A study of resistance spot weldability of metallic coated steels and PVD coated electrodes

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A STUDY OF RESISTANCE SPOT WELDABILITY

OF METALLIC COATED STEELS

AND PVD COATED ELECTRODES

A thesis submitted in fulfilment of

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ABSTRACT

The resistance spot weldability characteristics of three commercially available electrode compositions, Cu/Cr, Cu/Cr/Zr, and Cu/Zr have been investigated when welding three metallic coated sheet steels: aluminium 45% zinc, galvanised and galvanneal steels. Electrodes were evaluated using weldability lobes and electrode life tests. The aggressive nature of the erosion process encountered for Al-45%Zn and galvanised steels masks the influence of small additions of alloying elements such as Zr on electrode life. However, for galvanneal steel where the erosion process is more gradual, the Cu/Cr/Zr electrode proved to be the most effective in obtaining maximum life.

The development and composition of alloy layers which form on the tips of each electrode used to weld galvanneal steel have been identified from the outside as: a surface oxide sublayer (ZnO), a porous Fe-Zn sublayer (Γ phase: Fe₃Zn₁₀), a hard and brittle gamma (γ) brass (Cu₅Zn₈) sublayer, and a ductile beta (β) brass (CuZn) sublayer, and then the Cu/Cr substrate.

The feasibility of depositing a surface coating onto Cu/Cr electrodes to mitigate the formation of alloy layers and thus extend electrode life was also investigated. Physical vapour deposition of Cr using unbalanced magnetron sputtering and filtered arc evaporation extended the life of Cu/Cr electrodes by 100% from approximately 420 to 840 welds when welding Al-45%Zn sheet steel.

Although extension of electrode tip life was achieved it has been established that the life determining failure mechanism of coated electrodes is by gross plastic deformation of the electrode tip due to the extreme temperatures and repeated compressive forces generated during the welding operation. It is therefore proposed that future work should aim to improve the mechanical properties of the electrode material in order to provide a strong base capable of supporting a thin liquid metal resistant coating. This is essential to take full advantage of the benefits that thin film coatings have to offer.
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CHAPTER 1

INTRODUCTION
**Introduction**

Resistance Spot Welding is a process where joining of sheet steel occurs by the passage of a high current through the workpieces to be joined, via a pair of clamping electrodes. This results in a weld nugget at the point of highest resistance to the passage of current, ie. the sheet to sheet interface or 'faying surface'. Electrodes must possess high electrical conductivity to minimise electrode heating, and high thermal conductivity to dissipate heat from the contact area between the electrode tip and the workpiece. Electrodes should also exhibit high hot strength to resist deformation caused by the application of high welding force. In addition, to maximise electrode life limited or no alloying reaction should occur between electrode and sheet metal. Resistance spot welding electrodes are exposed to high temperatures and compressive stresses during welding, which soften the electrode and can lead to rapid deterioration.

The significant increase in the usage of metallic coated steels has raised new concerns over electrode deterioration. The increased welding currents and times required to weld metallic coated steels over those employed on uncoated steels provide the driving force for the metallic coating to alloy with the copper electrodes [1]. This alloying frequently causes non uniform pitting of the electrode face as well as electrode edge alloy build up. Generally, the shape, dimensions and surface condition of the electrode tips deteriorate when welding these steels. Current density and distribution during welding are greatly affected by such variations in electrode condition which affects nugget development. The tip life of electrodes used to weld metallic coated steels may be as low as 250 welds [2] depending on the coating composition, while electrodes used for welding uncoated steels may exhibit a life in excess of 50,000 welds [3].

It is therefore, not surprising that a considerable amount of research has been devoted to the problem of accelerated electrode wear caused by metallic coated steels. However, almost all of the effort has been aimed at optimising the welding operation modifying
electrode geometry \([4-6]\), electrode current \([7-9]\), electrode force \([10-11]\), sheet thickness \([12]\), coating thickness \([1, 5, 7, 13]\), coating composition \([6, 14, 15]\) and electrode composition \([8, 13, 16, 17]\). The alloying reactions that take place between the electrode and the metallic coating are the primary cause for accelerated electrode wear, yet very little effort has been devoted to the analysis of this interaction and the development of means to control it. An understanding of these mechanisms is considered to be essential and indeed a pre-requisite for devising a satisfactory solution to mitigate the extent of detrimental alloy layer formation.

In an effort to combat the rapid deterioration of electrode tips, numerous new electrode materials have emerged to weld metallic coated steels \([8, 13, 16, 17]\). Each material has characteristic properties which will affect the performance of the electrode. However, information regarding the specific alloy compositions and the electrode manufacturing route are not often specified, and there is significant variation amongst different electrode manufacturers. Published reports of electrode performance are highly contradictory and no clear cost advantage has been demonstrated by using alternative electrode compositions \([16, 18, 19]\). A more detailed review of spot welding and the effect of operating parameters on both weldability lobes and electrode life test results and electrode degradation are provided in Chapter 2.

The alloying process is initiated at the interface between the electrode and workpiece and therefore a surface engineering solution to the problem is a logical alternative. The deposition of a thin film coating onto the working face of an electrode may provide a solution by acting as a barrier to coating/electrode interdiffusion and thus retard alloy formation. However, to act effectively any coating must satisfy a stringent set of criteria.

It is important to consider the coating method to be used in conjunction with the coating material because the coating structure and properties will be highly dependant on the
deposition parameters. Physical vapour deposition (PVD) appears to be the most promising coating technology capable of depositing a wide range of material with the desired properties for electrodes. These may include, *inter alia*, refractory metals, and intermetallic compounds such as nitrides in single or multi-component form. A distinct feature of all PVD coatings is the high adhesion which is only achievable with thorough sample preparation and careful monitoring of deposition parameters. The coating must be contamination free, have a uniform structure and adhere well to the electrode if it is to endure the rigours of the welding operation. Finally, the cost and ease of deposition must be realistic if the process is to be transferred to an industrial environment. Chapter 3 describes the physical vapour deposition techniques of sputtering and evaporation. The effect of coating parameters, equipment, material preparation and coating structure are discussed.

The requirements of an electrode are varied and many and any candidate coating material must demonstrate, *in toto*, superior properties. Electrical conductivity must be high enough to avoid excessive resistance heating which will decrease the efficiency of the operation and the elevated temperatures may accelerate coating degradation. For similar reasons the coating should be heat conductive, to transfer heat away from the workpiece. The coating must be strongly bonded to the electrode and remain continuous during the welding process. The mechanical properties of the coating are also important as it must withstand the compressive forces experienced during welding and the subsequent deformation of the base electrode. Thermal and mechanical shock will also be experienced. The mechanical performance of the coating will be strongly affected by the nature of any residual stresses. A successful coating must not react with zinc or aluminium at elevated temperatures. This will depend on the temperature, diffusivity, and concentration of alloying elements. The coating must also be pore free otherwise liquid metal will penetrate through to the coating. A study on the resistance of metallic materials to molten zinc showed that the only resistant elements were tungsten, boron and silicon with molybdenum and chromium showing moderate
A number of refractory alloys (Mo-Ta, Mo-W) and metal borides (Fe-B, Mn-B) also proved highly resistant to zinc degradation. The materials most resistant to molten zinc tend to be hard and brittle which contradicts the mechanical requirements of the coating which indicates a compromise may have to be made between chemical resistance and the mechanical and electrical properties to achieve an optimum coating. It can be appreciated that selection of a candidate coating material is a formidable task. In this work, refractory coatings of Cr, Mo and Nb were considered with emphasis on Cr as the major coating.

The experimental procedure, more specifically the details of weldability lobe construction, electrode life tests and coating techniques are presented in Chapter 4. The results presented in Chapter 5 contain weldability lobes for Cu/Cr, Cu/Cr/Zr and Cu/Zr electrodes used to spot weld Al-45%Zn, galvanised and galvannealed coated steels, with the electrode life test results for the above combinations. The alloy layers which form on the electrode tips on electrodes used to weld galvanneal steel have been examined using SEM analysis, microhardness and x-ray diffraction. The effect of thin film coatings deposited onto Cu/Cr electrodes by PVD techniques on, weldability lobes, and electrode life are also covered. The mechanism of electrode failure has been documented. Possible explanations for the observed behaviour of both uncoated and coated electrodes are presented in the discussion, in Chapter 6. Recommendations have been made in light of the results obtained and identified possible areas for future work.
CHAPTER 2

RESISTANCE SPOT WELDABILITY OF METALLIC COATED STEELS
2.1 INTRODUCTION

For industries using large volumes of sheet steel, the most commonly used joining technique is resistance spot welding. Even with the challenge from laser welding, the process still offers cost effective welding, flexible manufacturing approaches and extremely high weld quality, particularly with the switch over from manual to robotic spot welding on automobile production lines. However, the introduction of lighter gauges of steel for body panel fabrication and the requirement of improved corrosion resistance in automobile bodies has led to a significant increase in the application of metallic coated steels.

The use of metallic coatings has seriously altered the spot weldability behaviour of sheet steels in two ways. Firstly, the low melting point coating alters the contact resistances. Since contact resistance is a surface property, the contact resistance of a coated steel is typically that of the coating, which is usually much lower than that for an uncoated steel and consequently the overall electrical resistance is reduced (Figure 2.1). To compensate for a decrease in contact resistance, an increase in welding current or welding time is required to maintain the minimum heat input for weld nugget formation. If this is not achieved weld nugget size falls, reducing weld quality and strength. This is best seen through the equation for the total heat generated during welding, which is of the form

\[ H = kI^2Rt \]  

Eqn 2.1

where \( H \) is the heat generated (joules), \( I \) is the welding current (amps), \( R \) is the total weld resistance (ohms), \( t \) is the time of current flow (sec.) and \( k \) is an empirical constant.
Secondly, interactions occur between the spot welding electrodes and the metallic coated steel. The high temperatures and pressures which develop with repeated welding, due to the increase in welding current or welding time, provide the driving force for these interactions which results in alloying of the metallic coating with the copper electrodes. The two effects combine to rapidly accelerate the rate of wear of electrodes used for welding metallic coated sheet steels. The tip life of electrodes used to weld metallic coated steels may be as short as 250 welds, while electrodes used for welding uncoated steels may exhibit a life in excess of 50,000 welds. The composition and geometry of the electrode plays a critical role in the spot welding of metallic coated steels, since the alloying reactions that occur between the coating and the electrode ultimately determine electrode life.

The degradation mechanism is understood to be a chain of processes which begins with the alloying of the electrode tip face with the metallic coating of the sheet steel, primarily around the edge of the electrode tip. As welding proceeds, the alloy layers grow in...
thickness until they are stripped away as a result of sticking. Sticking occurs when the coating solidifies, while the electrode tip is still in contact with the steel substrate. Retraction of the electrode tip strips alloy layers away and accelerates further erosion and pitting. To accelerate the removal of the coating from the sheet/sheet interface and the electrode/sheet interface and reduce welding time, higher electrode forces are recommended when welding metallic coated steels. High electrode forces require higher currents and result in increased electrode deformation. Impact, high temperature deformation, face erosion and alloy build up on the edge of the tip combine to cause an increase in electrode tip diameter. A gradual increase in contact area causes a corresponding decrease in current density resulting in welds of decreasing nugget size. Eventually a stage is reached where the welding nugget falls below an acceptable size, unless an adjustment is made to the current.

A considerable amount of research has been devoted to the problem of accelerated electrode wear caused by metallic coated steels. However, almost all of the effort has been aimed at optimising the welding operation by analysing the electrode geometry, electrode tip surface condition, electrode force, weld time, sheet and coating thickness, coating composition, current, cooling rate and electrode composition. The alloying reactions that take place between the electrode and the metallic coating are the primary cause for accelerated electrode wear, yet very little effort has been devoted to analysis of this interaction and the development of means to control it.

2.2 WELDABILITY TESTS

There are two universally accepted weldability tests for sheet steel, weld lobe current ranges and electrode life tests. The weldability of sheet steel is altered by changes in welding parameters and electrode set up and can therefore be characterised by a welding
lobe which displays the range of welding time and current settings within which satisfactory welds may be made. This is illustrated in Figure 2.2

![Welding lobes for 1.2 mm uncoated and galvanised steels](image)

Figure 2.2   Typical welding lobes for 1.2 mm uncoated and galvanised steels [4].

The lower curve represents the conditions at which a specified minimum nugget diameter will form while the upper curve represents the conditions at which metal expulsion will occur. A wider lobe is more useful since it allows a greater range of currents to be used. Welding lobes which display low current values are also beneficial in that, lower currents result in lower power consumption and hence reduced welding costs. Generally welding lobes of metallic coated steels are higher than those of uncoated steels due to the increased current requirements. The exact position and size of welding lobes is dictated by electrode geometry, electrode tip condition, electrode force, sheet and coating thickness, coating composition, test method and analysis of results.

An electrode life test aims to define the point at which weld quality deteriorates to an unacceptable level, where the electrode needs to be redressed or replaced. Although there is no universal standard, it is commonly accepted that a weld nugget diameter which falls
below 80% of the initial electrode tip diameter is unacceptable. The point at which this occurs is open to interpretation as electrode tip diameters are known to increase with alloy build up and then decrease as the alloy layers break, or are stripped away. This causes the electrode tip diameter to oscillate and often results in weld nugget sizes falling to the minimum acceptable size before the electrode tip diameter recovers and allows the size of the welding nugget to return to an acceptable level. Therefore, tests are usually extended beyond the first signs of minimum weld diameter to ensure the end point is reached. The end point is finally reached when the current density falls below the required level because the applied current is acting over too large a surface area. The life of the electrode is dictated by the same factors listed for welding lobes.

2.3 COATING PROCESSES

In the following sections, references will be made to different grades of metallic coated steels. It is therefore, appropriate at this stage to briefly describe some of these steels. Metallic coated steels can be broadly categorised into four groups as shown in Table 2.1.

<table>
<thead>
<tr>
<th>METALLIC COATING</th>
<th>TYPICAL COMPOSITION</th>
</tr>
</thead>
<tbody>
<tr>
<td>METALLIC COATING</td>
<td>Zn</td>
</tr>
<tr>
<td>Zinc</td>
<td>Balance</td>
</tr>
<tr>
<td>Zinc/Aluminium</td>
<td>43.4</td>
</tr>
<tr>
<td>Zinc/Iron Alloy</td>
<td>Balance</td>
</tr>
<tr>
<td>Electrodeposited</td>
<td></td>
</tr>
</tbody>
</table>

Table 2.1 Typical composition of common grades of metallic coated steels [21]
Zinc coatings, with a typical composition shown in Table 2.1 are referred to in this review as hot dipped galvanised (HDG). The aluminium suppresses the growth of zinc/iron alloys at the surface of the strip immediately after it is immersed in the bath of molten zinc. The strip is air cooled naturally until a fine spangle forms as the coating solidifies. The cooling rate is not critical to achieve normal properties and appearance. In continuously hot dipped zinc coatings, the base steel and the main zinc coating are separated by an extremely thin iron/zinc alloy layer [21].

Zinc/Aluminium coatings will be referred to as Al-45%Zn. The silicon controls the growth of unwanted alloy layers. In the microstructure, several phases can be seen. Immediately adjacent to the steel base is an iron rich interfacial layer containing iron, aluminium and silicon. The body of the coating comprises three phases: dark zinc rich areas, light aluminium-rich areas and silicon rich plate like areas. There are discrete areas of both zinc rich and aluminium rich metal to give both sacrificial protection by the zinc and surface aluminium oxide barrier protection. The cooling rate for this coating is more critical to achieve the desired coating structure and corrosion resistance, compared to HDG [21].

Zinc/iron alloy coatings will be referred to as galvannealed. These coatings have a fully alloysed zinc/iron coating. A furnace is placed around the strip as it emerges from the molten zinc to maintain the coating temperature until the zinc has fully alloyed with iron from the steel base. No trace of the spangle formation and the accompanying surface roughness is present. The galvannealed coating has a smooth dull matt greyish finish ideal for painting, hence its widespread use in automobile body panels. The lead increases the fluidity of the molten metal and the aluminium ensures the formation of the correct alloy type. The microstructure of galvannealed coating is typified by two zinc/iron alloy layers: a high iron content near the interface and a low iron content (~ 10%) near the surface [21].
Electrodeposited coatings will be referred to as electrogalvanised (EG). In this process, the metallic coating is deposited onto the steel (cathode) via electrolytic deposition of metal ions from an electrolyte solution. Electrogalvanising is a low temperature process and coating weight is controlled via the main process parameters of line speed and current density. The coating is electrodeposited without any intermetallic layers present at the steel/coating interface [22].

2.4 WELDING PARAMETERS

When resistance spot welding metallic coated steels, the electrode tip life may have a significant effect on the productivity of the operation and therefore methods for improving tip life are particularly important. Numerous methods exist which can be used to improve tip life, however, not all of these are economically or practically viable. The most important variables which are involved with resistance spot welding are the size and geometry of the electrodes, electrode force, welding time and welding current. A satisfactory weld, which has acceptable mechanical properties, may be produced only if a correct combination of these parameters is used. In order to improve the weldability of coated steels for industrial use, many studies have been conducted on welding parameters and their effect on electrode tip life. The following sections review each of these welding parameters and aim to explain the significance of each parameter with regard to tip life.

2.4.1 Weld Current

It is widely accepted that metallic coated steels require much higher weld currents than equivalent thicknesses of uncoated steel [1]. The primary reason for the higher currents is that the surface contact resistance of the coated steel is much lower than for uncoated steel as explained previously. The electrodes act as heat sinks, and since there is no
buffer zone at the outer surfaces of the parts to be joined a higher welding current is then required to overcome the greater heat loss and the reduced heat generation due to the high electrical conductivity of the coating. The higher temperatures of uncoated steels (due to higher contact resistances) would normally tend to diminish the heat flow between the interface weld location and the electrode tip. Orts [23] has proposed that the increased current requirements result from the molten coating being displaced by the electrode pressure, and spreading around the electrode and between the sheets, increasing the contact area and thus decreasing the current density. The current must still flow through the electrode/work contact area and the electrode faces become much hotter than they would on bare steel. This requires more critical control of the welding current as there is a narrowing of the weld lobe. Reports of increases in welding current requirements for galvanised steel vary from 25 to 100% [7, 8].

An investigation of the weldability of zinc vapour deposited steels and galvannealed steel sheets by Morita et al [9] showed that electrode life increased virtually linearly with welding current.

![Figure 2.3](image)

Figure 2.3 Effect of welding current on the electrode life [24].
This result is supported by Tanaka et al [25] who showed that with galvannealed and electrogalvanised steels electrode life increased uniformly with welding current. Increasing welding current decreases the weld time required and thus reduces the amount of alloying and erosion that can occur per weld. However, a maximum current value exists at which point the heating and cooling cycle is so severe that electrode life is reduced. From an industrial point of view high currents might not represent the most efficient welding program, even though welding times are reduced, since increased welding current requires more power, and hence greater cost.

### 2.4.2 Weld time

Coated steels require an increase in welding time which has been reported to vary from 50 to 100% greater than that required for equivalent gauges of uncoated steels [13]. The increased welding time is needed to displace the metallic coating from the sheet/electrode interface and sheet/sheet interface so that sufficient heat can build up to form the molten pool necessary to create a nugget. Excessively long or short weld times are considered to result in electrode life being reduced [25]. Long weld times allow more heat to travel from the faying surfaces to the electrode tips creating higher tip temperatures and increasing the time available for coating metal diffusion. Short weld times result in a more severe heating and cooling cycle permitting contamination to build up on the electrode tips leading to large button sizes which decrease current density. This is supported by the observations of Kimchi and Gould [16] who concluded that intermediate weld times exhibited the longest electrode life.

Large increases in weld time are not acceptable under production conditions, since the increased electrode/coating contact time leads to a reduction in electrode life and production rates. To avoid excessive weld times an accompanying increase in weld current is also required.
2.4.3 Electrode Force

The force exerted by the electrodes holds together the two surfaces to be joined. The applied force also influences welding behaviour as shown by Lake and Nealon [10]. Small variations in force (less than 25%) did not alter lobe width or position significantly, although at extremes of force, lobe position was changed considerably. A high force raised current requirements, as the contact area between the electrodes and the workpiece resulted in a lower contact resistance. A low force reduced current requirements, due to the increased contact resistance. These extremes do not provide optimum welding conditions because a low force may be insufficient to clamp the work pieces together allowing premature expulsion, while a high force may result in severe indentation of the electrode into the sheet surface.

Under light pressure, the area of contact between the electrode and the workpiece is through the peaks (i.e. the machined surface of the electrode tip and the rough surface of the coating) which represents only a small fraction of the projected contact area, thus the resistance is high. Under high pressure the peaks deform and flatten, increasing the contact area, which reduces the resistance [26].

