure are given in Cullity [51] and Azaroff [52].

3.5 Surface Topography of Hot Dipped Galvanized Steel

The surface roughness parameters were measured on a Talysurf 5 in the Tribology laboratory of the National Research Council in Vancouver. This is a surface texture stylus type measuring machine of modular design produced by Rank Taylor Hobson, in England. The stylus movement data is processed through a computer to produce the roughness and waviness parameters, with the corresponding profile graphs.

The stylus is carried on the end of a balanced beam and kept in contact with the surface by a light spring. The beam is supported by a skid behind the stylus, which rests on the sample surface and follows the general surface contours. Surface topography measurements are made by recording the vertical movement of the stylus as it traverses the sample surface at a given rate. The output data is stored in a PC file.
Measurements were carried out on laboratory prepared hot dipped steel sheets, on which the direction of withdrawal from the galvanized bath was marked. The measurements consisted of three traverses parallel to, and three perpendicular to, the withdrawal direction. The traverse measuring length was 17.5 mm. The roughness parameters determined from the measurements included the average roughness, $R_a$, the peak-to-valley depth, $R_{\text{max}}$, the average slope, $\Delta_a$, and the average wavelength, $\lambda_a$ as defined in section 4.4.1.

The galvanized sample was mounted on the worktable of the Talysurf 5 instrument with double-sided masking tape. The stylus was then moved with respect to the table and the vertical movement of the stylus recorded during the traverses for a given sample. In one series of tests the roughness of the shiny component of a spangle was compared to that of a frosty component. In these cases, the traverse path was carefully confined to the specific area being examined, using an assessment length of 5.6 mm and a cut-off length of 0.8 mm.

Surface contours across specific grain boundaries between spangles were determined. In this case, a number of parallel scans were made across the grain boundary at intervals of 100 $\mu$m or less, from which three-dimensional contour maps of the grain boundary region were produced. To complement the surface topography measurements, the thickness of the galvanized layer was determined for each sample. The thickness was measured using a Mitutoyo thickness gauge, at ten specific points on the sample surface, and the results averaged.

### 3.6 Solute Element Addition and Segregation Studies

The furnace and crucible arrangement are shown in Figure 3.1, and described in section 3.1.1. The 1000 gram melt was contained in a graphite crucible of 76.2 mm inside
diameter and 127 mm height. Bath temperatures were measured with chromel/alumel thermocouples having 0.127 mm diameter wires, with the thermocouple output recorded with a Kipp & Zonen recorder, using an ice/water bath cold junction as previously described.

In one series of experiments the composition of the galvanized layer after redipping was determined with the use of radioactive tracer. A small amount (~0.5 grams) of Tl$^{204}$ was added to bath 2, (see Table 3.1) at 480 °C, thoroughly mixed, and then allowed to equilibrate for 10 minutes.

Tl$^{204}$ has physical properties very similar to that of lead. It is a $\beta$ emitter (0.783 MeV, 2.7 yr. half-life) which makes it very suitable for autoradiography, since photographic film is sensitive to $\beta$ radiation.

Test samples of galvanized steel sheet 101.6 mm in length, 38.1 mm width and 0.475 mm thickness were dipped vertically into the bath containing Tl$^{204}$ at 475 °C, held for 10 seconds in the bath, then vertically lifted out rapidly and allowed to cool in air.

In another series of experiments, additions of lead, aluminum, antimony, and tin were made to the zinc melt to make up baths 3 to 8 in Table 3.1. The purity of the zinc and the alloy additions was 99.95 % or better. The same test samples as above were vertically hand-dipped in the baths at 475 ± 3 °C, held for 10 seconds, withdrawn rapidly and air cooled. At least four individual sheets were dipped and examined for each test condition.

3.6.1 Autoradiography of the Galvanized Steel Sheet

Test samples 40 mm in length, 30 mm in width an 0.475 mm in thickness, were cut from the redipped sheet, then autoradiographed by placing the large surface of the sample against a sheet of photographic film (double-sided no screen Kodak X-ray film). The film was on a glass plate to ensure that it remained flat. The sample was left on the film for approximately 16 hrs, then removed, and the film processed. The local presence
of radioactive thallium in the galvanizing layer resulted in darkening of the film adjacent to the local region.

In some samples, part of the galvanized layer was removed locally by fine grinding with 600 grit silicon carbide paper. After polishing, washing, and drying, the sample surface was again autoradiographed. In some areas where there was a bump on the surface, the entire galvanized layer was removed in polishing. This produced a tapered section of the layer around the bump which could then be examined in the autoradiograph.

### 3.6.2 Metallography of Dipped Samples

Following dipping, the samples were sheared to remove the undipped portion of the specimen. Along with the as-received galvanized piece, four samples, each 20 mm in length, 5 mm wide, and 0.475 mm thick, were clipped together with a Struers metal clip. The assembly was then vertically mounted in a translucent cold setting resin (Quick-mount). After the resin had set, the assembly was successively ground on 240 to 600 grit silicon carbide paper, coarse polished with 3 μm diamond paste using kerosine lubricant, followed by fine polishing with 0.06 μm alumina powder using an alcohol/glycerine mixture on a low nap polishing cloth.

After polishing the samples were etched using amyl nital (1 drop of nitric acid in 5 ml amyl alcohol) and examined under an optical microscope. Measurements were then made of the thickness of the new galvanized layers from the observed cross sections. These were then compared to the as-received galvanized sample that had been polished and etched at the same time.

The galvanized sections were also examined by microprobe analysis. Prior to examination in the Cameca SX50 microprobe analyser, the samples were coated with an evaporated layer of carbon. Using an acceleration voltage of 30 kV and a beam current
of 30 nA, the concentration of lead and/or antimony was measured across the galvanized layer at 1 to 2 μm intervals. The concentration of zinc and iron was monitored to establish the position of the Fe/Zn interface.

3.7 Volume Shrinkage Analysis During Coating Solidification

The depressions at grain boundaries have been attributed to volume shrinkage during galvanized coating solidification. In order to test this hypothesis, theoretical volume shrinkage calculations were made of the surface depression due to volume shrinkage as a molten zinc layer solidifies on the sheet steel.

3.7.1 Problem Formulation

Consider a rectangular volume element of the melt of unit depth, length 2L, and height $H_0$, at time $t = 0$, as shown in Figure 3.4. Calculate the solidification shrinkage that would be associated with the freezing from both ends of this volume element. Because of symmetry, half of the volume element may be considered in carrying out the calculations. As a small volume of solid $x H_0$ is formed, the melt level will drop a small amount from $H_0$ to $H_1$. As solidification progresses, the level of melt will continuously drop until the available liquid is consumed, leaving a shrinkage cavity. The following assumptions are made in order to carry out this calculation.

1. A moving vertical interface is maintained during solidification.

2. Freezing occurs uniformly from the two vertical ends.

3. The initial molten melt height $H_0$ is uniform at time $t = 0$ before freezing commences.
Dendritic solidification would result in shrinkage between the dendrite branches, reducing the possible shrinkage at the grain boundaries. Assumptions 1 and 2 take all the shrinkage to the grain boundary.

The initial volume of the molten layer is: $H_o L$. Let the volume shrinkage associated with the solidification of the whole layer be $\beta$. When a small volume of solid $x$ is formed, there is a corresponding drop in the liquid level that accompanies that solidification, and a volume balance is obtained as follows:

- Volume shrinkage when $x$ solidifies = $x H_0 \beta$
- Volume liquid drop = $(H_o - H_1)(L - x)$

Volume balance:

$$x H_o \beta = (H_o - H_1)(L - x) \quad (3.1)$$

For a particular case this is expressed as:

$$H_1 = H_o - \frac{H_o \beta x}{L - x} \quad (3.2)$$

For a general case the above equation is expressed as:

$$H_n = H_{n-1} - \frac{H_{n-1} x \beta}{L - nx} \quad (3.3)$$

where $n$ is the number of successive steps in the freezing direction.

The successive drop in the liquid level was calculated for different values of $L$ and $x$ from the above equation. The values chosen for $\beta$ were the reported volume shrinkage for a given melt, including 3.5% for pure lead and 4.2% for pure zinc. Other values are used to test the effect of large volume shrinkage on the shape of the calculated volume shrinkage curves.
### Table 3.1: Nominal Chemical Composition of the Galvanizing Baths Used

<table>
<thead>
<tr>
<th>Bath No.</th>
<th>Alloy Type</th>
<th>Concentration wt.%</th>
<th>Pb</th>
<th>Sb</th>
<th>Al</th>
<th>Cd</th>
<th>Fe</th>
<th>Sn</th>
<th>Zn</th>
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<td>SHG</td>
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<td>-</td>
<td>-</td>
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<td>2</td>
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<td>-</td>
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<td>-</td>
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<td>-</td>
<td>Bal</td>
</tr>
<tr>
<td>4</td>
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<td>0.08</td>
<td>-</td>
<td>0.35</td>
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<td>-</td>
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<td>-</td>
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<td>-</td>
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<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>Bal</td>
</tr>
<tr>
<td>6</td>
<td>3R2-4</td>
<td>2.0</td>
<td>-</td>
<td>0.27</td>
<td>-</td>
<td>-</td>
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<td>-</td>
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<td>-</td>
<td>-</td>
<td>-</td>
<td>0.2</td>
<td>Bal</td>
</tr>
</tbody>
</table>
Chapter 3. EXPERIMENTAL PROCEDURES

Figure 3.1: Schematic drawing of furnace and crucible for bulk supercooling measurements.
Figure 3.2: Schematic drawing of furnace, crucible, and dipping arrangement of experimental steel sheets.
Figure 3.3: Schematic drawing of micro-thermocouple assembly during coating solidification.
Figure 3.4: Schematic drawing of the solidification process in a control volume.
Chapter 4

OBSERVATIONS

4.1 Thermal Supercooling During Galvanizing Melt Solidification

4.1.1 Thermal Analysis Of Bulk Melt

Tests were undertaken to determine whether the bulk melt of the zinc galvanizing baths supercooled to a significant extent prior to solidification. The tests carried out and the results are listed in Table 4.1. Typical cooling curves are shown in Figures 4.1 to 4.3. In these measurements, the cooling rate (°C/s) is determined from the slope of the curve before the start of solidification.

Three repeat measurements (Tests 1 to 3, Table 4.1) with the high purity zinc melt gave an average plateau temperature of 419.2°C. The scatter of the three measurements is 0.7°C about the freezing temperature. A typical cooling curve from these measurement (Test 2, Table 4.1) is shown in Figure 4.1. A plateau of 125 seconds duration is observed at 419.5 °C. The plateau temperature drops approximately 1 degree in the 125 seconds. There is no indication of supercooling at the start of the freezing plateau.

Three repeat measurements (Tests 4 to 6) in an air cooled alloy bath (Zn + 0.11 %Pb + 0.30 %Al) are also listed in Table 4.1. A typical cooling curve (Test 4, Table 4.1) for this alloy is shown in Figure 4.2. In this case the plateau duration is shorter at about 45 seconds, and this plateau occurs at 419.5 °C. A small depression ahead of the plateau temperatures in these measurements indicate that a supercooling of 0.5 °C occurred prior
to solidification. This estimate is the difference in temperature between the bottom of the supercooled region and the observed starting temperature of the plateau.

When the alloy melt is cooled in an oil bath (Tests 7 to 9), cooling is much more rapid, and a shorter plateau of approximately 1 second duration is observed. A typical cooling curve from this measurement is shown in Figure 4.3. There is no evidence of supercooling at the start of the plateau.

4.1.2 Thermal Analysis of Galvanized Layer Melt

Three tests were carried out to demonstrate that a thermocouple welded to a steel sheet produced cooling curves which are related to the solidification of the zinc galvanizing layer. Cooling curves from a standard dipping test (Table 3.1, Bath 2) are compared to cooling curves for a reheated galvanized sheet and for an oxidized steel sheet dipped with the standard procedure but to which no zinc is attached during cooling. The results are shown in Figure 4.4. The as-received galvanized test sample normally dipped and cooled resulted in curve A. A plateau of approximately 10 seconds duration is observed close to the melt liquidus temperature. There is no plateau present in the cooling curve B of the reheated galvanized sheet nor in curve C for the oxidized sheet.

The results of fourteen tests carried out with thermocouples welded to the centre of as-received galvanized sheet are listed in Table 4.2. The galvanizing baths are listed in Table 3.1. In all of the tests a freezing plateau of 5.0 to 7.2 seconds duration is observed. A maximum supercooling of 0.5 °C is observed prior to the start of solidification in one of the tests based on the difference in temperature between the bottom of the supercooled region and the observed starting temperature of the plateau.

The results of three additional tests carried out using the thermocouples which passed through the as-received galvanized sheet and are beaded by the galvanized layer (Figure 3.3) are shown in Figure 4.5. The curves are all similar, exhibiting slightly sloping
freezing plateaus of varying duration. In general, these curves are very similar to the results for the welded thermocouples shown in Table 4.2. Note that the cooling curves were obtained from a Zn + 2 % Pb galvanizing bath.

4.1.3 Optical Pyrometer Measurements

Temperature measurements for a standard as-received sheet sample dipped in the galvanizing bath, as observed with a thermocouple welded to the back of the sample and simultaneously with an optical pyrometer, are shown in Figure 4.6. Curve A is the thermocouple output and B is the output of the optical pyrometer. In the first 13 seconds the sample is dipped into the melt and withdrawn to the position where the optical pyrometer measures the surface temperature. After 13 seconds both curves dropped at roughly the same rate. However, the temperatures indicated by the optical pyrometer are approximately 130 °C below the thermocouple results. In addition, the freezing plateau in curve A of between 30 and 35 seconds is not evident in curve B.

The emissivity setting of the optical pyrometer was established using the clean top surface of the bath. In several tests the galvanizing bath was allowed to cool and solidify. A typical result is shown in Figure 4.7, in which curve A is from the thermocouple and B is from the optical pyrometer. Shortly after solidification starts at S, there is a large drop in the temperature determined by the optical pyrometer, of nearly 80 °C, followed by a rise of approximately 20 °C and a short plateau. Without curve A, this could be interpreted to indicate that the liquid has supercooled by 20 °C at the start of solidification. However, curve A clearly shows that solidification had commenced prior to the drop in the optical pyrometer results. Cooling curves obtained with changes in emissivity setting are shown in Figures 4.8 (a) and (b). Note that even with changes in emissivity setting the thermocouple results are not equal to those of the optical pyrometer.
4.2 Coating Appearance and Spangle Size

The observations will consider the surface topography of the galvanized layer, described by the spangle size and contrast, the relative coating roughness, and the spangle orientations.

4.2.1 Pure Zinc Coating

The surface of the sheets galvanized in the pure zinc bath had a bright pebble-like appearance as shown in Figure 4.9(a). The grain size is small, typically less than 1.5 mm in diameter, and not spangled. Examination at low magnifications did not reveal any dendritic structure, but when the sample was examined under a stereo-microscope at about fifty times magnification, dendritic and cellular structures are revealed within the grains as shown in Figure 4.9(b). Some dendrite spikes are randomly located on the grain boundaries.

4.2.2 Zinc Coatings Containing 0.0 to 2.09 % Pb

Adding lead to pure zinc causes spangles to form and the grain size to markedly increase. This is shown in Figures 4.10 (a) to (l) for lead additions up to 2.09 % Pb. With 0.04 % Pb added to pure zinc the grain size remained small (~ 1.5 mm) and regular. Increasing the concentration to 0.06 % Pb resulted in the formation of dendritic spangles and a doubling of the grain size. Both shiny and dull regions can be observed on the coated surface.

With further increases in lead additions the dendrites in the spangles became more pronounced, the spangles more clearly defined and larger, and grooving at spangle boundaries became more severe.

The increase in spangle size with lead concentration up to 0.22 % Pb is shown in
Figure 4.11 (a). Spangles formed and started to grow between 0.05 and 0.06 % Pb, then increased in diameter rapidly as the lead increases to 0.10 % Pb. Above this level the diameter increased slowly and then stopped increasing above about 0.22 % Pb at a spangle diameter near 13 mm, Figure 4.11 (b).

4.2.3 Zinc Coatings Containing 0.0 to 2.0 % Sb

The results of antimony addition to the galvanizing bath are shown in Figures 4.12 (a) to (g). At an antimony concentration of 0.025 % the grains remained small (1.5 mm), but the surface did become a little more shiny and smoother (Figure 4.12 (b)) with these small additions. Increasing the antimony concentration to 0.05 % from 0.025 % resulted in the grains growing to twice their original diameter, and the dendritic structure becoming more clearly defined. However, the grains did not have the characteristic appearance of spangles. Increasing the antimony concentration to 0.075 % resulted in the formation of large spangles on the galvanized surface, with shiny and dull segments having grain diameters of about 7 mm. With 0.1 % Sb addition (Figure 4.12 (e)) feathery spangles formed with well-defined dendrites having secondary branches inclined at about 60° to the primary branches.

