

TIN PLATING USING LIQUID DYNAMIC COMPACTION

by

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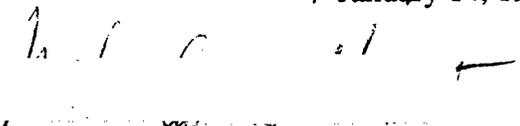
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Abstract

Commercially pure tin was spray coated on a plain carbon steel substrate using the Liquid Dynamic Compaction (LDC) spray deposition process. Using linear ultrasonic gas atomization dies (USGA) and nitrogen atomizing gas, nineteen spray coatings were made. Spray coating parameters varied during the work were pouring slit size, mass of tin melt, atomizing gas pressure, pouring temperature of the tin melt, flight distance from the dies to the substrate, substrate surface finish, and substrate temperature. Coatings were evaluated for appearance, continuity, and adhesion. Overspray powder from the atomization was also collected and examined to determine the effects of spray conditions on the size and shape of the powder.

In the as-coated state, the best results were obtained with thin coatings. It was found that thin coatings could best be achieved with a small atomized particle size and low metal spraying rate. A narrow pouring slit and high atomizing gas pressure combined with a small charge of molten tin produced the desired effect. The condition of the substrate was also found to be very important to adhesion. Substrates roughened by sand blasting displayed far better adhesion than smooth substrates. Also, it was found that preheating of the substrates led to heavy oxidation, preventing good wetting of the substrate by the tin spray, and interfered with the desired rapid quenching of the melt spray on impact with the substrate.

Some coated samples were post-processed by reflowing, a procedure in which the coated steel is heated to slightly above the melting point of tin. The purpose of reflowing is to spread and smooth the tin coating and promote formation of an intermetallic layer of FeSn_2 at the interface. Reflowing was performed by conductive heating both in argon and in hydrogen and by inductive heating in air both with and without a flux cover applied to the sample. Although reflowing did appear to improve the mechanical properties of the coatings, the appearance of the coating and the degree of coverage of the basis metal remained constant at best and deteriorated severely in many cases. In no case was there conclusive evidence that formation of an intermetallic layer at the tin/steel interface had occurred during reflowing.

Samples were also rolled at room temperature at reductions sufficient to slightly deform the steel basis metal. Rolling dramatically improved the quality of the tin surface in terms of smoothness and brightness and also greatly improved the adhesion of the tin. However, it was found that some minimum quality level of as-coated coverage and adhesion was required for rolling to have a significant beneficial effect.

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1. Introduction

Coating of a base material with a metal is a process of great commercial and technological importance. Such coating is done for a variety of reasons, including decoration, corrosion resistance, wear resistance, heat resistance, enhanced electrical or thermal conductivity, and surface chemistry modification for joining by welding, brazing, or soldering. The metals commonly used as coatings include tin, zinc, lead and lead alloys, nickel, chromium and chromium alloys, aluminum, cadmium, silver, gold, and platinum. The base metals and alloys used are too numerous to list, but in most cases the basic principle is to coat a relatively cheap base material with a more expensive material which has more desirable properties.

The most common coating technique, in terms of volume production, is electroplating, used mostly for the production of thin coatings. Electroplating is also used for thick coatings on higher cost specialty parts, but is most ideally suited to continuous production of coated sheet. There are numerous other methods, however. Electroless plating is also used for thin coatings, especially on base materials ill suited to electroplating. Hot dipping still finds some use for manufacture of thick coatings of low melting metals such as tin and lead and their alloys and zinc. Roll bonding is also used for thicker coatings, particularly aluminum and other corrosion resistant claddings. Explosive bonding of metal-metal composites is also a type of coating. Finally, plasma spraying and other thermal spray techniques are used for some specialty coatings.

However, there are environmental issues involved in electroplating which open the way for its potential replacement. Most electroplating baths have a pH which deviates significantly from neutrality, and many types also employ toxic chemicals, particularly cyanides. Storage, handling, and disposal or destruction of the bath chemicals is expensive and exposes workers to health risks. In most cases, however, electroplating continues to be used because other currently available coating methods are either not applicable or not economically feasible.

A method which has largely been unexplored for coating is spray deposition. Spray deposition involves atomizing a molten stream of metal which partially solidifies in flight and then impacts and fully solidifies as a dense deposit on a substrate. Most work on spray deposition has been in the area of shaped preforms. There is also interest in spray deposition for production of sheet and strip. What both of these have in common, however, is that the deposit is intended to be removed from the substrate to stand alone as the finished product. However, there is no reason that the deposit must be removed; instead, the technique can be used to spray a coating onto the substrate, much as flame

spraying techniques are used for coating. Sheet forming spray deposition techniques can easily be used to coat sheet, while shaped preform production methods have possibilities for coating more complicated shapes.

Coating by spray deposition has several advantages over current coating techniques. Compared to electroplating and electroless plating, spray deposition would remove the need for chemical baths and the associated handling and disposal hazards and costs; a high-speed spray coating line has the potential to match or exceed the production rates of electroplating and do it in less space. For production of clad materials, sheet spraying apparatus could easily be used to apply the cladding, removing the steps of aligning and holding materials for roll-bonding.

Spray coating also provides opportunities not available with current techniques. It is possible to coat with alloys not easily electroplated and in any desired composition which can be made in a melt. Also, with the exception of some cases of very high melting coatings on very low melting bases, it is possible to coat any material onto any other. Additionally, this technique can be used for metal coating of ceramics and possibly high-melting polymers. Finally, spray coating can be used for applying limited coatings, such as covering only one side of a sheet or repairing damaged coatings.

With these ideas in mind, it was decided to experiment with spray coating using a simple and easy, but still commercially important, system. Tin plating of steel is easy to set up, as tin has a low melting point and can easily be melted in a normal atmosphere with no special handling considerations. Because of its low melting point, tin can be contained in metallic crucibles and tundishes which can be made from easily machinable aluminum.

It was determined from this work that with limited preparation of the steel substrate and limited post-processing of the coated part, a good quality tin coating can be achieved. The primary criteria for characterizing the quality of the coating were surface appearance and coating adhesion. It is expected, based on these results, that other coating materials can be made to work with any number of base materials.

2. Literature Survey

2.1 Tinplate

The term tinplate refers to sheet steel coated on both sides with a continuous layer of tin. Tinplate is the most important commercial use of tin currently, accounting for 40% of the world's consumption of tin, approximately 80,000 tons each year. Because of the relative thicknesses of the average tin coating and average base material, this tin consumption corresponds to a total mass of finished tinplate produced each year of over 10 million tons.¹ Table 1 lists some standard thicknesses for specifications of tinplate; however, for special parts tin plated for highly corrosive environments, the tin thickness can be as great as 45 μm .²

Production Method	Designation	tin mass in g/m^2	tin thickness in μm
electrolytic	ASTM 25	5.6	0.38
	ASTM 50	11.2	0.77
	ASTM 75	16.8	1.15
	ASTM 100	22.4	1.54
	ASTM 125	28.0	1.92
hot dipped	1.25 lb	25	1.71
	1.50 lb	30	2.06
	1.7 lb	33	2.26
	2.0 lb	40	2.74

Table 1: Thickness of commercially produced tinplate^{3,4,5}

Tin coatings are typically designated by mass, either as g/m^2 or in the more archaic pounds per basis box (1 lb/bb = 11.2 g/m^2); thicknesses in μm have also been provided.

The steel sheet used for tinplate varies from 0.15 to 0.49 mm, in increments of 0.01 mm.

Tin is one of the oldest metals known to man. In ancient times, it was used both as an alloying element with copper to make bronze and also alone for jewelry. Early uses of tin were as a decorative material. The bright appearance of tin and its ability to form a clear and protective oxide and maintain its pleasing appearance led to the use of tin as decoration on other materials, originally attached by adhesives or by hammering studs on wood or leather. In fact, the original use of tin as a coating was probably more for decoration than protection.⁶

Early tin coatings were probably applied not by melting the tin but by heating the metal under a flux and then rubbing a small ingot of tin on the heated surface until a smooth and complete coating was achieved. The early materials tinned were also those used largely for decorative items, bronze and copper, suggesting that the tinning was for decoration rather than protection. It is not known when iron was first tinned, or tin

coated, but tinned iron from as early as the tenth century has been found, and a twelfth century author, Theophilus Rugerus, wrote "Whatever you wish to tin over in iron, file first and before you touch it with the hand throw it in the pot of melted tin with grease and stir with tongs till it becomes white."⁷

The process described above is basically the process used for tinning iron until the late nineteenth century, although it still refers to the tinning of finished items rather than the production of tinplate. Evidence seems to indicate that production of tinplate, specifically tinned iron sold in sheets with the intent of fabrication of the already tinned product, began in Germany sometime in the fourteenth century.

These initial tinplates were made from hand hammered wrought iron sheet and were made by hot-dipping (as described by Theophilus), although it appears that by that time, or shortly thereafter, an early form of pickling using such acidified fermentation products as vinegar and sour beer had been developed to better prepare the iron for tinning. The spread of the tinplate industry was very slow, not taking root in the other industrial European nations until the eighteenth century and not reaching America until the nineteenth.⁸

Early tinplate, however, was still mostly decorative and found use in such items as tableware (including plates and cups) and cookware, boxes, lanterns, and candle-holders. In fact, in some instances tinplate competed as a cheap substitute for pewter and silver. The major breakthrough for the tinplate industry came in 1810 when Nicolas Appert discovered a method of preserving sterilized foods in sealed containers. By 1812, John Hall and Bryan Donkin were producing "tinned" food. Today, packaging of various types consumes over 90% of the worldwide production of tinplate.⁹

The rapid growth of the canning industry spurred equally rapid growth in tinplate production through the nineteenth century and into the early stages of the twentieth. There are several good reasons for the use of tinplate as a food packaging material. Tinplate has a pleasing, shiny appearance and good corrosion resistance to most external atmospheres and most food acids (although a few do corrode untreated tin severely). In the case where the tin is attacked by the packed contents, the tin and its corrosion products are not harmful to humans, making the packaging safe. Because the majority of the mass of the tinplate is from the base iron or steel, the cost of the material is low compared to other safe, corrosion resistant materials. The surface chemistry of tin is important, as it makes the cans easy to solder (the original joining method for the long-used three piece can with a wrapped and soldered body and two soldered endplates) and also allows for easy application and good adhesion of organic coatings. Finally, the tin-steel bonding in tinplate is strong enough that the mechanical properties of the tinplate

are basically those of the base metal; thus, tinplate may be shaped, forged, blanked, or drawn as well as the base steel, and in some cases even better due to the lubricity of the tin coating.

Although hot-dip tinning was a fairly mature technology by the beginning of the nineteenth century, several important developments have occurred in the tinplate industry since then. These can be divided into two major groups: improvements in the base metal and improvements in the tinning process. The major base metal improvements in tinning paralleled the growth of the iron and later the steel industry. The single most important advance in tinning was the introduction of electrolytic tinning.

For the first several centuries of tinplate manufacture, hammered iron sheet was used as a base material. However, by the turn of the eighteenth century, a rolling mill had been established in Pontypool, England, for the production of iron sheet. By 1730, this sheet was being used to produce tinplate.¹⁰ Rolled iron became the standard until it was replaced by rolled steel in the late nineteenth century. However, at that time the rolling was still done by the Hot-Pack Process, in which sheets were doubled over and hot-rolled as a pack, then separated for the final cold rolling. This was a slow, labor-intensive batch process and was eventually replaced in 1927 by continuous cold-rolling, which was augmented in 1936 by the introduction of continuous annealing.¹¹ Advances since then in steel-making technology have allowed the tinplate base to become thinner and of higher quality, and cleaner steels allow for better tinning. In addition, the use of continuous operations in the steel making and fabricating industries has carried over to tinplating. All modern tinplate is made with continuous cold-rolled and continuous annealed base steel, and most tin plating facilities operate continuously, making use of coiled rather than cut steel.