There are practical high and low pressure limits. A limiting high pressure exists above which the contact resistance approaches a constant value. Operating in that range accelerates electrode deterioration because of lowered contact resistance and increased current requirements. A limiting low pressure is determined by the need for enough force to contain the molten metal and form a nugget rather than expel it.

Saito et al [5] investigated the effect of an increase in weld force from 2.7kN to 3.8kN for a hot dipped galvanised steel, while maintaining other parameters constant. This caused a sharp increase in the electrode tip life from ~300 to ~2300 welds as shown in Figure 2.4. The higher electrode force widened the weldable current range. The rate of increase of
the electrode tip diameter was noticeably reduced compared to the electrode subjected to a lower force, leading to the conclusion that the reduction in the rate of tip wear was primarily responsible for the increased life.

![Graph showing effect of increasing electrode force on tip life](image)

**Figure 2.4** Effect of increasing electrode force on tip life [5].

Nealon and Lake [11] investigated the effect of an increase in weld force from 1.6kN to 2.4kN for Al-45%Zn coated steel which almost doubled tip life, from ~200 to ~400 welds. A further increase to over 3kN results in a return to the lower tip life. Baker and Meitzner [27] achieved similar results for Zincalume® with maximum tip life being achieved at 2.4kN; an increase to 2.9kN resulted in a 45% decrease in electrode life. Conversely, Dickinson [13] reported the use of electrode forces lower than those used for uncoated steels resulted in more consistent weld diameters and increased electrode life. Jud [18], however, has noted maximisation of tip life with a force about 20% greater than for uncoated steel which seems to be in accordance with the literature in general. Nealon and Lake [11] concluded that electrode force does not appear to be a critical variable when welding zinc coated steels, unless extremes of force are used.
2.4.4 Electrode Composition

Electrodes must possess high electrical conductivity to minimise electrode heating, and high thermal conductivity to dissipate heat from the contact area between the electrode tip and the workpiece. Electrodes should also exhibit high hot strength to resist deformation caused by the application of high welding force, and to maximise electrode life, by providing resistance to alloying. The most commonly used electrode composition in Australia is Cu-0.8%Cr (J47 Alloy) since it exhibits the best all round properties. There is, however, a growing tendency to use different types of electrode material to increase electrode tip life.

One such material used is aluminium oxide dispersion strengthened copper which has a higher strength than the standard spot welding electrode materials which reputedly diminishes the extent of electrode tip deformation. Dickinson [13] and Jud [18] report electrode lives of four times that of standard electrodes at elevated temperatures. The major disadvantage with this type of electrode is a four to five times increase in cost over copper chromium (Cu-Cr) electrodes. Kimchi and Gould [16] have shown that although the aluminium oxide dispersion strengthened material has improved high temperature characteristics, this is not necessarily translated into an increased electrode life when evaluated using conventional life tests. They examined the electrode life characteristics of three electrode materials, Cu-Cr, copper zirconium (Cu-Zr) and Al2O3 dispersion strengthened copper (DSC) when spot welding hot dipped galvanised steel. The Cu-Zr electrode demonstrated the longest life, of 3500 welds, the Cu-Cr electrode followed with 2500 welds, the DSC electrode exhibited the shortest life of 1700 welds. The rate of increase in contact area of the electrode with the workpiece is often used as a measure of electrode performance since it is proportional to the rate of decrease in current density. In view of the electrode life results it was surprising that the rate of growth of the Cu-Zr and Al2O3 DSC electrode tips were very similar. Inspection of the surface condition showed the DSC electrodes were characterised by small, uniformly distributed pits on the
electrode face. The other electrodes however, show one or two large pits on an otherwise smooth face. Across the entire diameter, the electrodes appear to grow at roughly the same rate, however, as the Cu-Cr and Cu-Zr electrodes grow, large pits develop, concentrating current in one or two hot spots on the periphery of the electrode. The face of the DSC electrodes are more uniform so no current concentration occurs. This results in failure at a much smaller face diameter and a fewer number of welds.

Kumagai and Nagata [19] using hot dipped galvanised steels showed that the life of Al₂O₃ DSC electrodes is comparable to that of copper chromium zirconium electrodes (Cu-Cr-Zr), ~1000 welds when the Al₂O₃ content is 0.57wt%, even though the electrodes show greater resistance to alloying and mushrooming of the electrode tip. The continual mechanical impact on the electrode tip gradually spreads material towards the periphery. The forces which enlarge the tip, create cracks, reduce current density and shorten electrode life. The cracking at the tip is associated with a hard and brittle alloy layer, Cu-Zn beta (β) phase, which is formed at the surface of the electrode and develops along the crystal boundaries of the base material Al₂O₃ DSC. Increasing the Al₂O₃ content to 0.89wt% increased the thickness of the Al₂O₃ which formed on top of the Cu-Zr alloy layer at the electrode tip. This increase prevented the Cu-Zn alloy layer from spalling, and made nugget formation more stable as crack propagation became more difficult. Electrode life was increased to double that of Cu-Cr-Zr electrodes.

Other electrode materials exist which are known to increase electrode life. Cu-Zr electrodes are reported to increase tip life over standard Cu-Cr electrodes [16], the zirconium is thought to have the effect of inhibiting pick up on the electrode surface as well as reducing the grain boundary penetration [22]. Refractory based metal inserts including powder composites of molybdenum copper or tungsten copper containing a discontinuous refractory phase in a copper matrix are reported to increase electrode life, although at substantially greater cost [8, 17]. Saito et al [5] trialed a compound electrode with an insert. The core of the compound electrode was made from a conventional
chromium containing copper base alloy and was covered with pure copper of lower strength. This type of electrode was found to last twice as long as conventional copper base alloy electrodes, used to weld zinc vapour deposited sheet steel. The electrode tip was characterised by a convex wear profile which maintained a relatively small face diameter and extended electrode life.

Many of the reported improvements in tip life due to changes in electrode material are for particular conditions and as a result they are rarely achieved in other environments, especially in industry[11].

2.4.5 Electrode Geometry

2.4.5.1 Electrode Profile

It is generally accepted that the truncated cone electrode profile shown in Figure 2.5 with an included angle between 90° and 140° is the most suitable for industrial applications. While the extended tip or the pimple tip electrode has been shown to be superior in experimental trials where alignment is exact, its lack of mechanical strength can create difficulties if misalignment occurs [28]. Radiused electrodes are suitable where electrode misalignment or poor part fit up is likely to be a problem. They are, however, prone to rapid alloying with the zinc metallic coating resulting in rapid electrode degradation [10].

![Figure 2.5](image_url)  
**Figure 2.5**  Resistance spot welding electrode tip profiles.
Howes [4] showed that changing the included angle of the electrode tip had little effect on weld lobe width, but altered lobe position and electrode life. Decreasing the included angle from 120° to 90° moved the welding lobe to lower current values for both Al-45%Zn and hot dipped galvanised steels. Electrode life was found to increase to varying degrees with the decreasing included tip angle (Figure 2.6). It was suggested that the increase in electrode tip life for electrodes with a reduced included angle was due to the higher angle of incidence between the electrode shoulder and sheet surface. This allows alloy detachment from the periphery of the electrode to occur more easily. Regular removal of the build up maintains a high current density resulting in a large weld size. A more recent study by Howes [6] showed that a decrease in included angle from 120° to 90° for both electrogalvanised and galvannealed steels resulted in a decrease in electrode life, although no obvious reason was apparent.

Figure 2.6. Electrode tip life test results [4].
Bowers and Eager [29] studied the effect of non-uniform current distribution across the electrode face as a factor influencing electrode wear. Computer modelling was employed to produce a voltage map of each electrode shape. From the voltage map the current density profile at the electrode face was calculated. The ratio of the current density at the electrode shoulder (or face edge) to the current density at the face centre was found to decrease with increasing included angle. As the current density distribution approached 1, i.e. uniformity, electrode erosion became more evenly distributed across the face. Therefore, an electrode with a 90° included angle should outperform the 120° included angle.

2.4.5.2 Tip Diameter

Tip diameter is not readily changeable since product design usually dictates the size of weld required and thus the tip diameter to be used. Howes [6] showed that increasing tip diameter from 5mm to 7mm yielded a small improvement in tip life for electrodes used for hot dipped galvanised steel (650 cf 800 welds), while for Al-45%Zn steel tip life was seen to increase by a factor of four (350 cf. 1300 welds), see Figure 2.6. Nealon and Lake [10,11] proposed that for a larger electrode tip the relative current density of the face centre compared to the face edge is lower for a larger diameter. The reason for this effect is the formation of cavities which reduce the contact area and produce sufficient current density around the periphery of the weld area to result in fusion. It must be remembered that increased diameters require greater welding currents and therefore increased cost, and are only suitable where the improvement in electrode tip life is substantial. Contrary to the findings of Howes [6]; Gould [25] reported that increasing electrode tip diameter caused a decrease in electrode life when used to weld hot dipped galvanised steel. A tip diameter of 4.8mm exhibited a life of 3000+ welds while a tip diameter of 7mm exhibited a life of 1250 welds; reasons for this observation were unclear. Gould noted electrode tip diameter at failure was independent of the welding time used. This was considered very surprising as radically different face topographies were observed at different welding
This suggested that on average, the electrode life was controlled by electrode facial area rather than any particular aspect of electrode topography.

Saito et al [5] showed that current requirements were increased from 10 kV to 14 kV when increasing tip diameter from 5.1mm to 6.4mm although weld lobes were seen to increase in width when welding hot dipped galvanised steels. Electrode tip life was seen to increase by approximately 1000 welds for the three steels investigated (Figure 2.4). Figure 2.7 shows clearly that steels 1. & 3., both of which exhibit considerably shorter tip lives than steel 2., display a greater rate of increase of electrode face diameter with increasing number of welds.

![Figure 2.7 Changes in electrode face diameter with number of welds [5].](image)

Saito et al [5] concluded that in terms of electrode wear rate the change in the electrode face diameter with increasing number of welds is more important than the absolute value of electrode face diameter itself.
2.4.6 Coating Process and Composition

The composition of the metallic coating will have a strong influence on the electrode tip life as it is the coating which comes into contact with the electrode tip. Zinc coated steels can be produced by several methods, ie. hot dipped, fully alloyed or electrolytic. The coating process and composition, combined with the electrode composition will determine the various alloy layers which will form and their effect upon electrode tip life.

Natale [14] compared hot dipped galvanised (HDG) to electrogalvanised (EG) steels and found the latter showed consistently superior electrode life performance, even though similar current levels were required for welding products of comparable weight (Figure 2.8.). It was reasoned that the thin aluminium oxide film on the surface of the hot dip galvanised coating resulted in the poorer life as the enriched alloy layer increased electrode alloying. Significant differences in coating structure exist between hot dip and electrogalvanised steels. Hot dipped galvanised coatings have cast structures with thin intermetallic Fe-Al and Fe-Zn phases present in layered form at the zinc/steel interface. Electrogalvanised coatings have electroplated structures without any intermetallic layers present. The different structures of the hot dipped galvanised and electrogalvanised zinc iron coatings would result in different contact resistances. The resistance at the interface between the electrode and the workpiece is increased for hot dipped galvanised steel causing higher temperatures at the electrode surface.
Figure 2.8  Increased current levels for welding galvanised vs. uncoated steels [15].

Figure 2.9  Relative electrode life behaviour of galvanised and electrogalvanised steels [15].

Current levels required for producing acceptable welds are higher for zinc coatings, than zinc/iron coatings, regardless of whether the process was hot dipped galvanised or electrogalvanised [14] (Figure 2.9). The reduced currents required for welding galvannealed steels compared to hot dipped galvanised can be related to the increased electrical resistivity, higher melting point and reduced shunting tendency of the alloyed products. Electrode life improvement for electrodes used to weld galvannealed steels
results from higher electrical resistivity (lower welding current), higher coating melting
temperature, (reduced electrode alloying) and lower thermal conductivity than unalloyed
zinc coatings. Generally speaking, EG-ZnNi products (an electrogalvanised coating
containing 12%wt nickel) induce the least rapid wear of the welding electrodes, due to the
formation of a unique dual layer alloy which consists of ductile brass inner layer which
protects the copper electrode substrate. EG-ZnNi coatings are followed in wear
susceptibility by the galvannealed and electrogalvanised coatings, while hot dip
galvanised coatings cause the most aggressive electrode wear [15]. It is believed [2, 15]
that the aggressive wear problem is caused by trace addition of aluminium in hot dipped
galvanised coatings of 0.2 - 0.4wt%. Aluminium is needed however, to improve
adherence between the coating and the steel. The extremely poor performance of
Al-45%Zn would confirm this hypothesis.

Gould and Peterson [30] demonstrated that different coatings result in different electrode
tip lives when welded under the same conditions. Their results were in disagreement
with the general observations. Using the total number of welds to failure, galvannealed
exhibited the shortest life (1500 welds), with increasing lives for Fe-Zn electrocoated
(2300 welds), HDG (2800 welds), EG (4300 welds), and uncoated steel (>8000 welds).
From these results, the steels can be classified into three distinct groups, these are
uncoated steels, free zinc coated steels (hot dip galvanised and electrogalvanised), and Fe-
Zn alloy coated steels (galvannealed and Fe-Zn electro coated steels). No explanations
were offered to explain the extremely poor performance of the alloy coated steels.

Howes [6] also investigated the effects of different coatings on electrode life. Al-45%Zn
displayed the shortest life (350 welds), with increasing lives for the hot dipped galvanised
steels (650 welds), electrogalvanised (3500 welds) and galvannealed steels (5500 welds).
These results are in agreement with the majority of published data. Ostyn and Rubben
[31] confirmed the superior performance of galvannealed steel. They found that the
presence of the intermetallic, more resistive zinc-iron layer in galvannealed sheets results
in a lower welding current than galvanised steels leading to an increased life. Only Gould and Peterson seem to be in disagreement with the result observed for galvannealed steel. Even though welding conditions used by Howes [2] and Gould and Peterson [30] were similar, their results show that even small variations in operating conditions can cause considerable differences in results. These differences would be even more evident on the production line where parameters are less closely monitored.

Howes [4] has shown that coating composition readily affects electrode life when process variables are altered. A hot dipped galvanised steel showed little improvement in electrode life when the electrode tip diameter was increased from 5mm to 7mm. However Al-45%Zn yielded an increase in electrode life of four times for exactly the same increase in tip diameter.

Aluminium [32] is added to the zinc coating to inhibit the growth of iron zinc intermetallics during the hot dipped galvanising process. Its presence, even in small quantities in the alloy layers, which grow on the electrode tip as welding proceeds, alters the weldability of the coated steel and severely reduces electrode life [2, 6]. Brittle pockets containing aluminium form in the alloy layers which are easily broken away leaving a pitted electrode face. As more material is deposited on the electrode face more is stripped away. Gradually the weld quality deteriorates until a point is reached where unsatisfactory welds are achieved. This is especially noticeable in Al-45%Zn coated HDG steel. A similar erosion process occurs on electrodes used to weld other coated steels such as hot dipped galvanised, fully iron alloyed (galvannealed) and electrogalvanised zinc coated steel. However, the erosion rate is much slower due to the small amount or complete absence of aluminium in the coating of these steels. The order of decreasing rate of degradation is Al-45%Zn followed by hot dipped galvanised then galvannealed and electrogalvanised steels. The high iron content of the galvannealed steel coating contributes to the lowering of the electrode degradation rate when welding this
steel type. It is suggested that iron may have a stabilising influence over the diffusion of both zinc and aluminium into the copper, or of the copper into the complex alloy layers.

Pavlik [32] investigated the effect of aluminium in a galvanised coating. It was shown that button failure between two sheets with essentially the same coating composition was markedly different suggesting that aluminium was not responsible for weld metal failure. Failure was observed to occur in the weld metal rather than the heat affected zone surrounding it. It was concluded that the sulfur in the base metal led to the formation of alpha MnS in the weld, as one particular steel had a higher sulfur content than the other. Despite this, there is general agreement in the literature on the detrimental effect of aluminium [2, 6, 15].

2.4.7 Coating Weight

Several investigators [1, 5, 7, 13] have indicated that tip life decreased as coating thickness was increased for hot dipped galvanised, electrogalvanised and galvannealed steels. Natale [14] explained that increased shunting at both the electrode/sheet interface and the faying plane, along with the need to displace more coating at the faying plane, required increased currents as zinc coating weight increased. These increased currents, combined with increased zinc pick up at the sides of the electrodes, result in reduced electrode life. Figure 2.8 illustrates the deleterious effect of increased coating weight for hot dipped galvanised (HDG-Zn) and electrogalvanised (EG-Zn) steels.

Saito et al [5] proposed that since hot dipped galvanised steels are generally larger in coating weight than the zinc alloy electroplated steels, the electrode tip life is indeed shorter for HDG steel. Morita [9] showed, for both zinc vapour deposited steels and galvannealed steels, that electrode life becomes shorter when steel sheets with a higher coating weight are welded and concluded that electrode life strongly depends on the coating weight.
Howe and Kelley [33] found that electrode tip life improved with increasing coating weight for electrogalvanised steels, a result which seems to contradict the general trends observed in the literature that increased coating weight has a detrimental effect on electrode tip life. They proposed that the higher tip temperatures which developed when welding steels of thinner coatings appeared to be more detrimental to the electrode face than the increased alloying and pitting associated with thicker coatings. Alternatively, the poorer electrode life observed for material with lower coating weights may be a consequence of the lower welding currents employed at the lighter coating weights. The lower current levels limit the current range and subsequently, can result in reduced tip life. Mathieu and Patou [34] support this observation for the case of hot dipped galvanised steels. When similar welding currents are employed, more heating of the tip face occurred as the amount of zinc present at the electrode/sheet interface decreased.

Howe [12] conducted analyses on the electrode face to measure wear rates for ZnNi electrogalvanised sheet steel and found that coating weight had no discernible effect on wear, but rather the substrate thickness was the factor altering electrode life, with the thinnest substrate producing the highest wear rates. Since all tests were terminated after 10,000 welds, only end of life estimates were made and from these no conclusions could be drawn on the effect of coating weight on electrode life. Therefore, electrode face wear rates were compared instead for each different coating weight. No trend in wear rates was evident as coating weight increased.

2.4.8 Sheet Thickness

Dickinson [13] reported that thinner materials resulted in a faster wear rate of the electrode tips than thicker materials. The percentage increase in current to weld galvanised steel when compared to uncoated steel was greater for the thinner materials. since the loss of heat from the joining surfaces to the electrodes was greatest with thinner workpieces. This resulted in greater electrode heating which led to faster electrode deterioration.
Therefore, the greater the ratio of zinc coating thickness to substrate thickness, the greater the effect of the coating on reducing electrode life.

Howe [12] found that sheet thickness had a considerable effect on electrode wear rate and hence, electrode life on the weldability of Zn-Ni electrogalvanised steel sheet. A decrease in electrode face wear rate was observed as sheet thickness was increased causing a subsequent increase in electrode life. Electrode topography was smoother for the electrode used on a 1mm sheet than for 0.6mm sheet. The iron content on the electrode face was seen to increase with increasing sheet thickness. The Fe/Ni rich layer on the electrode tip appeared to retard brassing and loss of electrode material, thus reducing electrode wear. This trend was also affected by the welding parameters since the thinner sheet was subjected to less welding force which increased the electrode/sheet interface resistance, and could consequently cause higher temperatures at the electrode faces.

2.5 ELECTRODE DEGRADATION

2.5.1 Alloy Layer Composition

Howes [2] investigated four coated steels and analysed the alloy layers formed on the electrode tip at the completion of each electrode life test. The electrode tip was sectioned for SEM examination as shown in Figure 2.10
A concentration of aluminium was found in the alloy layers of electrodes used to weld galvanised, galvannealed, and Al-45%Zn coated steels. Figures 2.11 & 2.12 are micrographs of Cu/Cr electrodes used to resistance spot weld galvannealed and Al-45%Zn coated steels. Iron was found in each of the alloy layers, although it was not distributed uniformly across the electrode tip face, except in the case of the galvannealed steel. Areas in the alloy layers which were observed to have high concentrations of aluminium, but little iron, were prone to rapid erosion. This occurred for the hot dipped galvanised, and in particular Al-45%Zn steels, but not for the galvannealed or the electrogalvanised steels. Electrogalvanised steel coatings contain no aluminium which explains the absence of rapid erosion. The galvannealed coatings have a lower aluminium content than hot dipped galvanised steels and increased iron content, which is believed to have a stabilising influence over diffusion and the formation of intermetallics. Lavery and Williams [8] support this observation, finding that fully alloyed coatings (galvannealed) provide increased tip life which is attributed to the higher hardness of the coating and to the increased iron content in the coating reducing the necessary welding current.
Figure 2.11  Electrode alloying during resistance spot welding of galvannealed steel [2].