The average grain diameter as a function of antimony concentration up to 0.2 % Sb in the galvanizing bath is shown in Figure 4.13 (a). The results are very similar to that obtained with lead additions, Figure 4.11 (a), showing a rapid rise in diameter above about 0.04 % Sb.

Above 0.2 % addition (Figures 4.13 (b) and 4.11 (b) for antimony and lead respectively), the grain diameter appears to be constant to 2 % addition. The depressions at the grain boundaries appeared to be appreciably larger for the 2.09 % Pb (Figure 4.14 (a)) as compared to the 2.0 % Sb addition (Figure 4.14 (b)).
4.2.4 Single Solute Element Additions to the Galvanizing Bath

The relative effect of lead, antimony, bismuth, tin, cadmium, and magnesium for concentrations near 0.20 % (Table 4.3) on the structure of the galvanized layer is shown in Figures 4.15 (a) to (f). Additions of bismuth in the range of 0.025 to 0.20 % gave results similar to that reported for antimony. Large spangles with a mostly frosty appearance are observed, with a strong dendritic structure for the 0.20 % addition. Small non-spangled grains are observed with 0.025 % additions.

With additions of tin, cadmium, and magnesium up to 0.20 % to the zinc bath, the grains in the galvanized layer remained small (Figures 4.15 (a), (b), and (c)). For tin addition, the grain size is less than 1.5 mm and highly dendritic. The reflectivity of the surface is dull, with a frosty appearance, compared to the large spangles obtained with lead, antimony, and bismuth additions. Addition of cadmium gave results very similar to those observed for tin. Magnesium additions resulted in surfaces with a dull matte, silvery appearance, and grains did not exhibit a dendritic structure. With the addition of lead, antimony, and bismuth (Figures 4.15 (d), (e), and (f)), large spangles are formed.

4.2.5 Zinc Coating with Multiple Solute Additions

Considering the multiple bath additions (Table 4.3), it is observed that when tin is added to a Zn + 1.0 % Cd bath, the grain size remained small and dendritic (Figure 4.16 (a)). When 0.25 % Pb is added to this bath, large and highly dendritic spangles formed (Figure 4.16 (b)). The same effect is produced with Zn + 0.25 % Bi + 0.25 % Sb as would be expected since both elements are known to be spangle formers (Figure 4.16 (c)). Addition of 0.15 % Al to the bath did not change the spangle size.
Chapter 4. OBSERVATIONS

4.3 Spangle Orientation

Examples of the back reflection Laue photographs obtained are shown in Figures 4.17 and 4.18. In Figure 4.17 all the zones pass through one point, the (0001) pole. The angle this pole makes with the normal to the sample surface can be measured directly with the Greninger chart. In Figure 4.18, the (0001) pole is not in the picture, clearly indicating that the basal plane is inclined to the sample surface at a large angle.

The results for seven galvanized sheets produced from galvanizing baths of different compositions are listed in Table 4.4. Measurements made by Midler, as part of this investigation is listed in Table 4.5.

The overall results clearly indicate that the orientation of the spangle with respect to the sheet surface varies widely. In Table 4.4, $\theta$ varies between 17 and 80 degrees for different bath compositions, and in Table 4.5, it varies between 8 and 62 degrees for the same bath composition. The measured $\theta$ does not appear to be dependent on spangle size. Samples 1 and 2 of Table 4.4 had small spangles of 1 to 1.5 mm diameter, samples 3 to 7 had large spangles of 10 to 15 mm diameter. However, the $\theta$ values for samples 1 and 2 are similar to those for samples 3 to 7.

Note that in some cases, adjacent spangles have nearly the same $\theta$, as in samples 3 and 7 in Table 4.4 and sample 4 in Table 4.5. Typically, however, there is a wide range of orientation difference between segments in one spangle as shown in samples 3, 5, and 6 in Table 4.4 and sample 4 in Table 4.5.

Typical spangles examined in this study are shown in Figures 4.19 (a) and (b). These macrostructures show that the spangle sectors are not separately nucleated but emanated from the same central nuclei. The secondary electron images shown in Figures 4.20 (a) and (b) show that the primary dendrite arms are continuous across the centre of the spangle. The lead X-ray map in the vicinity of the centre (Figure 4.20 (c)) does not show
any concentration or depletion of lead in the region. The observed variation of lead in the areas of each spangle sector is believed to be associated with different velocities of growth of the primary and secondary dendrite arms during coating solidification.

A closer examination of the shiny and frosty sectors does reveal the differences in the surface topography in these regions as shown in Figures 4.21 (a). There is a sharp and clearly defined interface between the frosty (top) and shiny (bottom) sectors in this figure. It is quite clear from this figure that the frosty sector is considerably rougher than the shiny sector. This observation is in agreement with the results of the surface roughness parameter measurements. The marked differences in the surface topography of the shiny and frosty sectors is further emphasized by Figure 4.21 (b) obtained at a higher magnification. A lead X-ray map shows a slightly higher density of lead in the frosty sector as compared to the shiny sector, Figure 4.21(c). The observed peaks in the line scan across the sample surface (at the location marked A-A in Figure 4.21 (b)) is shown in Figure 4.21 (d)). The high lead peaks in this line scan are clearly associated with higher lead concentration in the frosty sectors. It is believed that the localised lead concentration is associated with interdendritic segregation of lead during coating solidification which is not unexpected.

4.4 Surface Topography of Hot Dipped Galvanized Steel Sheet

On the basis of visual examination, the surface topography appears to change appreciably when spangle growth occurs in the galvanized layer. The spangles are strongly dendritic, exhibiting spikes, shiny and dull segments, and depressions at the grain boundaries between the spangles. The top and bottom square markers in all of the graphs shown in Figures 4.22 to 4.29 indicate the maximum and minimum roughness parameters recorded for six scans. The circles represent the average values. The solid line in the
graphs is the line of best fit drawn through the average data points.

4.4.1 Lead Addition to the Galvanizing Bath

The results for twelve samples containing lead concentrations from 0 to 2.09 % Pb are listed in Table 4.6. In each case the results for three scans parallel (P) and transverse (T) to the withdrawal direction are shown, in addition to the grain size and the galvanized layer thickness. The average roughness parameter, $R_a$, as given in Equation 4.1, is the most widely used parameter, and is defined as the arithmetic mean of the departures of the surface profile from the mean line, i.e.

$$R_a = \frac{1}{L} \int_0^L y(x) \, dx,$$

where $x$ is the profile length and $y$ is the height. The peak-to-valley distance, $R_{max}$, is the maximum distance between the highest peak and deepest valley within the traverse length, $L$. The arithmetic mean of the surface profile slope within the profile length ($L$), expressed in degrees, is $\Delta_a$. The average wavelength, $\lambda_a$, of the surface profile within the traverse length ($L$) is:

$$\lambda_a = \frac{2 \pi R_a}{\Delta_a}\ \ (4.2)$$

The variation of $R_a$ with lead content is shown in Figure 4.22. Below 0.04 % Pb the $R_a$ values are low and constant with little scatter. Above 0.04 % Pb, the average $R_a$ increases by roughly a factor of 2, showing large fluctuations in the average values and a wide spread between maximum and minimum values. Above 0.12 % Pb, $R_a$ values tend to drop, some showing less scatter.

The grain size as a function of % Pb for the samples has been shown previously in Figure 4.11. Grain size, corresponding to spangle formation, increases rapidly above 0.04 % Pb to 0.11 % Pb, then increases slowly above the latter value.
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The maximum peak-to-valley distance, $R_{\text{max}}$, is shown as a function of % Pb in Figure 4.23. The general dependence of $R_{\text{max}}$ on % Pb is similar to that of $R_a$. The significance of $R_{\text{max}}$ with respect to the layer thickness can be evaluated by comparing $R_{\text{max}}$ to the minimum thickness of the layer, shown in Figure 4.24. Below 0.04 % Pb the average minimum layer thickness is 33 $\mu$m. At higher lead concentration, the average minimum layer thickness increases to 45 $\mu$m.

The variation of the surface slope, $\Delta_a$, and wavelength, $\lambda_a$, with % Pb is shown in Figures 4.25 (a) and (b) respectively. The slope increases significantly as spangles form above 0.04 % Pb and remains relatively constant until the high lead levels are reached, after which it decreases. The wavelength shows more scatter between 0.06 and 0.11 % Pb than at the very low and very high concentrations, but the average values are roughly independent of % Pb with the exception of 2.09 % Pb, Table 4.6. In this case $\lambda_a$ is much higher than all other values.

4.4.2 Antimony Addition to the Galvanizing Bath

Previous observations have shown that antimony produces spangles in the galvanized layer similar to those observed with lead additions. As a result, a series of surface roughness measurements were made for antimony additions to a pure zinc bath. The results are listed in Table 4.7, including data for the corresponding grain size and galvanized layer thickness.

The values of the roughness parameter, $R_a$, are plotted as a function of antimony concentration in Figure 4.26. It is noted that $R_a$ is relatively constant up to 0.08 % Sb with modest scatter at a value of 2. There is a small increase in $R_a$ at 0.10 % Sb with a very wide scatter band. However, this is primarily due to one large value in the six scans. The values of $R_a$ at 0.2 % Sb are similar to that at 0.1 %, and drops at 2.0 % Sb, Table 4.7.
The grain size as a function of antimony concentration was previously shown in Figure 4.13. As with lead, the grain size (and spangle formation) increases rapidly starting in the vicinity of 0.04 % Sb and at a slower rate at higher concentrations. However, with the antimony additions there is no increase in surface roughness, $R_a$, as the grain size increases with antimony concentration increasing up to 0.08 %. Even so, the increase in $R_a$ once the antimony concentration is greater than 0.075 % is small.

The maximum peak-to-valley distance, $R_{\text{max}}$, for % Sb is shown in Figure 4.27. Following the $R_a$, there is only a small increase in height above 0.075 % Sb, with $R_{\text{max}}$ being below that of lead up to this concentration. The minimum coating thickness of the galvanized layer for antimony concentration in the galvanizing bath is shown in Figure 4.28. The result is similar to that for lead, with appreciable scatter in the minimum values plotted.

The values of the average slope, $\Delta_a$, and average wavelength, $\lambda_a$, are plotted as a function of antimony concentration in Figures 4.29 (a) and (b) respectively. The $\Delta_a$ is observed to increase rapidly with increasing % Sb up to 0.20 % Sb, dropping to a low level for the 2 % Sb, Table 4.7. This is markedly different compared to the case in Figure 4.25 (a) for lead, which shows a small increase. This is more evidence that the dendrite morphology for the antimony additions is different from that for the lead additions, indicating a smoother, more inclined, faceted structure for antimony. The average wavelength, $\lambda_a$, is relatively independent of the antimony concentration, being a little higher at 0 and 2 % Sb and a little lower at 0.075 and 0.20 % Sb (Figure 4.29 (b)). In general, $\lambda_a$ is larger for the lead additions at 750 $\mu$m, compared with about 500 $\mu$m for antimony additions.
4.5 Single and Multiple Element Addition to the Galvanizing Bath

The surface roughness, grain size, and the minimum layer thickness for 0.20 or 0.25 % additions of bismuth, tin, magnesium, and cadmium as well as lead and antimony are listed in Table 4.8. The results for the surface roughness parameters for the single solute element additions are plotted as a function of the surface tension of the elements, and shown in Figures 4.30 (a) to (d). The relationship of $R_a$ and $R_{max}$ with the surface tensions of the added solute elements is shown in Figures 4.30 (a) and (b) respectively. The average roughness, $R_a$, and peak-to-valley depth, $R_{max}$, drops between bismuth and antimony, then increases progressively to magnesium and then drops with cadmium. The highest $R_a$ and $R_{max}$ are observed for magnesium.

A similar plot for the average slope, $\Delta_a$, and the average wavelength, $\lambda_a$, are shown in Figures 4.30 (c) to (d) respectively. There is considerable scatter in the values of these roughness parameters, with no apparent correlations between the values and the surface tensions of the added solutes. The minimum coating thickness of the test samples appear to be independent of the surface tension of the solute additions as shown in Figure 4.31.

The results of the surface roughness parameters for nine galvanizing baths (alloys 1 to 9) are listed in Table 4.9. The average of the roughness parameters are plotted in Figures 4.32 and 4.33. There is considerable scatter in the results. For $R_a$ and $R_{max}$ maximum values are observed for alloys 4 and 6; for $\Delta_a$ the maxima are for alloys 1 and 4; and for $\lambda_a$ the maxima are for alloys 5 to 8. There is no clear pattern for the alloys examined.

The surface roughness parameters in adjacent shiny and frosty spangle sectors produced from four different galvanizing baths (alloys 1 to 4) are given in Table 4.10. The surface roughness parameters $R_a$ and $R_{max}$ are shown in Figures 4.34 (a) and (b) respectively. The results indicate that $R_a$ and $R_{max}$ are higher in the frosty sectors for all the
galvanizing baths investigated. The same observation is made of the average slope, $\Delta_a$, as shown in Figure 4.35 (a); however the average wavelength, $\lambda_a$, as shown in Figure 4.35 (b) is higher in the shiny sector.

### 4.6 Effect of Cooling Rate

The effect of cooling rate on spangle size and surface roughness of a Zn-2 % Pb bath galvanized coating was investigated. Three cooling rates were used, air cooling (2.5 °C/s), oil quenching (39.1 °C/s) and water quenching (860 °C/s). It was observed that at higher galvanized sheet steel cooling rates, the grain size was small, typically less than 0.5 mm. The water quenched sheets buckled as a result of the quenching process.

The result of the measured surface roughness parameters are listed in Table 4.11. The average values are plotted in Figures 4.36 (a) through (d). The average roughness, $R_a$, is lowest for normal air cooling as compared to oil and water quenching as shown in Figure 4.36 (a). The peak-to-valley depth, $R_{\text{max}}$, is highest for the oil quenching consistent with the average roughness result.

The average slope, $\Delta_a$, and average wavelength, $\lambda_a$, are not significantly affected by the cooling rate, Figures 4.36 (c)) and (d). In general, the cooling rate had relatively little effect on the surface roughness of Zn-2 % Pb spangled surfaces.
4.7 Surface Roughness Profiles

4.7.1 Shiny and Frosty Spangle Sections

In the previous section the surface roughness was characterized by the average values of the roughness parameters and the scatter in the values. It is of interest to examine the surface profiles themselves, as recorded from the vertical movements of the stylus as it traversed the shiny or frosty segment of a spangle.

Typical roughness profiles of frosty and shiny spangle sectors for a Zn-0.20 % Sb bath are shown in Figures 4.37 and 4.38, respectively. The vertical and horizontal magnifications of the recorded data from the stylus movement are 2000 and 20, respectively. There are strong fluctuations in amplitude of between 12.5 and 13.9 \( \mu m \) for the frosty sector as compared to between 12.8 and 14.0 \( \mu m \) for the shiny sector. The surface roughness profiles of frosty and shiny segments from a Zn-0.25 % Bi alloy bath are shown in Figures 4.39 and 4.40 respectively. For a higher alloy bath composition (Zn + 0.25 % Sb + 0.25 % Bi) the frosty and shiny spangle section profiles are shown in Figures 4.41 and 4.42 respectively. These are very similar to Figures 4.39 and 4.40. The results from another alloy bath (Zn + 0.6 % Sn + 0.6 % Cd + 0.5 % Pb) are shown in Figures 4.43 and 4.44 for the frosty and shiny segments respectively. The frosty spangle profile graph (Figure 4.43) is essentially similar to the other corresponding profiles.

4.7.2 Random Surface Roughness Profile Graphs

The results of the random surface roughness profiles obtained from longer traverses (12 or 16 mm) to include boundaries between frosty and shiny spangles and the grain boundaries between spangles, are shown in Figures 4.45 to 4.51. The vertical and horizontal magnifications of the stylus data are 1000 and 20, respectively. The surface profile for a random length for a pure zinc bath is shown in Figure 4.45. The surface is irregular
with large peaks of 12 and 22 $\mu$m height above the general surface of the galvanized layer. The larger height is approaching one-half of the average thickness of the overall galvanized layer. The profile for the Zn-0.2 % Pb bath over 16 mm of traverse is shown in Figure 4.46. In this case we see a very large peak over 7.5 mm with a height of 50 $\mu$m.

Surface roughness profiles for Zn-0.2 % Sb and Zn-0.25 % Bi, both large spangled surfaces, are shown in Figures 4.47 and 4.48 respectively. There are large peaks and valleys in both cases, as well as small fluctuations superimposed on the larger features.

The surface roughness profiles for Zn-0.20 % Mg, Zn-0.25 % Cd, and Zn-0.20 % Sn are shown in Figures 4.49 to 4.51. These profiles exhibited wide fluctuations in amplitude, both long range and short range. The surfaces would be equivalent in appearance to the frosty spangle surface. Since the galvanized surface for these sheets does not exhibit large spangles, the absence of the large symmetrical hill contours observed in Figures 4.45 and 4.47 could be expected. The ranges of amplitude for Figures 4.49 and 4.51 are large, comparable to that observed with large spangles. The range for Zn-0.25 % Cd is smaller, (Figure 4.50) approximately 15 $\mu$m, in the area observed. This alloy exhibited a small diameter spangle structure.