The actual tinning process itself remained largely unchanged throughout the nineteenth and early twentieth centuries. Automated tinning machines replaced tinpots, and the development of a zinc chloride flux, which was added to the grease pots as a more effective fluxing agent, improved the efficiency of the tinning process, but the basic technique remained the same. Electrolytic tinning was known by the mid nineteenth century, as shown by an 1843 patent¹² for electrodeposition of tin, but the process developed very slowly, as shown by this 1883 comment: "Tinplates have been coated by the aid of electricity, but we do not hear of the process being extensively adopted. Possibly this method is only in its infancy, and ere long more may be heard of it."¹³ In fact, continuous strip electroplating did not appear on a large scale until first used in Germany in 1934. By the 1940s, electrolytic tinning had spread to the U.S. Since then its growth has been so rapid that today over 98% of all tinplate produced is electrolytic.¹⁴

Electrolytic tinplate offers several economic advantages over hot-dipped tinplate. Unlike hot-dipping, which requires handling of individual sheets, the electrolytic method is a continuous process, which speeds production and takes full advantage of the ability to use coiled steel directly in the tinplating line. In addition, electrolytic tin is generally less than 1/10 the thickness of hot-dipped tin (see Table 1). Given the costs of tin and steel (steel sells for about 10¢ per pound; a pound of tin costs \$3.25)¹⁵, even considering the relative quantities used, tin constitutes a major portion of the material cost, which makes the ability of electrolytic tinning to reduce the coating thickness a major economic factor. Electroplating also allows much better control of the thicknesses, and processes have even been developed for production of differential tinplate, with tin layers of differing thicknesses on the two sides of the sheet.

Other advances in tin plating have been made in post-processing of the tinplate, particularly with regard to electrolytic tinplate. Electrolytic tinplate typically undergoes a process called flow-brightening or simply reflowing. Reflowing is performed in-line, following the plating step, and consists of rapidly heating the strip to slightly above the melting point (typically either inductively or by resistance heating through conductive rolls) and then quenching in water. Since tin will completely wet a clean, oxide-free iron or low-carbon steel surface, the reflowing process smoothes the tin layer, which consists of islands of tin grown in the electroplating process. This serves three purposes. First, the reflowed tin has a smooth, shiny surface finish (assuming that the steel base was also smooth) which enhances its appearance, a matter of no small consequence in the tinplate industry. Second, the reflowing helps to insure that the coverage of tin on the base metal is complete. Finally, the interaction of molten tin and steel forms a thin layer of the intermetallic FeSn_2 , which improves the bonding between the tin and steel and also improves the corrosion resistance of tinplate used in food canning. This intermetallic layer is formed naturally during hot-dipping and is much thicker in hot-dip tinplate. Reflowing is not typically done on electrolytic tin coatings thicker than 8 μm .¹⁶

Further improvements in tinplate have been mainly in response to the demands of the canning industry for a material which displays better corrosion resistance, even to the harshest fruit and vegetable acids. Although the demands are primarily aesthetic, this is a major factor in such a consumer-driven industry. The two major areas of change have been in lacquer coating and treatment of the tin to form a more protective oxide layer. Often, the two processes are related, as the condition and treatment of the tin layer affects the adhesion of the lacquer.

Passivation treatments applied to tin have three major purposes: to prevent discoloration during processing or storage, to reduce discoloration due to sulfide staining,

and to prevent rusting during storage. The most common forms of passivation are based on the formation of a film of chromic oxide, typically either by immersion in chromic acid or by cathodic treatment in sodium dichromate (or the second followed by the first). In both cases, hexavalent chromium is reduced at the surface, either by local action currents in the case of immersion or by externally applied voltage in the case of cathodic treatments. Both treatments result in an oxide layer containing both stannous and stannic oxide and chromic oxide, although diffraction experiments have failed to identify any known chromium compounds. The chromium in the oxide film suppresses further oxide growth and also reduces sulfide staining (the discoloration of the tin layer and the package contents by the formation of black stannous sulfide in foods high in sulfur). As none of these protective coatings actually improve the resistance to fruit acids, their primary purpose, aside from packs high in sulfur, is to protect the outsides of cans from discoloration during baking of lacquers and subsequently during their shelf life. It should be noted that passivation films of high chromium content have been found detrimental to the wettability and adhesion of lacquer films, but as very thick tin oxide layers have been found similarly detrimental, a weak chromate treatment is considered optimal for these purposes.¹⁷

Lacquering of cans also serves three main purposes. First, although chromate passivation protects the cans to some degree from sulfide staining, a lacquer will do a much better job. Lacquers for cans to be used with sulfurous packs also have an addition of zinc oxide, which will react to form zinc sulfide with no discoloration. Second, some foods are discolored or suffer a loss of flavor due to interaction with dissolved tin. Although this is not harmful, it is undesirable. Lacquer coatings serve as a barrier to tin dissolution. Finally, in an effort to cut costs, thinner electrolytic tin coatings have come into common use, and in these cases the lacquer coating helps to provide corrosion resistance.¹⁸ It should be noted, however, that the use of tinfoil is still necessary to provide good adhesion of the lacquer, protection in the case of lacquer flaws, and corrosion resistance for the outsides of cans.

2.2 Electroplating

The first electroplating was done around 1800, when the development of batteries by Alessandro Volta made available a constant source of current. The process was of scientific interest, and plating of lead, copper, silver, and zinc was done. However, the process did not become commercially practical until the 1840s. The development of cyanide complexing baths allowed the formation of adherent deposits of silver, gold, copper, and brass. Prior acid baths had yielded poor plating adhesion due to undermining

of the basis metal by the bath. In 1925, a method of plating chromium electrolytically was introduced and found widespread application for decorative, corrosion resistant, and wear resistant coatings.¹⁹ The development of chromium plating sparked new commercial interest in electroplating in general. As mentioned, the first large-scale tin electroplating began nine years later, in 1934. Other metals commonly electroplated are copper, cadmium, zinc, silver, nickel, and alloys of copper and zinc, tin and zinc, tin and lead, and tin and nickel (which electrolytically deposit as a non-equilibrium SnNi compound).

In electroplating, the basis metal to be coated is made the cathode in an electrochemical cell. The cathodic reaction is reduction and deposition from the bath of the metal to be plated; evolution of hydrogen also occurs in some systems, particularly in chromium plating, but in many modern systems cathodic efficiency is very close to 100% and very little hydrogen is produced. Depending on the system, the anode may either be soluble or insoluble. In soluble electrode systems, the metal to be plated forms the anode and dissolution of the anode maintains the metal ion concentration in the bath. These anodes are themselves replaced when consumed. Other systems use insoluble anodes which are never replaced; in such systems, the metal ion concentration in the bath is maintained by additions of metal-containing chemicals.

Preprocessing of the basis metal is often vital to the quality of the plated deposit. Generally the preparatory steps include degreasing, alkali or electrolytic cleaning, and pickling, followed by a rinse before plating. Grease, dirt, and scale on the surface of the basis metal cause poor adhesion, so proper cleaning operations are crucial. However, the cleaning agents themselves are often detrimental to the effectiveness of the plating bath, making the rinse equally important. After plating, the parts must again be rinsed, both because the bath chemicals may damage the finished plating and to prevent exposure to dangerous bath chemicals during subsequent handling and use.

Central to the electroplating process is the bath itself. There are several important criteria used in selecting a bath. It must maintain a sufficient concentration of the metal to be plated in order to achieve reasonable plating currents. For conservation of energy and associated costs, the anode and cathode efficiencies of the bath should be as close to 100% as possible. This also prevents production of hydrogen at the cathode, which can cause embrittlement in high strength basis metals, and oxide filming of soluble anodes, which can cause drops in plating current. If the metal to be plated is noble to the basis metal, it is also necessary that the metallic ions be complexed such that they will not plate spontaneously on contact with the basis metal (which causes irregularity of the deposit and adversely affects adhesion); cyanide baths are often useful for this. The bath must

have sufficient throwing power, which is a measure of its ability to evenly plate parts at different distances from the substrate. A numerical measure of throwing power is given by the following:

$$TP = \frac{100 (K-M)}{K}$$

where

TP is throwing power,

K is the cathode/anode spacing ratio,

and M is the associated ratio of metal mass.²⁰

In the above, if the ratio of masses is equal to the ratio of the cathode-anode spacings, the bath is said to have 0 throwing power. For baths used to plate sheet, throwing power is not important as long as the anodes all dissolve equally; but when plating shaped parts or pieces with holes or other surface irregularities, throwing power is very important for an even and smooth coating. The brightness of the coating produced is also important, since many coatings are used for decorative purposes. Bath composition strongly affects the brightness of the coating and the range of plating currents over which brightness may be maintained. Additives are used for most common plating systems to improve brightness.

Where all of the above criteria can be met, other factors come into play. The bath should be stable; that is, it must not degrade during use, become irreversibly depleted of metal ions, or become clogged with precipitates formed from chemicals added to maintain the metal ion concentration. Most baths are designed to be used almost indefinitely, with occasional filtration. Although not many are, a good bath would be insensitive to impurity elements. Additional factors are safety and environmental issues. Heavily acidic baths require corrosion resistant container walls or polymer coatings, not only for the plating bath itself but also for the following rinse baths. Fixtures must be similarly protected. Cyanide-based baths present a danger of HCl evolution in contact with acids, requiring very strict rinse control after pickling, greater separation of pickling and plating tanks, and extra storage precautions.

There are four major systems used for tin plating: one alkaline and the others acid. The alkaline bath uses sodium or potassium stannate along with the appropriate (sodium or potassium) hydroxide. The anode is typically of the soluble type, but it must be polarized, a process known as filming, so that the tin will dissolve as the stannic (+4) ion. This causes a control problem in plating, as outside of a small range of operating currents, the anode will either dissolve as stannous tin, which does not plate out in the alkaline bath, or passivate, which drops the dissolution rate to virtually zero. It is possible to operate the bath with insoluble anodes and constant additions of alkaline stannates, but

this causes a buildup of sodium or potassium in the bath, which must eventually be discarded. Although, as will be seen, the acid baths offer several advantages over the alkaline system, the alkaline bath does offer reliable quality coating without use of special addition agents and is non-corrosive to plain carbon steel, which makes the tank, rolls, and fixtures much less expensive. However, the alkaline bath has largely gone out of use and accounts for only a small portion of electrolytic tinplate.²¹

As an alternative, three different types of acid baths are in use: Ferrostan, Halogen, and fluoborate. Ferrostan technically refers to the trade name of the tinplate made using this process by USX²², but it is commonly used to describe the process itself. The Ferrostan, or stannous sulfate, bath uses phenolsulphonic acid and dissolves the tin in the stannous (+2) state. The major advantage of this is that the current passed per mole of tin plated is only half what is required in alkaline baths using stannic (+4) tin. However, there are some drawbacks to the stannous sulfate system. Several addition agents, typically dihydroxydiphenylsulphone and monobutylphenylphenol sodium monosulphonate²³, are required. These additives serve three purposes. First, they prevent the stannous tin from oxidizing to stannic tin. Although this does not directly affect the plating, the stannic tin will eventually precipitate as stannic sulfate, which will form a sludge and eventually render the bath unusable if not removed. Second, the additives improve the wetting characteristics of the bath. Finally, the additives promote the formation of smooth deposits which have better brightness. Anode efficiency for the Ferrostan bath is 100%, but cathode efficiency is only around 95%, which can be beneficial with regards to maintaining the concentration of tin in the bath.