Mag: 1000x

Figure 2.12  Electrode alloying during resistance spot welding of Al-45%Zn steel [2].

Mag: 1000x
Saito et al [5] employed optical microscopy and surface profilometry to identify electrode alloy layers which developed during welding of galvannealed sheet steel and zinc vapour deposited steel (Figure 2.13). The two layers adjacent to the electrode face were both composed of Cu-Zn alloys, of varying thickness for different coating materials. Morita [9], using X-ray diffraction, identified these two layers as a hard and brittle gamma (γ) brass (Cu₅Zn₈) layer, and a ductile beta (β) brass (CuZn) layer. The outermost layer was zinc oxide, adjacent to a porous iron-zinc alloy (Γ phase: Fe₅Zn₇) layer.

<table>
<thead>
<tr>
<th>Steel</th>
<th>Electrode</th>
<th>Electrode Tip Face Shape</th>
</tr>
</thead>
<tbody>
<tr>
<td>Before Welding</td>
<td>Cu-Cr</td>
<td><img src="image" alt="Electrode tip shape" /> After conditioning welding</td>
</tr>
<tr>
<td>Galvannealed steel</td>
<td>Cu-Cr</td>
<td><img src="image" alt="Electrode tip shape" /> Fe-Zn (dark gray) Zn-Cu (white) Fe-Zn (light gray) Zn-Cu (yellow)</td>
</tr>
<tr>
<td>NB &gt; 6000 welds</td>
<td>Cu-Cr</td>
<td><img src="image" alt="Electrode tip shape" /></td>
</tr>
<tr>
<td>Zinc alloy electroplated steel</td>
<td>Cu-Cr</td>
<td><img src="image" alt="Electrode tip shape" /></td>
</tr>
<tr>
<td>NB = 1500 welds</td>
<td>Cu-Cr</td>
<td><img src="image" alt="Electrode tip shape" /></td>
</tr>
<tr>
<td>Zinc alloy electroplated steel</td>
<td>Cu-Cr</td>
<td><img src="image" alt="Electrode tip shape" /></td>
</tr>
</tbody>
</table>

Figure 2.13  Electrode tip shape after consecutive welds (roughness meter recording and optical microscope sketch) [9].
Figure 2.14 shows the concentration of elements and hardness distribution across the electrode tip. The iron-zinc alloy layer was formed by adhesion of the coating layer, whereas the brass layers were considered to be formed by the interdiffusion of copper from the electrode and zinc in the iron-zinc alloy adhering to the electrode face. When the Fe-Zn layer was thick, electrode tip life was observed to be relatively long.

Kumagai and Nagata [19] analysed the electrode tip of Al₂O₃ DSC and Cu-Cr-Zr electrodes used to weld galvanised steel. At the completion of the electrode tip life test an alloy build up of approximately 40 µm thick was identified, on the tip face of both electrodes, similar to that identified by Morita [9]. Many cracks were observed in these alloy layers, especially in the (γ) brass layer. The presence of aluminium and oxygen on the surface layer of the Al₂O₃ DSC electrode suggested a thin layer (a few microns) of Al₂O₃ had formed between the alloyed layer and the deposits (Fe, Zn). The Al₂O₃ layer is considered to suppress the deposit of material on the electrode face.
Tanaka et al [24] made similar observations about the tip of electrodes used to weld electrogalvanised steel. Some micro cracks occurred in the high hardness (HV 550) gamma (γ) brass region covered by the thick Zn-Fe-Cu alloy at the tip surface. This limited electrode tip life to ~3000 welds. Welding Zn-Ni coated sheet steel resulted in the development of a 50 μm alloy layer composed of a Zn-Cu-1.1%Ni alloy (α-β phases). There were no visible cracks, which extended the electrode tip life to ~7000 welds. The electrogalvanised(EG) and galvannealed sheet steels which resulted in a relatively short electrode life, were characterised by a concave profile of the tip surface. Alloy layers have developed on each tip surface. However, the thickness of the alloy layers in the long life electrode group of Zn-Ni sheet steels is considerably less than in the short electrode life group of electrogalvanised and galvannealed steels. Wristen [35] stated that the greater the depth of alloying, the shorter the life of the electrode, since the thicker alloy layer leads to higher temperatures due to the increased resistivity. Although the findings of Tanaka et al [24] would seem to substantiate this statement, Howes [2] refuted it, and concluded that the small rise in temperature would be unlikely to increase the wear rate sufficiently to account for the severe difference in observed electrode life.

Howe [12] investigated alloy layer composition on electrodes used to weld ZnNi electrogalvanised steel and found that the alloy formation is composed of 2 distinct layers, an outer thick, brittle intermetallic alloy layer and a ductile inner layer. The outer layer is composed mainly of zinc, small amounts of copper and substantial amounts of nickel and iron which are primarily concentrated near the surface. It is highly fractured which suggests it has a brittle nature. The alloy layer, adjacent to the electrode material, is composed of copper and zinc (β) brass and is ductile as shown by the lack of cracks and the termination of outer layer cracks as they meet this alloy layer. Howe [12] stated that the dual layer alloy formation is not found when welding free zinc coated sheets such as hot dipped galvanised and electrogalvanised. Tanaka et al [24], however, have shown that a dual layer formation is present on electrodes used to weld electrogalvanised steels. The beneficial effect of the ductile Fe-Ni rich layer at the surface of the electrode face in
retarding brassing and reducing electrode wear is believed to be due to the presence of iron. This is also believed to be one of the main factors responsible for the reduced electrode wear rates when welding galvannealed sheet steel [2, 33].

Howes [2] has suggested areas of low iron concentration and high aluminium concentration in the alloy layers may be the cause of the extreme brittleness of the electrodes used in the spot welding of galvanised steel. The areas of low iron on the electrode tips used for welding Al-45%Zn coated steels had noticeably higher hardness which led to rapid wear (Figure 2.12). The areas of rapid attack are prone to fracture and the development of pits. Coatings such as electrogalvanised, which contain no aluminium seemed to display slower rates of wear since the areas of rapid attack appeared to be less brittle. The effect of aluminium, in electrode tip layers is noticeably more harmful than zinc which explains the reduced life of electrodes used to weld galvanised steel compared with electrogalvanised steel. The presence of even higher concentrations of aluminium in Al-45%Zn coatings causes even more rapid degradation of the electrode tip. Iron however, has proved to be beneficial in minimising the severe effect of aluminium and decreasing the rate of erosion. Therefore, the small amount of aluminium present in galvannealed coatings has a minimal effect on electrode life.

2.5.2 Wear Mechanisms

Gould et al [3] provided a short description of the basic mechanism responsible for the degradation of electrode tips used to weld metallic coated steels. Zinc adhered to the electrode face from the very first weld. The zinc both alloyed with the electrode material and acted as a reservoir of zinc which diffused into the electrode. The electrodes occasionally bonded to the workpiece (sticking). Sticking occurred when the alloy layers froze before the electrode tip was retracted. It is thought that the low melting point zinc coating acted as a braze material or the electrode surface was directly forge welded to the substrate steel. When sticking occurred, retraction of the electrode tip resulted in the
removal of Cu and Cu-Zn alloys from the electrode tip evidenced by copper being found often on the surfaces of the weld. Electrode face edges were areas of both current and force concentration and as a result were seen to wear faster than the face centres. Also any discontinuity in the face such as a pit or a crack also tended to wear excessively. The electrode contact surfaces developed a mottled appearance with a small amount of brass build up around the face periphery. The weld surface was relatively free of zinc but showed evidence of copper pick up from the electrodes.

One of the main problems in reproducing results for electrode life tests is the irregularity with which electrodes wear. This was evident in Gould's [3] observation of the inconsistencies in the compositional profiles in the electrode cross sections. On the same electrode, one area of the face showed no zinc penetration with very little foreign material adhered to the free surface. In another area, there was massive build up of iron zinc alloys on the free surface and heavy penetration of zinc into the electrode.

Saito [5] stated that two factors tended to control electrode tip life, when welding metallic coated steels. (1) The weldable current range shifts towards the high current end and (2) the electrode tip alloys with the coated steel surface, increasing electrode tip wear. To this a third factor was also introduced, namely the wear pattern. An electrode tip used to weld galvannealed steel wore more quickly than that of a zinc alloy electroplated steel, yet the electrode tip life was observed to be longer. The tip was worn into an irregular convex pattern, but the tip diameter remained virtually constant. The wear of the tip is a complex phenomenon affected by alloying of the electrode tip with the coating materials of the steel, fracturing of the alloy layer, mechanical impact to the electrode tip face, temperature and pressure distribution in the steel sheets and the expansion, softening and indentation of the steel. This complexity has made elucidation of exact wear mechanism rather difficult, if not impossible.
The upper Cu-Zn layer on the tip of electrodes used to weld galvannealed steel was observed to have many cracks, running in the axial direction of the electrode, which were arrested by the layer adjacent to the substrate and then ran along the boundary between the two layers (Saito [5]). The detachment of the alloy layers in the electrode tip face is closely related to the cracks in the alloy layers. Fracture and delamination of the alloy layers is thought to arise from the cracks in the hard upper layer of Cu-Zn and to occur in the boundary between the two layers. The oscillations observed in the increase of electrode face diameter shown in Figure 2.7 for No. 2 steel were attributed to the separation of the alloy layer (including the Fe-Zn layers mentioned above) at the boundary between the two layers.

The gamma (γ) phase identified by Morita [9] in the alloy layers on electrodes used to weld galvannealed steel sheet was brittle and resulted in cracking and partial delamination as welding proceeded. Observations showed that the same phase continued to be formed in the delamination zone and that the electrode wear rate was thus strongly affected by gamma phase formation rate. For the first 1000 welds there was a sharp increase in the thickness of the gamma phase, beyond this there was little change in thickness owing to the repeated delamination and formation of the gamma phase. The gamma phase formation rate is faster during the welding of zinc vapour deposited steel than galvannealed steel, and was also faster for steels with a higher coating weight. This effect is believed to be the cause for faster electrode wear for materials of heavier coating weight or during the welding of non-alloyed materials at the same coating weight [9]. When welding alloyed coated steels or steels with a low coating weight the longer electrode life is due to a complex effect associated with the fact that electrode tip wear is suppressed by the slow formation rate of the gamma(γ) brass phase and that the nugget forming current range is wider.

The Cu-Zn alloy layer identified by Kumagai and Nagata [19] which formed on the Cu-Cr-Zr electrodes during welding of galvanised steel partially peeled off and as a result the
tip of the electrode softened from the high temperature. The tip diameter was seen to enlarge which reduced current density and eventually led to failure. Al₂O₃ DSC electrodes, through the formation of an Al₂O₃ layer on the surface of the electrodes, prevented the Cu-Zn alloy layer from breaking away, keeping the surface smooth and reducing the increase in tip diameter. This led to the production of weld nugget diameters of a satisfactory size even after repeated welding. The welding forces create cracks in the face tip and depending on the degree of development, shorten electrode life due to reduced current density.

Dykhno [36] proposed a theory for the probable mechanism by which low melting coatings break down during spot welding. The mechanism is considered as a complex process consisting of cold and hot bonding, thermal diffusion, electrical transfer and sublimation. The mechanism of adhesion is known to be one of sublimation. Sublimation is the transfer of a solid to a gas phase without passing through the liquid phase, by rapid heating.

When the electrodes are brought into contact with the workpieces and force is applied, the two contacting surfaces bond together. The region of greatest contact is around the periphery of the electrode which is confirmed by metallographic examinations of oblique sections. Bonding only takes place at the surfaces of contact spots. Once welding is underway the low melting point coating begins to melt in the actual contact zone. The molten coating wets the working surfaces of the electrode and intensifies hot bonding. The bond which is initially formed at micro-areas, gradually develops into macro areas. Thermal diffusion develops at the same time with the movement of atoms from the coating to the electrode tip. The powerful flow of electrons due to the welding current means that adhesion in the areas of actual contact is intensified by electrical transfer ie. directional movement by atoms of the metallic coating through the dividing boundary. In the area in which there is no direct contact between the metal being welded and the electrode, adhesion takes place by sublimation. Adhesion was greatest in the central zone
of contact, where the maximum temperature and pressure developed. Adhesion in macro areas of direct contact between the work and the electrode was small in comparison with the adhesion in areas where sublimation took place. In the central zone of true contact area, mass transfer is infinitesimal, compared with areas where there is no direct contact. This confirmed that adhesion of the coating as a result of hot bonding, thermal diffusion and electrical transfer cannot compare with mass transfer by sublimation. Away from the centre of the electrode towards the periphery, mass transfer becomes greater in the regions of direct contact and less in the gaps. This is due to the drop in temperature away from the electrode axis, and the amplification of deformation processes which intensifies bonding and an increase in current density which intensifies electrical transfer.

Welding ZnNi electrogalvanised steel led to the formation of a unique dual layer of alloys on the electrode tip face [12] as described in Section 2.5.1. After 10,000 welds there was little evidence of pitting of the electrode faces, which suggested that erosion of the electrode face, a common wear mechanism with coated sheet, was minimal. It was proposed that the lack of electrode face erosion was due to the presence of a dual alloy layer formation. As welding proceeds, the brittle outer layer provides a barrier which prevents the electrode tip material from alloying with the coating. It also behaves as an interface which occasionally breaks off and sticks to the weld surface. Once this brittle outer layer has broken away, the ductile inner layer still prevents any major erosion from taking place on the face of the copper electrode, as it prevents the zinc from the sheet coating coming into contact with the copper electrode base. This greatly reduces electrode face erosion and enlargement of the tip diameter and produces the low electrode wear rates observed.

Tanaka et al [24] summarised that electrode life in spot welding can be, more or less dominated by the reaction products formed at the tip surface. The relatively short life exhibited by electrogalvanised and galvanised sheet steels is probably due to the formation of micro cracks which accelerate electrode wear, probably by periodical
breaking away of the newly formed reaction products from the tip surface. Micro cracks develop due to the repeated pressure loading exerted on the electrode tip with each weld. By comparison, electrodes used to weld Zn-Ni electrogalvanised steel exhibit significantly longer life. This was attributed to the nickel disturbing the formation of Zn-Fe-Cu alloy at the tip surface during spot welding by delaying the diffusion of zinc in the electrode.

Howes [2] investigated the wear mechanisms of galvanised steel sheet. The copper levels observed on the surface of the welded sheet are similar to those of the surface layer of the electrode, indicating substantial transfer of matter from the electrode tip to the sheet surface. As each weld is performed the zinc coating vaporises which increases the concentration of the remaining elements in the coating. As the nugget forms these elements fuse along with the steel base and the electrode tip. As a result a crack is likely to form somewhere between the electrode tip and the steel substrate as the tip is retracted. The outer layer of the alloy on the electrode must be the remnant of the fused material between the electrode and the steel base. Some of this material also remains adhered to the steel base and some diffuses into the electrode enabling growth of the beta (β) brass layer. A similar mechanism for electrode erosion is believed to take place for electrogalvanised and Al-45%Zn coatings.

Howes [2] has also pointed out that once the zinc on the surface evaporates, the remaining aluminium content, both in the coating and in the alloy layers of the electrode is much more concentrated relative to zinc than in the coating prior to welding. For galvanised and galvannealed steels the concentration is 100 and 50 times greater respectively. Therefore the composition of the alloy in contact with the electrode surface is completely different from the coating. This is responsible for the inferior welding performance of galvanised steel in comparison with electrogalvanised steel, not the presence of a thin aluminium rich film on the surface of the metallic coating as proposed by Natale [14].
2.6 SUMMARY

What is clear from the above review is the inconsistency in the information produced by different sources and the difficulty in reproducing results. Gould and Peterson [30] investigated the tip life when welding a variety of coated steels. Electrode life results were seen to vary by up to 1200 spot welds within the same steel type (Table 2.2). Gould and Kimchi [37] attribute this to material or welding machine variability.

<table>
<thead>
<tr>
<th>ELECTRODE TIP LIFE TESTS</th>
<th>FIRST TEST</th>
<th>SECOND TEST</th>
</tr>
</thead>
<tbody>
<tr>
<td>UNCOATED STEEL</td>
<td>No failure</td>
<td>No failure</td>
</tr>
<tr>
<td>HOT DIPPED GALVANISED</td>
<td>4126</td>
<td>4499</td>
</tr>
<tr>
<td>ELECTROGALVANISED</td>
<td>5499</td>
<td>4934</td>
</tr>
<tr>
<td>GALVANNEALED</td>
<td>3872</td>
<td>2675</td>
</tr>
<tr>
<td>Fe - Zn ELECTROCOATED STEEL</td>
<td>3555</td>
<td>4429</td>
</tr>
</tbody>
</table>

Table 2.2. Effective electrode lives for each material [32].

Howe and Kelley [33] however, believe it is due to the variation between the electrode faces and the coating in which the topography and electrical characteristics of the electrode are constantly changing. Coating pickup/loss, alloying and pitting are competing processes which operate in an inconsistent manner, resulting in a pattern of wear which rarely repeats itself from test to test. Therefore each result must be considered individually and any conclusions which are drawn are dependent on the welding parameters and coating composition used in each particular test. This is not to say however, that general trends are not observed. The established trends are:
i) Electrode tip life is increased with an increase in welding current to a limit.

ii) Intermediate values of weld force and weld time optimise electrode tip life.

iii) Electrode tip life is decreased when coating thickness is increased.

iv) An included angle between 90 and 120° optimises electrode geometry. Tip diameter is generally dictated by weld requirements.

v) The presence of aluminium, even in small quantities in the alloy layers which grow on the electrode tip as welding proceeds alters the weldability of the coated steel and severely reduces electrode life. Brittle pockets containing aluminium form in the alloy layers which are easily broken away leaving a pitted electrode face. The order of decreasing rate of degradation in Al-45%Zn followed by hot dipped galvanised, the galvannealed and electrogalvanised. These steels have a decreasing aluminium content except in the case of galvanneal in which a high iron content is believed to stabilise the diffusion rates of aluminium and zinc.
CHAPTER 3

PHYSICAL VAPOUR DEPOSITION
3.1 INTRODUCTION

Most materials used in modern technology have differing requirements for surface and the bulk properties. The main requirements of the bulk are usually UTS, toughness, stiffness etc whereas the surface properties are usually corrosion resistance, wear, low friction etc. It is difficult to select a material which meets the required criteria for both, therefore the need for surface coatings arises. There is a range of coating methods available from various spraying techniques, electroplating, chemical vapour deposition (CVD) and physical vapour deposition (PVD). While each has its own advantages and disadvantages, evaporation and sputtering are currently the most widely applied forms of PVD. The potential of these PVD processes is being realised because of the ability to deposit a wide range of materials of uniform thickness at deposition rates which for some materials reach 70\(\mu\)m/min [38]. PVD is used to deposit coatings of metals and metallic alloys, ceramic compounds such as superconductor thin films, metal/ceramic and metal/polymer layered composites and semi-conductors onto substrates of virtually any material. Applications of PVD coated materials are found in every facet of modern product and manufacturing technology from microelectronic circuit fabrication to decorative coatings and tribology.

PVD is generally defined as a process used to deposit thin film coatings of physically generated atoms or molecules onto a substrate in a vacuum environment. There are currently many different PVD processes which can basically be divided into two; evaporation and sputtering. This categorisation is based on the physical mechanism used to produce the vapour flux of depositing individual atoms or molecules. Common to all PVD processes are:
1) A high vacuum chamber with low impurity gas levels and the provision for feeding controlled flow rates and/or maintaining partial pressures of one or more working gases such as argon or nitrogen.

2) A coating material source(s) capable of providing a well controlled quantity of vapour flux.

3) Carefully and reproducibly prepared substrate surfaces.

4) A substrate mounting assembly which controls substrate temperature and distance/orientation to the coating source.

The performance requirements placed upon high performance materials often exclude metallic and ceramic materials as suitable and hence provide the stimulus for the development of composite type materials using PVD thin films and coatings. In addition, the push to reduce manufacturing and material costs has also encouraged the applications of PVD technology. As a result, there is much interest in the field of PVD in the areas of process development and the development of improved materials with unique microstructures and properties.

This review will concentrate on summarising the current understanding of both sputtering and evaporation, in particular, unbalanced magnetron sputtering and filtered arc evaporation (the coating technologies employed in this work). This will include equipment design and operation, effect of process parameters on coating structure and properties, suitable coating materials and draw a comparison between sputtering and evaporation. A brief description of vacuum evaporation and sputtering is given below.