4.8 Pulldown at Grain Boundaries

When galvanized sheet containing large spangles is examined visually, large depressions are often observed at the grain boundaries between adjacent spangles. The effect is termed "pulldown" and is attributed to volume shrinkage during solidification, or volume shrinkage combined with surface tension effects in some way. Pulldown is particularly significant in the use of galvanized sheet in the production of smooth painted surfaces. The as-galvanized rough surface can be smoothed by temper rolling. This flattens the peaks, but does not fill the pulldown grooves. As a result, the surface contains a pattern
of grooves which are not filled by paint, making the surface unsatisfactory for this application. The grooves may also negatively influence the corrosion behavior of the sheet since the galvanized layer can be very thin at the bottom of the groove.

The surface contours in the vicinity of grain boundaries, on galvanized sheet produced from pure zinc baths and zinc baths with lead additions, were measured for a number of typical areas. This was done by making individual scans across grain boundaries and by generating three dimensional contour maps of the surface in the vicinity of grain boundaries.

### 4.8.1 Surface Profile Scans Across Grain Boundaries

Surface profile scans vary appreciably across different boundaries and at different points across the boundary. The profiles also changed with Pb content of the bath. An example of a surface profile for a Zn-0.11% Pb bath is shown in Figure 4.52, in which the grain boundary position is indicated by G. The profile shows a depression at the grain boundary with curving side walls on either side of the depression. The depression depth with respect to the surface to the left (h₁) and the right (h₂) as well as the average values (h₃) are given in Table 4.12. The groove width as a function of distance from the bottom of the groove is also given in Table 4.12. The groove width increases rapidly with distance from the bottom.

A similar profile across a grain boundary in a Zn-0.22 % Pb is shown in Figure 4.53. A surface depression is clearly evident at the grain boundary G, with relatively steep walls on either side of the depression. The groove depth with respect to the surface on either side, and the width as a function of the distance from the bottom of the depression are also listed in Table 4.12.

Increasing the bath lead content to Zn-2 % Pb markedly increases the depression depth, as shown in Figure 4.54. The average depression is nearly symmetrical about the
grain boundary, and had a peak on either side. The average depression depth in this case is 36.5 μm, compared to 8.2 and 7.9 μm for the 0.11 and 0.22 % Pb galvanizing baths respectively. The groove width as a function of the distance from the groove bottom is also listed in Table 4.12, and is plotted in Figure 4.55. Taking the minimum average thickness of the galvanized layer as 39.2 μm the grooves for the 0.11 and 0.22 % Pb baths reduced the layer thickness by about 20 %, and the 2 % Pb addition by about 93 %.

4.8.2 Three Dimensional Contour Surface Maps

The contour map of a galvanized surface from a pure zinc bath is shown in Figure 4.56, for a surface area 8 mm square. The surface is highly irregular with hills and valleys within a thickness of roughly 10 μm. The grain boundaries in the figure are indicated by G, and it is evident that there are depressions at the grain boundary. The surface contours at the grain boundary varied significantly both between different grain boundaries and along a given grain boundary. A second example for pure zinc with a surface area of 2.5 mm square is shown in Figure 4.57. In this case, the surface is relatively smooth with a horizontal grain in the center delineated by the grooves at the grain boundary surrounding the grain at G. The grooves are relatively shallow and similar in appearance around the grain.

Examples of the surface contours for a Zn-2.0 % Pb bath are shown in Figures 4.58 and 4.59. In Figure 4.58 the area shown is 10 x 12 mm and it is apparent that there are very large variations in the surface topography in the area shown. A very deep groove is observed at grain boundary G which progressively increases in depth from the back to the center of the surface. The contour also shows hills on either side of the valley, as well as a ridge to the right of G. The surface topography for a small area 4 mm square, shown in Figure 4.59, is much more regular. One deep groove associated with a grain boundary is clearly evident with symmetrical sloping walls on either side. Moving from
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the front to the back of the surface the depth of the grain boundary groove progressively decreased until it is part of a hill. A very small depression at the grain boundary is still evident in the back regions of the surface.

The surface contour for a galvanized layer from a Zn-0.22% Pb bath over a 4 mm square area is shown in Figure 4.60, with the grain boundaries indicated by G. The boundaries $G_1$, $G_2$, $G_3$ are observed to meet at a triple point. The groove for $G_1$ has a very steep wall (on the right) and a shallow inclined wall (on the left). The groove for $G_2$ appears symmetrical with shallow inclined wall on either side. There is no increase in groove depth, or significant change in groove morphology at the triple point. The overall surface roughness is comparable to Figure 4.56, for the pure zinc bath.

4.9 Redipped Galvanized Sheet and Segregation Studies

4.9.1 Galvanized Coating Appearance

The surface of the galvanized sheets after being redipped in the different baths appear different from one another and different from the as-received starting sheet. As reported in section 4.2, large spangles (greater than 10 mm diameter) were obtained with baths containing appreciable amounts of lead and antimony and small dendritic grains (less than 1.5 mm diameter) for baths containing 0.2% Sn. The as-received sheet is spangled with grains of 8 to 12 mm diameter.

The large difference in grain size and spangle formation between the lead and tin additions, for the same starting sheet, clearly indicates that the galvanizing bath composition (and not the original galvanized layer on the as-received sheet) determines the morphology of the final galvanized coating. This could only occur if the zinc layer on the as-received sheet melted, and mixed in the bath without significantly changing the bath composition.
4.9.2 Segregation Determined by Radioactive Tracers

The surface appearance of the as-received sheet redipped into bath 2 with $\text{Tl}^{204}$ added to the melt is shown in Figure 4.61. The surface is rough, spangled, and strongly dendritic. Three large dendrite branches are marked A, B, and C in the figure. Each of the branches had a clearly defined sharp central branch with secondary branches growing at approximately 60 degrees to the central branch. The secondary branches on one side of the dendrite appears light, and the other side dark. Light and dark regions are also present in some cases on either side of the secondary branches.

The autoradiography corresponding to the area shown in Figure 4.61 is shown in Figure 4.62. In the autoradiograph a dark region indicates a concentration of $\text{Tl}^{204}$. The dendrite branches A, B, and C in Figure 4.61 are clearly evident in Figure 4.62. The central spines of both the primary and secondary branches of dendrites B and C are depleted in $\text{Tl}^{204}$. The $\text{Tl}^{204}$ is concentrated along the branches but in an inconsistent way. Dendrite C, with light dendrites on the left of the primary spine and dark on the right in the optical image of Figure 4.61, had approximately the same $\text{Tl}^{204}$ concentration on both sides. However, dendrite A had a high concentration of $\text{Tl}^{204}$ above the spine, corresponding to a bright optical image in Figure 4.61 and low $\text{Tl}^{204}$ below the spine, corresponding to the dark image. The same occurs for dendrites D and E. In general, the bright areas on the optical image are associated with higher $\text{Tl}^{204}$ concentrations in the autoradiographs. There is no evidence that $\text{Tl}^{204}$ is concentrated at grain boundaries or in the regions where the secondary branches from different dendrites meet.

An autoradiograph of a bulk sample, solidified slowly from bath 2 containing $\text{Tl}^{204}$ is shown in Figure 4.63. The $\text{Tl}^{204}$ is uniformly distributed in the sample, illustrated by the uniform darkening. Some microsegregation is observed at small dendrites, the dendrite cores being depleted.
The sample shown in Figure 4.62 was mechanically polished to remove the galvanized layer on a bump in the sheet. The sample was then autoradiographed giving the results shown in Figure 4.64. The galvanized layer (unpolished) is marked A, the through thickness region of the layer is indicated by B, and the steel substrate by C. Note the presence of Tl\textsuperscript{204} in region A, and none in the steel substrate as expected.

A tapered section of the autoradiographed steel sheet is shown in Figure 4.65. The through thickness region is complex with light and dark bands being present, perpendicular to and inclined to the top surface. These bands are associated with the dendritic structure, similar to that observed on the top surface. Examining the dark bands, it is evident that Tl\textsuperscript{204} is present throughout the through thickness region with little change in concentration up to the steel surface. This could only occur if the initial galvanized layer remelted and moved away from the steel substrate to be replaced by the new galvanized bath material containing Tl\textsuperscript{204}.

4.9.3 Structure and Thickness of the Galvanized Coating

The alloy layer thickness for the lead containing baths without aluminum are shown in Figure 4.66 (a). The alloy layer thickness remains close to 17 \(\mu\text{m}\). The addition of aluminum reduces the alloy layer thickness to near 2 \(\mu\text{m}\) for lead concentrations of 0.20 and 2.0 \% as shown in Figure 4.66 (b). The total layer thickness for the lead containing baths varied between 38 and 53 \(\mu\text{m}\).

A cross section of the as-received sheet, observed optically, is shown in Figure 4.67 (a). The galvanized layer is marked A, the steel substrate marked B, and the alloy layer is marked C. The total galvanized layer thickness is 34 \(\mu\text{m}\), and the alloy layer is 2 \(\mu\text{m}\) thick. The corresponding cross section for a redipped sample is shown in Figure 4.67 (b). In this case the total galvanized layer thickness is 58 \(\mu\text{m}\), and the alloy layer is also 2 \(\mu\text{m}\) thick. Since the as-received galvanized sheet is produced commercially at high
strip velocities, and the redipped sample produced from a small bath and withdrawn by hand, the thickness of the galvanized layers could be expected to differ. The alloy layer thickness is the same in both the as-received and redipped sheet.

The cross section of a galvanized layer resulting from dipping the as-received sheet into a Zn-2 % Pb bath is shown in Figure 4.67 (c) and for a Zn-2 % Sb bath in Figure 4.67 (d). The total galvanized layer thickness in (c) and (d) are 46 μm and 42 μm respectively, and the alloy layer thickness is 16 μm in both cases. The much thicker alloy layer in Figures 4.67 (c) and (d) as compared to Figures 4.67 (a) and (b) may be due to the absence of aluminum additions to the bath for these samples. The thickness of the alloy layer is strongly dependent on the presence of aluminum in the galvanizing bath. The alloy layer thickness is however relatively constant at 16 μm, and independent of the lead concentration in the galvanizing baths without aluminum. The galvanized layer thickness for the hand-dipped samples of Figure 4.67 (b), and Figures 4.67 (c) and (d) are very similar (58, 46, 42 μm respectively).

4.9.4 Composition Across the Galvanized Layer: Zn-2 % Sb

Microprobe scans were carried out across the cross section of polished surface of both the as-received and redipped samples. The distribution of iron for two scans across the as-received galvanized sheet is shown in Figure 4.68 (a), and for the redipped sample in Figure 4.68 (b). In both cases, scanning from the steel substrate, there is a sharp transition in iron concentration between the substrate and the galvanized layer, the transition distances being several microns wide. The alloy layer transition in Figure 4.68 (b) is illustrated by the presence of iron after the sharp drop, the iron gradually decreasing in concentration over about 15 μm.

The distribution of antimony in the as-received galvanized layer and the redipped layer are shown in Figures 4.69 (a) and (b) respectively. Note the scale of % Sb in (b) is
larger than (a) by a factor of 32. The results shown in Figure 4.69 (a) show a very small amount of antimony present in the galvanized layer, close to the lower limit of detection of the microprobe. The levels of antimony normally expected in commercial galvanizing are between 0.04 and 0.08 % Sb, a little lower than what is reported here. There is a small peak at 50 μm from the start of the scan, near the metal/air surface which may be significant or an artifact resulting from the adjacent metal/air interface. The sample redipped in the Zn-2 % Sb bath, Figure 4.69 (b) shows that no significant antimony is present in the steel substrate, as expected, and large concentrations of antimony in the galvanized layer. The concentration of antimony varies appreciably from 0.5 to 7 % Sb across the thickness of the layer. The concentration for scan 2 is markedly different than scan 1. The scans for the as-received and redipped samples from Figure 4.68 are superimposed in Figures 4.70 (a) and (b) for scans 1 and 2 respectively. The difference in antimony concentration in the redipped sample and the very low concentration in the as-received samples is clearly apparent.

4.9.5 Composition Across the Galvanized Layer: Zn-2 % Pb

Microprobe measurements similar to those carried out in a galvanizing bath containing antimony were performed for a Zn-2 % Pb galvanizing bath. As before the position of the substrate/galvanized surface is determined from the sharp drop in iron concentration for a given scan. The specified lead concentration in the as-received sheet is 0.2 % Pb. The measured values vary widely, between 0 to 0.18 % Pb in 17 measurements and 0.20 to 0.39 in 12 measurements, indicating appreciable microsegregation of the lead in the galvanized layer.

Two microprobe scans across galvanized layers of samples redipped in the Zn-2 % Pb bath are shown in Figures 4.71 (a) and (b). Lead is present throughout the layer and is strongly segregated as indicated by the observed concentration variations. The
highest concentration observed is near 0.45 which is very much lower than the 2% bath composition. The difference can be attributed to the relative difficulty of measuring lead concentrations in the microprobe, the sensitivity being low since the Lα line is used for the measurements. The absolute accuracy is poor. However, the measurements on the as-received sheet shows that lead could be measured on a relative basis to between 0.1 and 0.39%. Accordingly, the observations that lead concentrations of 0.25 and 0.35% are within 5μm of the substrate/galvanized interface agrees with the antimony results that the zinc layer on the as-received sample melted and is replaced by liquid from the lead-rich bath when the sample was redipped.

4.10 Solute Concentration in the Grain Boundary Region

There are speculations that the concentration of lead in the spangle boundary region could be different than within the grains. A series of back scattered electron images of selected samples of the galvanized sheets were obtained in the vicinity of the grain boundary and at regions further from it. Lead X-ray maps and line scans in selected areas of the macrostructure were obtained.

The results obtained in the vicinity of two different spangle boundaries are shown in Figures 4.72 and 4.73. Figures 4.72 (a) and (c) and Figure 4.73 (a) show the BSE image at the grain boundary and its vicinity. Note the depressions at the boundaries in these figures. The lead X-ray map is shown in Figure 4.72 (b).

The concentration of lead across selected boundaries marked A-A and B-B in Figures 4.72 (c) and 4.73 (a) are shown in Figures 4.72 (d) and 4.73 (c) respectively. There is no evidence of higher lead concentration or depletion at the spangle boundaries.

The results obtained within two different grains are shown in Figures 4.74 and 4.75. Figures 4.74 (a) and 4.75 (a) are the BSE images in the regions examined. The lead X-ray
maps in these regions (Figures 4.74 (b) and 4.75 (b)) show that there is no significant variation in the lead concentration in either region. This result is quite similar to those obtained in the vicinity of the grain boundaries as previously discussed. The fluctuation in the lead concentration across the regions marked B-B in Figure 4.75 (a) and shown in Figure 4.75 (c) is quite similar to those previously shown in Figures 4.72 (d) and 4.73 (c) which is not unexpected. The presence of lead particles within the zinc matrix is shown in Figures 4.74 (c) and (d). The lead X-ray map (Figure 4.74 (d)) did show that lead segregated within the zinc matrix.

4.11 Volume Shrinkage During Galvanized Coating Solidification

The progressive volume shrinkage that occurred with the solidification of the molten coating layer on steel sheet was calculated using Equation 3.2. The results are plotted in Figure 4.76.