The Halogen bath, developed by DuPont,²⁴ uses stannous chloride in an aqueous solution with sodium fluoride, potassium bifluoride, and sodium chloride. Like the stannous sulfate bath, additives are required to prevent oxidation of the stannous tin and to produce a smooth, bright deposit. Typical agents are naphtholsulphonic acids, polyalkylene oxides, or gelatin. Again, the anode efficiency is 100%, with the cathode efficiency just above 97%. The Halogen bath allows very high cathode current densities and consequently is operated at very high speeds, typically in excess of 500 m/min. sheet speed.²⁵

The fluoborate process is a more recent development. While there is a great deal of interest in the system, it still accounts for only a small part of the tinplate produced today.²⁶ The bath is based on fluoboric acid and stannous fluoborate. Like the other acid baths, special additives are required to prevent oxidation of the stannous tin and to produce a smooth deposit. However, these addition agents work especially well; sludge formation can be reduced to the point that special filtering is not required, and the bath,

properly operated, produces an especially bright finish after reflowing. The fluoborate bath also offers the advantage of particularly high tin concentrations, and the efficiencies of both the anode and cathode approach 100%. Unlike the other three baths, which are operated at elevated temperatures (35°C for the Ferrostan process, and up to as high as 90°C for the alkaline stannate bath), the fluoborate bath can be run at room temperature. Bright coatings may be achieved over a wide range of current densities and temperatures.²⁷

However, all electroplating methods have environmental drawbacks to them. Electroplating processes create a large amount of toxic waste, which, for electroplating as a whole, can be broken down into seven categories: cyanides, hexavalent chromium, pH fluctuations, oil, heavy metals, phenols, and phosphates.²⁸ Although in tinplate manufacture, only pH fluctuations and tin are necessarily produced, some baths or bath additives include phenols, and passivation baths contain hexavalent chromium and often phosphates as well. Electroplating of other metals incorporates more dangerous chemicals. Although efforts have been made to reduce the use of cyanides, cadmium, copper, zinc, and silver are still commonly plated from cyanide baths.²⁹

What are the dangers of these various types of pollution? Cyanides and hexavalent chromium are extremely toxic, not only to people, but also to animal life. In many cases, the tolerance of aquatic animals to concentrations of cyanide and chromium are even lower than the tolerances for humans, leading to destruction of waterways by waste which might seem safe from a purely human point of view. Deviation of pH from neutrality can have similar effects, and also affect aquatic plant life as well. Oils present a similar danger, and will tend to form slicks on the surface of water, in addition to being mildly toxic and in some cases carcinogenic. Metals in the waste stream pose a health hazard, particularly cadmium but others as well, and many metals harmless to humans in plating waste concentrations will destroy sewage treatment bacteria if released through a municipal sewage system.³⁰ Simple dilution of the plating waste is not a solution. There is the issue of contamination at the spot of release, where dilution has not yet occurred, and also the issue of the number of facilities which might be dumping waste in an area. Because of this, most waste water ordinances restrict the concentrations of plating wastes to such low levels that they effectively require complete removal, even in the instance that discharge is into a sewage system.³¹

There are several sources of wastewater in the plating process: rinse water; intentional process solution dumps; spills, drips, and leaks; process treatment devices; ventilation systems; and accidental losses.³² Of these, rinse water is the greatest concern, for several reasons. Although proper methods of rinsing and optimal design of rinse

water flow can greatly reduce the amount of rinse water waste produced, it is impossible to eliminate it completely. Because of the sheer volume of rinse water produced, it must be treated and released as part of an in-line process, rather than stored for later treatment or destruction. Intentional dumping of process baths is rare, but does occur. Certain types of plating baths are unstable and will eventually become unusable. Also, in small job shops, where many different materials are plated, it may on occasion be cheaper to dispose of a bath than to store it until it is needed again. Spills, drips, and leaks can obviously be minimized, but not eliminated. Although small in volume, they cause the problem that all water which possibly contacts them must be treated as contaminated. Process treatment waste includes such things as filtrates from baths and the output from regeneration of ion exchangers used to clean waste waters of high volume and low contaminant concentration. Ventilation system waste comes from water and chemicals used to clean air ventilation outlets drawing toxic vapors away from process baths. Finally, there are accidental losses, which cannot completely be planned for and dealt with, and are usually the most catastrophic.

Although methods have been devised to deal with treatment of plating wastes,^{33,34,35} the issue of cost is still a major factor. There are several sources of increased cost in dealing with wastewater treatment.³⁶ There is a large capital investment in equipment for waste handling. In addition, there is the expense of skilled labor to operate and maintain the equipment and power to run it, all of which is operating expense not directly contributing to the production of the plated product. In many cases the chemicals required to neutralize or destroy the waste are more expensive than the initial cost of the material which is being destroyed.³⁷ Finally, there is the possibility of increased sewage disposal and water costs because of the possibility of contamination of sewage lines or local waterways. There is some financial recovery possible, as a well-run treatment facility may actually recover for reuse certain valuable chemicals or metals, but the operation still runs at a net loss (relative to free dumping).

As a final note on electroplating, it is worthwhile to mention that in addition to tinplate, electroplating is used on a wide range of metals and alloys. Basis metals plated cover a wide range, and the only real requirements are that the part be conductive and that it be resistant to any corrosive effects of the plating bath. It is also possible to electroplate non-conductive materials, in particular many polymers;³⁸ however, this requires first electroless plating with copper or nickel to give a conductive surface. In addition, fixturing is difficult, and electroplated coatings on plastics in general have far worse adhesion than those on metallic substrates.³⁹

2.3 Other Coating Methods

Aside from electroplating, there are many other coating methods in limited commercial use. As discussed, the major problem with electroplating as a process is its environmental side effects and the ever-rising associated costs. Most other coating processes currently available are much more environmentally friendly than electroplating. Some of these coating technologies have product performance-related characteristics which have given them the advantage in certain processing areas; however, various other factors, mainly cost or limited applicability, have held them to a minor role relative to electroplating in terms of volume of coated material produced.

2.3.1 Non-electrolytic Bath Plating Techniques

There are several methods of depositing metal coatings from an aqueous solution without an externally applied voltage. These can be divided into four categories: immersion plating, contact plating, non-catalytic reduction, and catalytic reduction (more commonly known as electroless plating). Of these, electroless plating is the most important commercially, although some of the others have seen limited use.

Immersion plating works by a displacement reaction. A noble metal can be plated onto a less noble metal by a simple displacement reaction, the base metal being dissolved and the noble metal deposited from solution. By use of suitable complexing agents, it is possible to vary the relative nobility of the metals so as to plate a normally less noble metal onto a normally more noble metal. The process does not occur uniformly over the part, but rather works by setting up local action cells in which some parts of the base metal act as the anode and dissolve while others act as the cathode, where plating occurs. Because of this, the thickness of the deposit is limited by the shutdown of the reaction, either because of growth of the deposited film over the anodic areas or because of passivation of the anodic areas. The maximum thickness is about 5 μm .⁴⁰ Immersion plating has been widely used with tin, more so than with any other material, especially for the tinning of aluminum pistons for internal combustion engines.^{41,42,43} This is done in a bath of sodium stannate operated at 175°F. A 3-5 minute immersion will produce a coating of 4-5 μm thickness. Immersion tinning has also been used for decorative coating of numerous small parts made of copper, brass, or steel, mostly using stannous chloride baths, and immersion plating of copper, nickel, and zinc (only onto aluminum and magnesium substrates) has also been done. Immersion plating was the standard method for gold plating prior to the development of electrodeposition.⁴⁴

Contact plating, discovered by Henry Bessemer in 1831 when he was immersion plating copper onto cast type metal in a zinc tray, works on the same basic principle as

immersion plating, but uses a third metal as the anode rather than dissolving the substrate. Bessemer's discovery was that instead of dissolving the type metal, his plating bath dissolved the zinc tray, which was in electrical contact with the type metal parts. The zinc dissolved and the copper plated out on both the zinc and the type metal. The advantage of this system over normal immersion plating is threefold. First, because there is a larger anode area, the plating reaction can proceed faster than in the case of simple immersion. Second, because the part does not have to serve as the anode, deposition can continue beyond total coverage of the part, and thicker deposits can be produced. Thirdly, it is possible to use contact plating to coat a base metal onto a noble metal without the use of special complexing agents, so long as the contact metal is less noble than that metal to be plated. Contact plating does, however, suffer from the problem that the contact point may wind up unplated. Also, the contact metal itself will also receive some cathodic action and will be plated also, slowing and eventually shutting off the anodic reaction.

There are additional problems which are shared by both immersion and contact plating. In both cases, the bath will become depleted of the plating metal quickly and will become useless unless chemical additions can maintain the metal concentration. On the other hand, the bath will become contaminated with the base metal dissolved from either the part or the contact metal. Finally, in many cases, undesirable side reactions will occur which decrease the efficiency of the bath or diminish the properties of the coating.

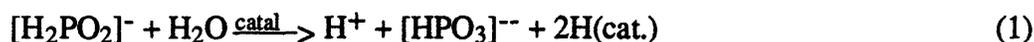
The last two types of non-electrolytic deposition do not rely on dissolution of metal. Both methods are similar, but one is non-catalytic while the other is catalytic. Non-catalytic chemical reduction is used to plate from an aqueous bath. A strong reducing agent is added to the bath which will cause the metal to plate out. The maximum coating thickness is similar to that for immersion plating. However, this method can be used to coat non-conductive materials. There are several drawbacks to the method, though. First, the plating ceases as soon as the surface is completely covered. Also, if the reducing agents are too strong, the deposit will be spongy and have an unsatisfactory appearance. Finally, the reaction, once started, will continue until the entire bath has been depleted of metal, rendering it useless for further plating and also causing material to plate on the container and any fixtures. Excess metal left in the bath after everything has been plated will precipitate as sponge metal. Commercially, the process is only used for deposition of silver and copper and non-conductive materials for decoration, silvering of mirrors, or providing a conductive coating.⁴⁵

Electroless plating is the most common of the non-electrolytic bath techniques. The reaction itself was first discovered in 1844, by Wurtz,⁴⁶ and in 1916 the first patent was

granted for the process.⁴⁷ The basic chemical reaction is reduction of nickel ions in aqueous solution by oxidation of hypophosphite. The reaction also produces elemental phosphorus, which becomes part of the coating, forming an alloy coating of 85-97% Ni and 3-15% P. The original technique was a non-catalytic reaction which deposited nickel in an uncontrolled manner. However, in 1946, Riddell and Brenner developed a method for autocatalytic selective deposition of nickel on steel. They called their process electroless plating, published several papers, and were eventually awarded two patents.^{48,49,50,51,52} The process used a similar bath, but rather than direct reduction of nickel by the hypophosphite, as shown below,



the nickel is reduced by hydrogen on the surface of the catalyst in the following series of reactions:



In this case, atomic hydrogen is formed on the catalyst surface by the oxidation of hypophosphite. The hydrogen then reacts with the nickel in solution to plate nickel and oxidize the hydrogen. The nickel surface itself acts as a catalyst, thus sustaining the reaction. A similar reaction deposits elemental phosphorus. It will be noted from these reactions that operation of the bath reduces the pH; if bath pH is allowed to drop below 3.0, plating will stop, so this reaction must be compensated for by the addition of chemicals such as sodium hydroxide. The reaction also depletes the bath of hypophosphite ions, and a side reaction which produces hydrogen gas rather than atomic hydrogen on the catalyst reduces the efficiency to about 33% (nickel atoms deposited per hypophosphite ion oxidized); hypophosphite must be added to the bath during operation to maintain plating. Also, it is occasionally necessary to precipitate the orthophosphite (HPO_3^{--}); however, this process is very expensive and often the bath is simply dumped instead. The plating rate is an exponential function of temperature, so baths are operated hot, typically above 167°F but below the boiling point of 217°F. Elevating the pH and hypophosphite concentration also increases plating rate, but the bath is metastable, and when a combination of sufficiently high temperature, hypophosphite concentration, and pH occurs, random precipitation of nickel occurs, with these precipitates then fueling the autocatalytic reaction and rapidly depleting the bath.