In simple sputtering a target of the coating material, and the substrate are contained in the vacuum chamber. The chamber is evacuated to a base pressure of $10^{-2}$ mTorr or less, and then an inert working gas, usually argon is leaked into the chamber to give a coating pressure of 10 mTorr or more. The target which is isolated from earth is negatively biased to 3000 volts [38]. This produces a glow discharge, the argon ions
produced are attracted to the target at high energies, and target atoms are ejected by a momentum transfer process. The ejected atoms arrive at the substrate and condense to form the coating.

Figure 3.1. Schematic of a planar-diode sputter deposition system [38].

In vacuum evaporation, an evaporation source and the substrate are contained in a vacuum chamber. The chamber is evacuated to a pressure usually less than $10^{-2}$ mTorr. The vapour source is either a resistance or induction heated crucible, a resistance heated filament or foil or an electron beam gun depending on the melting point of the material to be evaporated. This is energised to evaporate the charge and the vapour atoms travel in straight lines to condense on the substrate.
3.2 SPUTTERING

3.2.1 Introduction

In the process of sputtering highly energetic ions or neutral atoms strike the surface of a solid substrate causing ejection of one or more atoms or molecules by momentum transfer. The high energy particles are usually ions (and energetic neutrals) of an inert gas which are created by forming an abnormal glow discharge in argon. These ions strike the cathode and release material from the cathode surface usually in atomic form. The ions from the cathode will collide with any surface placed near it and result in it being coated. This is called 'sputter deposition'. Typically about 1% of the bombarding energy contacting the target produces sputtered particles while about 75% causes target heating and the remainder causes the emission of secondary electrons from the target. The sputtering yield which is defined as the number of target atoms per incident particle, depends on the target material, the bombarding surface, the energy of the
incident particle and the angle of incidence. The charge of the incident particle and the
temperature of the target have no effect on the sputtering yield. The process is widely
used due to its simplicity and sometimes superior capability over evaporation such as
alloy film deposition. In addition sputtering is a mechanical process while evaporation
is a thermally activated process. Evaporation kinetics are controlled by material
parameters such as the melting point and have an exponential relationship with
temperature so minor temperature fluctuations can result in major evaporant flux
changes. Sputtering allows greater control of the resulting atom flux with much less
variation in flux between different materials identically sputtered due to the mechanical
momentum transfer nature.

3.2.2 Equipment and Design

A typical sputter-deposition system consists of a high-vacuum pumped chamber, a
target which is the coating material source, a substrate holder, a working gas supply and
a high voltage RF or DC power supply. The target is generally in the form of solid
sheet or rod and is negatively biased to a large RF (13.56 MHz) or DC potential usually
-3000V. The target, therefore becomes a cathode relative to the earthed vacuum
chamber and substrate holder. The negative target voltage will initiate the formation of
a plasma provided the pressure in the chamber is about 7.5 m Torr. Usually the target
and the substrate holder are of equal size, flat, parallel and closely spaced.

Quite often modifications are made to the above standard system to enhance the
sputtering system. For example substrate heating or the application of a substrate bias
voltage to improve adatom mobility (surface diffusion), addition of a reactive gas to the
plasma to deposit a compound such as titanium nitride or the use of multiple sputter
targets to create multi layer or chemically graded films.
3.2.3 Coating Process

At the target surface the impinging inert gas ion/neutral must transfer sufficient kinetic energy to a target atom to overcome the local bonding forces and remove an atom from the target surface. The collision of an energetic ion/neutral results in a momentum transfer to the atoms within a few atomic distances from the impact site. Any sputtered atom will have acquired a sufficiently large momentum component oriented away from the target surface. Atoms sputtered from a surface will have energies in the 10 to 40 eV range with increasing energy as atomic number of the sputtered atom increases. Increasing the energy of the bombarding ions does not appreciably increase the average sputtered atom energy. Below about 25 eV no sputtering occurs while above this level sputter yield increases steadily with increasing ion energy [39].

3.2.4 Sputtering Methods

While there are several different sputtering systems, the two most common are planar diode sputtering and magnetron sputtering, both are used commercially and in research and development.

3.2.4.1 Planar Diode Sputtering

The name is derived from a sputter source which consists of two flat, parallel electrodes, one being the target electrode and the other being the substrate or substrate holder. The target electrode is usually about 10 to 30 cm diameter and in a DC system will be negatively biased (cathode). The substrate electrode acts as the anode in this diode arrangement and is either grounded or negatively biased to a low voltage of -100V if low energy ion bombardment of the growing film is desired.
Planar diode sputtering systems display the following characteristics

1) The current densities at the cathode are low causing low sputter rates
2) The working gas pressures are high, resulting in collision dominated transport of ions and neutral atoms.
3) The substrates are in contact with the plasma and are constantly being bombarded with energetic particles leading to significant heating (uncoated substrates may reach 500°C) [38]

The following is a typical set of planar-diode operating parameters [39]:

- a cathode current density of 10 A/m².
- a cathode voltage of -3000 V
- a working gas (Ar) pressure of 75 m Torr
- a cathode to substrate separation of 40 mm
- a deposition rate of about 60 nm/min

A high working gas pressure is needed to sustain the glow discharge plasma which results in a short mean free path for ions accelerating out of the plasma toward the cathode meaning that multiple ion-neutralisation collisions occur. The high gas pressure and corresponding multiple scattering events for a sputtered atom mean that much of the material sputtered from the target is deposited somewhere else than on the substrate due to diffusion through the vapour. A collision dominated transport of sputtered atoms reduces the efficiency and increases the cost of the deposition process. This is illustrated in Figure 3.3.
Figure 3.3. Schematic diagram of different processes occurring in conventional planar diode sputtering [40].

3.2.4.2 Magnetron Sputtering

A highly successful alternative method of increasing the degree of ionisation over the planar diode is the magnetron. Magnetron sputtering is a very controllable process which permits relatively high deposition rates and significantly lower substrate heating when compared to conventional sputtering as well as uniform deposition over large substrate areas [41-43]. Consequently, magnetron sputtering is competing for applications formerly reserved for evaporation. The deposition rate is linearly dependent on target power and with, in general, low substrate heating[44, 45]. The operation of magnetrons rely on influencing the motion of electrons with an applied magnetic field. While this motion is described by a simple equation,

\[ m \frac{dv}{dt} = qE + q(v \times B) \]  

Eqn 3.1
where $m$, $q$, and $v$ are the mass, charge and velocity respectively of the charged particle, i.e. electron moving in the electric field $E$ and magnetic field $B$. The actual motion can be quite complex and difficult to visualise [46]. The lowest achievable pressures are employed to run deposition plasmas to minimise the reflection of sputtered atoms back towards the target, and the scattering of the sputtered atoms on their path to the substrate. Such low pressures cause the cathode glow region to expand and fill most of the chamber, sustained by ionisation produced by energetic secondary electrons which have been accelerated across the cathode sheath from the sputtering process. Most of the applied voltage appears over this sheath which accelerates the electrons to enter the plasma with high energies (300-500 eV). Magnetically enhanced glows improve the sputtering process by increasing the path length of such electrons so that they lose all of their energy to ionising collisions in the plasma before they reach the anode or walls. A magnetic and/or electrostatic trap is required over the cathode surface to achieve this. The magnetron source is a diode source modified by the addition of a moderate strength magnetic field to trap secondary electrons emitted by the cathode and accelerated to high energies near the cathode. The energetic electron spiral in the magnetic field which increases their path length along which they continue to cause ionisation of neutral atoms. The intense ionisation is responsible for rapid sputtering and rates of deposition of 1.8 μm/min have been reported [39]. The increased ionisation allows the glow discharge to be sustained at typical working gas pressures of 1.1 m Torr, a reduction of about 50 times below that required for a planar diode. Lower target voltages than for a planar diode are employed (300-600V) [47].

To maintain electrical neutrality in the conducting plasma, the ions also move with the electrons towards the substrate. The substrate when biased will behave like a conventional plasma probe. At all bias voltages less than the anode potential, a constant ion flux will leave the equipotential plasma, to be accelerated across the substrate sheath to the substrate. Also arriving at the substrate is a flux of non-thermal energetic electrons, which must have enough energy to overcome the sheath potential to reach the
substrate. Important parameters are the current measured at -100V bias, which should be all ion current since all electrons are repelled, the self bias voltage, when the number of electrons collected equals the number of ions, and the electron current at zero bias voltage [46].

The significant reduction in operating pressure results in magnetron sources functioning more efficiently than planar diode sources. The increased mean free path reduces the possibility of a sputtered atom being involved in a collision and causes close to line of sight deposition. A greater proportion of sputtered atoms are deposited onto the substrate due to reduced scattering but this also causes more variability in coating thickness. This is often overcome by motion of the substrate during coating.

There are a variety of geometrical arrangements which give efficient magnetron effects. The two most widely used are the planar magnetron and the unbalanced magnetron. The basic configuration of a planar magnetron is shown below.

![Diagram of a magnetron](image)

**Figure 3.4.** The magnetic field in a magnetron traps the electrons which drift around the magnetic tunnel [40].

A water cooled cavity lies behind the cathode and contains the magnetic assembly which produces the characteristic tunnel over the cathode. The operation involves the
trapping of the secondary electrons by the magnetic tunnel, which must be closed to accommodate the various drift modes. The secondary electrons spiral back and forwards along field lines, with reflections as they approach the negative cathode surface and they drift around the magnetron track. As the electrons collide with inert gas atoms, they produce more electrons and ions and are scattered on average outwards, ultimately reaching the anode surfaces with small amounts of remnant energy [46]. The efficiency of the ionisation process in the magnetron cavity allows intense plasma discharges capable of providing high sputtering rates to be maintained at moderate and near constant voltages, even at low pressures. Deposition rates will depend on the radial position of the substrates. Typical operating conditions for magnetrons are [44]:

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cathode current density</td>
<td>200 A/m²</td>
</tr>
<tr>
<td>Discharge voltage</td>
<td>800 V</td>
</tr>
<tr>
<td>Argon pressure</td>
<td>1 mTorr</td>
</tr>
<tr>
<td>Cathode erosion rate</td>
<td>12 A/min</td>
</tr>
<tr>
<td>Deposition rate</td>
<td>200 nm/min</td>
</tr>
</tbody>
</table>

3.2.4.3 Unbalanced Magnetron Sputtering

An unbalanced magnetron configuration is made by adding an extra fringing field to the usual magnetron trap. By placing more magnetic poles on the outer magnetic ring than in the centre an unbalanced configuration is achieved. The motion of the secondary electrons in an unbalanced magnetron field is more complex than in the balanced situation. The electrons are trapped initially by the magnetron tunnel, and move back and forth along field lines while drifting around the track. After suffering many ionising collisions, the secondary electrons will leave the primary magnetron trap, to enter the fringing field region. Even though the field is small in this region it is of sufficient strength to prevent the electrons moving across the field lines to the chamber walls or the anode as the electrons now have little energy. The field configuration is a
magnetic bottle with an electrostatic reflector (the cathode) at one end. To leave the trap, the electrons have to move towards the substrate. For unbalanced magnetrons, over 90% of the electron current flows through the substrate.

![Diagram](image)

Figure 3.5. The magnetic field in an unbalanced magnetron is different from the balanced magnetron beyond the magnetic tunnel [40].

3.2.5 Effect of Substrate Bias

The growth of vapour and sputter deposited thin films at low substrate temperatures produces films with many defects which affect the physical properties of the material. This defective structure is caused by the geometric shadowing of regions due to the finite size of the deposited atoms. The structure depends on substrate preparation, angles of incidence, energies and rate of arrival of incoming particles and on any movement of the atoms after deposition due to thermal or bombardment induced motion. Ion bombardment of the growing film can significantly alter the microstructure of the film by promoting atomic motion during deposition.
When the substrate is biased negatively, the electrons from the plasma are repelled and the heating effects associated with electron bombardment are reduced. As the negative bias is increased the amount of ion bombardment of the substrate and growing film increases, which increases the temperature of the substrate. The advantages of ion assisted deposition are increased hardness [48], improved adhesion, and higher density films [49] with a fine grained microstructure. Adhesion is improved by [50]

1. Desorbing loosely bonded impurity species.
2. Generating an increased density of nucleation sites for coating growth.
3. Overcoming activation energies for forming interface compounds
4. Promoting a compressive stress state in coatings and
5. Enhancing adatom surface mobility.

When a bias is applied to a substrate, particle bombardment occurs which results in back-sputtering and the deposition rate is decreased. The application of a negative bias will also lead to deposition of atoms of the substrate holder and the mask onto the substrate as well as substrate heating.

3.2.6 Film Morphology

Thornton [39] has extended a microstructural zone model originally devised by Movchan and Demchishin [51] for evaporated films to include gas pressure/ion energy which makes it equally applicable to sputtered coatings (Figure 3.6). Distinct microstructural zones are found to be roughly defined by temperature to melting point temperature (T/T_m) ratios and gas pressures. At low temperatures of less than 0.15 T/T_m the coating atoms have limited mobility and the structure is columnar, with tapered outgrowths and weak open boundaries. An open columnar structure results from a low substrate temperature which prohibits sufficient adatom surface diffusion to compensate for shadowing of the intercrystallite valleys by the crystallite peaks. A
fibrous structure, Zone T occurs for temperatures between 0.15 and 0.45 T/T_m. Although the structure remains columnar, the columns are finer, and more dense with parallel boundaries, normal to the substrate surface primarily due to the increased surface diffusion. These boundaries are stronger than those for Zone 1 although there is still a high defect density. At 0.45 to 0.75 T/T_m the films are fully dense due to rapid surface diffusion with a very coarse columnar microstructure. Extensive coarsening is largely due to effects of bulk diffusion. At substrate temperatures above 0.75 T/T_m the structure is of large equiaxed grains or columnar grains with low defect densities and hence low internal stresses because the high temperatures allow development of stress free grains which form easily by recrystallisation.

Figure 3.6. Thornton zone model showing microstructure as a function of relative substrate temperature and chamber pressure [52].
3.3 EVAPORATION

3.3.1 Introduction

Deposition of materials via the process of evaporation involves a heated source material which under high vacuum at sufficient temperature liberates atoms or molecules by sublimation or vaporisation of the solid or liquid material placed in the source. The vapour stream is transferred from the evaporation source, through the vacuum with little scattering and deposits onto the substrate. These particles then condense on the substrate surface and film surface, followed by rearrangement of atoms or modifications of chemical bonds on the surface. An evaporation system consists of a vacuum chamber, a vacuum pumping system, a gas inlet system for chamber venting, an evaporation source(s) and a specimen holder.

Evaporation of a material requires energy to be supplied to atoms or molecules of the condensed phase to overcome attractive interatomic or intermolecular forces and provide kinetic energy to vapour species leaving the surface of the material. Thermal energy which enhances the thermal motion of species at the surface of a material to be evaporated is supplied by heating the source material at sufficiently high temperatures to liberate large amounts of atoms or molecules from the condensed phase.

3.3.2 Equipment and Design

Vacuum chambers are generally constructed from a non-magnetic stainless steel usually in the shape of a rectangular box or cylinder with multiple doors or ports with adequate access for loading substrates, coating materials and general cleaning and maintenance. The exact design of the chamber is governed by the type, size and number of samples to be coated. Doors are usually sealed with rubber ‘O’ rings but where ultra high vacuums
are required then soft metal copper gaskets are preferred. A fixture to support and position the substrate during deposition may be a rod or plate or it may move in order to improve coating thickness uniformity over complex shaped substrate surfaces. Vacuum evaporation is a ‘line-of-sight’ process and for substrates with intricate shapes complicated movements are required to ensure a uniform coating. Evaporation systems are equipped with heating and cooling facilities as temperature readily affects substrate cleanliness, film adhesion, residual stress and microstructure.

The pumping system used must be capable of rapid pump down to the required vacuum (10^{-3} Pa/7.5 \times 10^{-3} \text{ mTorr}) and maintain it during deposition. This is usually achievable using a roughing pump/high vacuum pump combination. Most vacuum systems use an oil diffusion pump backed by a mechanical pump incorporating a liquid nitrogen cooled baffle or trap between the diffusion pump and the chamber to eliminate oil vapour contaminating the coating chamber (Figure 3.7). Practical pump down times widely vary from theoretically calculated times since outgassing from chamber walls that are covered with thick powdery deposits can be great and is increased by the radiant heat from the vapour sources.
3.3.3 Evaporation Sources

An evaporation source provides a controlled flux of vapour from a liquid by evaporation or from a solid by sublimation dependent on the relationship between the vapour pressure, temperature and melting point. The material to be evaporated is contained by a material with which it does not react, otherwise contamination of the coating by impurities occurs. Types of evaporation sources most commonly used are resistance heating (including crucible sources), electron beam heating and cathodic arc.

3.3.3.1 Resistance Heating

The source, usually a resistance heated wire or metal foil must have sufficient power density to attain a temperature which will cause evaporation of the coating material.
3.3.3.2 Electron Beam Sources

There are two main types of electron beam sources those in which the source of electrons is a hot filament and those in which the electrons are generated within a plasma. Electron beam sources allow for controlled evaporation via a large range of power densities and the extremely high temperatures achievable. The source material, of virtually any ceramic or metal is contained in a water cooled copper hearth, since the material in contact with the copper hearth doesn't melt, no contamination of the source occurs. The disadvantages come in dealing with differences in vapour pressure among different elements in an alloy source material, preventing expulsion of macroscopic droplets from the melt pool because of transient excessive heating or entrapped gas, and maintaining a constant evaporation rate. Electron beam sources are used for high melting point metals such as titanium.

3.3.4 Cathodic Arc

3.3.4.1 Introduction

Arc evaporation sources operate at low voltages and high currents allowing efficient evaporation of material through multiple arc discharges across flat metal substrates which act as the cathode. An intense plasma is established adjacent to the cathode
which causes a high degree of ionisation of the metal and non metal flux. The simple design and operation of the source allows a range of source sizes to be used. There is no effective liquid on the source surface as melting occurs rapidly, so any source orientation is possible. Cathodic Arc Physical Deposition (CAPD) is characterised by

1) A very high percentage of ionisation of the emitted vapour, 30-100%
2) The emission of ions that have multiple charges.
3) High kinetic energy of the emitted ions, 10-100eV.

This yields many benefits in terms of coating quality and appearance. They are

1) High film adhesion and density.
2) High deposition rates and superb coating uniformity.
3) High quality stoichiometric reacted coatings over a wide range of processing conditions.
4) Low substrate temperatures during deposition.
5) Retention of alloy composition from target to deposited film.

CAPD has established itself to be a high deposition rate process with superior film quality for hard coatings. Promising results have been reported for TiN, CrN, ZrN, Ti C,N, and Ti Al,N [54]. However, of major concern in this process is the formation of micron and larger size droplets called 'macroparticles' which deposit on the substrate causing a rough and dull coating undermining the integrity of the coating especially in decorative and corrosion protective coatings. Efforts to overcome the problems associated with macroparticles has seen the development of a range of techniques the most successful being the Filtered Arc Deposition System (FADS).
3.3.4.2 Arc Ignition

A cathodic arc plasma deposition (CAPD) system includes a vacuum chamber, cathode, arc power supply, arc igniter, anode, and a substrate power supply (Figure 3.8). An arc is ignited in vacuum interrupters when the electrodes are drawn apart to open the circuit. The most commonly used method is to make momentary contact to the target surface with a contactor, the open circuit voltage of the arc power supply being the potential difference between the target and the contactor. This is reliable provided a molybdenum or tungsten contactor is used to prevent the possibility of the contactor becoming welded to the target as the surface temperature of the target increases. The arc moves in a random fashion across the source material unless magnetically guided and causes evaporation in a continual series of flash evaporation events. The eroded material sustains the arc. The cathode spot is a neutral plasma which ranges from 1 to 20 µm in diameter and is an intense source of photons, electrons, metal atoms, and micron sized droplets of cathode material. Electron atom collisions result in the formation of positive ions in a region close to the cathode spot surface. Some of these ions are accelerated back to the cathode and may be responsible for initiating new arc sites. Typical arc voltages and currents range between 15 to 50 volts and 30 to 400 amps, respectively.
Figure 3.8. General construction of cathodic arc evaporation sources [55].

The cathode spot causes very rapid heating of the surface in its immediate vicinity and emits material in a manner similar to flash evaporation. The high local current density rapidly heats a small volume of the target surface, explosive evaporation occurs, and the cathode spot simultaneously migrates to another location to repeat the process. The flux emitted from an arc source consists almost entirely of ions and microdroplets. A CAPD system results in a high degree of ionisation (as high as 100%) of the emitted material and neutral metal vapour constitutes only a small fraction (1-2%) of the mass transfer. The majority of microdroplets are emitted from the cathode at low angles (0 to 30°) while the ions are ejected predominantly in a direction perpendicular to the plane of the cathode (Figure 3.9).