It is observed in Figure 4.76 that the gradient of the shrinkage curves became steeper (shrinkage becoming more severe) as the value of $\beta$ increases. These calculated curves are compared to the profiles across grain boundaries previously shown in Figures 4.52 to 4.54. Note that the volume shrinkage of zinc on solidification is 4.2 %. By directly superimposing these theoretical curves on the profiles across the boundaries, Figures 4.77 to 4.79 for a Zn-0.11 % Pb, Zn-0.22 % Pb and Zn-2.0 % Pb galvanizing baths, were obtained. The calculated shrinkage curves clearly did not coincide with the grain boundary profiles. If we consider Figure 4.79, the pulldown at the spangle boundary is much deeper than that predicted for a zinc bath solidified normally. This observation indicates that volume shrinkage does not account for all the pulldown observed at spangle boundaries.
Table 4.1: Bulk Melt Thermal Analysis Results

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<tr>
<th>Test No.</th>
<th>Bath Temp. (°C)</th>
<th>Cooling Medium</th>
<th>Cooling Rate (°C/s)</th>
<th>Plateau Temp. (°C)</th>
<th>Plateau Duration (s)</th>
<th>Supercooling (°C)</th>
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<tr>
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<tr>
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</tr>
<tr>
<td>8</td>
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</table>

Notes:
A: Air cooling.
B: Oil quenching
Tests 1 to 3 Bath No. 1 Table 3.1. Pure Zn $T_{mp} = 419.5$ °C
Tests 4 to 9 Bath No. 2 Table 3.1.
Table 4.2: Solidifying Zinc Coating Thermal Analysis Results

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<th>Sample No.</th>
<th>Tmax</th>
<th>Cooling Rate</th>
<th>Plateau Temp.</th>
<th>Plateau Duration</th>
<th>Average Coating Thickness</th>
<th>Supercooling</th>
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Tests 8 to 14 Bath No. 4 Table 3.1.
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Table 4.4: Angle Between the Basal Plane and the Sheet Surface

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Table 4.5: Angle Between the Basal Plane and Sheet Surface (Zn-2% Pb)

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Table 4.6: Grain Size and Surface Roughness Dependence on Bath Lead Concentration

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Notes:
P: Traverse parallel to withdrawal direction.
T: Traverse perpendicular to withdrawal direction.
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Chapter 4. OBSERVATIONS

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Notes:
P: Traverse parallel to withdrawal direction.
T: Traverse perpendicular to withdrawal direction.
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## Chapter 4. OBSERVATIONS

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Notes:
P: Traverse parallel to withdrawal direction.
T: Traverse perpendicular to withdrawal direction.
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### Chapter 4. OBSERVATIONS

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Table 4.10: Surface Roughness Parameters in Shiny and Frosty Spangle Sectors

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<tr>
<th>No.</th>
<th>Added Element</th>
<th>$R_a$ (μm)</th>
<th>$R_{max}$ (μm)</th>
<th>$\Delta_\alpha$ (deg.)</th>
<th>$\lambda_\alpha$ (μm)</th>
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<tr>
<td></td>
<td>(wt.%)</td>
<td>S</td>
<td>F</td>
<td>S</td>
<td>F</td>
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<tr>
<td>1</td>
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</tr>
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<td>3</td>
<td>0.25%Bi+</td>
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<td></td>
<td>0.6%Cd+</td>
<td>0.5%Pb</td>
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Notes:
S: Shiny spangle sector.
F: Frosty spangle sector.
Table 4.11: Surface Roughness Dependence on Cooling Rate: Zn-2% Pb Galvanizing Bath

<table>
<thead>
<tr>
<th>Cooling Medium</th>
<th>Cooling Rate (°C/s)</th>
<th>Trace</th>
<th>( R_a ) (µm)</th>
<th>( R_{max} ) (µm)</th>
<th>( \Delta \alpha ) (deg.)</th>
<th>( \lambda_a ) (µm)</th>
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<td>P</td>
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<td>T</td>
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Table 4.12: Groove Depth versus Width During Galvanized Coating Solidification

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<th>Groove Width</th>
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</table>
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Figure 4.1: Cooling curve from air cooled pure zinc melt.

Figure 4.2: Cooling curve from air cooled alloy melt (Zn + 0.11 %Pb + 0.30 %Al).
Figure 4.3: Cooling curve from oil quenched alloy melt (Zn + 0.11 %Pb + 0.30 %Al).

Figure 4.4: Cooling curves from thermocouples spot welded to steel sheet.
Figure 4.5: Cooling curves from micro-thermocouples during galvanized coating solidification (Zn + 2 %Pb bath).

Figure 4.6: Cooling curves from spot welded thermocouple and optical pyrometer during galvanized coating solidification.
Figure 4.7: Cooling curves from the solidifying galvanizing bath melt (Zn + 0.04 % Pb + 0.15 %Al bath).
Figure 4.8: Cooling curves with changes in emissivity setting.

(a) Emissivity setting: 0.26.

(b) Emissivity setting: 0.35.
Figure 4.9: Photomacrographs of a pure zinc coating on steel sheet.

(a) Magnification 8X.

(b) Magnification 51.2X.
Figure 4.10: Photomacrographs (a) to (l): effect of lead concentration (0.0 to 2.09% Pb) on spangle size and morphology. Magnification 3X.
(c) Zn-0.04% Pb.

(d) Zn-0.06% Pb.
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(e) Zn-0.07% Pb.

(f) Zn-0.08% Pb.
(g) Zn-0.09% Pb.

(h) Zn-0.11% Pb.
(i) Zn-0.13% Pb.

(j) Zn-0.15% Pb.
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(k) Zn-0.22% Pb.

(l) Zn-2.09% Pb.
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Figure 4.11: Grain size versus lead concentration.

(a) Pb concentration: 0.0 to 0.22%.

(b) Pb concentration: 0.0 to 2.09%.

Figure 4.11: Grain size versus lead concentration.
Figure 4.12: Photomicrographs (a) to (g): effect of antimony concentration (0.0 to 2.0% Sb) on spangle size and morphology. Magnification 6X.
(d) Zn-0.075\% Sb.
(e) Zn-0.10% Sb.

(f) Zn-0.20% Sb.
(g) Zn-2.0% Sb.
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Figure 4.13: Grain size versus antimony concentration.

(a) Sb concentration: 0.0 to 0.20%.

(b) Sb concentration: 0.0 to 2.0%.

Figure 4.13: Grain size versus antimony concentration.
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(a) Zn-2.0% Pb bath.

(b) Zn-2.0% Sb bath.

Figure 4.14: Photomacrographs obtained from high Pb and high Sb galvanizing bath. Magnification 8X.
Figure 4.15: Photomacrographs (a) to (f): effect of single solute element additions on spangle size and morphology. Magnification 8X.
(c) Zn-0.20% Mg.

(d) Zn-0.20% Pb.
(e) Zn-0.20% Sb.

(f) Zn-0.25% Bi.
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(a) Zn + 1% Cd + 0.5%Sn.

(b) Zn + 1% Cd + 0.5%Sn + 0.25% Pb.

Figure 4.16: Photomacrographs (a) to (c): effect of multiple bath addition on spangle size and morphology. Magnification 8X.
(c) Zn + 0.25% Bi + 0.25% Sb + 0.15% Al.
Figure 4.17: Back reflection Laue photograph from spangle orientation study; a sector with basal plane (diffraction spot A) shown on photo.

Figure 4.18: Back reflection Laue photograph from spangle orientation study; a sector with basal plane not shown on photo.
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(a) Shiny/frosty spangle sectors.

(b) Completely frosty spangle. Magnification 6.4X

Figure 4.19: Macrographs of typical galvanized sheet surface selected for spangle orientation study.
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Figure 4.20: Secondary electron image of a spangle selected for orientation study.

(a) Magnification 100X

(b) Magnification 400X

Figure 4.20: Secondary electron image of a spangle selected for orientation study.
(c) X-ray map for lead of the area shown in (b).
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Figure 4.21: A secondary electron image in a shiny/frosty spangle sector.

(a) Magnification 100X.

(b) Magnification 400X.
(c) X-ray map for Pb of the area shown in (b).

(d) Line scan for Pb across the position marked A-A in (b).
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Figure 4.22: Average roughness parameter versus lead concentration.

Figure 4.23: Maximum peak-to-valley depth versus lead concentration.
Figure 4.24: Minimum coating thickness versus lead concentration.
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Figure 4.25: Changes in the surface slopes and the wavelength of roughness peaks and valleys versus lead concentration.

(a) Arithmetic mean of surface slopes ($\Delta a$).

(b) Average wavelength of surface peaks and valleys ($\lambda a$).
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Figure 4.26: Average roughness parameter versus antimony concentration.

Figure 4.27: Maximum peak-to-valley depth versus antimony concentration.
Figure 4.28: Minimum coating thickness versus antimony concentration.
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Figure 4.29: Surface slopes and the wavelength of roughness peaks and valleys versus antimony concentration.

(a) Arithmetic mean of surface slopes ($\Delta a$).

(b) Average wavelength of surface peaks and valleys ($\lambda a$).
Figure 4.30: Changes in surface roughness parameters with the surface tension of added solute element.

(a) Average roughness parameter ($R_a$).

(b) Maximum peak-to-valley roughness parameter ($R_{max}$).
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(c) Arithmetic mean of surface slopes (Δα).

(d) Average wavelength of surface peaks and valleys (λα).
Figure 4.31: Minimum coating thickness versus the surface tension of added solute element.
Figure 4.32: Surface roughness parameters in selected galvanizing baths.

(a) Average roughness parameter.

(b) Maximum peak-to-valley depth ($R_{\text{max}}$).
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(a) Arithmetic mean of surface slopes ($\Delta a$).

(b) Average wavelength of surface peaks and valleys ($\lambda a$).

Figure 4.33: Surface roughness parameters in selected galvanizing baths.
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Figure 4.34: Surface roughness parameters within the shiny or frosty segments in selected galvanizing baths.

(a) Average roughness parameter.

(b) Maximum peak-to-valley depth.
Figure 4.35: Surface roughness parameters within the shiny or frosty segments in selected galvanizing baths.

(a) Arithmetic mean of surface slopes (Δa).

(b) Average wavelength of surface peaks and valleys (λa).
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(a) Average roughness parameter ($R_a$).

(b) Maximum peak-to-valley depth ($R_{\text{max}}$).

Figure 4.36: Surface roughness parameters versus galvanized steel sheet cooling rate.
(c) Arithmetic mean of surface slopes ($\Delta a$).

(d) Average wavelength of surface peaks and valleys ($\lambda a$).
Figure 4.37: Surface roughness profile within the frosty sector of a Zn-0.2%Sb bath coated steel sheet.

Figure 4.38: Surface roughness profile within the shiny sector of a Zn-0.2%Sb bath coated steel sheet.
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16.0

PROFILE LENGTH (mm)

Figure 4.39: Surface roughness profile within the frosty sector of a Zn-0.25%Bi bath coated steel sheet.

16.0

PROFILE LENGTH (mm)

Figure 4.40: Surface roughness profile within the shiny sector of a Zn-0.25%Bi bath coated steel sheet.
Figure 4.41: Surface roughness profile within the frosty sector of a Zn + 0.25%Sb + 0.25%Bi bath coated steel sheet.

Figure 4.42: Surface roughness profile within the shiny sector of a Zn + 0.25%Sb + 0.25%Bi bath coated steel sheet.
Figure 4.43: Surface roughness profile within the frosty sector of a Zn + 0.6%Sn + 0.6%Cd + 0.5%Pb bath coated steel sheet.

Figure 4.44: Surface roughness profile within the shiny sector of a Zn + 0.6%Sn + 0.6%Cd + 0.5%Pb bath coated steel sheet.
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Figure 4.45: Surface roughness profile across a pure zinc bath coated steel sheet.

Figure 4.46: Surface roughness profile across a Zn-0.20% Pb bath coated steel sheet.
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Figure 4.47: Surface roughness profile across a Zn-0.20% Sb bath coated steel sheet.

Figure 4.48: Surface roughness profile across a Zn-0.25% Bi bath coated steel sheet.
Figure 4.49: Surface roughness profile across a Zn-0.20% Mg bath coated steel sheet.

Figure 4.50: Surface roughness profile across a Zn-0.25% Cd bath coated steel sheet.
Figure 4.51: Surface roughness profile across a Zn-0.20% Sn bath coated steel sheet.
Figure 4.52: Surface profile across the grain boundary in a Zn-0.11% Pb bath coated steel sheet.

Figure 4.53: Surface profile across the grain boundary in a Zn-0.22% Pb bath coated steel sheet.
Figure 4.54: Surface profile across the grain boundary in a Zn-2.0% Pb bath coated steel sheet.

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Figure 4.65: A tapered section of the as solidified sample. Magnification 5X
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(a) Pb concentration: 0.0 to 0.22%.

(b) Pb concentration: 0.0 to 2.0%.

Figure 4.66: Alloy layer thickness versus lead concentration.
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Figure 4.67: Photomicrographs of the cross-section of selected galvanized steel sheets. Magnification 500X

(a) Coating from a Zn + 0.20% Pb + 0.15% Al bath.

(b) Coating from a Zn + 2.0% Pb + 0.27% Al bath.

(c) Coating from a Zn-2.0% Pb bath.

(d) Coating from a Zn-2.0% Sb bath.
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Figure 4.68: Iron concentration across the galvanized layer thickness.

(a) Fe concentration in the as-received steel sheet.

(b) Fe concentration in the redipped steel sheet.
Figure 4.69: Antimony concentration across the galvanized layer thickness.

(a) Sb concentration in the as-received steel sheet.

(b) Sb concentration in the redipped steel sheet.
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Figure 4.70: Antimony concentration in the as-received and redipped sheets.

(a) Sb concentration in the as-received and redipped steel sheets.

(b) Sb concentration at about 8 μm from location shown in (a).

Figure 4.70: Antimony concentration in the as-received and redipped sheets.
(a) Fe concentration in the as-received and redipped steel sheets.

(b) Pb concentration in the as-received and redipped sheets.

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(c) BSE image at 300X.
(a) BSE image at 400X.

(b) X-ray map for Pb of the area shown in (a).

Figure 4.73: SEM image of galvanized steel sheet surface in the vicinity of a grain boundary.
(c) Line scan for Pb across area marked B-B in (b).
Figure 4.74: SEM image of a galvanized steel sheet within a given grain.
(c) BSE image of (a) at 1700X.

(d) X-ray map for Pb of the area shown in (c).
(a) BSE image at 400X.

(b) X-ray map for Pb of the area shown in (a).

Figure 4.75: SEM image of a galvanized steel sheet surface within a given grain.
(c) Line scan for Pb across the area marked B-B in (a).
Figure 4.76: Calculated theoretical volume shrinkage curves during galvanized coating layer solidification.

Figure 4.77: Superimposing calculated theoretical volume shrinkage curves on measured profile across spangle boundary in a Zn-0.11% Pb bath.
Figure 4.78: Superimposing calculated theoretical volume shrinkage curves on measured profile across spangle boundary in a Zn-0.22% Pb bath.

Figure 4.79: Superimposing calculated theoretical volume shrinkage curves on measured profile across spangle boundary in a Zn-2.0% Pb bath.
Chapter 5

DISCUSSION

5.1 Thermal Supercooling During Galvanizing Melt Solidification

The cooling curves for the pure zinc and galvanizing bath bulk liquids gave good thermal plateaus. The plateau temperatures correspond to the melting temperature of pure zinc and the alloy to within better than ± 1 °C, which is reasonable for the temperature measuring system used. If the liquid is supercooled prior to solidification, a depression in the cooling curve should be observed prior to the well defined plateau. The extent of supercooling is taken as the difference between the minimum temperature reached in the depression and the starting plateau temperature. In the present measurements for pure zinc no depression was observed and therefore no supercooling occurred.

In the literature it is reported that the liquid zinc on a galvanized sheet supercools prior to solidification. The amount of supercooling reported varies widely, from 0 °C to 23 °C. The present measurements show that the supercooling required to activate nucleating sites in pure zinc, and typical galvanizing baths, is less than 1 °C. This is in agreement with the measurements on pure zinc droplets reported by White [53], but different from the value of 23 °C reported by Kim and Patil [9].

The observed differences in the cooling curves shown in Figure 4.4 are clearly associated with the solidification of the galvanized coating on the redipped sheet. Upon heating the as-received galvanized sheet (Table 3.1, Bath 2) in an electric furnace it is likely that the alloy phase at the steel/zinc interface grows during reheating of the galvanized layer.
to encompass the entire layer. On cooling, with no liquid present, no freezing plateau is observed. When an oxidized steel sheet was dipped and removed from the bath, no liquid remained on the steel sheet. As a result no freezing plateau is observed, as expected.

The results clearly indicate that the cooling obtained from galvanized samples to which a thermocouple had been welded is related to the cooling of the zinc layer, as indicated by the plateau in the curve. Accordingly, if the liquid supercools prior to solidification, there should be a drop of temperature below the plateau at the onset of solidification. The results of temperature measurements made with fine thermocouple wires (Figure 4.5), passed through the sheet and joined by the galvanizing layer (Figure 3.3), are consistent with the measurements made with thermocouples spot welded to the sheet, both showing well-defined plateaus. This is further evidence that the welded thermocouple results are indicative of the temperature of the galvanized layer during solidification.

The large difference between the cooling curves obtained with thermocouple A, Figure 4.6, and with an optical pyrometer B, is attributed to the changes in the emissivity of the sample surface. The absence of a freezing plateau in curve B suggests that the optical pyrometer is not as sensitive to the local temperature of the galvanized layer as the thermocouple.

The supercooling observed in the galvanized layer is below 1 °C as listed in Table 4.2. The plateaus are clearly delineated, and in the case of sample 4 are within 1 °C of the liquidus temperature. Since no depression of temperature is observed before the plateau, the present results clearly indicate that there is no significant melt supercooling during galvanizing, any supercooling being less than 1 °C.

Temperature measurements of bulk melt with an optical pyrometer, as shown in curve B, Figure 4.7, show that the melt temperature drops by 80 °C and an apparent supercooling of 20 °C occurs before solidification. However, the simultaneous thermocouple
measurement curve A, clearly shows that solidification has commenced prior to the sharp drop in temperature indicated by the optical pyrometer. Clearly the 20 °C drop is not due to supercooling, but due to a marked change in the emissivity of the sample surface as the surface changes from liquid to solid, since there is an overall 80 °C apparent drop in temperature.