Preparation of materials for electroless plating is similar to that for electroplating. The material must be clean and free of oxides. In addition, several metals are catalytic poisons, including lead, tin, zinc, cadmium, antimony, arsenic, bismuth, molybdenum,

vanadium, tungsten, and zirconium; these metals cannot be plated by this technique and their presence at the surface of any part to be plated may cause poor plating results.⁵³

Electroless nickel plating is by far the largest volume application of this process, and has found widespread use. The process can be used on parts which are hard to electroplate because of size or shape or fixturing difficulties. It can be used on non-metallic materials, although coatings on plastics and ceramics are not nearly as adherent. The Ni-P alloy formed is harder and more corrosion resistant than electrolytic nickel. The process is also useful for plating certain materials (Al, Mg, Be, and certain superalloys) to improve wetting by solders or brazes. Electroless copper has also found some use for plating of printing circuit boards, due to the ease of plating difficult shapes on non-conductive parts; however, electroless copper coatings are typically overplated with electrolytic copper.

Electroless plating, however, suffers from several drawbacks. The reducing agents used in the process cost more than the electricity which would be required to electrodeposit identical coatings, making the process economically unfavorable. Also, very thick coatings cannot be formed, rendering the process less effective for parts to be used in highly corrosive applications. The Ni-P alloy produced in electroless nickel plating, although stronger and more corrosion resistant than other coatings, is brittle and has poor flex and impact resistance and hot hardness, and the presence of P in the coating makes the parts difficult or impossible to weld.

A problem of all the nonelectrolytic techniques is that they share the environmental costs of electroplating. All still make use of chemical baths and require similar cleaning and rinsing. Further, since the baths of nonelectrolytic processes eventually degrade and must be disposed of, the environmental problem is in some ways even worse.

2.3.2 Hot Dipping

Although hot dipping is no longer much used for production of tinplate, it still finds application for other coatings, particularly of zinc and lead, but to a lesser degree also for production of some tinned parts. In all cases, the process is basically the same. The part to be tinned is first cleaned and pickled. After that it is fluxed, and then immersed in a bath of molten metal. An intermetallic layer grows at the interface and the thickness of the final coating is largely determined by the duration of immersion in the bath. Upon removal, the piece is cooled to dry the coating (sometimes by forced convection to reduce oxidation of the coating). All hot dip processes suffer the limitation of working only with low melting coating alloys and the requirement to keep a large bath of metal in the

molten state during the operation. In addition, the bath eventually becomes contaminated with the basis metal.

Zinc hot dipping or hot dip galvanizing is in widespread use for steel construction parts, especially those which will be exposed to chlorides in service. The properties which make zinc an excellent coating are slow corrosion rate, galvanic protection of the basis steel, and the ability to paint the zinc layer easily for decorative or protective purposes. The flux used is zinc-ammonium-chloride, which, depending on the process, is either floated as a foam on top of the bath (wet galvanizing) or placed on the part as an aqueous solution which is then evaporated before immersion (dry galvanizing). The intermetallic layer in zinc hot dipping is much more complex than that formed in tinning; it has several layers and the exact composition is a function of immersion time and bath and basis metal composition. The corrosion resistance of final product is proportional to the coating thickness, and thicknesses in excess of 610 g/m^2 ($43 \text{ }\mu\text{m}$) are standard.⁵⁴

Hot dipping of lead alloys, called terne plate, is also widely practiced, and continuous dipping lines have been developed for production of terne strip. The material finds wide use for underhood automotive parts as well as fuel tanks and some outdoor building materials, due to the high corrosion resistance and good weldability, solderability, and paintability of the terne coating. Because pure lead will not alloy with iron, 2-25% tin and sometimes antimony are added to the lead bath. The process for terne dipping is identical to that for tin dipping. Coating thicknesses range from 60 to 250 g/m^2 , which is approximately 5 to $22 \text{ }\mu\text{m}$.⁵⁵

2.3.3 Chemical Vapor Deposition

For specialized applications, chemical vapor deposition has found some use in depositing metallic coatings. The process is expensive and has several other drawbacks as well. The gases used are often toxic or corrosive, and require special handling and disposal in addition to being a possible safety hazard. The substrate for CVD is generally held at elevated temperature in order to allow deposition, which requires special atmospheric control and also can destroy any heat treatment previously performed on the part to be coated. CVD does, however, offer certain advantages. Although the substrate is held at high temperature, it is possible to deposit refractory metals or ceramics at temperatures far below their melting points; for this reason the process is mostly used with nickel, chromium, tungsten, and tungsten carbide coating. The properties of the deposited layer can be controlled to achieve near theoretical density. Control of grain size or orientation as well as epitaxial growth are possible in some cases. In addition, the coating has good bonding and the process has good "throwing power".⁵⁶

There are two different types of CVD process, displacement and decomposition. In a displacement reaction, the basis metal is absorbed into the gas stream and the coating metal deposited in an exchange. In order for this reaction to continue beyond formation of a very thin layer, the coating must diffuse into the substrate. Although this provides excellent bonding and is often beneficial in terms of surface properties, it does require an especially high operating temperature; also, thickness of the deposit is limited by diffusion and the time required grows exponentially with coating thickness. In a decomposition reaction, the gas decomposes, leaving the coating material on the surface. Due to high substrate temperatures, some diffusion of the coating may occur, but it is not necessary for continued coating, and the deposition rate is constant with time.⁵⁷

2.3.4 Vacuum Techniques

Three main vacuum techniques are in use for coating: evaporation or physical vapor deposition, sputtering, and ion plating. All three see limited use in the coating industry, mainly because of high cost and low plating rates. The processes are operated in some degree of vacuum, although for sputtering and ion plating the chamber is backfilled with inert gas at low pressure to allow a plasma to be lit.

Evaporation is the simplest of the three. The material to be deposited is evaporated. Heating is by refractory metal wires or foils or, more commonly, in small crucibles heated by radiation or conduction from a resistance wire. In some cases evaporation is by electron beam, with the coating material continuously fed and serving as its own crucible. This has the advantage of being usable with high melting materials and in continuous operation. The vapor then spreads throughout the chamber and coats all surfaces, including the chamber walls and the cooler parts of the evaporation apparatus. Coating thickness is a function of distance from the source, and parts must be moved to ensure an even coating. The composition of an alloy coating is determined by the melt composition and the relative vapor pressures, rather than by the bulk composition of the starting stock. Evaporated coatings are typically very thin. Some uses include coating mirrors and reflectors for lamps and scientific instruments and producing light attenuation coatings for anything from sunglasses to microscopes. Evaporation works equally well for coating ceramics and plastics as for coating metals. Some application has been found for wear and corrosion resistance coatings on high strength steels, as there is no concern over hydrogen embrittlement as would be the case with electrolytic or electroless plating. The process has also been used to apply M-Cr-Al-Y hot corrosion resistant coatings on turbine blades. Using electron beam evaporation, it is possible to build an apparatus for continuous coating of sheet, but these are very slow, operating at sheet speeds of only 5

m/min. for decorative coatings and only a few cm/min. for heavier corrosion or wear-resistant coatings.⁵⁸ By far the largest volume of commercial evaporation coating, over 99%, is done with aluminum, mainly for electronic circuitry and decorative coatings. Aluminum is easy to evaporate and has a bright finish. Decorative coatings of aluminum and some reflective coatings (depending on the application) are covered with a clear lacquer to protect the very thin coating from physical damage.⁵⁹ It should be noted that despite its low melting point, tin has a very low vapor pressure and is thus difficult to apply by physical vapor deposition.

Sputtering is similar to evaporation except in the manner in which the coating material enters the vapor phase. A plasma of some inert gas, typically argon, is lit, using the target of coating material as the cathode and an operating voltage in the range 0.5 to 5 kV. This causes bombardment of the target by high energy (10 to 40 eV) argon ions, which dislodge atoms from the target. These then deposit on the part and inside the sputtering chamber. Rates of deposition are very slow, a maximum of 30 nm/sec for metals, less for ceramics, and the process is very inefficient, as most of the energy goes into heating the target rather than dislodging atoms (relative to evaporation, sputtering has 3-10 times the energy cost, depending on the vapor pressure of the material). However, sputtering does have two advantages, both due to the fact that the coating material enters the vapor phase by mechanical, rather than thermal means. First, the sputtering rate is similar for all target materials for a given ion bombardment energy, regardless of the vapor pressure. Second, the rate of sputtering of all components of the target is proportional to their fraction of the target, so the composition of the deposited coating is the same as that of the target. The primary use of sputtering is in deposition of aluminum alloys, refractory metals, and oxide insulation layers on microcircuits; however, it has also been used for chrome plating of plastic auto body parts, TiN wear resistant tool coatings, and MoS₂ lubricant coatings.⁶⁰ The slow rate of deposition and the high cost of operation make this process unsuitable for any large-scale sheet plating operations.

Ion plating, or ion vapor deposition, combines some features of both evaporation and sputtering. The part is placed in a vacuum chamber in which a plasma of inert gas is lit. The plasma cleans the surface of the part for a few minutes. Next, standard evaporation techniques are used to introduce metal vapor into the discharge. The vapor is then ionized and accelerated towards the part, where it forms a solid coating. This concentrates the deposition of the evaporated material on the part, increasing the plating rate to as high as 25 $\mu\text{m}/\text{min.}$, although 3-5 $\mu\text{m}/\text{min.}$ is more common. Also, continuous cleaning of the part surface and redeposition of the etched coating gives the process a

high "throwing power" and provides very even coverage, even over an uneven surface. The process is currently used for aluminum coating of titanium and high strength steel spacecraft fasteners and for undercoats for electroplating, but its high cost and the long cleaning time limit its applicability.⁶¹

2.3.5 Thermal Spraying

Thermal spray technology for coating was developed in 1910 by Swiss inventor M.U. Schoop.^{62,63} Schoop's initial work was done by pouring a molten metal stream into a jet of high pressure air, a process which had previously been used for atomizing liquids, and placing a substrate in front of the gas jet. Based on this molten metal process, Schoop and his co-workers developed methods using powder and wire as feed stock. Today, there are four methods of spray coating: molten-metal spraying, flame spraying (used with both powder and wire), electric arc spraying, and plasma spraying.

Schoop's original molten-metal technique was developed further by addition of apparatus to aspirate molten metal from a bath through a pinpoint hole. It was this process which eventually led to the Mellozing pistol (so named for the company which first produced it), invented by Jung and Versteeg in 1924. The Mellozing pistol resembles a large handgun with a container for molten metal and a gas inlet. Molten metal from a separate furnace is fed in and kept hot by a natural gas flame inside the gun (which also pre-heats the high pressure air). The metal is aspirated from the chamber and sprayed. When empty, the chamber is refilled. The Mellozing pistol is simple to construct, runs off a regular natural gas line, and uses simple compressed air. Also, because the metal is melted separately and fed as liquid, the feed stock for the gun can be ingots. However, there are several disadvantages. The gun is cumbersome and is not effectively portable, due to the need for the melting furnace to feed it. Also, the parts wear out very rapidly, particularly when used with zinc, and only low melting metals can be sprayed, with aluminum as the upper bound. Finally, the gun must be kept stable and the spray is horizontal only.⁶⁴ Today, this process sees very little use.

The difficulty of containing a melt for metal spraying and the limitations this imposed on possible coating materials spurred developments of new techniques which could use solid feed stock. Flame spraying was the second idea developed by Schoop and his colleagues, and is still in wide use today. Rather than using a feed of molten metal, the original flame spraying guns used a powder feed. This caused some difficulty at the time because metal powders were not widely available and were often irregular in shape and size and therefore tended to jam the gun. The modern powder spraying process was developed by Fritz Schori, who devised a feed system based on three gas streams.