The anode in the discharge circuit can be either an isolated electrode or the vacuum chamber itself. In the latter case the chamber is connected to the positive side of the arc
power supply and the internal components are grounded. For a discrete anode, the electrode is isolated from the vacuum chamber and connected directly to the positive side of the arc power supply. This arrangement has the effect of deflecting the path of the ions emitted from the cathode. It is possible by careful selection of anode size and position relative to the cathode to deflect some part of the coating flux which would otherwise be deposited onto the chamber walls. This results in increased deposition rate, improved target utilisation and the anode collects material that would otherwise be deposited on the wall of the chamber which reduces the need for frequent maintenance.

Figure 3.9. Cathode spot region of a vacuum arc [56].

The mechanism of material erosion from the cathode is that of crater formation which has been attributed to:
1) Intense Joule heating and resultant explosive evaporation due to the high current
density in the cathode spot.
2) Fracture of the cathode material by thermoelastic stresses.
3) Expulsion of material by the local electric field and
4) Expulsion of material resulting from the plasma pressure.

3.3.4.3 Microdroplets

The emission of microdroplets by cathodic arcs is of great significance in the deposition
of thin film as the microdroplets become macroparticles in the deposited film.
Macroparticles are the primary reason that CAPD films are restricted to tribological
applications. Microdroplets range in size from the sub micron to several microns in
diameter. The size and population of microdroplets is affected by the choice of cathode
material, operating parameters, and designs of the sources that reduce or eliminate
them. Materials with higher melting points emit more ions and fewer microdroplets.
Once the cathode material is selected, the number and size of microdroplets is affected
by cathode to substrate geometry, arc current, magnetic field, gas species, and pressure.
The geometry of the coating system affects the concentration of macroparticles on the
substrate as microdroplets are emitted at low angles up to 30° to the cathode surface.
Lower arc current reduces the size and concentration of microdroplets emitted while
higher reactive gas pressure has a similar effect. Selecting the optimum operating
conditions reduces the effect of macroparticles although cannot totally eliminate them.
The emission is heaviest from low melting point materials and from slow moving arcs.

Two theories exist to explain macroparticle emission. McClure [57] has suggested a
theory based on plasma emission where ions from the ion cloud directly above the
cathode spot are accelerated towards the liquid surface of the active cathode spot. The
vapour jet recoil force presses inward on the molten metal and material is pushed
towards the edge of the crater leading to the observed distribution of macroparticles.
Boxman and Goldsmith [58] proposed a theory based on explosive emission where the electron emission is concentrated on small surface protrusions which are rapidly heated by electron emission until they eventually explode at a peak pressure of 20 GPa. The impact from the explosion generates other surface defects and other sites for the process to be repeated.

Microdroplets can be eliminated by using electrostatic/magnetic ion optics to separate the ions from the microdroplets and hence deposit a macroparticle free coating. The most commonly used method of macroparticle elimination makes use of low angle shielding to intercept the flux of microdroplets although this significantly reduces the deposition rate. An increase in arc spot velocity induced by an applied magnetic field known as steered arc [59] decreases the period that the spot remains stationary and hence reduces the volume of material melted and explosively emitted from the crater.

Another method uses a diffuse arc in which the discharge extends over the surface of the target and the target is in a molten state. No microdroplets form in this mode. Aksenov[60] developed a system to eliminate macroparticles using a plasma optic system to deflect the path of the ions in the emission flux. The plasma optic comprised a curved metal tube having a longitudinal magnetic field of several hundred Oersteds and a radial electric field of tens of volts. The ions are separated from the microdroplets allowing the production of macro-free coatings. Measurements of the radial ion current density profile at the end of the plasma optic system indicated a high degree of ion focussing along the axis of the system (Figure 3.10). The paths of neutral atoms and microdroplets are unaffected by the magnetic and electric fields and followed linear paths and are collected on the inner surface of the duct. Further work has seen the development of the filtered arc deposition system based on the earlier work of Aksenov.
3.3.4.4 The Cathodic Arc Source

The cathodic arc source consists of a source material (cathode), an anode arrangement, an igniter and a means of confining the arc spot to the surface of the cathode. There are three primary methods to control the arc, the absence of which will allow the arc to migrate at random over the surface. Any discontinuity will trap the arc leading to rapid erosion at that point producing a crater. Some sources employ a passive confinement border to keep the arc on the surface of the target, boron nitride being the preferred material. Another method employs boundary shields which extinguish the arc when it leaves the surface of the target [62]. Sources using boundary shield confinement are limited to a few inches in diameter which limits coating uniformity. A further difficulty with such sources arises from the need to repeatedly re-ignite the arc, since it is extinguished each time it leaves the target surface. Film quality is adversely affected by each re-ignition event where an intense pulse of microdroplets is emitted from the source, resulting in a high concentration of macroparticles. Passive confinement borders allow the production of larger area cathodes which provides good coating thickness uniformity over large area substrates. Any melting of the cathode induced by
the arc spot is restricted to microscopic areas, the cathode therefore remains solid and can be mounted in any orientation. In addition the passive border does not extinguish the arc, hence the source remains ignited for long periods and re-ignition is rare.

The third method of controlling the arc is to use a magnetic field to guide or steer the arc across the target surface (Figure 3.11). The benefits are more uniform deposition and some reduction in microdroplet emission resulting from the increased velocity of the arc spot over the cathode surface. A simple stationary magnetic field coil is positioned behind the target to both guide the arc and to increase the velocity of the arc spot over the target surface. The resultant motion of the spot produces a significant improvement in deposition uniformity, since the arc can be steered over the full area of the source. A development of this incorporates several magnetic coils arranged one within another. By switching the power between the coils and thus capturing the arc in another field loop, it is possible to broaden the erosion groove and hence considerably increase target utilisation.
3.3.4.5 Coating Process

As for all deposition processes, pre-cleaning is of vital importance to ensure good adhesion between the substrate and the coating. Grease and oil can be removed can be removed in a vapour degreasing system while oxides are removed in either alkaline or acid solutions followed by ultrasonic agitation.
Once the parts to be coated are loaded the chamber is pumped down to a predetermined level. High energy ion bombardment using ions from the arc source are used to clean the substrates further. The arc source is ignited and a high negative bias voltage (400 to 800 Volts) is applied to the substrate. The ion-bombardment sputter cleans the surface of the substrate removing any residual thin oxide layer or foreign contaminants. The substrate is also heated by this ion bombardment and modified by ion induced damage. The bias voltage is reduced to its normal coating level (50 to 200 Volts) and the arc current is adjusted to its deposition level, and the coating process begins.

3.3.5 Temperature Control

Thin film deposition relies on elevated temperatures to enhance film adhesion, control the morphology of the growing film and to activate the reaction between metal and reactive gas in a reactive deposition process. Initially, coating is conducted at as high a temperature as the substrate can tolerate to ensure good adhesion, although high ion energies reduce this requirement. As coating thickness increases the temperature is reduced because film morphology is more a function of ion bombardment than of temperature.

The high energy density at the substrate produces rapid heating during the high bias stage and during deposition, especially for a thick coating. To avoid overheating and keep the substrate temperature within narrow limits the total power can be adjusted either by the arc current or the bias power.

One unique advantage of CAPD is its ability to deposit fully reacted hard coatings at low temperatures (150-200°C) whereas other PVD processes require temperatures in excess of 400°C to ensure full reaction. This result is derived from higher ion energies and the higher degree of ionisation achieved in the CAPD process [62].
3.3.6 Film Morphology

During the early stages of deposition, growth occurs at discrete nuclei until a continuous surface film forms. Outward growth then proceeds to produce in many cases a columnar structure. The coating microstructure which develops is largely based upon substrate temperature which controls the key growth mechanisms of adatom surface diffusion and bulk diffusion, surface roughness, generated shadowing of surface regions from the line of sight evaporated atoms, the rate of deposition and the angle of incidence of the vapour stream and the gas pressure. Higher substrate temperatures increase both surface and bulk diffusion kinetics since the activation energies for these processes are both related to the melting point of the bulk coating material. At high temperatures where surface diffusion is rapid, the effects of any topographic shadowing are decreased and a smoother film results. High temperatures also promote recovery, recrystallisation, and grain growth processes within the growing film, thus producing a more dense and defect free coating.

Evaporated coatings are very similar to those obtained by sputter deposition and follow the zone growth model originally devised by Movchan and Demchishin [44] and then expanded upon by Thornton [39]. Thornton's model (see section 3.2.6) was the result of work which demonstrated that sputter deposited coatings were affected by an increase in argon pressure in the same way that a decrease in deposition temperature would reduce $T/T_m$. Reduction of the $T/T_m$ ratio reduces adatom mobility since this is a thermally activated process which is exponentially related to the temperature. An increase in pressure causes more collisions of the evaporated atoms to occur prior to impacting the substrate. The energy of the impacting particles is severely reduced which thereby reduces the energy deposited in the surface. This reduces the local substrate temperature and hence reduces the adatom mobility.
Modification of the microstructure and chemistry of an evaporated film is achieved by continuous low energy ion bombardment before and during the coating process. The continuous collisional mixing occurring in the upper few atomic layers by low energy bombardment is an effective way to achieve high adatom mobilities at low substrate temperatures. Furthermore, the incorporation probabilities of high vapour pressure or low solubility elements are increased.

### 3.3.7 Adhesion

Adhesion is considered one of the most important prerequisites of engineering coatings for use in tribological environments. If the interface adhesion is poor coating detachment may occur and lead to premature failure. The high deposition energies involved in CAPD results in strong atom-atom bonding, surface intermixing at the coating substrate interface and elimination of voids at the interface producing excellent adhesion. The high bias applied to the substrate to sputter clean the surface prior to coating also serves to heat the substrate further improving adhesion. Figure 3.12 shows on a molecular scale the variation between a high energy coating such as filtered arc compared to a low energy coating such as electron beam evaporation. Low energy coatings are characterised by atoms which stick where they arrive due to low mobility, resulting in a poor density coating filled with voids and impurity atoms as in Figure 3.12a. In Figure 3.12b, the positive ions are attracted to the negatively charged substrate with sufficient energy to clean off surface atoms and diffuse to low energy sites resulting in higher density coatings with less contamination.
In addition, the high energy bombardment stage deposits a thin layer of the unreacted or partially reacted target material which greatly enhances the adhesion and hence performance due to the better matching of expansion coefficients between the coating and the substrate. The thickness of the interlayer is relatively small (<200 nm) otherwise the interlayer may have a detrimental effect. For example, a titanium interlayer has been shown to lead to substantial increases in adhesion [67-70]. Rickerby [68] has shown that wear resistance is also increased for an increased interlayer thickness. The origins of improved adhesion have been attributed to two factors. (a) Chemical Gettering Effects: titanium reacts chemically at the surface to dissolve weak oxide layers, and (b) Mechanical Effects: the titanium interlayer acts as a soft compliant layer which reduces the shear stress across the coating/substrate interface and hinders crack propagation in the interfacial region. During coating, an increase in adhesion is observed with increasing bias from 0 V to 100 V. Above this level little improvement in adhesion is observed although the coating structure changes from a columnar structure at 0 V bias to a nearly equiaxed structure at 400 V bias. Even though the number of macroparticles in the film was reduced, the deposition rate was also reduced.
3.3.8 Filtered Arc Deposition System (FADS)

Aksenov [60,71,72] originally developed a plasma optic system to deflect the path of the ions in the emission flux. He demonstrated that a toroidal magnetic field may be used to remove neutrals and macroparticles from an arc source. The plasma duct filter is a quarter torus with a magnetic field parallel to the walls of the torus. The equation which relates the transport of a low density plasma along a toroidal field is given by

\[
\frac{r}{u} > \frac{1}{v_0}
\]

Eqn 3.2

Where \( u = \frac{Mc^2}{ZeRH} \) \( u \) is the velocity of the centrifugal ion drift in the field, \( M \), \( Z \), and \( v_0 \) are the mass, charge, and longitudinal velocity, respectively, of the ions, \( R \) is the radius of curvature of the magnetic lines of force, \( l \) the length of the toroidal field, \( r \) the radius of the plasma duct, \( c \) the speed of light, \( e \) the electronic charge, \( H \) magnetic field strength, and \( E \) electric field strength.

The magnetic plasma duct method of filtering macroparticles from arc discharges is successful at obtaining a low energy, high intensity particle beam. It is the most effective method to date to filter macroparticles although when used in conjunction with some of the other methods discussed it proves even more successful.

The filtered arc [73] has been used to deposit a wide range of materials (Figure 2.13), such as aluminium, titanium, vanadium, copper, niobium, zirconium, tantalum and molybdenum at deposition rates of up to 40 \( \mu \)m/h [74]. Compound films such as titanium nitride and molybdenum nitride as well as VN, ZrN, NbN and Fe3N4 have been prepared by introducing reactive gases into the deposition chamber. In the case of filtered arc this is possible without poisoning the cathode since the source is situated along the duct, away from the site where the gas is introduced. Highly transparent
Oxide films for optical systems have been deposited by introducing oxygen to the chamber [74].

The primary attraction of the filtered arc in addition to the high quality metal and compound films is the extremely high rates of deposition achievable. It is expected that future developments will result in multiple cathodes and industrial scaling of the technology.

Figure 3.13. Schematic representation of the filtered arc deposition system.
3.4 COMPARISON: Sputtering vs Evaporation

The principal differences between sputtering and evaporation are:

1) Sputtering offers a wider range of coating materials.
2) A higher percentage of ionisation in the metal vapour and high fraction of metal ions compared to gas ions in arc evaporation provides higher deposition rates.
3) Evaporation provides less substrate heating per atom deposited.
4) Sputtering provides better coating adhesion.
5) Sputtering provides more dense coating microstructures.
6) The presence of macroparticles in arc evaporation.

Sputtering allows the deposition of virtually any material and although the range of materials suitable for evaporation coating is substantial, difficulties are encountered as the melting point of the coating material increases. Maintaining uniform composition while evaporating alloys and compounds can be a problem. Sputtering however, is limited by low deposition rates and extensive substrate heating due to ion bombardment. The emergence of magnetron sputtering has to some extent relieved some of these problems by increasing deposition rates and reducing substrate heating. Magnetron deposition rates are still generally lower than those for evaporation. One major attraction of magnetron sputtering is the ability to uniformly deposit coatings over large substrate areas. This then favours comparably with evaporation on a deposition per unit area basis due to the large area ability of magnetrons. Large areas can be coated by evaporation but it generally requires multiple evaporation sources which causes difficulty due to the extreme sensitivity of the evaporation rate to the electric power input to the heating source [75].
The majority of techniques used to deposit hard coatings for industrial applications have stemmed from sputtering and arc evaporation. Variations in the two methods originate from differences in the process of particle emission from the target material. In sputtering, the accelerated ions (of 0.2 - 1.0 keV energy) strike the target surface, and the target atoms are emitted by momentum transfer. In arc discharge, the metallic particles are evaporated from a molten pool where power densities of $10^{10}$ W/m$^2$ are concentrated. The emitted species in sputtering exhibit energies of 10 eV per sputtered atom, while in arc evaporation they are 0.1 to 1.0 eV per metallic atom and about 50 eV per ion of evaporated material. The ionisation energies are also observed to vary widely with about 1 to 10% of the supplied energy resulting in sputtering and about 80% in the case of Ti evaporation. These variations in ionisation energy and particle energies influence the growth of the film in very different ways.

Vyskocil et al [76] compared the number of sputtered atoms per unit time with the number of evaporated atoms per unit time and concluded that evaporation produces four times the number of atoms as sputtering per unit time for the same target power. There is also a significant variation in the efficiency of utilisation of energy delivered to the cathode in both systems. The power loss on target is 90 - 95% of input power in magnetron sputtering, in arc evaporation it is only 30%.

3.5 THIN FILM COATINGS FOR ELECTRODES

The volume of information available through public domain literature is scant. It is suspected that a substantial amount of research is being conducted in industrial laboratories which is not being published. Work which has been published is reported with little regard to detail and has provided no solid foundation for further work. As a
result a thorough systematic investigation of the effect of thin film coatings on the performance of spot welding electrodes is warranted.

Gobez [77] deposited a number of coatings on Cu/Cr/Zr electrodes in order to weld zinc coated steels. Cobalt, tantalum and nickel coatings reduced electrode life whilst TiN and Mo coatings slightly increased wear resistance. No rationale was provided for the selection of coating material, nor was the coating technology specified. Little detail was given in the report regarding substrate preparation and deposition conditions which are considered critical for optimum coating development. In addition no report of failure mode of the coated electrodes was given, which would have helped to identify possible improvements.

In a recent project, TiN was shown to increase the life of Cu/Cr electrodes by 70% when welding an Al-45%Zn coated steel [78]. The coatings were deposited by a commercially available cathodic arc process, with little scope for optimisation of the deposition parameters for this application. Improvement was only achievable when multiple layer coatings were employed to overlap coating impurities such as pinholes.

In 1984 the Toyota Motor Company [79] released a patent which outlined improvement in electrode tip life by coating an electrode with 20-70 μm of chromium. The patent was general specifying the chromium coating could be deposited by a range of coating techniques such as electroplating, metal spraying, vacuum coating, ion plating or sputtering. No information was provided regarding the improvements which could be achieved using such a coating.

It would appear from the above that a number of coating materials show promise in extending electrode life. Previous work has not endeavoured to match coating properties to the required material criteria and have not optimised coating conditions. Consideration of the coating requirements indicates there must be a trade off between
thermal, mechanical, electrical, chemical and structural properties. It is inevitable that extensive trials need to be undertaken to fully investigate the feasibility of coating electrodes to increase their life when welding metallic coated steels.
CHAPTER 4

EXPERIMENTAL PROCEDURE
4.1 RESISTANCE SPOT WELDABILITY TRIALS

4.1.1 Electrodes

The electrodes used were 90-degree (included angle) truncated cone type electrodes each machined to 5.0 ± 0.5mm diameter. This type of electrode was utilised for weld lobe construction, electrode life tests and all coating trials. The composition of the electrodes tested is typically

<table>
<thead>
<tr>
<th>ALLOY</th>
<th>HARDNESS</th>
<th>ELEC. COND.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu - 0.8%Cr</td>
<td>174Hv20</td>
<td>80% IACS</td>
</tr>
<tr>
<td>Cu - 0.3%Zr</td>
<td>152Hv20</td>
<td>90% IACS</td>
</tr>
<tr>
<td>Cu - 1.0%Cr - 0.05%Zr</td>
<td>160Hv20</td>
<td>85% IACS</td>
</tr>
</tbody>
</table>

Table 4.1 Electrode alloy composition and properties. Electrical conductivities are expressed as a percentage of the conductivity of the International Standard for Annealed Copper (I.A.C.S.)

Figure 4.1 Spot welding electrode and electrode tip configuration
The condition of the cutting tool on the lathe used to machine the electrode tip to the required diameter seriously affects the surface finish of the electrode and hence contact area and ultimately tip life. The cutting tool was sharpened prior to construction of the three weld lobes for each coated steel. This eliminated any variation in surface finish on the electrode tip between tests.

Alignment of the electrode tips is crucial to maintain consistent current density. Carbon paper imprints of actual contact area are obtained by bringing the electrode tips into contact with a sheet of carbon paper between them.

### 4.1.2 Metallic Coated Steels

The materials used for this work were all 0.8 mm base thickness, metallic coated steels, supplied by BHP STEEL, Sheet and Coil Products Division. Three classes of coated steels were investigated, namely:

1. Hot Dipped Galvanised
2. Al-45%Zn
3. Galvanneal

Chemical compositions and coating weights for each steel are presented in Table 4.2. The coating thicknesses are not consistent for all three samples, thus comparison between the three is not strictly valid. Kimchi [37] reports that differences of 2:1 in thickness make only a small difference to electrode life. It is however, acknowledged that increased coating weight has a detrimental effect on electrode life and since hot dipped galvanised and Al-45%Zn products are generally heavier in coating weight than galvanneal, the electrode tip life is indeed shorter with them.
### COATING COMPOSITION

<table>
<thead>
<tr>
<th></th>
<th>Al (wt%)</th>
<th>Fe (wt%)</th>
<th>Pb (wt%)</th>
<th>Si (wt%)</th>
<th>Coating Mass (g/m²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al-45%Zn</td>
<td>56.7</td>
<td>1.66</td>
<td>1.39</td>
<td></td>
<td>150</td>
</tr>
<tr>
<td>Hot Dip Galvanised</td>
<td>0.30</td>
<td>0.13</td>
<td>0.14</td>
<td></td>
<td>275</td>
</tr>
<tr>
<td>Galvanneal</td>
<td>0.17</td>
<td>9.02</td>
<td>0.08</td>
<td></td>
<td>80</td>
</tr>
</tbody>
</table>

Table 4.2  Coating composition of each coated steel used in this investigation.