Tests were carried out in which the emissivity setting of the optical pyrometer was varied to see if one setting could be found which gave temperature measurements which matched the thermocouple measurements. The results are shown in Figures 4.8 (a) and (b). With an emissivity setting of 0.26, Figure 4.8 (a), the optical pyrometer reading is higher than the thermocouple reading by about 25 °C before freezing and near 10 °C after freezing. The optical pyrometer cooling curve exhibits a short plateau and a slight rise, at times different from the simultaneous thermocouple curve. With the emissivity set at 0.35, Figure 4.8 (b), the optical pyrometer temperatures are higher than those from the thermocouples above freezing temperatures and lower after freezing. In the freezing region, the optical pyrometer temperature drops steeply as the thermocouple temperature plateaus. The estimated "noise" from the optical pyrometer temperature is between 8 to 12 °C.

These results indicate that even with emissivity adjustments, the temperature measured by an optical pyrometer during the solidification of either bulk melt and a galvanized layer is not reproducible, reliable, or accurate. Accordingly, on the basis of the present observations, the reported values of supercooling obtained using an optical pyrometer are not considered valid.
5.2 Surface Topography of the Galvanized Sheet

5.2.1 Bath Composition and Surface Roughness Parameter

The observed differences in spangle size and morphology in the galvanized sheets examined are directly related to the chemical composition of the galvanizing bath. The surface topography of galvanized sheets is also strongly dependent on the bath composition. Accordingly, changing bath compositions to change or control the spangle size or morphology will also change the smoothness of the surface of the galvanized layer.

The variation of surface roughness ($R_a$) and average peak-to-valley depth ($R_{\text{max}}$) with lead concentration is shown in Figures 4.22 and 4.23. Both roughness parameters increase as the lead concentration increases. The increase in $R_a$ above 0.04 % Pb is clearly associated with the formation of spangles.

The results indicate that $R_a$ and $R_{\text{max}}$ decrease with increasing lead concentration above 0.12 % Pb, as the spangle diameter increases. The decrease may be attributed to both a smoothing of the large spangle surfaces, and a reduction in the number of grain boundaries traversed in a scan. There are generally large surface perturbations at the grain boundaries.

The observed fluctuation in the average values, and the wide spread between the maximum and minimum values are associated with the dendrite growth pattern on the galvanized surface. If a line traverse is made across a large number of secondary or tertiary dendrite arms as compared to a traverse parallel to the dendrite arms the average roughness parameters would be higher in the transverse direction. Hawthorne and Yick [56] reported that for a ground surface the average roughness parameter ($R_a$) in a direction transverse to the ground direction is higher.

The significance of the observed maximum roughness height, $R_{\text{max}}$, with respect to the galvanized layer thickness can be appreciated by comparing Figures 4.23 and 4.24.
Considering a minimum coating thickness of $32 \, \mu m$, the average peak-to-valley depth, $R_{\text{max}}$, $(10.9 \, \mu m)$ constitutes $34 \%$ of the galvanized layer thickness. When the lead concentration is below $0.04 \%$, $R_{\text{max}}$ was about $26 \%$ of the minimum coating thickness. At lead concentrations greater than $0.04 \%$, $R_{\text{max}}$ increases to about $36 \%$. This result is associated with different dendrite morphologies for galvanizing baths of different composition.

It is desirable to keep the average peak-to-valley depth within a narrow limit since any wide variation in this parameter can have an adverse effect on the paintability and smoothness of the surface. The observed increase in the average slope, $\Delta_a$ (Figures 4.25 (a)), and the average wavelength, $\lambda_a$ (Figure 4.25 (b)), above $0.04 \%$ Pb are associated with spangle formation and the increased average surface roughness (Figure 4.22).

These results show that the average peak-to-valley depth, $R_{\text{max}}$, as well as the average wavelength, $\lambda_a$, are significant parameters in assessing the surface roughness (profile amplitude and wavelength) of a galvanized sheet. By controlling these parameters within narrow limits it should be possible to obtain better paint adhesion, and reduced paint cracking, during subsequent drawing or other forming operations.

The effect of changes in the antimony concentration in the galvanizing bath on measured surface roughness parameters are similar to those obtained for lead. This result is not surprising since either lead or antimony added to the galvanizing bath results in the formation of large spangles. The observation that $R_a$ (Figure 4.26) and $R_{\text{max}}$ (Figure 4.27) are approximately constant (within $2 \, \mu m$) for an $0.075 \%$ Sb bath as compared to $0.04 \%$ Pb (within $1.6 \, \mu m$) Figure 4.22, suggests that the dendrite morphology with the antimony additions is different on a microscale than for the lead additions that produced smoother surfaces.

Increasing the antimony concentration in the bath increases the grain size, as shown in Figure 4.13. The average roughness parameter is independent of the spangle size up to
0.075 % Sb, and then increases a small amount with higher antimony concentration. The minimum coating thickness of the galvanized layer for antimony addition (Figure 4.28) is similar to that obtained for lead addition (Figure 4.24). The observed fluctuation in $R_{max}$ is similar to that obtained for lead addition.

A visual examination of the galvanized surface shows that the spangle boundary depression becomes larger as the lead concentration in the bath increases as previously discussed. With antimony, the spangles are smoother and the grain boundary depression smaller for comparable lead and antimony concentrations. This observation may be due to differences in the spangle boundary geometry (depth and width).

The observation that the average slope, $\Delta_a$ (Figure 4.29 (a)), increases rapidly with increase in antimony concentration up to 0.20 % Sb, and then drops to a low value at 2.0 % Sb is different from that obtained for lead over the same concentration range (Figure 4.25 (a)). This is further evidence that the spangle morphology for the antimony addition is different than for lead, indicating a smoother, and more inclined faceted structure.

5.2.1.1 Shiny and Frosty Spangle Sectors

The result of the surface roughness parameters in the shiny and frosty sectors of selected spangles are shown in Figures 4.34 and 4.35. It is evident from Figures 4.34 (a) and (b) that both $R_a$ and $R_{max}$ are appreciably higher for the frosty sectors than for the shiny sectors in all cases. Note that the values of $R_a$ and $R_{max}$ are much lower than that obtained on the longer random scans, discussed previously, due to confining the scan path to one spangle section.

For $\Delta_a$ shown in Figure 4.35 (a), in all cases the frosty segment has a much higher slope than the shiny segment, by a factor of 7 for the Zn-0.25 % Bi bath, for example. The average wavelength, $\lambda_a$, is small for the frosty segments (Figure 4.35 (b)) and consistently higher for the shiny segments, with the value for the shiny segments still much smaller
than that observed in the random scans described previously.

5.3 Bath Composition and Surface Roughness Profile Graphs

5.3.1 Shiny and Frosty Spangle Sectors

The typical surface roughness profile graphs for selected shiny and frosty spangle sectors are shown in Figures 4.37 to 4.44. The surface roughness profile for the frosty sector in Figure 4.37 can be compared to that in the shiny sector of the same spangle shown in Figure 4.38. It is observed that the surface fluctuations in the shiny sector are about 1.2 \( \mu \text{m} \) as compared to 1.4 \( \mu \text{m} \) in the frosty section, with 4 peaks outside this range. The wavelength of the fluctuations is in general much longer than that of the frosty section, with occasional fluctuations of short wavelength. There are wide depressions at 0.5 and 1.5 mm along the traverse which are not present in the frosty segments.

The frosty section profile in Figure 4.39 is generally similar to that of Figure 4.37. The profile height is larger in Figure 4.39, from 11.5 to 15 \( \mu \text{m} \) and the wavelength shorter over much of the traverse. The shiny segment Figure 4.40 shows a much flatter surface after the first 0.5 mm traverse with profile heights between 13 to 14 \( \mu \text{m} \) and a combination of short wavelengths imposed on a generally long wavelength pattern. The large peaks in the first 0.5 mm of the traverse are associated with the transition between the frosty and shiny segments.

The similarity between profile graphs shown in Figures 4.39 and 4.40 and those of Figures 4.41 and 4.42 show that adding 0.25 % Sb to the Zn-0.25 % Bi bath has no significant effect on the roughness in these selected areas.

The frosty spangle profile, Figure 4.43, is similar to the other profiles shown. However, in this case, the amplitude is more regular and smaller than the others, between 12 and 14 \( \mu \text{m} \). The wavelength is similar to the others. The shiny profile, Figure 4.44, is
anomalous. The first 2 mm of the traverse shows appreciable amplitude fluctuations with long wavelengths; the traverse from 2 to 4 mm is very flat, between 13.2 and 13.4 \( \mu m \) with short and long wavelength fluctuations. This difference between the starting section of the traverse and the second half of the traverse is present, to some degree, in all the shiny section profiles shown. This difference is associated with the transition from a frosty to a shiny spangle section.

5.3.2 Random Surface Roughness Profile Graphs

The complexity of the surface topography of the galvanized sheets is clearly brought out in the results of the random surface profile graph of selected samples shown in Figures 4.45 to 4.51. Considering the large spangled sheets (Figures 4.46 to 4.48), broader and larger peaks and valleys are commonly seen. The profile for Zn-0.2 % Pb bath over 16 mm of traverse is shown in Figure 4.46. In this case a very large peak, over 7.5 mm, with a height of 50 \( \mu m \) is present. This is a large spangle consisting of a shiny sector (on the left), with a relatively smooth profile, and a frosty section (on the right) with a rougher profile. The cross section of one spangle arm, at least in this case, consists of two planes, one shiny and one frosty, forming a broad symmetrical cap running along the galvanized surface.

Considering Figures 4.47 and 4.48, the large non-symmetrical valley at 9 to 12 mm distance (Figure 4.47) is the surface contour across a grain boundary between two spangles. The symmetrical hills in Figure 4.48 indicate a series of dendrite branches in a spangle are being traversed, most surfaces being frosty since they have local small and short wavelength fluctuations. In Figure 4.48 the maximum to minimum fluctuation in the field of view is large, 30 \( \mu m \), in a layer thickness of 44 \( \mu m \) (Table 4.8).

Considering the small diameter spangled coatings (Figures 4.49 to 4.51), the surfaces are equivalent in appearance to a frosty spangle surface. Since the galvanized layer does
not exhibit large spangles, the absence of the large symmetrical hill contours observed in Figures 4.45 and 4.47 are expected. The ranges of amplitude for Figures 4.49 and 4.51 are large, comparable to those observed for large spangle layers. The range for Zn-0.25 % Cd is smaller, (Figure 4.50) approximately, 15 \( \mu m \) in the area observed. Note that this alloy exhibits a small spangle structure. These results also show that a smaller spangle size is not synonymous with a smoother surface. Even for the pure zinc bath coating with small grains (Figure 4.45), the surface profile is highly irregular with large peaks of 12 \( \mu m \) and 22 \( \mu m \) above the general irregular surface of the galvanized layer.

The observed peaks and valleys in these surface profile graphs are clearly associated with the crossing of spangle sector boundaries as well as the crossing of spangle grain boundaries. This observation confirms the previous quantitative data that the average roughness parameters are consistently higher in the frosty sectors than the shiny sectors of a given spangle. The superimposed fluctuations on the larger features are associated with the crossing of dendrite arms in the spangles during the measurement.

The weldability of galvanized sheets is dependent on the surface roughness of the sheets, particularly the amplitude and the wavelength of the irregularities. Fostini et al. [57] reported that the average wavelength parameter in a galvanized surface, is an important surface parameter that determines the electrode life during the spot welding of galvanized sheets. They noted that coatings which had wavelengths of less than 0.5 mm passed the weld electrode life test. This suggests that if this parameter could be controlled within narrow limits, higher productivity and lower cost could be achieved during the welding of galvanized steel sheet.

5.3.3 Surface Tension and Surface Topography

Adding lead to a galvanizing bath lowers the surface tension of the bath melt a small amount, since the surface tension of lead is less than that of zinc. The addition of lead
also changes the structure of the galvanized layer. The surface roughness may thus be related to the surface tension of the alloying addition to the bath. The surface roughness parameters are plotted against the surface tension of the alloying elements in Figures 4.30 (a) to (d).

The observed drop in the values of $R_a$ and $R_{max}$ between the surface tensions of bismuth and antimony are related to the influence of such additions on spangle size and morphology as previously discussed. The result that the average roughness parameter for tin and magnesium additions are higher than those of the characteristically large grain size (low surface tension) additions such as lead, bismuth, and antimony show that the coating texture is related to both the spangle morphology and size in some way. The galvanized coating thickness is not a strong function of the added solutes as shown in Figure 4.31; this observation is not unexpected.

### 5.4 Multiple Solute Addition to the Galvanizing Bath

The average of the minimum coating thickness for the normal experimental galvanizing conditions is about 36 $\mu$m, relatively independent of the solute additions to the bath (Figure 4.31). The variation in roughness of the surface with different alloying additions is therefore not due to differences in layer thickness.

The effect on surface roughness of adding lead to the bath can be assessed by comparing alloys 1 and 2 in Figure 4.32 (a). Adding 0.25 % Pb (alloy 2) to the galvanizing bath reduces the $R_a$ by about 32 % (from 2.2 $\mu$m to 1.5 $\mu$m). Removing the lead (alloy 5) and adding some aluminum increased the average roughness to 3.6 $\mu$m. Similarly, the addition of 0.27 % Al to 0.19 % Pb bath (alloy 6) also resulted in a higher value of the average roughness than for alloys 1 to 3. Without the cadmium (alloy 4) and lower tin levels, $R_a$ increases appreciably. Adding 2 % Pb or Sb to the bath (alloys 7 and 8) does
not significantly increase the value of $R_a$ above the levels shown for alloys 1 to 3. Adding 0.25 % Bi (with $R_a = 2.6$) to 0.25 % Sb (with $R_a = 1.6$) had the unexpected result of a low value of $R_a$ of 1.3. The $R_{\text{max}}$ values tends to follow the $R_a$ values for the nine alloys with considerable scatter in the data.

Tin by itself added to cadmium does not reduce the $\Delta_a$ (alloy 1). Adding lead to a Zn + 1 % Cd + 0.5 % Sn bath markedly reduced the average slope, $\Delta_a$, (alloys 1 to 3) Figure 4.33 (a). Alloys 6, 7, and 8 all contained lead and all had low values of $\Delta_a$. Alloy 4 also contain lead, but the average slope, $\Delta_a$, is higher than for alloys 6 to 8. This may be due to the presence of tin in the bath, producing a highly dendritic coating structure during solidification. It is not clear why this is so. Alloy 5 had $\Delta_a = 1.0$ whereas a 0.20 % Sn has $\Delta_a = 3.9$ (Figure 4.30 (c)), suggesting that the 0.15 % Al addition had markedly influenced the surface morphology which is unexpected. In alloy 9, $\Delta_a$ is about the same as for the cases when antimony and bismuth are the individual additions.

The $R_a$ and $R_{\text{max}}$ values for the cadmium primary addition (alloys 1, 2, and 3) all remained low even with the large additions of tin and lead as compared to the other baths (Figures 4.32 (a) and (b)). This suggest that the cadmium primary addition probably determines the overall surface topography of the galvanized sheet. This speculation is supported by the result shown for alloy 4 without cadmium and lower tin concentration than alloy 1 but with a much higher value of $R_a$. This same trend is noted for $R_{\text{max}}$ (Figure 4.33 (b)).

These observations may be due to the influence of the primary tin present in this alloy bath; producing a highly dendritic and small grain structure. There is no significant increase in the average roughness value for the high lead and antimony baths as shown in Figure 4.32 (a) for alloys 7 and 8. These results clearly indicate that there are certain minimum amount of element type and concentration that determines the overall surface texture of the galvanized sheet.
5.4.1 Shiny and Frosty Sectors

Comparing the surface roughness of the shiny and frosty sectors shows that the frosty sectors are rougher on a microscale level than adjacent shiny sectors. This is shown in Figures 4.34 (a) and (b) for $R_a$ and $R_{\text{max}}$, and in Figure 4.35 (a) for $\Delta_a$. The three roughness parameters are all higher in the frosty sector.

Comparative surface profile graphs in the frosty (Figure 4.37) and shiny (Figure 4.38) spangles show that the profile amplitudes are higher and closer together in the frosty regions as compared to the shiny regions. This gives a qualitative confirmation of the varying degrees of roughness in the two regions. The observed strong fluctuations in amplitude between 12.5 and 13.9 $\mu$m (Figure 4.37) and variations in wavelength in the 4 mm scan is associated with the rougher spangle morphology in these localized regions. The fluctuation in the shiny sector is much less at between 12.8 and 14.0 $\mu$m (Figure 4.38) as expected. The effect of different bath composition within these localized regions is to modify the extent of amplitude fluctuation and the wavelength within these regions.