The combustible gas is ignited to form an annular flame. The powder-laden air is introduced inside the annular flame by low-pressure, preheated compressed air (which must be kept very dry to prevent excessive oxidation of the powder), while the high-pressure air flows outside the flame from a second annular outlet. In this process, the powder is broken up very little, so the droplet size tends to be the initial powder size.⁶⁵ Powder spraying is still used today for applications such as spraying of catalytic coatings and electrically insulating oxide coatings.⁶⁶

Two years later, Schoop and his co-workers expanded the flame-spraying process to use wire feed stock. This eliminated the problem of powder feed jamming and also greatly expanded the materials which could be sprayed, although materials difficult to draw to wire were still not used (for certain cost-blind applications, rods of material which cannot be drawn are centerless ground to the wire size [typically $\frac{1}{8}$ "] and fed back-to-back into the sprayer). The gun uses an annular flame surrounded by the high-pressure spray, just like the powder gun, with the rod fed into the back of the flame at a constant rate by a set of rollers. The only real disadvantage of this process relative to powder spraying is that the flame must be extremely hot to melt the rod quickly enough for reasonable spraying rates,⁶⁷ which for modern guns can reach 30 kg/hr. Wire spraying is today used for such applications as production of zinc and aluminum corrosion resistant coatings and is far more common than powder spraying.⁶⁸

Electric arc spraying was also developed by Schoop, with the assistance of Bauerlin, in 1914. His first efforts used a wire of feed stock and a carbon rod, but it was quickly discovered that using two wires of feed stock worked more effectively and without the worry of wear on the carbon electrode. When the gun is operated, an electric arc is struck between the two wires at up to 80V. The arc melts the tips of the wires, which are in a spray of high-pressure air. As compared to flame spraying techniques, the electric arc process is much simpler, requiring no combustible gas (in fact, requiring only an air compressor and electric power supply) and operating at lower cost with greater output. However, the process does require an appropriate electrical supply. Also, in some alloys, the composition of the feed stock is altered by evaporation of constituents during the arc melting.⁶⁹ A modern electric arc gun is capable of spraying up to 55 kg/hr.⁷⁰ Work has also been done on the use of induction heating for wire spraying. Although this method works well for spraying in special atmospheres, it is inefficient compared to arc melting.⁷¹

The final type of thermal spraying is plasma spraying. The plasma spray gun works by lighting a plasma between two water-cooled electrodes in the spray gun. Inert gas, usually argon or nitrogen, is fed in from the back to maintain the plasma. A hole in the

front electrode allows a jet of extremely hot air to escape. Powder injected near the front electrode is melted by the plasma and carried out by the jet of escaping air and sprayed on the substrate. This process can be used with ceramics as well as metals, due to the high temperature of the spray. Spraying rates for plasma guns can reach 9 kg/hr. Plasma spraying is used for coatings such as electrically resistant oxide layers and wear resistant coatings of high-melting materials like chrome-nickel-boron alloys and tungsten carbide.⁷²

A second type of plasma spraying, called transferred arc plasma spraying, electrically links the front electrode of the plasma gun with the substrate. A secondary circuit conducts electricity to the substrate through the spray. This heats and possibly melts the substrate. Transferred arc spraying requires less energy than standard plasma spraying at the same deposition rate and yields better bonding and denser coatings; however, it requires an electrically conductive substrate and will also damage any heat treatment on the substrate.⁷³

All sprayed deposits (except transferred arc spraying) have similar characteristics, and the preparation of the substrate and post-processing of the deposit is similar for all systems. The surface preparation for metal spraying is simpler than for other coating techniques. The substrate must be clean and grease free, but need not be pickled or electrocleaned. In order to assure good adhesion, however, the surface is typically roughened by blasting (sand or grit) or by rough threading (in the case of cylindrical parts). Adhesion is mechanical, with the blasting or threading allowing the initial layers of the coating to attach. Further layers interlock with the irregular shapes of previous layers, forming a solid piece by mechanical keying. The metal stream carries very little heat to the surface due to cooling in flight, and there is little or no metallurgical bonding or interdiffusion between the coating and the basis metal. This low heat transfer does, however, make thermal spraying suitable for coating of plastics and glass or even wood and cloth. All metal spray coatings share two characteristics: rough surface and porosity. The former is generally undesirable for aesthetic reasons. The latter ruins any corrosion resistance, although it can be useful for retention of lubricants. Most deposits are only 85-90% dense, but coatings thicker than 230 μm have been found to have no interconnected porosity from surface to substrate. In order to smooth the surface and seal the porosity, several methods can be used. They include burnishing, rolling, swaging, wire brushing, and shot peening. In some cases, organic sealants can be used to close up the porosity, but this is unsuitable for high temperature or high friction applications where the sealant would melt or degrade.⁷⁴

Several uses of thermal spraying have already been mentioned. In general, the low coating rate of thermal deposits makes them unsuitable for mass production, and they tend to find use on parts which cannot be coated easily by other methods. Thermal spray is especially effective for coating with oxides and carbides, which cannot be made as thick deposits by any other means. Rust-proofing of large or irregular structures can be easily accomplished with spraying guns, and spraying over welds and rivets in completed parts is easily possible. However, due to the uneven distribution of metal in the spray cone, the quality and evenness of the sprayed deposit is controlled by the skill of the gun operator or the precision and pattern of automated spraying apparatus.⁷⁵

2.4 Powder Metallurgy and Rapid Solidification

As mentioned, even before Dr. Schoop built his first spray coater, the ability of gas atomization to make metal powders was known. In recent years, there has been a great interest in powder metallurgy (PM) for industrial applications. Powder metallurgy production of parts consists of several steps: production of powdered metals, consolidation of powder, and shaping and densification. The last two may be performed in combination or individually in either order, depending on the process used. This processing route offers several advantages in both economics and performance.

Economically, the advantages of powder metallurgy lie in three main areas: efficient use of materials and energy, reduced costs in production of short runs, and reduced labor and tooling costs through elimination of forming operations.⁷⁶ Because powder production yields are very high, efficient use of materials and the energy required for solidification processing of metals is achieved. In such a price competitive market, the savings in energy, materials, and time costs from yields approaching 100% are important. By selecting an appropriate consolidation and densification method, the tooling required for production of parts by PM can be considerably simpler than that required for typical hot and cold working. Also, the basic powder production methods remain the same regardless of the material used or the final shape desired; only the consolidation methods and tooling must be varied to switch from production of one finished part to another. Similarly, since PM parts can often be formed to net or near net shape, depending on the precision required for the application, a multiple step process of forming, machining, and finishing a part can often be replaced by single consolidation step which may optionally be followed by surface finishing and minor machining for precise tolerances. It should be noted, however, that powder processing itself is a slower and more costly route than traditional ingot or continuous cast solidification processing, so the economic potential of PM processing can only be fully realized in the production

of short run or difficult to machine parts where the elimination of finishing tooling and labor offsets the increased cost of the powder stock over bar, rod, sheet, or ingot stock.

On top of the potential economic advantages, PM provides several unique property improvements due to the rapid solidification of metallic powders. The high supercooling of the melt during powder processing techniques leads to substantial departures from equilibrium, including enhanced solid solubility and formation of non-equilibrium crystalline and even glassy phases. In addition, the rapid solidification of particles leads to a very fine dendrite spacing which, combined with the extended solubility, virtually eliminates segregations and massively reduces the size of inclusions. High solidification rates also give powders a very fine grain size (on the order of 10 μm), which enhances the strength of the material if this can be maintained throughout the manufacturing process. Even finer grain sizes ($< 0.1 \mu\text{m}$) can be achieved through crystallization of glassy materials. These microstructural features have several beneficial effects on the properties of finished parts. Metal powders are inherently isotropic, unlike traditional ingot parts, which typically have a strong anisotropy, either from solidification or from rolling and forging operations. Furthermore, the reduction of segregation and the small size of inclusions increases the toughness and fatigue strength of many PM alloys and allows higher tolerance for impurities, which is especially important for recycled material.⁷⁷ PM processing also offers unique alloying capabilities, such as mechanical alloying of compositions not normally possible by ingot technology, and production of parts with insoluble reinforcements, such as oxide dispersion strengthened (ODS) alloys⁷⁸ and fiber reinforced, metal-matrix composites.^{79,80,81,82} Currently the majority (60-70%) of PM parts go into automobile manufacture. Other applications include turbine discs and oxide dispersion strengthened turbine blades.⁸³

Powder metallurgy starts with the production of powders. Several methods are currently in use; these can be broadly broken into chill processes and powder processes. Chill processes make use of a water-cooled rotating wheel, and include melt-spinning, melt extraction, and twin roller quenching. In all processes, molten metal is brought into contact with the wheel and rapidly solidified to form flakes, ribbons, or sheet. Chill processes achieve very high cooling rates, on the order of 10^5 to 10^6 K/s. The product is then typically broken up to provide small flakes, although for applications such as transformer cores and soft magnetic materials large, thin, continuous sheets may be produced. Powder processes produce powders directly through atomization, either by use of a spinning cup or rotating electrode or by gas atomization. Gas atomization techniques can be broken down into three types: subsonic gas atomization, sonic gas atomization, and ultrasonic gas atomization. Subsonic gas atomization produces the lowest cooling

rates, 10^0 to 10^2 K/s, and the largest powder sizes. Sonic gas atomization, which is used in the Osprey process, achieves cooling rates on the order of 10^3 to 10^4 K/s. Ultrasonic gas atomization, which is used in the Liquid Dynamic Compaction process, has the highest cooling rates, 10^4 to 10^5 K/s, and the smallest powder sizes as well as the narrowest distribution of powder sizes.⁸⁴

Although for some applications powders can be used directly, in most cases it is necessary to consolidate them to manufacture a part. Several methods are available, including pressing and sintering, powder forging, hot pressing, hot and cold isostatic pressing (HIP and CIP), powder rolling, extrusion, metal injection molding (MIM), and cold forging. The type of process selected will determine the cost of the tooling and the consolidation operation, the amount of densification and the degree of anisotropy of mechanical properties. In all processes, the basic steps are elimination of trapped gas, filling of large voids, plastic flow into small voids, and diffusional bonding of the particles. It is important in this processing that any oxide skin which may be present on the particles is broken down to insure full densification and good diffusional bonding.⁸⁵

2.5 Spray Deposition and Liquid Dynamic Compaction (LDC)

Although PM processing offers several benefits in terms of economics and properties, it still fails to approach the economy of conventional castings for production of simple shapes such as bar stock and sheet metal. Powder metallurgy also requires complex and expensive equipment to keep the powder clean and oxide-free during the multi-step process of going from powder production to finished part. In addition, it is often too expensive to fully densify PM parts or impossible to do so without the special PM properties degrading due to grain growth or coarsening of inclusions and intermetallics at high temperature. Thus, the PM parts are used at less than theoretical density. Finally, oxide levels in PM parts can be too high for some applications.

One solution to these problems is spray deposition. Originally developed by Singer⁸⁶ at the University College of Swansea, spray deposition combines gas atomization with collection of particles on cooled substrate to form a solid deposit of high density. If deposition is done in an inert atmosphere, the deposit will have much lower oxide content than an equivalent PM part and can subsequently be handled without need for protective atmosphere or worry of excessive oxidation. The deposit can be directly rolled, forged, or HIPed to full density. The process retains the improved properties of powder metallurgy, since the material is still rapidly solidified by the gas atomization and the impact with the cooled substrate; however, using spray deposition, it becomes economically feasible to produce bulk simple shapes like sheet and strip with higher

quality than conventional castings and lower cost than conventional casting or powder metallurgy.