4.1.3 Spot Welding Apparatus

Weld lobe construction and electrode life testing was conducted on a Schlatter 120 kVA pedestal style, spot welder located at BHP Research, Port Kembla Laboratories. The current values (RMS), electrode force, voltage and energy are monitored via an IBM personal computer which is interfaced with the welding machine. The welding machine controller settings employed throughout this work were: squeeze time 25 cycles, hold time 3 cycles and an off time period between welds of 40 cycles. Squeeze time is the time allowed for the electrodes to reach maximum clamping force. Hold time is the time for which electrodes remain in contact with the workpiece after the current is turned off. The clamping force on the electrodes was 2.5 ± 0.1kN.

4.1.4 Weld Lobe Construction

Weldability lobes were constructed in accordance with the method adopted by BHP Research. In all cases, data for current, force, voltage and energy were recorded for each weld period. Triplicate tests were performed for each electrode material. The lobes are
constructed between 5 and 13 cycles (1 cycle = 1Hz) at 2 cycle increments. This represents the most practical and economical welding schedules for the steels to be used. Each lobe has an upper and lower curve, the upper curve represents the point of expulsion (the point where molten metal is blown away from the weld area interface in a mass of sparks), the lower curve represents the minimum conditions to produce an acceptable weld nugget diameter. The minimum acceptable weld nugget diameter is defined as 80% of the original tip diameter, i.e. 4.0mm. At each weld time the current is stepped up in increments of approximately 0.2 - 0.3 kA until the minimum acceptable weld nugget diameter is reached. The destructive peel test is used to assess average weld nugget diameter. The weld is peeled apart and the nugget diameter measured in the X and Y direction using a Vernier Calliper to obtain the average weld nugget diameter. Once the first minimum nugget diameter has been recorded two subsequent tests in four at the same current level must also display a weld nugget greater than
or equal to the acceptable minimum. The recorded current value on the lobe is the average of
the three current readings. The weld lobes plotted represent the average of three repeated
lobes.

The point of expulsion, for each weld time is found by increasing the weld current in
increments of 0.2 - 0.3 kA until molten metal is blown from the weld interface. Then at the
same current level two subsequent tests in four must demonstrate expulsion. The recorded
current value is the average of these three readings.

4.1.5 Electrode Life Test

An intermediate weld time of 7 cycles was chosen for all life tests as it produces optimum
performance in each electrode. Long weld times create higher tip temperatures and increase
the amount of coating metal diffusion into the electrode, while short weld times result in a
more severe heating and cooling cycle increasing alloy build up which reduces current
density. To avoid expulsion, which results in rapid electrode wear, the welding current was
set just below the expulsion level for each steel sample. Triplicate life tests were carried out
for each material. Each life test is carried out by spot welding continuously on strips 1m long
by 40mm wide, monitoring the deterioration of the electrode tip and weld quality. Peel tests
are conducted at 100 weld intervals. As the weld nugget diameter approaches 80% of the
original tip diameter, peel tests are conducted every 40 welds. Termination of the electrode
life test is established once the averaged weld nugget diameter falls below the acceptable
minimum.
4.2 ELECTRODE TIP EXAMINATION

4.2.1 Scanning Electron Microscopy.

Each electrode selected for SEM examination was sectioned along its axis, mounted and prepared metallographically. The alloy layers which had developed on the electrode tips (Figure 5.5) were examined in a Leica S440 scanning electron microscope (SEM) using the back scattered detector to enhance compositional variations across the alloy layers. The composition of these alloy layers was detected using an Oxford Pentafet Energy Dispersive Spectroscopy (EDS) Unit and analysed by a Moran Scientific Multi Channel Analyser. The analytical technique was standardless semi-quantitative analysis. Contaminants and trace elements were ignored and the results were normalised to a total of 100%. Results are based on the average of at least three spot analyses.

4.2.2 Microhardness Testing.

Electrodes were prepared in the same manner as for electron microscopy. Microhardness testing of the alloy layers was conducted on a Zeiss 80 optical microscope equipped with MHT-4 microhardness system located at BHP Research, Port Kembla Laboratories. The minimum load of 5g was employed for all tests. Results are based on the average of at least three readings. Measurements were obtained for the substrate and both brass layers. However the iron zinc and zinc oxide surface layers were observed to crumble under the force of the indenter due to the brittleness of these layers. No results were obtained for these layers.
A Leco Microhardness tester (M-400-H1) installed at the University of Wollongong was used to measure the hardness of chromium coated copper/chromium electrodes at the completion of weldability tests to investigate plastic deformation of the electrode tips. A load of 100g was employed for all samples. Results for used electrodes are based on the average of at least three readings.

### 4.2.3 X-Ray Diffraction

X-ray diffraction (XRD) was conducted on a Siemens D5000 θ–2θ diffractometer configured in the conventional Bragg - Brentano geometry. The system was operated with Cu Kα radiation (λ = 0.15406 nm), with a LiF post-specimen monochromator. The peak resolution was limited by the 2θ step size of 0.02°. A step time of 10 seconds was used to scan the 2θ from 30-90°. The Cu Kα2 contribution was filtered from the spectra using the Siemens DIFFRAC-AT software package. The truncated cone of each electrode was removed from the tip leaving a cylinder of ~7mm diameter coated with alloy build up at one end. The depth of penetration into the alloy layers was insufficient to detect the presence of all expected phases. Hence, after a full scan the tip was ground down 15-20 μm and then re-scanned.

### 4.3 THIN FILM DEPOSITION BY PVD TECHNOLOGIES

#### 4.3.1 Electrode Preparation

Electrodes were machined on a lathe to a diameter of ~4.6mm prior to being mounted vertically in cold resin, with the tip facing downwards. The process of grinding and
polishing removed material from the electrode tip until the diameter increased to $5.0 \pm 0.5$ mm using $1 \mu m$ diamond spray for the final polish on napless cloth. At all times care was taken to ensure that the electrode remained perpendicular to the polishing wheel, otherwise electrodes brought into contact when welding were not properly aligned causing hot spots which accelerated tip deterioration. The resin mount was removed from the electrodes which were ultrasonically cleaned in acetone and ethanol before being placed in the coating chamber.

4.3.2 Cathodic Arc Evaporation (CAE)

Coatings were deposited onto the copper based alloy electrode tips using a cathodic arc evaporation unit at Balke - Durr, Germany. A commercially used multiple arc chamber was employed to deposit approximately $10 \mu m$ of CrN. Temperature was maintained below $350^\circ$C. No other details on deposition parameters could be obtained.

4.3.3 Unbalanced Magnetron Sputtering (UMBS)

Coatings were deposited onto the copper based alloy electrode tips using an unbalanced magnetron at CSIRO's Division of Applied Physics (the magnet M3 of [41] was used). Deposition was conducted in a diffusion pumped chamber, $300$ mm in diameter and $300$ mm long. After evacuating the chamber to a base pressure of less than $3 \times 10^{-6}$ Torr, the working pressure was set at $0.2$ Pa ($10^{-3}$ Torr) with flowing argon at a rate of $20$ sccm. The magnetron power was $400$W, and a small d.c. supply was used to bias the substrate. A metal plate with an aperture masks the samples. The source to substrate distance was $60$ mm. Samples were sputter cleaned at $-400$V bias for one minute prior to coating at $-100$V for various times.
The sputter chamber was designed for small thin film samples, not bulky electrodes which
created problems achieving suitable coating temperatures. A thermocouple was used to
ensure the electrodes achieved a temperature suitable for adequate adhesion. The highest
achievable temperature in a realistic time of 2 hours was 200°C.

4.3.4 Filtered Arc Deposition System (FADS)

Coatings were deposited onto the copper based alloy electrode tips using a Filtered Arc
Deposition System (FADS) at The Royal Australian Mint. The process parameters chosen
for depositing metallic chromium coatings are listed below. Electrodes were cleaned in a
vapour degreasing bath of simmering trichloroethylene for 2 minutes and finished with 10
minutes in an ultrasonic bath of ethanol. Sputter cleaning of the electrode substrates was
performed for one minute. The bias voltage was set to -900V and the beam current, 100mA.
Samples were heated by a 5 amp radiant heater and monitored via a pyrometer to a
temperature of approximately 350°C. Base pressure was reduced to 7 x 10^-6 Torr, coating
pressure was slightly less once coating began caused by the gettering effect of the chromium
stream. To initiate the coating process the bias voltage was reduced to -100V and the beam
current was increased to 500mA. Temperature was maintained at approximately 350°C while
coating deposition was conducted.
Figure 4.3  An unbalanced magnetron sputtering chamber and pumping system.
Figure 4.4  A filtered arc deposition system consisting of chamber, pumping system, control panel and monitoring devices.
CHAPTER 5

EXPERIMENTAL RESULTS
5.1 UNCOATED ELECTRODES

The results are divided into two sections, Section 5.1 covers uncoated electrodes, Section 5.2 covers PVD coated electrodes. Each section contains weldability lobes, electrode life test results and an investigation of the mechanisms by which electrodes fail.

5.1.1 Weld Lobes

Three weld lobes were constructed for each electrode composition used to weld each coated steel in an effort to reduce any scatter in the data. Each test was conducted in exactly the same manner as the previous test. However, as a multi parameter system it is extremely difficult to maintain all variables exactly the same and hence this amount of scatter was not unexpected. Figures 5.1, 5.2 & 5.3 show the weld lobes for the Cu/Cr, Cu/Cr/Zr & Cu/Zr electrodes respectively against each coated steel. The current values are an average of the three tests. The results obtained are displayed in tabular format in Appendix A. The lobes all exhibit the conventional shape, ie. decreasing weld time required an increase in current and vice versa.

The weld lobes for galvanneal are observed to lie approximately 1 kA below those of Al-45\%Zn for all electrode compositions. The weld lobes constructed for Al-45\%Zn lie 0 - 0.7 kA below those for hot dipped galvanised. The weldable current range for galvanneal, is very narrow, approximately 0.75kA, compared to approximately 1.2 kA for hot dipped galvanised and Al-45\%Zn.
Figure 5.1  Weldability lobes for Cu/Cr electrodes used to spot weld each different coated steel.

Figure 5.2  Weldability lobes for Cu/Cr/Zr electrodes used to spot weld each different coated steel.
Figure 5.3 Weldability lobes for Cu/Zr electrodes used to spot weld each different coated steel.

5.1.2 Electrode Life Data

Figure 5.4 shows that maximum electrode life was achieved when welding galvanneal steel, irrespective of electrode composition. The life of electrodes used to weld galvanneal steel averaged 5000 welds; 5 and 12 times the life of electrodes used to weld galvanised (1000 welds) and Al-45%Zn (400) steels, respectively. The data is tabulated in Appendix B.

The life of electrodes used to weld Al-45%Zn and hot dipped galvanised steels is almost identical regardless of electrode composition, whereas noticeable variation exists for galvanneal. The life of a Cu/Cr/Zr electrode used to weld galvanneal exceeds that of Cu/Cr by 1100 welds and Cu/Zr by 1500 welds. In an attempt to elucidate the reason
for variation in electrode life exhibited when welding galvanneal it was decided to subject these electrodes to further microstructural examination.

![ELECTRODE LIFE TEST RESULTS](image)

**Figure 5.4** Electrode life data for all electrode compositions and all coated steels.

5.1.3 Electrode tip examination

5.1.3.1 SEM Examination

Electron micrographs of cross sections of each electrode after 1000 welds on galvanneal steel are shown in Figures 5.5, 5.6, & 5.7. A complex alloy layer is observed to build up on the surface of electrode tips. For each electrode tip, 4 sublayers varying in composition and thickness have been identified. Table 5.1 is a summary of the
the appearance and thickness of each sublayer. The elemental composition of each sublayer has been established using EDS spot analysis and is shown in Table 5.2. The boundaries are well defined and the composition of each sublayer is fairly constant throughout the thickness of each particular sublayer. According to the chemical compositions, the following phases are likely to exist. The innermost sublayer is a ductile beta (β) brass of approximate composition 52% Zn, 48% Cu. The sublayer adjacent to (β) is a brittle gamma (γ) brass, 63% Zn, 36% Cu. The composition of these brass sublayers was almost identical for all electrodes. The thickness of (β) brass for Cu/Cr and Cu/Cr/Zr electrodes was very similar, (5-15 μm). The brass sublayers, ie. (β) and (γ) for the Cu/Zr electrode were 15-25 μm thick. The (β) and (γ) brasses are continuous for each electrode composition except Cu/Zr which displays cracking in the (γ) brass layer which is arrested at the (β) brass interface. An Fe-Zn sublayer was present which separates the brass sublayers from a very porous, brittle ZnO surface layer. The composition and thickness of this Fe-Zn sublayer is strongly dependent on the composition of the electrode. The thickest layer was observed for the Cu/Cr/Zr electrode (30-60 μm) followed by the Cu/Cr electrode (20-40 μm) for which both sublayers are seen to be continuous. The Cu/Zr electrode displayed a discontinuous thin (0-10 μm) Fe-Zn sublayer which, judging by the extensive cracking in the (γ) brass sublayer, provides little mechanical or physical protection to the underlying brass layers. The Cu/Cr and Cu/Cr/Zr electrodes display a continuous ZnO surface sublayer which is approximately 60-90 μm thick. Extensive cracking is also prevalent in the ZnO sublayer on the surface of Cu/Zr electrode, which was measured to be approximately 30 μm thick.
Figure 5.5  Electrode alloying during resistance spot welding of galvanneal steel using Cu/Cr electrode.

Figure 5.6  Electrode alloying during resistance spot welding of galvanneal steel using Cu/Cr/Zr electrode.
Figure 5.7 Electrode alloying during resistance spot welding of galvanneal steel using Cu/Zr electrode.

<table>
<thead>
<tr>
<th>Sublayer</th>
<th>Cu/Cr (μm)</th>
<th>Cu/Cr/Zr (μm)</th>
<th>Cu/Zr (μm)</th>
<th>Cu/Cr Appearance</th>
<th>Cu/Cr/Zr Appearance</th>
<th>Cu/Zr Appearance</th>
</tr>
</thead>
<tbody>
<tr>
<td>β-Brass</td>
<td>15</td>
<td>15</td>
<td>25</td>
<td>continuous</td>
<td>continuous</td>
<td>continuous</td>
</tr>
<tr>
<td>γ-Brass</td>
<td>10</td>
<td>10</td>
<td>20</td>
<td>continuous</td>
<td>continuous</td>
<td>cracked</td>
</tr>
<tr>
<td>Fe-Zn</td>
<td>20-40</td>
<td>30-60</td>
<td>0-10</td>
<td>continuous</td>
<td>continuous</td>
<td>cracked</td>
</tr>
<tr>
<td>ZnO</td>
<td>50-90</td>
<td>40-60</td>
<td>20-30</td>
<td>continuous</td>
<td>continuous</td>
<td>cracked</td>
</tr>
</tbody>
</table>

Table 5.1 Summary of characteristics of each sublayer formed on the tip of electrodes used to weld galvanneal steel.
## COMPOSITIONAL ANALYSIS

Alloy layers in electrode tip region

**Copper Chromium Electrode: Life 4880**

<table>
<thead>
<tr>
<th>wt %</th>
<th>Cu alloy</th>
<th>β - Brass</th>
<th>γ - Brass</th>
<th>Fe - Zn</th>
<th>ZnO</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>99.4</td>
<td>51.7</td>
<td>38.4</td>
<td>5.2</td>
<td>5.5</td>
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<tr>
<td>Zn</td>
<td>47.6</td>
<td>59.7</td>
<td>42.4</td>
<td>58.2</td>
<td></td>
</tr>
<tr>
<td>Fe</td>
<td>0.4</td>
<td>1.7</td>
<td>51.6</td>
<td>33.8</td>
<td></td>
</tr>
<tr>
<td>Al</td>
<td></td>
<td></td>
<td></td>
<td>0.6</td>
<td></td>
</tr>
<tr>
<td>Cr</td>
<td>0.6</td>
<td>0.3</td>
<td>0.2</td>
<td>0.9</td>
<td>1.9</td>
</tr>
</tbody>
</table>

**Copper Chromium Zirconium Electrode: Life 5990**

<table>
<thead>
<tr>
<th>wt %</th>
<th>Cu alloy</th>
<th>β - Brass</th>
<th>γ - Brass</th>
<th>Fe - Zn</th>
<th>ZnO</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>99.6</td>
<td>51.5</td>
<td>33.2</td>
<td>1.8</td>
<td>4.1</td>
</tr>
<tr>
<td>Zn</td>
<td>47.9</td>
<td>64.8</td>
<td>39.4</td>
<td>60.9</td>
<td></td>
</tr>
<tr>
<td>Fe</td>
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<td>1.4</td>
<td>58.2</td>
<td>31.8</td>
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</tr>
<tr>
<td>Al</td>
<td></td>
<td></td>
<td></td>
<td>0.9</td>
<td></td>
</tr>
<tr>
<td>Cr</td>
<td>0.3</td>
<td>0.2</td>
<td>0.5</td>
<td>0.4</td>
<td>0.1</td>
</tr>
<tr>
<td>Zr</td>
<td>0.1</td>
<td>0.1</td>
<td>0.4</td>
<td>0.1</td>
<td>0.4</td>
</tr>
</tbody>
</table>

**Copper Zirconium Electrode: Life 4410**

<table>
<thead>
<tr>
<th>wt %</th>
<th>Cu alloy</th>
<th>β - Brass</th>
<th>γ - Brass</th>
<th>Fe - Zn</th>
<th>ZnO</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>99.3</td>
<td>53.2</td>
<td>36.6</td>
<td>18.6</td>
<td>2.5</td>
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<td>Zn</td>
<td>46.5</td>
<td>62.4</td>
<td>61.2</td>
<td>83.8</td>
<td></td>
</tr>
<tr>
<td>Fe</td>
<td>0.1</td>
<td>0.8</td>
<td>20.0</td>
<td>12.4</td>
<td></td>
</tr>
<tr>
<td>Al</td>
<td></td>
<td>0.2</td>
<td>0.1</td>
<td>0.9</td>
<td></td>
</tr>
<tr>
<td>Zr</td>
<td>0.7</td>
<td>0.2</td>
<td>0.1</td>
<td>0.1</td>
<td>0.4</td>
</tr>
</tbody>
</table>

Table 5.2 E.D.S. spot analysis of sublayers present in each alloy layer developed on the tip of electrodes used to weld galvanneal steel.
5.1.3.2 Microhardness testing

The microhardness of all sublayers on different electrodes after 1000 welds on galvanneal steel was measured. Meaningful results were obtained for the substrate and both brass sublayers. The hardness of both the Fe-Zn and surface ZnO sublayers could not be determined unambiguously because they crumbled under the indentation force, due to their brittle nature. The results are listed in Table 5.3. As expected the hardness values of the same sublayers on different electrodes were very similar.

### Microhardness of alloy layers (Micro Vickers 5gf)

<table>
<thead>
<tr>
<th></th>
<th>Cu alloy</th>
<th>β - Brass</th>
<th>γ - Brass</th>
<th>Fe - Zn</th>
<th>ZnO</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu-Cr</td>
<td>136.1 VMH5</td>
<td>242.1 VMH5</td>
<td>566.6 VMH5</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Cu-Cr-Zr</td>
<td>122.9 VMH5</td>
<td>220.7 VMH5</td>
<td>572.7 VMH5</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Cu-Zr</td>
<td>128.3 VMH5</td>
<td>221.3 VMH5</td>
<td>550.6 VMH5</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 5.3Microhardness of the alloy layers which develop on different electrode tips.