5.5 Pulldown at Grain Boundaries

5.5.1 Surface Profile Scans Across Grain Boundaries

The present results clearly indicate that surface depressions and peaks occur in the vicinity of grain boundaries on the galvanized layer surface. Grain boundary depressions increase with increase in lead bath content. The depression depth is 8.2 $\mu$m for 0.22 % Pb as compared to 36.5 $\mu$m for 2.0 % Pb (Figures 4.52 to 4.54). With an average minimum coating thickness of 39.2 $\mu$m, the effective galvanized layer thickness would be reduced by about 20 % for 0.22 % Pb and about 93 % for 2.0 % Pb. Since the corrosion resistance of the galvanized layer is directly related to the coating thickness, the presence of large depressions seriously influences the corrosion resistance of the layer.
The depression observed at the grain boundary might be attributable to volume shrinkage, since the grain boundary is in the region where the last liquid solidifies. This can be examined by calculating the surface contour of two adjacent grains in the galvanized layer solidifying towards each other. As solidification progresses volume shrinkage associated with the solidification will result in the growing crystals becoming progressively thinner. The solidification volume shrinkage for zinc is 4.2%.

Assuming a planar solid-liquid interface, perpendicular to the steel sheet surface, theoretical volume shrinkage curves are calculated (Figure 4.76) using reported volume shrinkage parameters for zinc and other metals. The calculated curves (Figure 4.76) are directly superimposed on the profile graphs across specific boundaries (Figures 4.52 to 4.54) for a direct comparison between them. The comparative graphs are shown in Figures 4.77 to 4.79 for the 0.11 % Pb, 0.22 % Pb, and 2.0 % Pb baths respectively. These graphs indicate that volume shrinkage alone on solidification cannot account for the observed depressions at spangle boundaries.

These depressions could be associated with the change in the surface tension of the zinc resulting from the low surface tension alloy additions, since pulldown is primarily associated with large spangles. It is possible that towards the end of solidification the alloy additions concentrate at the liquid/air interface due to surface oxidation and absorption and influence the surface tension of the melt to a far greater extent than that anticipated on the basis of the amount of alloy added to the bath. It is not clear how the effect of the alloy additions could be demonstrated to change the surface tension leading to pulldown as described above.

The observation that grain boundary depression becomes more severe with increased lead concentration may be associated with a longer solidification time. This could occur if the increased lead concentration expands the local freezing range of the alloy within the interdendritic regions. The subsequent filling of solidification shrinkage void could
cause the spangle boundaries to be deeper and wider.

5.5.2 Three Dimensional Contour Surface Maps

The surface contours in the vicinity of grain boundaries are clearly delineated in the three dimensional maps shown in Figures 4.56 to 4.59. Depressions of the surface are clearly evident at the grain boundaries, and in some cases small peaks adjacent to the depressions. The depressions are smaller in pure zinc, as compared to alloy baths. Depressions and general surface contours can vary appreciably along a given grain boundary. The effect of increased lead concentration in the bath on grain boundary depression, is further demonstrated in the three dimensional maps.

The general surface contours, including the grain boundary depression are believed to be associated with the spangle size and morphology in the galvanized layer. Larger spangle sizes produce larger depressions. The presence of large depressions on the layer surface is of major concern in quality control, since the depressions are visible on painted surfaces, and cannot be removed by temper rolling.
5.6 Galvanized Layer Thickness and Segregation Studies

5.6.1 Redipped Steel Sheets

In the present experiments, commercially galvanized sheets were used as the starting material. This eliminated the necessity for deoxidizing and cleaning the steel sheet surface prior to galvanizing. It is therefore necessary to show that starting with galvanized sheet is equivalent to using clean steel sheets for examining the solidification of the galvanized layer.

When the galvanized starting sheet is dipped into the bath for ten seconds, it is shown that effectively all the initial galvanized layer remelts and moves away from the steel sheet to mix in the bath, without significantly affecting the bath composition. That this occurs is shown using a number of different techniques.

The liquid layer on the steel sheet when it is removed from the bath has the composition of the bath. Consider first the change in bath composition due to the remelting of the galvanized layer on the starting sheet, assuming complete mixing of the melt. The calculated volume of the galvanized material on the steel sheet prior to redipping is 0.39 cm³ weighing 2.78 g.

The composition of the coating material is zinc containing 0.20 % Pb and 0.15 % Al and the corresponding weights are 5.6 x 10⁻³ g for lead and 4.2 x 10⁻³ g for aluminum. Redipping the sheet in a small bath of 1,000 g, the concentrations of lead and aluminum in the bath would be increased by 5.6 x 10⁻⁴ % (5.6 ppm) and 4.2 x 10⁻⁴ % (4.2 ppm) respectively, which is negligible. A similar calculation for a larger galvanizing bath of 11,350 g and a larger steel sheet (7.62 x 20.32 cm) gives values of 1.96 x 10⁻⁴ % (1.96 ppm) and 1.47 x 10⁻⁴ % (1.47 ppm) for lead and aluminum respectively, which again is negligible.

The initial evidence that the galvanized layer on the starting sheets remelt is that
different galvanizing baths give markedly different macrostructures in the galvanized layer, starting with the same material. Further evidence comes from the radioactive tracer studies and microprobe scans across the galvanized layer. In both cases the tracer added to the melt, or the alloy added to the melt are detected within several microns of the steel sheet surface. This could only occur if the starting galvanizing layer remelted and moved away from the steel surface to within several microns of the steel surface.

5.6.2 Segregation Determined by Radioactive Tracer Technique

The autoradiographs in Figure 4.62 clearly indicate that Tl$^{204}$ is segregated on a microscale in the galvanizing layer; this is associated with the dendritic structure. Solute is depleted in the primary and secondary dendrite spikes and concentrated between the branches. This is consistent with the normal dendritic growth process in which the thin primary stalk grows rapidly into the liquid, solute being rejected laterally as defined approximately by the phase diagram. If the secondary branches are also spikes, then these will also act as primary branches and segregate solute laterally as they grow.

There is considerable variation in the distribution of Tl$^{204}$ within the frosty or shiny sector in the identified dendrite branches (A, B, C, D, and E), shown in Figure 4.62. Note that the bright and dark optical images shown in Figure 4.61 corresponds to the shiny and frosty sectors in a given dendrite. One can compare the dendrite branches B and C (Figure 4.62) with relatively uniform Tl$^{204}$ concentration in both sectors of the dendrites to A and D which show different concentrations.

Looking at the segregation of Tl$^{204}$ in the identified dendrite branches, spangle segments exhibit different amounts of segregation as evidenced by the different degree of darkening in an inconsistent way. This could result from two factors. In one case if the secondary dendrite branches grow along the melt/air surface there would be an apparent depletion of solute in this segment, since the branches are depleted. Alternatively, if the
secondary branches grow along the steel/melt interface there is upward non-dendritic growth to the air/melt interface resulting in a higher apparent solute concentration at the air/melt interface. With dendritic segments growing on inclined planes apparent concentrations could vary between the two cases of surface growth. In general, the shiny sectors tend to have a higher concentration of Tl\textsuperscript{204} than the frosty sectors.

There is no clear evidence that Tl\textsuperscript{204} is concentrated at the grain boundaries, or where adjacent spangles meet. This indicates that effectively all the segregation is on a microscale, between adjacent dendrite branches and that the bulk residual liquid does not increase in concentration as solidification progresses.

The observation that the added Tl\textsuperscript{204} is relatively more uniformly distributed in the solidified bulk sample (Figure 4.63) as compared to the galvanized coating (Figure 4.62) is attributed to the large and highly dendritic spangles formed during solidification of the galvanized coating.

5.6.3 Structure and Thickness of the Galvanized Coating

The galvanized coating consists of an alloy layer adjacent to the steel surface and a spangled zinc layer between the alloy layer and the air interface. The thickness of the alloy layer (Figure 4.66 (b)) depends on the presence of aluminum in the bath. If no aluminum is present the alloy layer is thick, as has been reported in the literature [20]-[24]. In the present results, the alloy layer thickness for both 0.2 % and 2.0 % Pb is the same with 0.15 % Al in the bath. Without aluminum, the alloy layer takes up approximately 37 % of the coating thickness as compared to about 4 % in the baths with aluminum.

In considering the nucleation site of the spangles, the above observations indicate that the nucleation sites are not related to the alloy layer. Since the spangle size is independent of alloy layer thickness, the nucleation sites are also independent of thickness. The alloy
layer structure appears to remain the same as the alloy layer thickens. Accordingly, if the nucleation sites are related to the alloy structure, the sites should be the same for thin and thick alloy layers.

The thickness of the alloy layer at the steel/zinc interface is reduced when aluminum is added to the bath [20]-[24]. The present results are in agreement with this as shown by comparing Figures 4.67 (a) and (b) with an aluminum free coating in Figures 4.67 (c) and (d). The result that both the as-received galvanized sheet and the redipped sheet have the same alloy layer thickness (2.0 µm) is clearly associated with the presence of aluminum in both baths. This could occur if all the original coating was redissolved and a new one formed; or alternatively the relatively pure outer zinc layer was dissolved during redipping, leaving the original alloy layer which did not grow during the redipping process.

The as-received steel sheets were produced commercially on a continuous galvanizing line at high strip velocities as compared to laboratory hand dipped samples. The observed increase in the coating thickness from 34 µm to 58 µm for the as-received and redipped sheets respectively, may be associated with the differences in the two dipping methods. The similarities between the total coating thickness shown in Figure 4.67 (b) and those of Figures 4.67 (c) and (d) despite the differences in the galvanizing bath composition is consistent with earlier reports that coating thickness is dependent on both the dipping time and temperature.

5.6.4 Solute Concentration Across the Galvanized Layer

As part of the evidence to demonstrate the dissolution and removal of the galvanized layer and the starting test samples, EMPA scans for antimony were made across the galvanized layer for a starting sheet, Figure 4.69 (a) and after dipping in an antimony rich bath Figure 4.69 (b). The antimony concentration varies extensively across the
galvanized layer in both the starting and dipped sheets. The scan on the dipped sheet shows antimony from the bath is present in the layer within 5 μm of the sheet surface, indicating the remelting and dispersal of the original galvanized coating.

Samples from a lead rich bath show large fluctuations in lead concentration, similar to antimony, as shown in Figure 4.71 (b). The maximum level shown is 0.45 %, appreciably lower than the 2 % concentration in the bath. This difference is attributed to the relative difficulty of measuring lead concentrations in the microprobe, the sensitivity being low since the La line is used for the measurements. The observation that lead concentrations of between 0.25 and 0.35 % are within 5 μm of the steel/coating interface agrees with the antimony results that the original coating on the sheets is replaced with the new bath when the sample is redipped.

The variation in concentration of both antimony and lead across the galvanized layer is attributed to the dendritic growth of the layer. The layers in both cases exhibited a highly dendritic, spangled surface. This would lead to low solute concentrations in the primary and secondary branches and irregular higher concentrations in the interdendritic regions. The small difference in the segregation pattern between antimony and lead is attributed to the small difference in the spangle morphology in the two cases.

5.6.5 Distribution of Solute in the Grain Boundary Region

Since the grain boundary region is the last to solidify, it will contain a higher concentration of solute rejected during solidification raising the concentration of the bulk residual liquid. The tracer experiments showed no increase in solute concentration in the grain boundary region.

Similar results were obtained from the SEM observations. X-ray maps for lead of two separate spangle boundaries shown in Figure 4.72 (b) show a relatively uniform distribution of lead in the boundary region. In addition, concentration scans A-A and
B-B across grain boundaries in Figure 4.72 (c) and Figure 4.73 (a) also showed no lead segregation (Figures 4.72 (d) and 4.73 (c) respectively). Accordingly, there is no significant segregation of lead in the boundary region, in agreement with the radioactive tracer results.

Considering segregation within individual spangles, the results show that there is no significant macrosegregation present. The lead X-ray maps for two grains, Figures 4.74 (b) and 4.75 (b) show no significant variation in the overall lead concentration across the grains, similar to that observed in the grain boundary region. Macrosegregation of lead is observed, as shown in the lead X-ray map in Figure 4.74 (d). This is associated with segregation of lead laterally from the growing primary and secondary dendrite branches, producing small areas rich in lead between the dendrite branches in the last liquid to solidify.

5.7 Spangle Size and Morphology During Galvanized Coating Solidification

The present observation that certain bath additions are necessary for the formation of spangles in the galvanizing layer is in agreement with previous reports [7,9]. The minimum lead addition of 0.03 % required for spangle formation reported by Kim and Patil [9] is also in agreement with the present results.

A mechanism proposed to account for spangle formation [7] is that the addition of lead to the bath lowers the overall surface tension of the bath resulting in some way in the formation of large spangles during solidification. This suggests that there should be a correlation between the surface tension of the melt addition, spangle formation, and spangle size.

The amount of alloying addition to the bath is small. If the change in the galvanizing bath surface tension is taken as a linear function of the zinc and alloying element surface
tensions, based on the relative mass of lead and zinc, the change of bath surface tension would be very small. With a surface tension of pure zinc of 760 ergs/cm and lead 473 ergs/cm, the combined surface tension by concentration on adding 0.2 %Pb would be 759.4 ergs/cm. There is no clear basis for evaluating the new surface tensions in this way, but it appears likely that the small alloy addition has a very small effect on the overall surface tension. As a result, to examine the effect of surface tension, the values of the alloy additions themselves are used, since it is not clear what role surface tension has in the solidification of the galvanized layer.

When the grain size in the galvanized layer for a series of 0.2 % alloy elements is plotted against the solute surface tension (Figure 5.1), it is evident that the grain size decreases with increasing surface tension. Both bismuth and antimony produce larger spangles than lead, for the same alloy addition, and both have smaller surface tensions.

It is possible that the bath additions might change the number of effective nucleating sites in the bath, increasing the number to give a fine grain size, or decreasing the number by chemical dissolution, to give large spangles as proposed in the literature [7]. On the basis of the present results, it is difficult to see how antimony and bismuth, and to a lesser extent, lead, would dissolve active nuclei to produce large grains whereas tin, cadmium, and magnesium would not.

In the multiple addition observations, the spangle size is determined by the specific addition of antimony, bismuth, or lead. Additional elements have no significant effect. Since pure zinc has a small grain size to start with, only the removal of active nucleating sites could be considered to account for the large spangle size. There is no evidence that this did occur.

From the present results it is clear that spangle formation is strongly related to dendritic growth, since dendrites form a very marked component of the spangle structure.
Accordingly, spangle formation and size could be related to the manner in which the dendrite growth occurs in the galvanized layer, particularly on the effect of solute additions on dendritic growth.

Zinc has a hexagonal close packed structure. Dendrites grow primarily in the basal plane (0001) in the \(<1\bar{1}00>\) directions and to a lesser extent in the [0001] direction \([35]\). When zinc is cast in a chill mold, the basal plane tends to be oriented parallel to the chill, near the chill face, and perpendicular to the chill away from the chill face \([38,39]\). There is no evidence that small alloy additions to zinc change the dendrite orientations, and therefore on the basis of an orientation argument of preferred growth, result in larger grains or spangles.

The thermal conditions associated with dendritic growth have been investigated extensively by observing dendritic growth in supercooled pure materials; both in transparent liquids and metals. The velocity approximately increases as \((\Delta T)^2\), where \(\Delta T\) is the thermal supercooling of the melt at the start of solidification. Velocities of 3 cm/s are observed in pure tin at supercoolings near 10°C \([54]\).

Based on the results of the temperature measurements, large thermal supercooling did not occur during coating solidification. Therefore, it is highly unlikely that the large thermal supercoolings reported by Kim and Patil \([9]\) and Cameron and Harvey \([7]\) control the rate of dendritic growth or the spangle size during galvanized coating solidification.

The large spangle size could be associated with a marked increase in dendrite velocity. If under given thermal conditions dendrite growth rates could be enhanced, then in a given period of time they would grow longer distances. If this controlled the grain size, then there would be a direct correlation between dendrite velocity and grain size. Accordingly, if small solute additions to a melt can change the dendrite growth velocity, then this might account for the formation of large spangles resulting from small alloy additions.

It is proposed that when the dendrite spikes form, the solute alloy addition in the
melt is rejected in large part into the melt since it has very limited solid solubility. This produces constitutional supercooling at the solid/liquid interface which is the reason that dendritic growth occurs. Solute rejected at the dendrite tip is primarily lateral to the dendrite growth direction. As a result, the highly concentrated solute along the side walls of the dendrite spike inhibit further growth. The dendrite tip sees a very thin layer of concentrated solute, closely related to the dendrite tip curvature. The thin layer of highly concentrated solute at the dendrite tip strongly influences the dendrite tip curvature by changing the surface tension of the solid/liquid interface. Solute with a lower surface tension will lower the surface tension at the dendrite tip which will reduce the radius of curvature and increase dendrite tip velocity. Experimental and theoretical analysis of dendrite growth clearly shows that decreasing the surface tension of the solid/liquid interface increases dendrite velocity.