Singer's initial system used a single circular sonic gas atomizer and produced an axially symmetric spray cone from a circular melt delivery tube. Although this produced good properties, the deposit was thicker in the center than at the edges, and direct rolling of the material was difficult. Singer then proposed solving the problem with either a series of nozzles or a single scanning nozzle. The latter idea was eventually developed into the Osprey Process.^{87,88}

The Liquid Dynamic Compaction process is similar to the Osprey Process in basic operation, but uses an ultrasonic gas atomizer (USGA) instead of the sonic gas atomizer used by Singer. The USGA atomizing die makes use of a Hartmann shockwave device, in which the introduction of high pressure inert gas into a resonance chamber creates shock waves, forcing the gas out of the atomizing nozzle at velocities up to Mach 3 and frequencies in the range of 20-100 kHz. This high velocity pulsed gas jet atomizes the metal stream much more efficiently than the sonic gas atomizer, producing smaller particle sizes and higher cooling rates.⁸⁹ Liquid Dynamic Compaction originally made use of a single circular atomizing die similar to the Osprey atomizer; however, further developments led to a linear die design, with two opposing linear atomizing dies placed on either side of a narrow slit through which the molten metal was introduced. Rather than a spray cone, the linear dies produce a spray "tent", which forms a deposit with a central section of nearly constant thickness, ideal for subsequent rolling to sheet. Further, the dies can be made arbitrarily long for production of sheet of any desired width.

During operation of any spray deposition system, there are three possible deposition regimes. In the rapid heat extraction regime, the heat input to the substrate and previously deposited layers from the melt spray is small compared to the ability of the substrate to extract heat. The particles are rapidly quenched upon impact at rates up to 10^3 K/s. Such a deposit has fine, equiaxed grains and almost no segregation, as there is no growth across prior particle boundaries; however, the particles do not completely fill the voids left by the solidification of previous layers and the density is low. At slightly higher rates of heat input to the substrate, the new particles arrive before the previous layer has completely solidified. A steady state is reached in which approximately one layer of particles remains semi-solid on the surface of the deposit at all times. This allows for some lateral spread of the deposited material, which helps to fill voids and increases the density of the deposit. Because only a thin layer is molten, solidification is still fairly rapid and small grain size and low segregation are maintained; however, there is grain growth across the prior particle boundaries, which are eliminated in the semi-

solid layer. Grain structure in such a region can be either equiaxed or Widmanstätten. If the heat input from the melt exceeds the heat extraction capabilities of the substrate, a large liquid layer builds up which will experience a large degree of lateral spreading and will solidify slowly, exhibiting properties similar to a conventional casting. All benefits of rapid solidification will be lost in such a case.⁹⁰

Currently, spray deposition has found some limited commercial applicability. Using a rotating substrate, spray techniques have been used to make preforms for short seamless tubes and to spray form cast iron finishing rolls for rolling mills. The Osprey Process has also been used to spray near net shape preforms for turbine discs. Very little experimentation has been done on the use of spray deposition for producing coatings; although in one experiment, Singer⁹¹ sprayed coated steel with an aluminum layer which possessed mechanical properties superior to those of a hot dipped aluminum coating.

3. Experimental Procedure

3.1 Spray Coating Apparatus

The spray coating apparatus consists of an aluminum tundish which sits in a linear ultrasonic gas atomization (USGA) chamber with a gas impingement angle of 45° . The pouring slit is an integral part of the tundish; the dimensions of the tundish and slit are given in Table 2 (two sets of slit dimensions are given, as the slit was narrowed during the course of the work). The atomizing dies are affixed to a $3/8$ " (9.5 mm) thick aluminum plate which is mounted at the corners on four steel angles, placing the atomizing slit 730 mm off the base. The angles have holes in them along their height which can be used for support rods for the substrate, allowing the flight distance to be easily varied. Figure 1 shows the tundish.

An aluminum stopper rod is used to prevent the tin from pouring through the slit before atomization. The stopper rod is made from a block of aluminum machined to a knife edge with an included angle of 45° which fits snugly into the pouring slit. The block is attached to a $1/2$ " (12.7 mm) aluminum rod, which is used to hold it in place prior to atomizing, and is removed to start the metal flow.

Two flat steel plates connected to a 110 V wall plug are attached to the sides of the tundish, allowing direct resistance heating. The plates are held on by a stainless steel wire. The tundish is electrically insulated from the rest of the atomization stand by a ceramic fiber sheet and glass tape and is also wrapped in a thick layer of fiber insulation for better retention of heat. A thermocouple is inserted about $1/4$ " into a small hole in a lower outside corner of the tundish to measure the tundish temperature during heating and atomization.

The dies are connected to a gas supply through a pair of U-bent (2" radius) $3/8$ " O.D. copper tubes which meet in a tee. Another short length of $3/8$ " tubing with one 90° bend goes from the tee to a solenoid valve, used to fire the atomizing gas; a pressure gauge on the downstream side of the solenoid is used to determine atomization pressure during the run. From the valve, a five foot length of $5/8$ " O.D. flexible tubing connects to a gas stand with a regulator. The gas stand is capable of taking input from up to four gas cylinders and is rated to provide output at up to 1500 psig; however, only one cylinder was needed to provide sufficient pressure and flow rate for the tin coating runs.

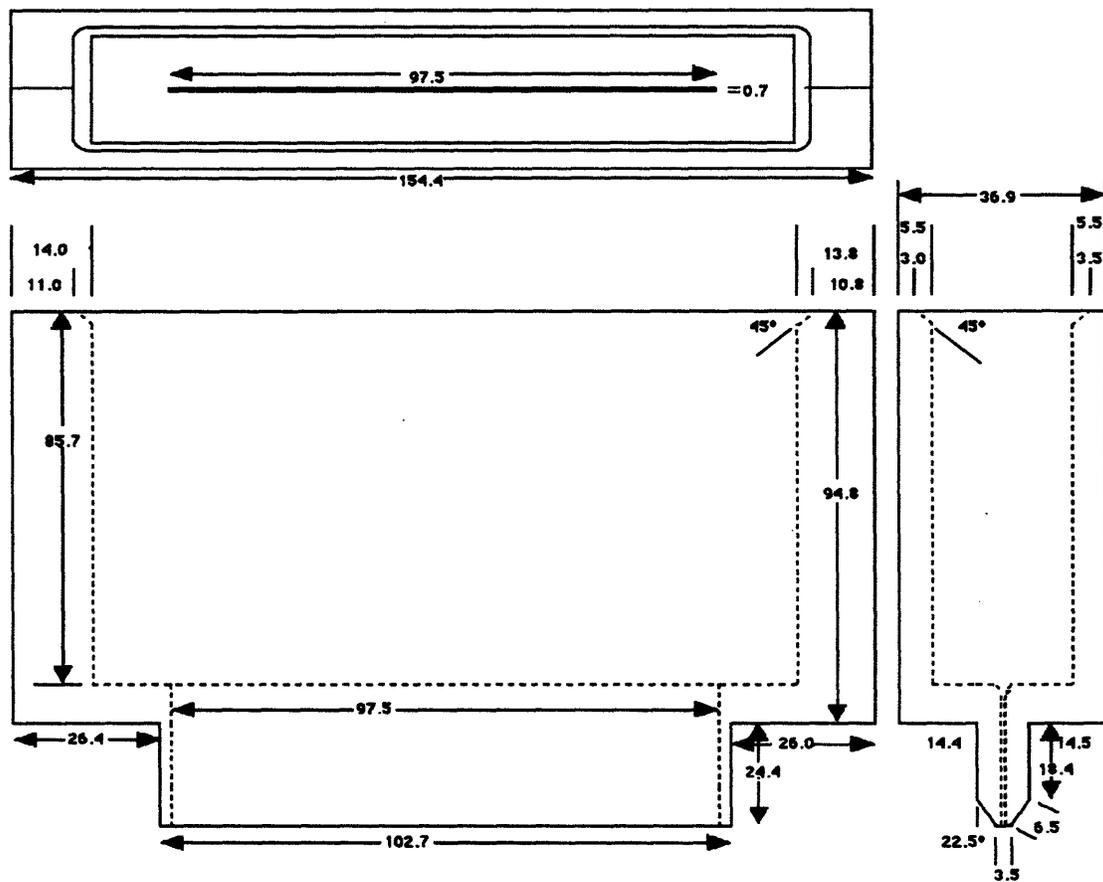
The substrate is placed on a thin steel sheet three feet long which is placed on supports under the atomizer and can be pulled under the atomization spray. The substrate was manually translated, as no mechanical method could be devised which provided

sufficiently high substrate speed and did not introduce as many inconsistencies as manual translation.

Figure 2 shows the entire coating apparatus

3.2 Characterization of the Coating Apparatus

Before any runs were performed using tin, the performance characteristics of the tundish and slit, the dies, and the gas supply were determined. For the tundish, the important characteristics were the nature of the flow through the slit and the tundish heating curve. For the atomization dies, the relationship between static and dynamic pressures was determined. For the slit/die unit, the aspiration at the slit during



Tundish for tin coating experiments. All measurements in mm.

Figure 1: Tundish for tin coating.

atomization was measured.

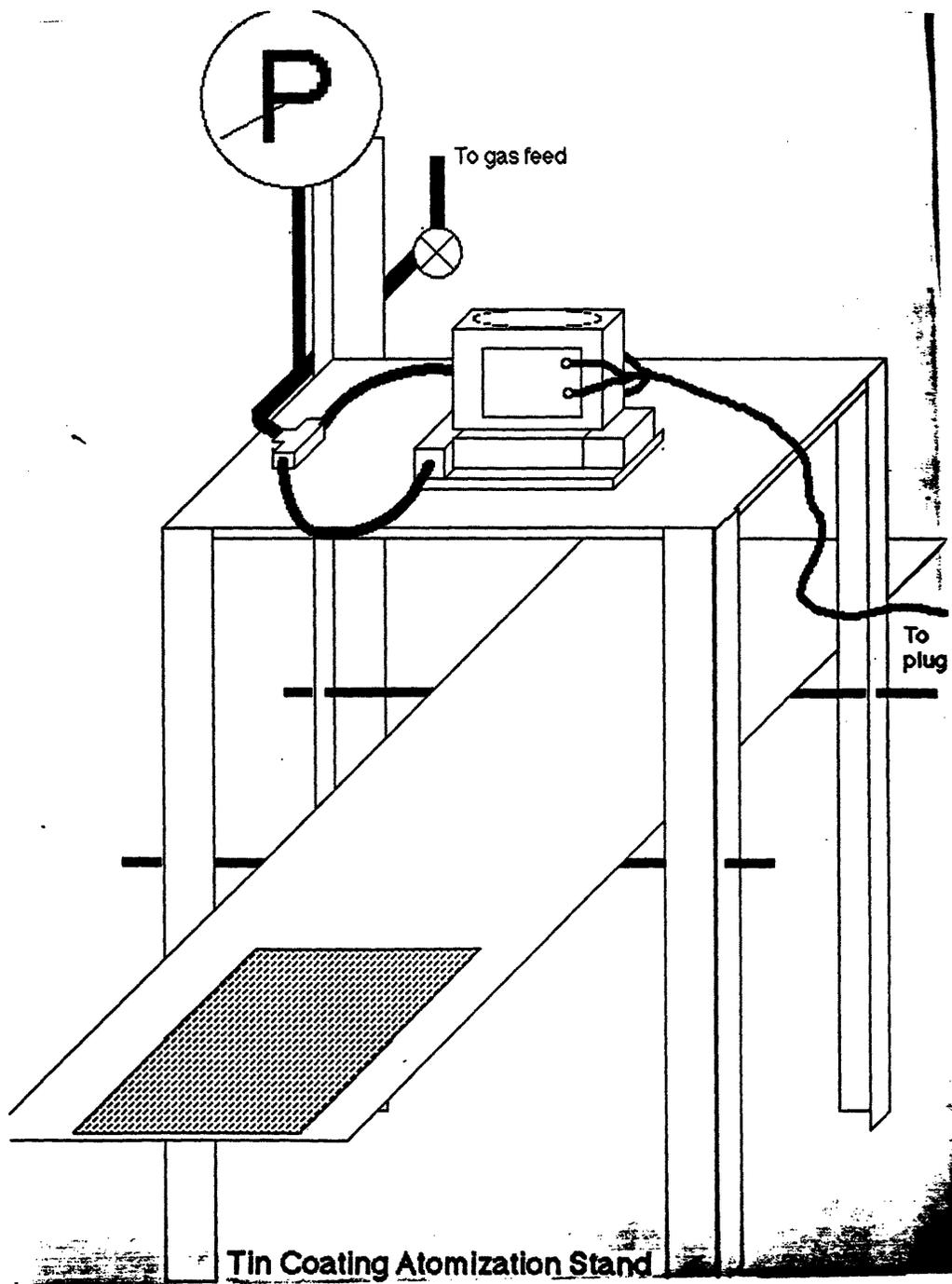


Figure 2: Tin Coating Atomization Stand.