5.1.3.3 X-Ray Diffraction

Figure 5.8 shows the x-ray diffraction spectrum obtained for a Cu/Cr electrode tip used to produce 1000 welds using galvanneal coated steel. The electrode tip has been ground down 30 μm to reveal the sublayers. Figure 5.9 shows three superimposed x-ray diffraction spectra of a Cu/Cr electrode tip. The tip has been examined three times: in the as received condition, after removing 15 μm by grinding and after 30 μm had been removed. The results obtained after successive grinding and x-ray diffraction of the tip suggest that, the following sublayers are formed in sequence from the outer
surface: a zinc oxide sublayer (ZnO), an iron-zinc sublayer (Γ phase: Fe₃Zn₁₀), a gamma (γ) brass (Cu₅Zn₈) layer, and a beta (β) brass (CuZn) layer, and finally the Cu/Cr substrate.
Figure 5.8  X-ray diffraction pattern from an electrode tip, ground 30 µm into the alloy layer to improve detection of each phase.
Figure 5.9  Three x-ray diffraction spectrums of one electrode tip which has been examined after successive grinding.
5.2 PVD COATED ELECTRODES

5.2.1 Weld Lobes

Weldability lobes were constructed to investigate the effect of thin film PVD coatings on the current and time requirements to achieve satisfactory welds. All weld lobes were constructed for one steel, Al-45%Zn. This is because of the aggressive nature encountered with Al-45%Zn steel which allowed quick evaluation of coated electrodes. A limitation on the number of coated electrodes meant only one lobe was constructed for each case whereas the lobes in Section 5.1 are the average of three. Figure 5.10 shows weld lobes for a CrN coated Cu/Cr electrode and an uncoated Cu/Cr electrode used to weld Al-45%Zn coated steel. The CrN was deposited in a commercial cathodic arc chamber and is approximately 10 μm thick. Figures 5.11 and 5.12 are weld lobes for Cr coatings deposited on Cu/Cr electrodes by unbalanced magnetron sputtering and filtered arc evaporation respectively. The coatings are approximately 3 and 4 μm thick. The results are presented in tabular form in Appendix C.

The weld lobe for the CrN coated electrode is observed to lie approximately 1 kA below that of an uncoated electrode which indicates a substantial reduction in either weld current or time can be accommodated to produce a satisfactory weld. The weld lobes of Cr coated electrodes deposited by both sputtering and filtered arc also lie below that for an uncoated electrode although not to the same extent as CrN coated electrodes. The improvement varies from 0.3 - 1.0 kA.
**WELD LOBES: CrN COATED AND UNCOATED ELECTRODE**

![Graph](image)

Figure 5.10  Weldability lobes for CrN coated (commercially deposited by cathodic arc) Cu/Cr electrodes used to spot weld Al-45\%Zn metallic coated steel.

**WELD LOBE: Cr SPUTTER COATED AND UNCOATED ELECTRODES**

![Graph](image)

Figure 5.11  Weldability lobes for sputter deposited Cr coated Cu/Cr electrodes used to spot weld Al-45\%Zn metallic coated steel.
5.2.2 Electrode Life Data

The electrode life results shown in Figure 5.13 and Table 5.4 indicate that the application of thin film coatings have been successful in achieving substantial improvement in electrode life over uncoated electrodes. Three coating systems were trialed: CrN deposited by cathodic arc, Cr deposited by unbalanced magnetron sputtering and Cr deposited by filtered arc evaporation. A 50% extension in electrode life was achieved for CrN coated electrodes. A 100% extension of electrode life was achieved for both Cr coatings deposited by magnetron sputtering and filtered arc evaporation. Additional electrode life tests were conducted to investigate the effect of improved surface finish without a coating on Cu/Cr electrode tips created by the polishing operation. Electrode life improved by 40% over machined uncoated
electrodes. All coating trials (except Test 14) were conducted on Al-45%Zn to provide a relatively quick result. Exact details are provided in Table 5.5.

<table>
<thead>
<tr>
<th>COATING</th>
<th>ELECTRODE LIFE (ave.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Uncoated</td>
<td>420</td>
</tr>
<tr>
<td>Polished</td>
<td>580</td>
</tr>
<tr>
<td>CrN</td>
<td>606</td>
</tr>
<tr>
<td>Cr - sputter</td>
<td>815</td>
</tr>
<tr>
<td>Cr - filtered arc</td>
<td>880</td>
</tr>
</tbody>
</table>

Table 5.4 Summary of average life results for each coating system.

![COATED ELECTRODE LIFE RESULTS](image)

Figure 5.13 Chart of electrode life for different coating systems.
<table>
<thead>
<tr>
<th>TEST</th>
<th>COATING</th>
<th>STEEL</th>
<th>METHOD</th>
<th>THICKNESS</th>
<th>LIFE</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Uncoated</td>
<td>Al-45%Zn</td>
<td>N/A</td>
<td>N/A</td>
<td>420</td>
</tr>
<tr>
<td>2</td>
<td>Uncoated</td>
<td>Al-45%Zn</td>
<td>Polished</td>
<td>N/A</td>
<td>580</td>
</tr>
<tr>
<td>3</td>
<td>CrN</td>
<td>Al-45%Zn</td>
<td>Cathodic Arc</td>
<td>10 μm</td>
<td>720</td>
</tr>
<tr>
<td>4</td>
<td>CrN</td>
<td>Al-45%Zn</td>
<td>Cathodic Arc</td>
<td>10 μm</td>
<td>620</td>
</tr>
<tr>
<td>5</td>
<td>CrN</td>
<td>Al-45%Zn</td>
<td>Cathodic Arc</td>
<td>10 μm</td>
<td>480</td>
</tr>
<tr>
<td>6</td>
<td>Cu/Mo</td>
<td>Al-45%Zn</td>
<td>Mag. Sputtering</td>
<td>1 μm/2 μm</td>
<td>520</td>
</tr>
<tr>
<td>7</td>
<td>Nb/Cr</td>
<td>Al-45%Zn</td>
<td>Mag. Sputtering</td>
<td>1 μm/2 μm</td>
<td>440</td>
</tr>
<tr>
<td>8</td>
<td>Cr</td>
<td>Al-45%Zn</td>
<td>Mag. Sputtering</td>
<td>3 μm</td>
<td>840</td>
</tr>
<tr>
<td>9</td>
<td>Cr</td>
<td>Al-45%Zn</td>
<td>Mag. Sputtering</td>
<td>3 μm</td>
<td>800</td>
</tr>
<tr>
<td>10</td>
<td>Cr</td>
<td>Al-45%Zn</td>
<td>Mag. Sputtering</td>
<td>6 μm</td>
<td>830</td>
</tr>
<tr>
<td>11</td>
<td>Cr</td>
<td>Al-45%Zn</td>
<td>Filtered Arc</td>
<td>2 μm</td>
<td>750</td>
</tr>
<tr>
<td>12</td>
<td>Cr</td>
<td>Al-45%Zn</td>
<td>Filtered Arc</td>
<td>4 μm</td>
<td>940</td>
</tr>
<tr>
<td>13</td>
<td>Cr</td>
<td>Al-45%Zn</td>
<td>Filtered Arc</td>
<td>6 μm</td>
<td>820</td>
</tr>
<tr>
<td>14</td>
<td>Cr</td>
<td>Galvanneal</td>
<td>Mag. Sputtering</td>
<td>3 μm</td>
<td>6000</td>
</tr>
</tbody>
</table>

Table 5.5  Electrode life results, including details of each coating system.
5.2.2.1 Compound Coatings

Initial coating trials were carried out by a commercial coater using a cathodic arc system to deposit CrN on electrodes. The coating was approximately 10 μm thick. Although some encouraging results were achieved (Test Nos. 3, 4 & 5), significant variation was observed in the three electrode pairs tested. Figure 5.14 shows that the CrN coating had particles and agglomerates on the surface of the coating, ranging in size from 0.5-10μm. These are micro-droplets from the deposition process, which are a characteristic feature of arc evaporation, due to the tendency of the arc to occasionally dwell on a spot. Figure 5.15 shows a higher magnification image of the surface in which an equiaxed structure and a number of pinholes can be seen in the coating. Also a foreign particle 40 μm long can be seen embedded in the coating in Figure 5.16. This particle has severely disturbed the coating structure and created an area in which accelerated degradation would be expected.

![Figure 5.14](1471_15KV_10μm_WD17.png)  
**Figure 5.14** CrN coating deposited by cathodic arc on a Cu/Cr electrode tip: macroparticles and agglomerates are littered on the coating surface.
Figure 5.15  CrN coating: same as for Figure 5.13 but showing pinholes at high magnification

Figure 5.16  CrN coating: same as for Figure 5.13 but showing the presence of foreign particle which resulted in a large pore in the coating.
5.2.2.2 Refractory Metal Coatings

In an unbalanced magnetron sputtering chamber coatings of molybdenum (2µm) with a copper interlayer (1µm) (Test No. 6) and niobium (2µm) with a chromium interlayer (1µm) (Test No. 7) were deposited. No improvement in life was demonstrated for these two coatings, and no further trials of these coatings were undertaken.

5.2.2.3 Chromium Coatings

A number of preliminary sputter trials were conducted before adherent Cr coated electrodes were reproducibly prepared. Figure 5.17 is a SEM micrograph of a Cr coating, 6 µm thick deposited onto a Cu/Cr tip by unbalanced magnetron sputtering. Test Nos. 8, 9 & 10 demonstrate a 100% life improvement to approximately 815 welds. Figure 5.18 shows the chromium coating to be virtually free of any foreign particle contamination. For Test 14, Al-45%Zn was replaced with galvanneal, the coated steel used in the fabrication of automotive panels where the preferred joining technology is resistance spot welding. A life of 6000 welds demonstrated no improvement in electrode life, compared to an uncoated electrodes.

Time constraints and the availability of equipment restricted the use of the FADS system. A number of preliminary runs were conducted before any meaningful results were obtained. Test Nos. 11, 12 and 13 successfully demonstrate 100% life improvement over uncoated electrodes. Figure 5.18 is a chromium coating free of any contamination. In stark contrast to the coating deposited by cathodic arc (Figure 5.14) the FADS produced a macroparticle, defect free coating. The curved plasma duct, the steered arc and the focussing effect of magnetic coils contribute to produce a defect free coating. Although there is some variation in the FAD results, the degree of scatter associated with weld life tests prohibits any conclusions being drawn on variable coating thicknesses employed.
Figure 5.17  Cross section of a Cr coating deposited by unbalanced magnetron sputtering. The coating is 6 μm thick.

Figure 5.18  Chromium coating deposited using unbalanced magnetron sputtering: The coating quality is much better than for CrN.
5.2.3 Electrode Tip Examination

Figures 5.20 & 5.21 show the difference between an uncoated electrode tip and an electrode tip sputter coated with 3μm of chromium. The uncoated tip has been machined on a lathe, evidenced by machining grooves, to a diameter of 5 mm. The coated electrode has been polished to a 1 μm finish, which increases the true surface area even though the diameter is still 5 mm.

Figures 5.22 & 5.23 show the alloy layer build up after 200 welds and after further degradation of the electrode tip to the failure point of 840 welds. The steel used in the test was Al-45%Zn. The first evidence of noticeable alloy layer build up on coated electrodes occurred after 200 welds. Up to this point the quality of weld nugget on the steel was excellent. In fact the first sign of weld nugget deterioration was observed
after 350 welds. Deterioration occurred in the form of build up (and in some places removal) of zinc oxide around the perimeter of the electrode and hence an increase in electrode surface area occurred. Evidence of pitting around the perimeter of the electrode is also obvious. Observations on the degradation of uncoated electrodes showed that within the first 5 welds, excessive alloy layer build-up had occurred, judging by the poor quality of weld nugget on the steel surface and visual observation of the electrode face. In other words, the Cr coating significantly increased the life of electrodes and also improved the quality of weld nugget observed on the steel surface. Figure 5.23 shows an electrode surface which is heavily covered by zinc oxide. Severe pitting is evident; the two shiny regions in the centre are pools of solidified aluminium, zinc and copper.

Figure 5.20 An unused electrode tip machined to a diameter of 5mm. Magnification 11X
Figure 5.21  An electrode polished and sputter coated with 3 μm of Cr.
Magnification 11X.

Figure 5.22  A Cr coated Cu/Cr electrode tip after 200 welds on Al-45%Zn steel.
Magnification 11X.
After 200, 400 and 800, welds electrodes were removed from service, sectioned along their axis, mounted and prepared for SEM examination. Figures 5.24 to 5.28 are SEM micrographs of Cu/Cr electrode tips after increasing periods of service. The smooth electrode edge in Figure 5.24 is created by grinding the edge with fine grade paper to remove obstinate remains of the mounting resin from the polishing operation. Figure 5.26 shows an electrode edge which has not required further grinding to remove the mounting resin, hence showing the original machining grooves. The rapid rate and aggressive nature of the degradation process for Al-45%Zn is readily observable. EDS semi quantitative analysis was used to investigate the durability of the chromium coating. After 200 welds alloy layers had clearly formed and only small traces of Cr were evident. So badly pitted were the electrode tips at 400 and 800 welds that no trace of Cr was found.

Figure 5.23 A Cr coated Cu/Cr electrode after a complete life test (840 welds) on Al-45%Zn coated steel. Magnification 11X.
Figure 5.24  SEM micrograph of a Cu/Cr electrode coated with 3μm of Cr showing electrode tip wear after 200 welds on Al-45%Zn coated steel.

Figure 5.25  SEM micrograph of small pit observed on the face of the electrode in Figure 5.24.
Figure 5.26  SEM micrograph of a Cu/Cr electrode coated with 3μm of Cr showing electrode tip wear after 400 welds on Al-45%Zn coated steel.

Figure 5.27  SEM micrograph of electrode alloying on Cr coated Cu/Cr electrode tip after 200 welds on Al-45%Zn steel.
Figure 5.28  SEM micrograph of a large pit and subsequent alloy build up in the degraded region of an electrode after 800 welds on Al-45%Zn coated steel.

5.2.3.1 Microhardness Testing

Microhardness of the electrodes removed from service at 200, 400 and 840 welds (life test) was measured at 0.5mm intervals perpendicular to the electrode tip face, with an initial test at 0.2mm. Three areas were assessed: the centre, the left and the right edges of the electrode face. As the tips were badly pitted and worn a reference line was established from which all distance measurements were taken. A variation of approximately 60 VMH points is observed over the 3mm region tested. Beyond 3mm, the microhardness values are observed to be similar to those for an unused electrode.
Hardness of an unused electrode: 162 VMH_{100}

Figure 5.29  Microhardness profiles of electrode tips after 200, 400 and 800 welds. The load used was 100g.
6.1 UNCOATED ELECTRODES

6.1.1 Weld Lobes

Even though great care was taken to ensure that electrode tip alignment and weld force were set to, and maintained at correct values, the scatter in weld lobes was observed to be up to 1.0 kA (Appendix A), and reproducing results proved to be difficult. Such scatter reduced the effectiveness of a weld lobe as an accurate tool to establish strict welding schedules and therefore served only as a general guide to the weld time/current combinations that produced satisfactory welds. In spite of the difficulty associated with constructing weld lobes of low scatter, certain trends were observed which are worthy of further discussion.

The position of the weld lobes in current/weld time co-ordinates was found to be strongly related to the nature of the metallic coating on the steel surface and its weight, i.e. thickness. For instance, the weld lobes of galvanneal, for all electrode materials were located approximately 1 kA below that of Al-45%Zn and 1-2 kA below hot dipped galvanised (Figures 5.1, 5.2 & 5.3). Galvanneal is a fully alloyed Fe/Zn coating with a high Fe concentration which increases electrical resistivity and melting point, but reduces current shunting which reduces the current required to achieve a satisfactory weld compared to free zinc coatings (hot dipped galvanised and Al-45%Zn) [14].

Another possible explanation for lower weld currents is the effect of coating weight. The galvanneal alloy used in this investigation had a coating mass of only 80 g/m², and this might have influenced the welding lobe. Several investigators [1, 5, 7, 13] have indicated that a reduction in coating weight lowers welding currents required. Natale [14] has explained that increased shunting at both the electrode/sheet interface and the faying plane, require increased currents as zinc coating weight increased. This view is
not supported by Kimchi [37] who has shown that differences of 2:1 in coating weight made only small differences to current values and electrode life. However, it is not inconceivable that the disagreement amongst different researchers stems from the fact that a wide range of coatings have been used in different investigations. It is, therefore, possible that over one range of thicknesses, weld current is not affected whereas in another range, a relationship between the two does exist.

The reduction in weld current improves weldability of the product, reduces power costs and decreases the amount of thermal cycling which reduces the rate of metal diffusion and alloy build up. However, the reduced current shunting and increased electrical resistivity are unable to accommodate small fluctuations in power and machine set up; for a given weld time a smaller range of weld currents will allow production of a satisfactory weld. This is the cause of both the narrow welding window and higher scatter obtained for galvanneal than for either hot dipped galvanised or Al-45%Zn (Figures 5.1, 5.2 & 5.3).

6.1.2 Electrode Life Data

Similar to the reasons cited for welding lobes, the higher electrode life achieved when welding galvanneal, irrespective of electrode composition, is also largely due to the coating composition (Figure 5.2). The improvement in electrode life results from a higher electrical resistivity of the coating (lower welding current), higher melting temperature of the coating (reduced electrode alloying) and lower thermal conductivity than unalloyed zinc coatings [14].

The lower electrode life obtained for both Al-45%Zn and hot dipped galvanised also relates to the composition of the coating and is primarily due to the addition of Al to the Zn coating. Al is added to hot dipped galvanised, in small quantities, to inhibit the growth of Fe-Zn intermetallics during the hot dipped galvanising process and to
improve adhesion between the coating and the steel. In Al-45%Zn, Al is a major constituent added to improve corrosion resistance of the coating. The presence of Al in the coating, be it in small or large quantities, results in significant accumulation of Al in the alloy layers which grow on the electrode tip as welding proceeds. Brittle pockets containing Al form in the alloy layers which are easily broken away leaving a pitted electrode face. This alters the weldability of the coated steel and severely reduces electrode life. This is especially noticeable on electrodes used to weld Al-45%Zn coated steel which demonstrated a life in the range of 370 to 510 welds. Hot dipped galvanised displays a similar degradation process, albeit at a much slower rate due to a lower Al content in the coating. This is reflected in the life of electrodes used to weld hot dipped galvanised which ranged from 1190 to 1370 welds.

The electrode life for different coated steels can be summarised as follows. Taking hot dipped galvanised as the standard coating, the addition of significant amounts of Al in Al-45%Zn severely decreases the life owing to extensive interaction of the coating with the electrode. The presence of Fe in the galvanneal reduces the extent of interaction and counter balances the aggressive behaviour of Al (Figure 5.4).

In addition, the increased current requirements due to a heavier coating weight combined with added coating pick up at the sides of the electrode, contribute to the reduction in electrode life. An increase in coating weight means that a larger volume of molten material is displaced when an electrode tip mates with the steel. This inevitably leads to increased contact of an electrode with the metallic coating around the periphery of the electrode. Larger contact area with molten metal increases the likelihood of deleterious interaction between the electrode and the metallic coating which would eventually manifest itself as heavier build up on the electrode tip. Galvanneal has a similar Al content to hot dipped galvanised yet the life is much longer. It is believed that the high Fe content of the galvanneal coating contributes to the lowering of the electrode degradation rate when welding this steel type. It is suggested that Fe may
have a stabilising influence over the diffusion of both Zn and Al into the Cu, or of the Cu into the complex alloy layers [2]. This aspect is further elaborated in Section 6.1.3 when dealing with the degradation mechanism of electrodes.

In so far as the electrode composition is concerned, Al-45%Zn did not show any sensitivity and almost identical lives were obtained for all compositions. In the case of hot dipped galvanised and galvanneal, the highest lives were obtained when using Cu/Cr/Zr electrodes and the lowest for Cu/Zr electrodes. In order to explain this behaviour the role of alloying elements in Cu based electrodes and the nature of interaction between the electrode and metallic coating have to be considered.

Alloying elements are added to the Cu electrode material to improve the mechanical properties without significantly affecting the electrical properties of the electrode. Usually an improvement in one is at the expense of the other. Cr is added to increase hardness and load bearing ability of electrodes usually increasing electrode life. This is, however achieved by reducing electrical conductivity. Zr is also added to increase the hardness although it is not as potent a strengthener as Cr. Zr is less detrimental to the electrical conductivity of Cu yet electrode life is generally less than for Cr strengthened electrodes.

For galvanneal and hot dipped galvanised the explanations above were found to be true. In particular, the degradation process for the electrodes used to weld galvanneal coated steel is gradual and therefore the effect of alloying elements as outlined above becomes pronounced and identifiable. The life of the Cu/Cr/Zr electrode is clearly superior to the other electrode compositions and warrants further investigation. From an industrial viewpoint this is quite important as galvanneal is used extensively in automobile panel assembly and any improvements in electrode life will ultimately lead to reduced costs on the production line.
However for Al-45%Zn this was not observed to be true as the life values were reversed which demonstrates what a complex system is operating. The above mentioned explanation cannot account for the situation where the Cu/Zr electrode yielded the longest life. Undoubtedly, the aggressive nature of Al-45%Zn negates the load bearing explanation. Alternatively, where electrode life is so short, load bearing capacity may not be the dominating factor in determining electrode life and perhaps increased electrical conductivity is. However, no concrete evidence can be offered to explain the results obtained for Cu/Zr electrode.