The dendrite velocity is primarily related to the local thermal and solute conditions at the advancing dendrite tip. The tip can be approximately described as a paraboloid of revolution with a specified radius of curvature at the tip. In general, the tip radius decreases with increasing dendrite velocity. The solute environment ahead of a dendrite tip is complex. It depends on the segregation coefficient of the alloy addition, the tip curvature (and therefore the growth velocity), the diffusion of rejected solute into the melt, and fluid flow at the dendrite tip. These are mostly unknown factors.

The segregation coefficient for the alloy additions which produced large spangles are small antimony \((k=7.69 \times 10^{-4})\), bismuth \((k=1.02 \times 10^{-3})\) and lead \((k=2.2 \times 10^{-3})\). They are completely soluble in the melt at the levels added, but are hardly soluble in the solid. The other alloy additions tin \((k=1.09 \times 10^{-3})\), magnesium \((k=0.05)\), and cadmium \((k=0.60)\) which produced smaller or no spangles have low values of \(k\) for tin and higher values for magnesium and cadmium. Solute is clearly rejected ahead of the dendrite tips in all cases. The amount of solute present at the solid/liquid interface at the dendrite tip
could vary significantly (Table 5.1) between the alloy additions considered, and therefore the dendrite velocity could vary accordingly.

Considering the values of \( k \) shown in Table 5.1 it becomes readily apparent that highly concentrated solute could be present ahead of the growing zinc dendrites. This could affect the dendrite velocity.

The surface tension of the highly concentrated solute ahead of the dendrite tip could influence the curvature of the dendrite tip and thus the growth velocity of the dendrite. If the surface tension of the melt at the dendrite tip is low, the dendrite tip could have a small radius of curvature as sketched in Figure 5.2 (a). This dendrite would grow much faster than a dendrite with large radius of curvature as shown in Figure 5.2 (b). A large curvature could be associated with a high surface tension melt at the solid/liquid interface.

The present results show that large spangles are associated with solute element additions that have lower melt surface tensions. This could be accounted for if the lower surface tension of the solute reduces the tip curvature and increases the dendrite velocity. Observations have been reported and theories developed for dendritic growth, mostly in transparent materials, as a function of melt supercooling and solute additions. Typical surface tensions of various metals relevant to this study are listed in Table 5.2.

According to Nash and Glicksman [45] for a non-isothermal steady state dendritic growth, and for small undercoolings, the growth rate can be expressed as follows:

\[
V = 0.114 \left( \frac{\alpha_L \Delta S_f L}{\gamma_{SL} C_L} \right) \left( \frac{\Delta T C_L}{L} \right)^{2.65}
\]  

(5.1)

where

- \( V \) = Growth velocity

- \( \Delta T \) = Supercooling
Chapter 5. DISCUSSION

- $\Delta S_f$ = Entropy of fusion per unit volume
- $L$ = Latent heat of fusion
- $\gamma_{SL}$ = Surface tension
- $\alpha_L$ = Thermal diffusivity of the liquid
- $C_{PL}$ = Specific heat of the liquid

Equation 5.1 is based on the assumption that no side branching occurs during the dendritic growth. This assumption may raise questions as to the physical relevance of this equation to actual dendritic growth during coating solidification. It is believed that solutions to the steady state equations would furnish reasonable approximations to the average growth rate, and to the shape of the dendrite in the neighborhood of the tip. Any thermal interaction between the dendrite tip and the side branches up to about 7 times the radius of curvature at the tip would be small [45].

By substituting typical data for zinc ($\Delta T = 1$ to $2$ °C; $\Delta S_f = 1.74 \times 10^6$ J/m$^3$°C; $L = 1.02 \times 10^8$ J/kg; $\gamma_{SL} = 0.1$ to $1.0$ J/m$^2$; $\alpha_L = 1.7 \times 10^{-5}$ m$^2$/s; $C_{PL} = 498$ J/kg °C) into Equation 5.1, the dendrite tip velocity were calculated and a plot of the results versus surface tension is shown in Figures 5.3 (a) and (b). These figures show that as the surface tension is increased the velocity at the dendrite tip is decreased; resulting in smaller grain sizes. At lower surface tensions the dendrite tip velocity increases. The effect of increasing the amount of supercooling is to shift the velocity of growth to higher values (Figure 5.3 (b)) for a given interfacial energy. When this result is compared to the grain size observed on the coatings produced from baths containing lead, antimony and bismuth, there appears to be a possible relationship between the observed spangle size and the bath surface tensions. This result supports the contention that the mechanism of spangle growth is related to the effect of bath surface tension on dendrite growth velocity.
Since the primary factor leading to the growth of large spangles is the presence of a very thin, highly concentrated solute layer at the dendrite tip, with solute having a low surface tension, then only small amounts of solute are required in the melts. This also requires solute with very limited solid solubility in the melt. If these conditions are not met the spangle size will be small. All of these conditions are met by the alloy additions which produce large spangles, antimony, bismuth, and lead.

The growth of large spangles is clearly associated with the growth of long dendrite spikes, followed by secondary and tertiary spikes to complete solidification. The size of the spangles therefore is directly related to the growth of the primary dendrites which quickly establish the spangle diameter during galvanized coating solidification.

5.8 Formation of the Shiny and Frosty Spangle Sectors

On the basis of the present results, the entire spangle grows from one nucleus. Since the \{0001\} plate formed at the nucleus can be inclined at a large angle to the steel and air/melt surface, part of the plate intersects and grows along the steel/melt surface and part of the air/melt surface. The morphology of the spangle suggests growth is more complex.

There are six \{10\overline{1}0\} independent dendrite spikes growing in the basal plane from the nucleus, each of which have secondary branches inclined to the liquid surfaces. As a result each primary branch will have secondary branches. Some branches will be pointing toward the air surface and others to the steel surface.

The former will grow along the melt/air surface producing shiny segments. The latter grows along the steel/melt interface and produce frosty segments. The frosty appearance results from a relatively rough surface associated with shrinkage of the liquid as the dendritic branches thicken from the steel to the air/melt surfaces. The shiny segments
solidify from the air to the steel surface and therefore shrinkage will not affect the air surface topography. The observed shiny and frosty sectors in a typical spangle can therefore not be associated with crystallographic orientation differences between these sectors.

5.9 Spangle Orientation

Spangles generally exhibit alternate shiny and frosty segments. It is possible that the difference in appearance of the alternate segments might be due to an orientation difference between the adjacent segments. A consistent orientation difference was reported by Cameron et al. [6] between 2 and 12 degrees (Table 2.1), the frosty segment having a smaller angle $\theta$ than the shiny segments.

The present observations that the basal plane of the spangles is inclined to the galvanized sheet surface is in agreement with the previous reports of Cameron et al. [6] and Wall et al. [15]. The observations made by Jaffrey et al. [14] that only the mirror-like, feathery or dimpled topographies have their basal planes parallel to the surface of the sheet is not supported by this study.

The observation by Cameron et al. [6] that the frosty sectors are more nearly parallel to the plane of the sheet is not supported by this study. The present results show that the basal planes of the shiny/frosty spangle pairs can be inclined to the sheet surface at the same angle (samples 3 and 6, Table 4.4), as well as at different angles to the sheet surface (samples 5 and 7). To account for the orientation difference between the shiny and frosty spangle sectors, Cameron et al. [6] speculated that all of the sectors in a given spangle probably did not grow from the same nucleus. This appears highly unlikely.

Furthermore, since spangles clearly grow with a very strong dendritic structure, it follows that the spangle orientation, with respect to the steel surface, would be related to
the preferred dendrite growth direction in the basal plane. This is clearly not the case for the spangles examined in this investigation. The basal plane is oriented at large angles with respect to the steel sheet. With spangle sizes up to 15 mm diameter, and a layer thickness of less than 50 µm, dendritic growth cannot occur primarily in the basal plane of the galvanized layer.

The dendritic growth direction for zinc was determined in bulk pure liquid. In growth of dendrites in the galvanized layer we are considering growth in a very thin layer, equivalent to growth on a substrate, and in melts having a range of solute additions to the zinc. Accordingly, this raises the following questions.

1. Does dendritic growth in zinc (or other hexagonal systems) always grow in the basal plane in <1010> directions?

2. Is the dendrite growth rate different on a substrate as compared to the bulk growth?

3. Will the melt composition influence the dendrite orientation?

In response to question 1, concerning the dendrite growth direction, there is clear evidence in zinc and particularly in dendritically frozen water (which has a hexagonal structure) that dendrites often are bent and grow in the <1120> direction as well as <1010>. Examples are shown in Figures 5.4 (a) and (b), and 5.5 (a) and (b).

A typical frost ice dendrite growing on a glass plate photographed by Bentley [58] is reproduced in Figure 5.4 (a). Note the curly and fern like morphology of the dendrite structure. A sketch of an ice dendrite growing on a glass substrate reported by Lindenmeyer [59] is reproduced in Figure 5.4 (b). In addition to the curly dendrite morphology shown in Figure 5.4 (a), two other morphologies have been observed and photographed by Bentley [58]. These photographs are reproduced in Figures 5.5 (a) and (b). Figure 5.5 (a) shows the dendrite arms going off at an angle of approximately 60 degrees
to each other forming a herring-bone pattern. Similar results have been observed in this study, particularly in the large spangle coatings. Figure 5.5 (b) shows that the dendrite branches can be inclined at a different angle than 60 degrees; in this case the departure is approximately 90 degrees, giving a fir-tree structure. These figures clearly show that dendrite growth direction can vary appreciably depending on the growth conditions which are often complex.

There is clear evidence that dendrites grow appreciably faster on a substrate than in bulk liquid. This is shown in the results reported by Lindenmeyer et al. [55] for ice (a hexagonal material) growing dendritically from water. The growth rate is a function of the melt supercooling and substrate. At a supercooling of 3 °C the dendrite velocity increases from about 0.3 cm/s for free growth, to 1.2 cm/s for growth on a glass rod, and 3.0 cm/s for growth on a brass plate.

The addition of solute to the melt can have a marked effect on orientation of the growing dendrites. This is shown in the results of Lindenmeyer [59] on sodium chloride solutions in Figure 5.6. As the amount of sodium chloride increased in the solution, for a given liquid supercooling, the angle between the basal plane and growth direction increased. At 2 °C supercooling the orientation between the basal plane and growth direction increased from 1 ° for 0.001M solution to 24 ° for 0.4M solution. Similar results are obtained [59] for sugar solutions, as shown in Figure 5.7. Since the dendrite velocity increases with melt supercooling, the orientation of the basal plane changes at lower dendrite velocities with increasing solute content.

In the present investigation in pure zinc the basal plane formed a large angle (40 °) with the sheet surface (which is effectively parallel to the growth direction). It may be that there is sufficient impurity in the zinc used to effectively provide enough solute to cause the dendrite directions to deviate from the basal plane. It is also noted that dendrite growth is confined to a thin liquid layer which will define the growth direction,
starting from a single nucleus.

The present results suggest that a spangle starts from a single nucleus with the basal plane inclined to the plate surface. As the individual dendrite arms fan out from the nucleus, and grow side branches forming shiny and frosty segments, the individual branches can change their orientation depending on local thermal and solute conditions. As a result all of the segments in a spangle do not have the same basal plane orientation with respect to the plate surface.
Table 5.1: Estimated Segregation Coefficient and Interface Composition in Alloy Systems Investigated

<table>
<thead>
<tr>
<th>Alloy System</th>
<th>Estimated K</th>
<th>Interface Composition (C₀/K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn-Al</td>
<td>0.20</td>
<td>1</td>
</tr>
<tr>
<td>Zn-Pb</td>
<td>0.0022</td>
<td>90.91</td>
</tr>
<tr>
<td>Zn-Sb</td>
<td>0.000798</td>
<td>250</td>
</tr>
<tr>
<td>Zn-Bi</td>
<td>0.00102</td>
<td>200</td>
</tr>
<tr>
<td>Zn-Cd</td>
<td>0.6</td>
<td>0.33</td>
</tr>
<tr>
<td>Zn-Sn</td>
<td>0.00109</td>
<td>200</td>
</tr>
<tr>
<td>Zn-Mg</td>
<td>0.05</td>
<td>4</td>
</tr>
</tbody>
</table>

Table 5.2: Surface Tension of Elements Commonly Added to Zinc Bath

<table>
<thead>
<tr>
<th>Element</th>
<th>Surface Tension (dynes/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>860</td>
</tr>
<tr>
<td>Zn</td>
<td>760</td>
</tr>
<tr>
<td>Cd</td>
<td>590</td>
</tr>
<tr>
<td>Mg</td>
<td>583</td>
</tr>
<tr>
<td>Sn</td>
<td>566</td>
</tr>
<tr>
<td>Pb</td>
<td>470</td>
</tr>
<tr>
<td>Sb</td>
<td>395</td>
</tr>
<tr>
<td>Bi</td>
<td>375</td>
</tr>
</tbody>
</table>
Figure 5.1: Grain size versus the surface tension of melt addition.
(a) Low surface tension solute melt.

(b) High surface tension solute melt.

Figure 5.2: Effect of melt surface tension on dendrite tip geometry.
Figure 5.3: Calculated dendrite tip velocity versus melt surface tension.

(a) Supercooling of 1°C.

(b) Supercooling of 2°C.
(b) Sketch of ice dendrite growing on a glass substrate [58].
Magnification 1.5X

(b) Sketch of ice dendrite growing on a glass substrate.

Figure 5.4: Random growth of dendrites on a glass substrate.
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(a) Dendrite branches growing at approximately 60 degrees to each other [58].

(b) Dendrite branches growing at approximately 90 degrees to each other [58].

Figure 5.5: Morphology of frost ice dendrites growing on glass substrate.
Magnification 1.5X
Figure 5.6: Angle between the growth direction and the basal plane as a function of the supercooling of various sodium chloride solutions.
Reference [59]
Figure 5.7: Angle between the growth direction and the basal plane as a function of the supercooling of various sugar solutions.
Reference [59]
Chapter 6

SUMMARY AND CONCLUSIONS

6.1 Mechanism of Spangle Formation

On the basis of the experimental observations spangle nucleation and growth during galvanized coating solidification occurs as described below.

1. The molten zinc layer on the steel sheet is less than 50 μm thick. The temperature gradient in this thin layer of liquid is very small, sufficiently so to consider the liquid to be at a uniform temperature.

2. As the liquid cools, heterogeneous nucleation occurs at temperatures just below the liquidus (within 1 °C). Nucleation does not occur preferentially at the steel/zinc or zinc/air interface. The nuclei grow as small plates with the basal plane in the plane of the plate, oriented at random with respect to the plane of the steel sheet.

3. If lead, antimony, or bismuth are in the melt, these are rejected at the edge of the plate resulting in the formation of relatively sharp dendrite spikes growing in the <1010> directions in the basal plane. The spikes reach the melt surface very quickly either at the steel/melt or air/melt interface. In either case the spike will continue growing along the interface at a high velocity in a direction along the surface parallel to the projection of <1010> on the surface.

4. Since there are six equivalent directions (<1010>) in the basal plane, six primary dendrites can grow from the initial nucleus producing a spangle of six fold symmetry.
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However, depending on the orientation of the nucleus and the local temperature and solute conditions during growth, all six dendrites will not grow at equal rates, producing spangles with less than six fold symmetry.

5. The large spangles produced when lead, antimony, or bismuth are added to the melt are a result of the increase in dendrite velocity of the primary spikes. These additions have very low solubility in zinc. As a result when growth occurs the additions are strongly rejected at the growing interface. The high concentration of the addition at the interface, changes the dendrite tip curvature as a result of the low surface tension of the alloying element. The dendrite tip radius is decreased, resulting in an increase in dendrite velocity. When the dendrite reaches the melt surface, there is a further increase in dendrite velocity enabling the dendrite branch to grow rapidly over large distances.

6. The large spangles result from the very rapid growth of the primary \( <10\bar{1}0> \) spikes. These establish the overall size of the spangle. The space between the primary spikes is filled in by secondary spikes at a slower rate. The process continues as the spikes thicken, with the possible addition of tertiary spikes until the liquid has solidified.

7. This large spangle diameter is a direct result of the high dendrite velocity. It is likely that the supercooling required to activate the heterogeneous nuclei, even though small, is not a unique value, but occurs over a small range of temperatures. As the liquid cools the heterogeneous nuclei requiring the least supercooling will become operative. If dendritic growth is slow, the liquid between the growing grains continues to cool activating more nuclei. This then produces a relatively small grain size. Growth is still dendritic. If dendritic growth is rapid, the dendrite spikes cover a much larger region of the melt before more nuclei are activated. Once
a spike grows into a region the latent heat evolved will raise the local temperature of the melt reducing any local supercooling present and stopping the growth of new grains.