Pouring characteristics of the tundish and slit were checked initially using water instead of tin. First water was poured into the open tundish top with no stopper rod. It was determined that for total water input less than about 80 to 100 ml, fully developed flow never occurred. Instead, the water poured in three cylindrical streams, one from each end of the slit and one from somewhere near the middle. A fully developed flow yields a solid curtain of water exiting the slit and drawing together into a stream below the tundish under the influence of surface tension. This convergence occurs over a sufficiently large distance that the stream could be considered a uniform sheet at the atomization point, which for this setup is immediately below the slit exit. With larger charges of water, it was possible to achieve fully developed flow, but never instantaneously; some initial transient of separated flow was always observed. In any case, the last water to drain out was always in split flow, as the pressure head became insufficient. The larger the charge, the longer the period of fully developed flow.

For such a small charge amount, steady state flow was not possible; however, steady state conditions were achieved with water by holding the tundish under a running faucet. By varying the faucet flow rate it was possible to achieve steady state conditions with different heights of water in the tundish and different water flow rates through the slit. In all steady state flow conditions observed in which any amount of water could be made to stay in the tundish (rather than pouring directly through the slit) the flow out the bottom of the slit was fully developed. In all cases in which the entire slit could not be filled, the flow was split.

Experiments using the stopper rod to prevent water from flowing through the slit during filling of the tundish (at least in large quantities, as the plug did leak slightly) showed that fully developed flow could be achieved with smaller charges of water. As little as 50 ml produced the desired flow. In addition, if fully developed flow did occur, it

Tundish:	length:	126.5 mm
	width:	26.8 mm
	depth:	86.1 mm
	area:	3390 mm ²
	volume:	292 ml
Slit I	length:	97.5 mm
	width:	1.0 mm
	depth:	32.8 mm
	area:	97.5 mm ²
	volume:	3.2 ml
Slit II	width:	0.7 mm
	area:	68.2 mm ²
	volume:	2.2 ml

Table 2: Tundish Measurements

was present from the start with no initial period of separated flow. Again, the flow always split at the end of the pouring when the liquid level inside the tundish dropped too low.

The above experiments were performed with the 97.5 x 1 mm slit before any tin spraying was done. They were also repeated with the 0.7 mm wide slit. These experiments showed that the minimum charge size for fully developed flow had dropped to about 40 ml of water. Little time was spent characterizing behavior of the thinner slit without a stopper rod, as the initial testing showed that a stopper rod was always necessary to avoid an initial transient.

In all cases, elimination of the initial transient is vital to a good coating. Because the time required to coat the small test substrates used was less than a second, the tin actually atomized for the coating would come from the initial transient, preventing even coverage (it is, in fact, believed that this occurred in some runs, with expected incomplete coverage of the substrate).

The tundish was also tested to determine its heating characteristics. Heating of the tundish indicated that a temperature of 300°C could be achieved in slightly over twelve minutes and then the tundish would hold a temperature of 300°C ± 15°C for at least five minutes after the power was turned off. Although no measurements have been taken, use in tin spraying has shown that the tundish can be heated up to at least 400°C within a reasonable time. It has also been observed that placing the cold stopper rod in the tundish has a noticeable effect on tundish temperature (a 10°C drop in less than a minute with no continued heating after unplugging) and that the cold stopper never reaches the tundish temperature. This seems to have had little effect on atomizer performance. In early experiments, the stopper rod was heated to 300°C along with the tin in a furnace; however, it was later decided that the difficulty involved in handling and seating the hot stopper rod outweighed the advantages of heating it.

Characterization of the atomizing dies and gas supply system consisted of determining the effects of slit position in the dies, cylinder pressure, and gas stand outlet pressure on atomizing pressure (as measured at the pressure gauge downstream of the solenoid valve) and aspiration. This was done by firing the gas at five different regulator settings and three different slit positions. The results are presented in Table 3. With no shims, the bottom of the tundish rested directly on top of the dies. Shims were placed between the tundish bottom and the dies and were each 3.5 mm thick.

The results show that the atomization pressure varies linearly with regulator pressure over a wide range of pressures, being slightly less than 50% of the regulator pressure. Further work has shown this to be true up to a regulator pressure of 245 psig, which yields an atomization pressure of 120 psig. No variation of the atomization pressure with cylinder pressure was seen, although it was also observed that cylinder pressure dropped very little. It should be noted that the short duration of the tin runs has resulted in little gas use even during real runs.

It can be seen that in all cases the dies were aspirating with 0 or 1 shim, with the pressure change increasing with atomization pressure. With 2 shims, there was backpressure in all cases, again increasing with atomization pressure. For normal use, a condition of slight aspiration is desired so that tin continues to flow as the pressure head drops to zero. A greater amount of aspiration will result in more uniform flow; however, in this case the aspiration will be small compared to the pressure head over the brief duration of actual coating. For this reason, it was decided to operate the atomizer with

Cyl. Press. (psig)	Regulator Pressure (psig)	Atomizing Pressure, dynamic (psig)	Shims	Slit-die distance (mm)	dP (psi)
2300	40	10	0	13.0	-0.01
			1	9.5	-0.01
			2	6.0	+0.06
2250	60	25	0	13.0	-0.02
			1	9.5	-0.03
			2	6.0	+0.13
2200	100	45	0	13.0	-0.05
			1	9.5	-0.06
			2	6.0	+0.32
2100	150	70	0	13.0	-0.08
			1	9.5	-0.19
			2	6.0	+0.51
2100	200	100	0	13.0	-0.09
			1	9.5	-0.31
			2	6.0	+0.59

Table 3: Atomizing Gas Characterization.

Cyl. Press.: cylinder pressure prior to firing the gas

Regulator Pressure: pressure set for output from gas stand

Atomizing Pressure: pressure downstream from the solenoid valve during firing. This value will be somewhat higher than the actual dynamic pressure at the slit exit.

Shims: number of shims (3.5 mm) used to raise the slit.

Slit-die distance: separation of the plane of the slit bottom and the plane of the die outlet. In all cases, the slit is below the dies.

dP: the aspiration (negative) or backpressure (positive) as measured by the pressure difference inside the sealed tundish before and during firing of the gas.

the tundish sitting directly on the dies for improved stability and repeatability.

3.3 Tin Coating Procedure

There are certain constant procedures followed during every tin coating run. Others are variable by run. The general method of coating will be described, after which each of the parameters varied through the runs will be discussed.

First the atomization pressure was set at the regulator and checked by firing the gas and reading the atomization pressure at the gauge downstream from the solenoid valve. In all runs, the atomizing gas was nitrogen. Next the tin was weighed and melted. For the initial runs a graphite crucible was used. It was later replaced by a stainless steel beaker for better heat conduction when used on a hot plate and easier handling. The tin was melted either in a furnace or on a hot plate. Generally the furnace was preferred for better temperature control, but in some runs the furnace was used to heat the substrate to a different temperature and a hot plate was used to melt the tin with an immersed thermocouple measuring the melt temperature. When the furnace was used, the temperature of the furnace was measured by thermocouple and the tin was left long enough to equilibrate (over an hour to reach 400°C). Direct measurement of the tin temperature in the furnace was not attempted. In neither case was special atmosphere used, as the tin formed a thin solid oxide skin which protected the melt from further oxidation.

The tundish was electrically heated to the desired temperature and then unplugged, after which the stopper rod was inserted and seated. For some runs the stopper rod was also heated to or near the tundish temperature; whether the stopper was heated or not appears to have had no effect on the outcome of the runs. At this point the tin was poured into the tundish (after the oxide layer had been skimmed with a ladle). The tin handler then signalled for the gas to be fired and pulled the stopper rod. The substrate was pulled through the tin spray and when it was completely out the gas was shut off and the remaining tin allowed to drain through the slit and solidify in a single piece in a ceramic tray. This tin was then recovered and remelted for later use.

The substrates were all cut from a single piece of plain low-carbon steel having an initial thickness slightly less than 1 mm (≈ 0.93 mm). The piece was originally sheared into 16 9" x 9" pieces. After five runs it was decided that more efficient use of the base metal stock could be made by shearing these in half and using a 9" x 4.5" substrate (with the 9" axis in the translational direction) which would be completely and more uniformly covered by the spray. This also doubled the number of available substrates.

The following variables were altered during the course of the work: tin charge size, tin temperature, tundish temperature, slit size, atomization pressure, flight distance, substrate surface condition, and substrate temperature. Table 4 shows the conditions for all runs. These parameters can be divided into those which affect the atomization and those which affect the substrate-coating interaction; of course, to some degree the nature of the atomization affects the substrate-coating interaction. Charge mass, slit size, and atomization pressure primarily affect the spray, while tin and tundish temperature, flight distance, and substrate surface condition and temperature mainly determine the coating characteristics and adhesion.

Variation in the charge mass affects the metal flow rate and flow conditions. The larger the charge, the greater the pressure head forcing tin through the slit, thus the greater the metal flow rate. In the conditions of low aspiration under which the tin coating was done, the pressure head is the main determinant of metal flow rate. A smaller charge mass results in a greater gas to metal flow ratio, which produces smaller particles; however, it is possible that fully developed flow does not exist in some cases of low charge mass. The metal flow rate can also be varied with the slot size. There is a lower limit to the slot size which can be effectively used, particularly with an aluminum slit, as the atomizing gas cools the slit and will eventually freeze the melt if the flow rate is not high enough. Increasing the atomizing pressure will also act to decrease the particle size, without any metal flow problems; however, excessive atomization pressure disturbs the substrate and can even interfere with the adhesion of the coating.

The nature of the spray will affect the coating characteristics. The size of the particles places a limit on the minimum coating thickness. The melt enthalpy will affect the bonding of the coating. However, other factors directly modify the coating-substrate interaction. Bonding can be either mechanical or metallurgical. Roughening the substrate by sand blasting improves the mechanical bonding and was used for most runs. All substrates, whether blasted or not, were sanded with 120 grit paper to clean them; in the case of blasted substrates, sanding preceded blasting. Metallurgical bonding is dependent on formation of FeSn_2 at the interface between the tin and the substrate. As the intermetallic layer only grows at elevated temperature, heat must be provided either by preheating of the substrate or by superheating of the melt in excess of that normally needed for atomization. However, metallurgical bonding is also dependent on the steel surface being clean and oxide free, which means that preheating of the substrate will work against this unless atomization is done in an inert or reducing atmosphere.

The flight distance was varied greatly over the runs. Changing the flight distance has two major affects on the coating quality. As the flight distance gets shorter, the melt

enthalpy will be higher at impact with the substrate, which will result in better metallurgical bonding and denser deposits. As the flight distance becomes longer, the spray becomes more uniform and the possibility of shrinkage delamination of the coating is decreased along with the melt enthalpy. Most of the runs were made with a 13" flight distance. Attempts to shorten the flight distance resulted in instability of the substrate in the gas stream. Although this is only a problem on the scale of the current lab operation, it does require consideration of other possible effects of such high forces on the substrate. Several runs were made with greater flight distances.