From the above discussion it is obvious that a similar set of factors govern the electrode life just as they affect the position and size of weld lobes. Unfortunately, due to the complex nature and inter-relation of some factors, it is difficult to ascertain the exact contribution of each factor.

6.1.3 Degradation Mechanism

Based on SEM examination (Figures 5.5, 5.6, & 5.7) and x-ray diffraction analysis of the alloy layers on the electrode face, the following layers are formed in sequence from the outside: a surface oxide sublayer (ZnO), a porous Fe-Zn sublayer (Γ phase: Fe₃Zn₁₀), a hard and brittle gamma (γ) brass (Cu₅Zn₈) sublayer, and a ductile beta (β) brass (CuZn) sublayer (the Cu-Zn phase diagram [80] is reproduced in Appendix D), and then the Cu/Cr substrate. The Fe-Zn sublayer is formed by adhesion and transfer of the coating layer on the steel, to the electrode, whereas the brass layers are formed by the interdiffusion of the Cu from the electrode and Zn from the Fe-Zn sublayer [9].

The above mentioned layered structure is similar to those identified by Howes [2] although he did not carry out x-ray diffraction and relied entirely on elemental composition. The findings are also in agreement with Morita [9] who conducted a similar study, except for the Fe-Zn sublayer which he identified as a porous Γ phase
with a composition of Fe$_3$Zn$_7$. Morita did not cite any reference material as the source of his phase diagram or x-ray diffraction data. The Fe-Zn phase diagram [81] (reproduced in Appendix D from Hansen's Constitution of Binary Alloys) and x-ray diffraction JCPD databases have no record of any phase with a composition of Fe$_3$Zn$_7$ as identified by Morita. Unfortunately, in the absence of any information corroborating the existence of a Fe$_3$Zn$_7$ phase, it is not possible to concur with Morita's assertion regarding the formation of this phase on the electrode tip. Indeed, the present investigation has established that an Fe-Zn layer with a composition of Fe$_3$Zn$_{10}$ develops on the electrode tip. No other references could be found in the literature providing x-ray diffraction analysis of alloy layers formed on electrode tips.

Three interesting phenomena have been observed in the sublayers which develop on the tip of Cu/Zr electrodes used to weld galvanneal (see Figure 5.7). (1) The thickness of ($\beta$) and ($\gamma$) brass sublayers in each electrode are observed to vary. The Cu/Cr electrode, and the Cu/Cr/Zr electrode exhibit brass sublayers 10-15 $\mu$m thick whereas the Cu/Zr electrode exhibits brass layers 20-25 $\mu$m thick. (2) The brittle ($\gamma$) brass layer of the Cu/Zr electrode proved susceptible to cracking and subsequent delamination under repeated loading and pressure. (3) The Fe-Zn sublayer was severely cracked and EDS standardless analysis revealed substantial compositional variation of the Fe-Zn sublayer compared to the Cu/Cr and the Cu/Cr/Zr electrodes. The Cu/Cr and Cu/Cr/Zr tips both developed relatively thick and continuous (20-60 $\mu$m) Fe-Zn sublayers whereas for the Cu/Zr electrode the Fe-Zn sublayer is very thin (<10 $\mu$m), fractured and discontinuous. The Cu/Zr electrode contained ~60% Zn & 20% Fe while the Cu/Cr electrode contained ~40% Zn & 50% Fe, the Cu/Cr/Zr electrode contained ~40% Zn & 60% Fe.

Each of the above can be attributed to the inferior mechanical properties of the Cu/Zr electrode. The substrate cannot provide solid support for the alloy layers. Hence, the brittle Fe-Zn and ($\gamma$) brass sublayers crumble under repetitive impact forces and allow extensive influx of molten Zn. The higher Zn concentration of the Fe-Zn layer is
readily replenished at the interface with Cu resulting in thicker brass layers due to increased diffusion.

Irrespective of the cause of cracking, the (β) brass sublayer was an effective barrier to arrest cracks. However, the brittle (γ) brass layers fracture and spall away under repeated loading. The same phase was also seen to reform in the delaminated zone which suggests that electrode wear is strongly affected by the (γ) phase formation rate. A comparison of the (γ) phase formed on Cu/Zr electrodes, after 1000 welds, shows it to be nearly twice as thick as the sublayer on the Cu/Cr and Cu/Cr/Zr electrodes. Beyond this level however there is little change in thickness owing to recurrent delamination and reformation of the (γ) phase.

The preceding section has demonstrated that all sublayers formed on the electrode tip are equilibrium phases. It is not surprising that such a layered structure has developed because essentially a diffusion couple was established between the electrode and the steel. Indeed, the sequence of sublayers is in agreement with the Cu-Zn phase diagram. The low Zn phase (α) was indistinguishable from the substrate but (β) and (γ) brass phases were unambiguously identified. The high Zn phases in the phase diagram did not form in this system because of the presence of a significant amount of Fe which preferentially reacted with Zn. At the outermost sublayer, ZnO formed which is due to the reaction between zinc and oxygen, in the surrounding air.

It is interesting to note that equilibrium conditions were established in a short period of time. More specifically, the layered structures shown in Figures 5.5, 5.6 and 5.7 were obtained after 1000 welds. Bearing in mind that weld time was only 7 cycles (each cycle is about 20 ms. for a 50 Hz mains frequency). Therefore the total time at temperature amounted to approximately 2.5 minutes.
6.2 PVD COATED ELECTRODES

Both CrN and Cr displayed lower weld lobes than uncoated electrodes. The CrN coated electrodes exhibited the lowest weld lobe which was marginally lower than the weld lobes of Cr, deposited by both unbalanced magnetron sputtering and filtered arc evaporation. Electrode life testing revealed that all Cr coated electrodes achieved a 100% improvement in electrode life compared to uncoated electrodes. CrN coated electrodes displayed an improvement of 60% while refractory metal coatings of Mo and Nb yielded no improvement. A polished, uncoated electrode showed 40% improvement in electrode life. In this chapter explanations are offered for the above observations. After discussing the possible causes of variation in electrode lives, a life determining mechanism will be proposed. In the light of this several recommendations have been made to further increase electrode life.

6.2.1 Welding Lobes

To achieve an acceptable weld nugget, a certain amount of power is required. By using a constant current supply, the voltage is automatically adjusted to provide the set current. At a fixed current, any extra resistance, for instance, due to the presence of a coating would result in extra heat dissipation from the electrode. Obviously this wasted energy has to be compensated by increasing the input power. In other words, by increasing the current setting on the power supply to a higher value. However, the weld lobes of coated electrodes are observed to lie 0.3 - 1.0 kA below those for uncoated electrodes. The effect of the added coating resistance must be outweighed by another factor. The other major source of resistance is the interface between the electrode and the workpiece. As this is a surface property it is not surprising that it will be affected by the polishing procedure prior to coating. When an unpolished electrode is brought into contact with steel, the true area of contact is much smaller than the apparent area of
contact, i.e. the area described by tip diameter (Figure 6.1). The true area of contact is established on the tip of asperities which would be exposed to very high current density. Thus, at the tip of asperities, 'hot spots' will form. The increased area of true contact, of a polished electrode reduces the current density in the areas of true contact, hence the number or severity of hot spots decreases. Consequently lower temperature in the vicinity of the point of contact develops which reduces the driving force for alloying and diffusion.

The weld lobes constructed for each coated electrode were observed to lie below that of an uncoated electrode as explained above. However, no conclusive explanation can be offered for the CrN weld lobe lying below that for the Cr coatings, although the possibility of some chemical/metallurgical effect, due to the inert nature of CrN cannot be entirely ruled out.

Figure 6.1 Schematic diagram of a microscopic region of an electrode tip showing the increase in true surface area after polishing the electrode face.
6.2.2 Coating Quality and Electrode Life

A number of reasons given to explain weld lobe behaviour, are equally applicable to discuss electrode life. Such a relationship is not unexpected as both are created by spot welding and both are influenced by factors such as contact resistance, electrode and metallic coating composition. If the contact resistance of the electrode tip is lower then less electrical energy is dissipated as heat at the interface. The reduction in weld current due to a lower contact resistance of the coated electrodes may also contribute to the increased life of the coated electrodes as well as lowering the weld lobes.

6.2.2.1 Compound Coatings

It would appear from the results obtained to date that only a 60% gain in electrode life could be obtained by coating Cu/Cr electrodes with CrN. Extensions in electrode life are believed to come from the improved surface finish and the ability of the coating to act as a diffusional barrier between the electrode and the steel surface. In addition, the variability in electrode life is higher for CrN than in the case of uncoated electrodes and other coated electrodes. The source of coating degradation may lie in the coating structure. It was noted in Section 5.2.2.1 that the CrN coatings had defects including macro-particles, pinholes and foreign particle contamination. All of these defects may compromise the mechanical integrity of the coating and its resistance to Zn and Al attack. Once a route for metal infiltration has been established through the coating, alloying will occur and mechanical failure of the coating will quickly follow. This indicates the importance of a sound coating structure and the control of coating parameters if an effective coating is to be produced.

The selection of CrN as a compound coating was based on earlier work by Studdon [78] who investigated the suitability of TiN coatings on electrode tips. In this work, TiN was not considered a suitable candidate because of a number of defects. The popularity
of TiN for many applications stems from its high hardness, relative inertness and low friction. TiN bonds well to steel, but its adhesion to copper alloys is poor, although work has been carried out to improve adhesion by using Ti or Cr/CrN interlayers [82-83]. The thickness of TiN coatings are restricted by the build up of residual stress in the coating to about 5-6μm. The residual stresses in CrN are less severe than in TiN coatings and thicknesses of >50μm can be achieved. These shortcomings of TiN makes it an unsuitable coating for spot welding electrodes as concluded by Studdon [78]. It is worth mentioning that Studdon obtained electrode life improvement of 70% when spot welding Al-45%Zn coated steel with Cu/Cr electrodes coated with TiN (from 190 - 350 welds). However, to achieve this a double layer coating was required. It is documented that a second layer not only improves adhesion of the uppermost layer with the substrate but also provides improved protection from liquid metal erosion. Pinholes and voids which develop as a part of the first coating are covered by the second coating. In this current work only single layer coatings were deposited. All efforts by Studdon to improve electrode life using single layer coatings failed. It was concluded that the copper based alloy substrate was too ductile to support such a thin, hard and rigid coating.

For these reasons CrN was chosen, but even then no great improvement in electrode life was obtained, implying that, although the hardness and residual stresses of CrN are much lower than TiN, it is still regarded as being too uncompliant to be supported by a soft copper substrate.

6.2.2.2 Refractory Metal Coatings

The refractory metal molybdenum coating did not improve electrode life. Molybdenum does have a tendency to oxidise at high temperatures, and it is suspected that this, perhaps exaggerated by poor adhesion, was the reason for the poor life result for the Mo/Cu coated electrode. No explanation could be offered for the failure of the Nb/Cr.
6.2.2.3 Chromium Coatings

Metallic Cr was used to extend electrode life by 100% over uncoated electrodes using both unbalanced magnetron sputtering and filtered arc deposition techniques. A 40% improvement in electrode life was observed over the CrN coated electrodes. As was outlined in Section 2.5 there are many factors which contribute to the eventual failure of an electrode tip. It is therefore difficult to pinpoint exactly how the metallic chromium coating assists in prolonging electrode tip life. Although the primary aim of the coating is to prohibit or at least retard the alloying reactions which occur between the coating of the steel and the electrode tip, the preparation of the tip prior to coating may influence electrode life to some extent as was discussed in Section 6.2.1. To investigate this electrode life tests were conducted on Cu/Cr electrodes which had been polished but not coated. The improvement in electrode life of 40% over unpolished Cu/Cr electrodes gives some credence to the above hypothesis. From this it can be concluded that the coating operating in tandem with the improved surface finish combine to increase electrode life. The exact contribution of each factor, however, cannot be determined without further investigation.

The quality of the coatings deposited onto electrode tips in Figure 5.18 and 5.19 by unbalanced magnetron sputtering and filtered arc deposition respectively, are clearly superior to the CrN coating of Figure 5.14. The Cr coatings are free from foreign particles, pinholes and macro-particles. The reduction in the number of defects enhanced the mechanical integrity of coating and its ability to resist liquid metal attack from Zn and perhaps more importantly, from Al.

The fact that galvanneal is used extensively in the automotive industry for panel fabrication and joined by resistance spot welding warranted an electrode test with a coated electrode. A Cu/Cr electrode coated with 3 μm of Cr by unbalanced magnetron sputtering showed no improvement in electrode life when used to weld galvanneal. The
reason for this relates to the durability of the coating over 6000 welds. The alloying process is not as aggressive as for Al-45%Zn due to the absence of Al and the presence of Fe. However, over 6000 welds the coating deteriorates by cracking due to softening of the electrode, which allows liquid metal infiltration, alloying and eventually the coating spalls off.

6.2.3 Degradation Mechanism

In spite of certain improvements achieved in electrode life by Cr coating, the question of exact failure mode and life determining mechanism remains to be addressed. An insight into the degradation mechanism became apparent once microhardness testing of the weld tip had been conducted. After 200 welds, the region immediately behind the tip was found to have softened by 60 VMH compared to the as received condition. This is due to the extreme temperatures the electrode is exposed to at the tip for repeated periods of time. The metallic chromium coating is able to withstand the stresses of welding more readily than a compound coating such as TiN. However, such deformation of the electrode face could not be endured by any coating system. The coating would fracture providing sites for liquid metal infiltration and subsequent alloying. As brittle layers develop they crack and spall off removing with them sections of the coating. Any coating system must have a strong substrate capable of supporting it. Clearly the Cu/Cr alloy does not possess the mechanical properties required for operation at high temperature especially under repeated impact loading rigours of spot welding.

The thin film Cr coating served its purpose by providing a diffusional barrier to liquid metal infiltration and hence retarding alloy layer growth. Visual observation of weld appearance, which is a mirror of the electrode tip, showed weld quality deterioration to be prohibited for about 200 welds before the usual failure signs such as pitting became apparent. An electrode sectioned after 200 welds (Figure 5.24) shows evidence of tip
degradation and electrode edge alloy build up as well as deformation of electrode tip shape. EDS area analysis of the pit (Figure 5.25) yielded 2 wt% Cr amongst Cu, Zn and Al. Subsequent analysis at 400 welds and 800 welds yielded only trace quantities of Cr. This analysis suggests that the Cr coating is removed well before the end of the life test is reached.

6.2.4 Recommendations

The findings of Section 6.2.4 lead to the conclusion that electrode life of coated electrodes at this stage is ultimately dictated not by coating properties as would be expected but rather by mechanical properties of the substrate material. The observed softening phenomena associated with the use of standard Cu/Cr spot welding electrodes is the major stumbling block currently restricting major developments in the extension of electrode tip life when welding metallic coated steels. Future work in the area of electrode life development should focus on improving the high temperature characteristics of the electrodes.

As reported in Section 2.4.4 Dickinson [13] and Jud [18] both report electrode lives of four times that of standard electrodes at elevated temperatures when using aluminium oxide dispersion strengthened copper electrodes. The major disadvantage with this kind of electrode is the price which is about five times the cost over Cu/Cr electrodes. In addition to aluminium oxide dispersion strengthened copper, other alloys such as copper beryllium should be seriously considered. Maximum hardness is achieved for a beryllium content between 1.8 and 2.0wt%. Remarkable precipitation hardening occurs, with hardness values above 40 Rockwell C [84] (in perspective, this is in the range normally associated with steels). The addition of Be to Cu reduces the electrical conductivity and it is imperative that suitability of this material as a candidate electrode material should be thoroughly assessed. If Cu/Be proved to be satisfactory, it would provide an excellent low cost substrate material owing to its extremely high mechanical
strength. The role of a strong substrate cannot be overemphasised in any coating application and indeed it would be impossible to realise the full potential of a coating without a strong substrate to support it.

Others have tried alternative materials in the quest for improved performance. Refractory based metal inserts including powder composites of molybdenum copper or tungsten copper containing a discontinuous refractory phase in a copper matrix are reported to increase electrode life, although at substantially greater cost [8, 17]. These all merit further investigation as candidate materials for physical vapour deposited coatings. The main attraction of PVD is that they it can be applied to all potential electrode materials and designs.

Once a more suitable substrate has been established then considerable development needs to be conducted on the most suitable coating system. Ideally it is envisaged that a multi-layer coating would provide the most comprehensive protection against liquid metal attack. The coatings trialed in this work would undoubtedly have been enhanced with the addition of a second coating of CrN. As demonstrated in this work, the CrN coating displayed lower welding current. Therefore CrN is proposed as the top layer. The reduction in weld current associated with the CrN coating, hopefully reduces the temperature generated in the electrode with significant influence on the extent of plastic deformation in the electrode which, in turn, would enhance the performance of the electrode. The CrN layer needs to be supported by a thick Cr interlayer which will act as diffusion barrier to reduce the extent of inter diffusion and alloy layer build up. It is interesting to note that this coating architecture can be readily accommodated in PVD technology. It is possible to coat the electrodes with Cr and when the desired thickness has been achieved, nitrogen can be bled into the system to start reactive deposition of CrN. A final hard coating not only promotes a more durable system but also has the advantage of increased adhesion. Coupled with this is the secondary protection the outer coating provides over any pinholes or voids present in the first layer.
CHAPTER 7

CONCLUSIONS
CONCLUSIONS

The initial phase of the work examined the characteristics of three electrode materials used for resistance spot welding metallic coated steels. The electrode materials evaluated were: Cu/Cr, Cu/Cr/Zr and Cu/Zr. Metallic coated steel samples used were Al-45%Zn, galvanneal, and hot dipped galvanised. The electrodes were evaluated using standard weld lobe construction technique and conventional electrode life tests. Results from these tests were analysed and the conclusions are summarised below.

(1) The weld lobes of galvanneal (for all electrode compositions) were located below Al-45%Zn and hot dipped galvanised due to the increased electrical resistivity, higher melting point and reduced current shunting.

(2) When welding Al-45%Zn and hot dipped galvanised steels, no improvement in electrode life was obtained regardless of electrode compositions. In the case of galvanneal, the Cu/Cr/Zr electrode outperformed the Cu/Cr and Cu/Zr electrodes. The aggressive erosion process encountered for Al-45%Zn and hot dipped galvanised outweighs any influence the minor addition of alloying elements may have on electrode life.

3) The following sublayers were identified on the tip of Cu/Cr electrodes used to weld galvanneal steel: from the outer surface, a surface oxide sublayer (ZnO), a porous Fe-Zn sublayer (Γ phase: Fe₃Zn₁₀), a hard and brittle gamma (γ) brass (Cu₅Zn₈) sublayer, a ductile beta (β) brass (CuZn) sublayer, and then the Cu/Cr substrate.

4) The weld lobes for electrodes coated with CrN and Cr were approximately 0.3 - 1.0 kA below those of an uncoated electrode. A polished surface finish has
lowered contact resistance and hence reduced the current required to achieve a satisfactory weld.

5) Electrode life tests for electrodes coated with Cr deposited using the techniques of unbalanced magnetron sputtering and filtered arc deposition demonstrated a reproducible 100% improvement in electrode life from approximately 420 welds (for uncoated electrodes) to approximately 840 welds. This was only achieved when welding Al-45%Zn coated steel. It was apparent that coating thickness did not influence electrode life regardless of the PVD coating method.

6) The life determining degradation mechanism of coated electrodes has been identified as gross plastic deformation of the Cu based alloy substrate.

7) The major finding of this work leads to the recommendation that future work in this area should initially be aimed at the improving the high temperature properties of the substrate material. This must not however be at the expense of electrical requirements of spot welding electrodes which make resistance spot welding such an economical process.


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APPENDICES
# APPENDIX A  Weld Lobe Data

<table>
<thead>
<tr>
<th>STEEL COATING</th>
<th>WELD TIME (cycles)</th>
<th>Cu/Cr WELD CURRENT (kA/rms)</th>
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APPENDIX C  Coated Electrode Weld Lobe Data

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APPENDIX D: Cu - Zn Phase Diagram [80]

Iron - Zinc Phase Diagram [81]
PUBLICATIONS
'Surface Engineering of Spot Welding Electrodes.'
Presented at the 'Second Australian International Conference on SURFACE ENGINEERING', Adelaide, 7-10th March 1994.

'Optimising Resistance Spot Weldability of Metallic Coated Steels through Electrode Chemistry.'
R. Finlay & M. Samandi.