8. If a large number of nucleating sites are artificially introduced in the melt (as in the Heurtey process when zinc powder is blown into the melt) these are effective in reducing spangle size. In this case we have a large number of nuclei which can grow with effectively no supercooling. As a result a large number of nuclei are equally favoured for growth, producing a fine grain size, even with high dendrite velocities.

9. Large depressions (pulldown) are observed at the spangle boundaries. The depressions cannot be accounted for by volume shrinkage during solidification. No mechanism to account for the pulldown is evident. The depressions could be related to the surface tension of the melt. The higher solute concentrations in the last liquid to solidify could influence the melt/air surface tension at the boundary.

10. The surface roughness of the spangle is directly related to the dendritic growth. As the liquid between the dendrites solidifies shrinkage occurs. The periodic hills and valleys observed when the surface roughness is measured is associated with the dendrite spikes and volume shrinkage that occurs when the interdendritic regions solidify. Since the dendrite growth morphology can be complex, the surface roughness pattern can be correspondingly complex as is observed.

11. Solute segregation occurs in the spangles. Solute depletion occurs in the dendrite branches, consistent with with the phase diagram, the dendrite branch being the first to solidify. The solute is concentrated between the dendrite branches, in the last liquid to solidify as expected. No significant concentration above the general
Chapter 6. SUMMARY AND CONCLUSIONS

microsegregation occurs at the spangle boundaries, since nearly all of the segregation occurs interdendritically.

6.2 Conclusions

1. The present measurements indicate that the supercooling necessary to activate the nucleating sites in pure zinc and typical galvanizing baths is less than 1 °C. Changing the cooling rate by a small amount does not significantly influence grain size or spangle formation.

2. Since a thermal supercooling of less than 1°C was observed in the galvanized layer, nucleation could occur in the melt without the presence of more active nucleating sites at the steel or air surfaces. The results indicate that nucleation occurs in the body of the liquid of the galvanizing layer. Accordingly, mechanisms which attempt to account for the growth of dendritic spangles based on thermal supercooling cannot be justified.

3. Adding more nuclei in the form of solid zinc particles, as in the Heurtey process, would increase the number of nucleating sites and therefore decrease the grain size, as is observed. If a suitable nucleant could be added to the galvanizing bath such as TiB$_2$ in aluminum, this could reduce grain size. The particle density would have to be large, as is the case with TiB$_2$. There is no report in the literature that such nucleating agents have been found for zinc. In blowing the solid zinc particles on the galvanized layer, the liquid metal is cooled. It is unlikely that the cooling associated with the blowing decreases the grain size.

4. The spangle orientation results clearly show that the spangles are not parallel to the sheet surface but are inclined to the steel sheet at angles between 8 and 80
degrees. The shiny and frosty segments in a given spangle in some samples have the same inclination to the steel sheet; in other samples they have markedly different inclinations.

5. The growth of large spangles is clearly associated with the growth of long dendrite spikes, followed by secondary and tertiary spikes to complete solidification. The size of the spangles therefore is directly related to growth of the primary dendrites which quickly establish the spangle diameter.

6. The addition of elements lead, antimony, and bismuth at a concentration greater than 0.04 % to the galvanizing bath, resulted in the formation of large and highly dendritic spangles. The appearance of the spangles, shiny or frosty, varies a little with different solute additions at the same concentrations. A minimum solute addition is thus required to produce any significant grain growth, and after a limiting concentration is reached, further solute additions have relatively little effect on the grain size and spangle formation.

7. Additions of elements tin, cadmium, and magnesium produce relatively small grain sizes, similar to that obtained in a pure zinc coated steel sheet. These observations clearly show that different solute elements added to the galvanizing bath have markedly different effects on the nucleation and growth kinetics of the grains during the solidification of galvanized coatings.

8. Large spangles are obtained with alloy additions which have very limited solid solubility in zinc and which have low melt/vacuum interface surface tensions. Alloying additions do not remove nucleating sites, leading to larger grains, as reported in the literature. Spangle diameters decrease with increasing surface tension of the alloying element, other factors being kept constant. The amount of alloy addition
required to produce spangles is less than 0.1 %.

9. The manner in which some alloy additions produce large spangles is attributed to the alloy changing the dendritic growth conditions. The primary dendrite branches in spangles are long and thin, indicating that they grow at high rates. The growth rate, in the absence of thermal supercooling, could be controlled by constitutional supercooling at the dendrite tip. Higher dendritic growth rates are associated with smaller dendrite tip radii.

10. The primary factor leading to the growth of large spangles is the presence of a very thin, highly concentrated, and low surface tension solute layer at the dendrite tip. All of these conditions are met by the alloy additions which produce large spangles (antimony, bismuth, and lead).

11. The thickness of the galvanized alloy layer is reduced when aluminum is present in the galvanizing bath. Solute segregation in the galvanized layer is directly associated with the dendritic growth of the spangles during coating solidification. There is no indication of solute concentrations at grain boundaries which would result from interdendritic enriched solute being moved into the bulk liquid. Accordingly, the galvanizing melt exhibits microsegregation only.

12. The general surface topography of the galvanized sheets is related to the dendritic growth, and volume shrinkage that occurs as the interdendritic liquid solidifies. As long as strong dendritic growth occurs, and the metal shrinks as the liquid/solid transition occurs, then a relatively rough surface would be formed.

13. Large spangles are obtained by adding small amounts of alloys to the melts. The alloys are required to have low solid solubility in zinc, complete solubility in the
melt, and have a value of surface tension appreciably less than that of zinc. If these conditions are not met the spangle size will be small.

14. Small temperature changes as the liquid layer cools will have little effect on spangle size. Large temperature changes, such as quenching the galvanized layer in water, will eliminate spangle growth. However, quenching will generally cause the steel sheet to buckle, making quenching unsuitable for producing spangle free sheet.
BIBLIOGRAPHY


Appendix A

Justification for Negligible Internal Resistance to Heat Flow

A.1 Introduction

It has been shown in standard heat transfer text books [60] - [63] that if the Biot Modulus (the ratio of conductive to convective resistance to heat flow) is less than 0.1, the error involved in assuming negligible thermal gradients within a body during heating or cooling would not be greater than about 5%.

The Biot Modulus is defined as:

\[ Bi = \frac{hL}{K_s} \]  

where

\( h \) = convective heat transfer coefficient
\( L \) = a characteristic length (volume of the body divided by the surface area)
\( K_s \) = thermal conductivity of the solid

In heat transfer processes involving convection it is important to accurately determine the convective heat transfer coefficient, \( h \), that would be applicable under the given set of conditions. Standard techniques are either to obtain the heat transfer
coefficient from existing empirical correlation or to carry out specific experiments for their determination.

According to Pitts and Sissom [62] for forced convection turbulent flow of a liquid metal over a plate the following empirical correlation could be used:

\[
\text{Nu}_x = \frac{h x}{k_f} = 0.530 \sqrt{\text{Re}_x \text{Pr}}
\]  \hspace{1cm} \text{(A.2)}

According to Chapman [61] for laminar flow of air over a flat plate the following empirical correlation could be used:

\[
\text{Nu}_x = \frac{h x}{k_f} = 0.332 \text{Re}^{0.5}_x \text{Pr}^{0.33}
\]  \hspace{1cm} \text{(A.3)}

\[
\begin{cases}
    0.6 \leq \text{Pr} \leq 50 \\
    \text{Re} < \text{Re}_{x,c} \approx 5 \times 10^5 \\
    \text{properties at } t_m
\end{cases}
\]

In Equations A.2 and A.3:

- \( \text{Nu}_x \) = Nusselt number
- \( \text{Re}_x \) = Reynolds number
- \( k_f \) = Thermal conductivity of the fluid
- \( x \) = Local distance
- \( \text{Pr} \) = Prandtl number

According to Kreith [63] the average value of the heat transfer coefficient for laminar free convection during the cooling of a vertical plate is given by the following empirical correlation.
In the above equation:

\[
\text{Nu}_L = \frac{h_c L}{K_f} = 0.555 (G\!r_L \text{ Pr})^{0.25}
\]  \hspace{1cm} (A.4)

where the Grashof number is given as:

\[
G\!r_L = \frac{g L^3 \beta (T_s - T_f)}{\nu^2}
\]  \hspace{1cm} (A.5)

The convective heat transfer coefficient, \( h \), during the cooling of the steel sheet within the zinc bath is calculated from Equation A.2 [62]; and on exit from the bath, the convective heat transfer coefficient is calculated from Equation A.3 [61]. However, in the laboratory dipping experiments the convective heat transfer coefficient is calculated from Equation A.4 as suggested by Kreith [63].
A.2 Calculating the Reynolds Number

Typical continuous galvanizing lines operate at a strip velocity of between 0.51 to 2.54 m/s (100 ft/min to 500 ft/min). The majority of steel sheets commonly galvanized have thicknesses between 0.4 mm to 1.0 mm. The Reynolds number at given velocities is calculated from the following expression:

\[ Re_z = \frac{ux}{\nu} \]  

(A.6)

where

\[ x \] = Characteristic length
\[ u \] = Velocity
\[ \nu \] = Kinematic viscosity

The physical properties of molten zinc and air is obtained at the mean temperature (average of the sum of the initial steel temperature \( T_s \), and the molten zinc or air temperature \( T_f \)).

Reynolds number is calculated from the following data for the two velocities 0.51 and 2.54 m/s.

A.2.1 Steel Sheet Within The Zinc Bath

Data:
Appendix A. Justification for Negligible Internal Resistance to Heat Flow

\[ T_s = 458^\circ C \text{ (initial steel temperature)} \]
\[ T_f = 450^\circ C \text{ (zinc bath temperature)} \]
\[ T_m = 454^\circ C \text{ (mean temperature)} \]
\[ x = 3m \]
\[ \nu = 4.65 \times 10^{-7} m^2/s \]

By substituting the above data into Equation A.6 for the two velocities the Reynolds number is obtained.

For \( u = 0.51 m/s \) \( \text{Re}_x = 3.29 \times 10^6 \)

For \( u = 2.54 m/s \) \( \text{Re}_x = 1.64 \times 10^7 \)

Both values indicate turbulent flow.

A.2.2 During the Air Cooling of the Steel Sheet

Data:

\[ T_s = 450^\circ C \text{ (initial steel temperature)} \]
\[ T_f = 25^\circ C \text{ (fluid (air) temperature)} \]
\[ T_m = 237.5^\circ C \text{ (mean temperature)} \]
\[ L = 0.203m \]
\[ \nu = 3.933 \times 10^{-5} m^2/s \]
\[ K_f = 4.02 \times 10^{-2} W/m^\circ C \]
\[ \text{Pr} = 0.698 \]

The above data is substituted into Equation A.6 to obtain the Reynolds number during continuous cooling.
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For $u = 0.51 \text{m/s}$ $Re_x = 3.89 \times 10^4$

For $u = 2.54 \text{m/s}$ $Re_x = 1.94 \times 10^5$

Both values indicate laminar flow.

A.3 Calculating $h$ Values from Empirical Correlations

Considering the flow of zinc melt over the steel sheet surface the heat transfer coefficient is calculated from Equation A.2 for the two Reynold numbers previously calculated using the data below.

Data:

\[
Pr = 0.027
\]

\[
k_f = 58.3 \text{W/m°C}
\]

For $Re_x = 3.29 \times 10^6$ $Nu_x = 157.9$ $h = 3068.5 \frac{\text{W}}{\text{m}^2 \text{°C}}$

For $Re_x = 1.64 \times 10^7$ $Nu_x = 352.7$ $h = 6853.7 \frac{\text{W}}{\text{m}^2 \text{°C}}$

A similar calculation for the flow of air over the steel sheet surface using Equation A.3 for the two Reynold numbers previously calculated is given below.

Data:

\[
Pr = 0.698
\]

\[
k_f = 4.02 \times 10^{-2} \text{W/m°C}
\]

For $Re_x = 3.89 \times 10^4$ $Nu_x = 57.95$ $h = 0.78 \frac{\text{W}}{\text{m}^2 \text{°C}}$

For $Re_x = 1.94 \times 10^5$ $Nu_x = 129.3$ $h = 1.73 \frac{\text{W}}{\text{m}^2 \text{°C}}$
A.4 Calculating the Biot Modulus

The data below is substituted into Equation A.1 and the Biot Modulus calculated. The two thicknesses considered are 0.4 mm and 1 mm. The validity of the negligible internal resistance to heat flow is checked for the two cooling conditions (within the zinc bath and in air) during continuous hot dip galvanizing.

Data:

For a plate $L = \frac{Thickness}{2}$

<table>
<thead>
<tr>
<th>Strip thickness</th>
<th>$L$</th>
<th>$\frac{Thickness}{2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.4 mm</td>
<td>L</td>
<td>0.2 mm</td>
</tr>
<tr>
<td>1 mm</td>
<td>L</td>
<td>0.5 mm</td>
</tr>
</tbody>
</table>

$k_s = 36.5\text{W/m}^\circ\text{C}$

A.4.1 Cooling in the zinc bath

For $L = 0.0002$ m:

For $h = 3068.5 \frac{\text{W}}{\text{m}^2\circ\text{C}}$ $Bi = 0.017$

For $h = 6853.7 \frac{\text{W}}{\text{m}^2\circ\text{C}}$ $Bi = 0.038$

For $L = 0.0005$ m:

For $h = 3068.5 \frac{\text{W}}{\text{m}^2\circ\text{C}}$ $Bi = 0.042$

For $h = 6853.7 \frac{\text{W}}{\text{m}^2\circ\text{C}}$ $Bi = 0.094$

A.4.2 Cooling in air

For $L = 0.0002$ m:
Appendix A. Justification for Negligible Internal Resistance to Heat Flow

For \( h = 0.78 \frac{W}{m^2°C} \) \( Bi = 4.25 \times 10^{-6} \)

For \( h = 1.73 \frac{W}{m^2°C} \) \( Bi = 9.49 \times 10^{-6} \)

For \( L = 0.0005 \) m:

For \( h = 0.78 \frac{W}{m^2°C} \) \( Bi = 1.06 \times 10^{-5} \)

For \( h = 1.73 \frac{W}{m^2°C} \) \( Bi = 2.37 \times 10^{-5} \)

The above calculations have shown that the assumption of negligible internal resistance to heat flow for strip thickness up to 1 mm during the continuous hot dip galvanizing process is valid for the cases considered in this investigation.

A.5 Cooling of Laboratory Dipped Steel Sheets in Air

During the laboratory dipping experiments the steel sheet loses heat by natural convection and radiation. These two modes of heat transfer are considered in this analysis.

A.5.1 Calculating the Grashof Number

As noted previously the Grashof number is:

\[
Gr_L = \frac{g L^3 \beta (T_s - T_f)}{\nu^2}
\]

\[
\{ 10 < Gr_L \Pr < 10^9 \}
\]

Data:
Appendix A. Justification for Negligible Internal Resistance to Heat Flow

\[ T_s = 450^\circ C \text{ (initial steel temperature)} \]
\[ T_f = 25^\circ C \text{ (fluid (air) temperature)} \]
\[ T_m = 237.5^\circ C \text{ (mean temperature)} \]
\[ L = 0.203m \]
\[ \nu = 3.933 \times 10^{-5} m^2/s \]
\[ \beta = 3.355 \times 10^{-3} \]

The above data is substituted into Equation A.7 to obtain the Grashof number:

\[ Gr_L = 7.558 \times 10^7 \]

Since the Grashof number is less than $10^9$ the flow is laminar.

A.5.2 Calculating the Biot Modulus

Substituting the above data into Equation A.4 the Nusselt number and the convective heat transfer coefficient is obtained.

\[ Nu_L = 51.75 \quad h_c = 10.25 \frac{W}{m^2 \circ C} \]

Considering Radiative Cooling:

According to Chapman [64] the radiative heat transfer coefficient, \( h_r \), can be expressed as:

\[ h_r = \sigma \varepsilon (T_s^2 + T_f^2)(T_s + T_f) \quad (A.8) \]

where
Appendix A. Justification for Negligible Internal Resistance to Heat Flow

\[ \sigma = 5.64 \times 10^{-8} \frac{W}{m^2 K^4} \]

\[ \varepsilon = 0.15 \]

\[ T_s = 723 \text{ K} \]

\[ T_f = 298 \text{ K} \]

The above data is substituted into Equation A.8 to obtain the radiative heat transfer coefficient.

\[ h_r = 5.31 \frac{W}{m^2 \circ C} \]

The combined heat transfer coefficient during air cooling of the experimental sheets is:

\[ h_{comb} = 15.56 \frac{W}{m^2 \circ C} \]

The combined heat transfer coefficient is substituted into Equation A.1 to obtain the Biot number.

The Biot Modulus:

For \( L = 0.0002 \text{ m} \):

\[ Bi = 8.53 \times 10^{-5} \]

For \( L = 0.0005 \text{ m} \):

\[ Bi = 2.13 \times 10^{-4} \]

The above calculations have shown that the assumption of negligible internal resistance to heat flow during the cooling of the laboratory dipped steel sheets is valid for the cases considered in this investigation.