3.4 Post-Coating Processing

Two methods intended to improve the properties of the tin coatings were studied. The reflowing process has already been described. Various methods of accomplishing tin spreading by remelting were used. Also, many samples were rolled to improve the

Run #	Charge	Press.	Pour T	Tund T	Slit width	Fl. dist.	Sub sur	Sub T
1	400 g	70 psig	300°C	300°C	1.0 mm	15"	sanded	25°C
2	400 g	70 psig	300°C	300°C	1.0 mm	15"	sanded	210°C
3	305 g	70 psig	300°C	300°C	1.0 mm	13"	sanded	250°C
4	235 g	70 psig	330°C	300°C	1.0 mm	13"	sanded	230°C
5	370 g	70 psig	330°C	300°C	0.7 mm	13"	blasted	240°C
6	316 g	70 psig	400°C	285°C	0.7 mm	13"	blasted	25°C
7	410 g	120 psig	415°C	400°C	0.7 mm	13"	blasted	25°C
8	245 g	120 psig	400°C	400°C	0.7 mm	13"	blasted	25°C
9	260 g	120 psig	400°C	400°C	0.7 mm	7.5"	blasted	25°C
10	400 g	115 psig	400°C	400°C	0.7 mm	9.5"	blasted	25°C
11	246 g	120 psig	400°C	400°C	0.7 mm	9.5"	blasted	25°C
12	257 g	120 psig	400°C	400°C	0.7 mm	13"	blasted	25°C
13	245 g	120 psig	420°C	400°C	0.7 mm	13"	blasted	25°C
14	245 g	120 psig	400°C	400°C	0.7 mm	21"	blasted	25°C
15	250 g	115 psig	400°C	400°C	0.7 mm	17"	blasted	25°C
16	260 g	120 psig	400°C	400°C	0.7 mm	17"	blasted	25°C
17	343 g	120 psig	400°C	400°C	0.7 mm	17"	blasted	25°C
18	295 g	120 psig	400°C	400°C	0.7 mm	13.5"	blasted	25°C
19	273 g	120 psig	400°C	400°C	0.7 mm	17"	blasted	25°C

Table 4: Conditions for tin coating runs.

Charge: mass of tin used for atomization

Press.: dynamic atomization pressure.

Pour T: temperature of tin when poured into tundish.

Tund T: temperature tundish was heated prior to the tin being added.

Slit width: the width of the slit opening on the tundish.

Fl. dist.: the flight distance (distance from the slit to the substrate).

Sub sur: surface condition of the substrate.

Sub T: temperature of the substrate.

coating properties.

Attempts at reflowing the spray coated tin samples were made using three different melting techniques: conductive heating in an inert atmosphere, conductive heating in a reducing atmosphere, and inductive heating in air. The first effort was made inside a quartz tube under flowing argon. A set of custom end plugs were made which contained tubing for gas input and outlet, a thermocouple to measure the tube furnace temperature, and a pass-through hole for stainless steel wire (made by forcing the wire through the rubber stopper, so that it would be tight) which was used to move the specimens. Samples were placed on stainless steel foil boats to which the stainless wire was attached so that the boats could be pulled into and out of the hot section of the furnace, allowing the entire heating and cooling cycle to occur under a controlled atmosphere and reducing the amount of time the piece was at elevated temperature. Heating times varied from as great as 20 minutes to as little as 3 minutes, although samples heated for less than 4 minutes showed only superficial surface melting. Test coupons for inert gas remelting were 1" x 4.5" and were prepared by shearing.

A second set of attempts was made using a hydrogen furnace. Heating to 265°C was done at a rate of 8°C/min. followed by cooling at a similar rate, all under hydrogen gas. Test coupons for hydrogen remelting were 0.5" x 2.25" and were made by shearing.

Finally, in an attempt to better duplicate actual industrial reflowing practice, samples were induction heated to above the melting point of tin and then drop quenched in water. For this, test coupons 0.5" x 2.25" (prepared by shearing) were suspended by a fine copper wire in a 1.5" diameter by 2.5" high 6-turn coil connected to a Lepel Model T-10-3, 23.5 kW induction unit. Test samples of uncoated steel of the same size with thermocouples welded in 2 positions were used to determine the time required to heat the samples to 250°C as a function of power setting and sample mass. Heating time for actual test pieces was then determined based on the mass of the sample (the heat capacity of iron is twice that of tin, which nearly exactly cancels the heat of fusion of tin, causing the heat requirements to raise either iron or tin to 250°C to differ by only 10%). One piece was tested with no flux and one with ZnCl-based solder flux spread on the tinned side. In addition, a hot dipped part of the same dimensions was made by immersing a cleaned and fluxed piece of steel in molten tin and remelted under flux.

Rolling was also used to improve coating quality. This was inspired by the observation that the top-sheared edges (where the tin was deformed) of tin coupons cut for testing fared better in bend testing and showed greater resistance to peeling than the bottom sheared edges (where the tin was undeformed).

All samples were rolled at room temperature, either in one or several passes, to reduce the thickness of the tin coating. In most cases at least three passes were used, as multiple passes at the same roll gap were seen to improve the tin surface. In addition to better mechanical properties, rolling produced improved uniformity of the coating and a smoother tin surface, resulting in a more attractive finish. In most cases, the deformation was heavy enough to reduce the thickness of the steel also. All rolling was done on either 0.5" or 1" x 4.5" samples sheared from the coated sheet; the direction of rolling was transverse to the direction of substrate motion during deposition. For most runs four rolled samples were made, two sheared so that the tin was deformed on one edge, one sheared so that it was deformed on both edges, and one sheared so that the tin was not deformed. The coated sheet produced in one run was rolled as a single piece; rolling of this piece was in the direction of substrate motion during deposition.

In a few cases, samples were both rolled and reflowed, and some samples were rolled, reflowed, and then rolled again. In these cases, each individual step conforms to the process descriptions above.

3.5 Characterization of Coatings

The testing and evaluation methods used on the tin coatings are described below.

Physical appearance: Each coating was described and photographed. Qualitative evaluation of large-scale adhesion, surface uniformity, coating thickness, surface roughness, and fraction of surface which remained molten after impact was made.

Profile measurement: The thickness of each deposit was measured at several points along a line transverse to the direction of substrate translation. In cases of large-scale de-adhesion, this could be measured directly, in other cases the thickness of the tin plus steel was measured and the thickness of the steel subtracted out. Substrate thickness in this case was determined either by peeling the tin off or by measuring an uncoated section and taking this value as uniform.

Metallography: Samples of coated steel were cut or sheared and mounted in epoxy, polished, and viewed under a microscope, either etched or unetched. This was not done for many samples, as little new information was provided after a few samples had been observed. Metallographic preparation of the samples proved difficult, and in most cases the microstructure of the coating was of much less interest than its appearance and adhesion.

Bend testing: Coupons of coated steel 1/2" wide were bent to a 90° angle around mandrels of 1.75", 0.875", and 0.437" diameter. The strains produced in such a test are a function of strip thickness, which will vary with surface treatment of substrate, tin coating

thickness, and rolling. The maximum strains are approximately 3%, 6%, and 10% respectively for the three mandrels for a strip of average size. Strain was calculated individually for each strip tested. The strain for a bar in bending can be roughly calculated as follows. The bar will bend in such a manner as to minimize the strain energy. For a homogeneous bar, this means that the central plane of the bar will bend but will not be elongated or compressed. The tin coating on these test samples will cause deviation from that; however, because upwards of 95% of the sample undergoes plastic deformation and because the yield stress of tin is negligably small compared to that of the base steel, the plane of zero elongation can be assumed to be the central plane of the steel base metal. For a mandrel of given radius, r , the length of the test bar bent 90° which is in contact with the mandrel is given by

$$l = \frac{2 \pi r}{4}.$$

Discounting any change in thickness of the steel during bending, the plane of zero elongation then has a length given by

$$l_0 = \frac{2 \pi (r + \frac{1}{2} t_s)}{4},$$

where l_0 happens to also be the initial length of that segment of the test bar and t_s is the thickness of the steel base. The strain at any given position in the bar can then be determined as

$$\epsilon = \ln \frac{r+y}{r + \frac{1}{2} t_s},$$

where y is the position measured outward from the mandrel surface. The maximum strain will be at the outer surface of the tin, and will be given by

$$\epsilon_{\max} = \ln \frac{r + t_t}{r + \frac{1}{2} t_s},$$

where t_t is the total thickness of the piece.

The effect of bending on the coating was classified in one of four categories: no damage, lined, cracked, or cracked and peeled. Lining occurred only on rolled samples; in some cases the prior particle boundaries would become visible on the surface of the strained coating. Lined samples show no base metal through the deformed tin coating, so this result is a failure only in the sense of damage to aesthetic value of the coating. A sample which showed cracking suffered damage sufficient to reveal the base metal at the flaw. Samples which cracked and peeled developed cracks all the way across the test piece, and the tin delaminated from the base metal and remained straight as the piece was bent. After bending, the strips were straightened manually, except for those which cracked and peeled severely, in which case no additional damage could have been done by

straightening. Samples were again checked for cracking or peeling on straightening. It should be noted that in the case of many lined samples, the lining disappeared after the piece was straightened.

Reflowing: Samples which underwent reflowing were subjected to a similar series of tests. Profile measurements were not done, as the surface of the tin coating was generally too uneven to allow good measurements. Many reflowed specimens lacked sufficient continuity of the tin layer for any tests other than visual examination.

Rolling: Rolled samples also underwent the above tests. Profile measurements were done differently for rolled samples. For each individual sample to be rolled, three thickness measurements were taken from the center 1" of the length of the specimen. After rolling, three more were taken from the same area. In addition, the length of the piece was measured before and after to be used to calculate the amount of deformation of the steel.

If it is assumed that due to the nature of the rolling operation, most of the deformation goes into reduction of the thickness and elongation of the piece with little deformation in the transverse direction, then the amount of strain measured from the length increase can be taken as equal to the amount of strain in the flattening of the part, from which the percentage reduction can be calculated as follows:

$$\epsilon_{\text{elong}} = \ln \frac{l}{l_0}$$

$$t_f = t_0 \exp(-\epsilon_{\text{elong}})$$

$$\% \text{reduction} = \frac{t_f}{t_0}$$

where ϵ_{elong} is the true strain in the rolling direction, l and l_0 are the final and initial lengths of the strip, and t_f and t_0 are the final and initial thicknesses. This also gives the final thickness of the steel, which cannot be measured easily due to the difficulty of removing the rolled tin coating without damaging the substrate as well and which is necessary to calculate bending test strains. This method is an approximation, and it is evident that strains in the transverse direction (broadening of the strip) and curving of the pieces in the rolls have introduced significant error, as the final tin thicknesses calculated from this are less than those observed from mounted and polished sections and are sometimes less than 0.

Examination of overspray powder: The overspray powders from the first fourteen runs were collected and sieved to determine powder size distribution. For all but the first two runs, all particles larger than 589 μm were discarded as being unatomized droplets rather than actual powders (optical examination reveals this assumption to be true for > 95% by mass of these particles). Powders were sieved through the following screen

sizes: 125 μm , 63 μm , and 53 μm . In some cases, a 38 μm screen was used, but no powders ever passed through the 38 μm screen. Where considered applicable, powders were kept sorted by size and photographed for examination of shape.

4. Results

4.1 As Coated Samples

4.1.1 Physical Appearance

The first four runs all had very poor adhesion. The coatings from runs 1 and 4 slid off when the substrates were picked up. The coating from run 2 delaminated completely during cutting of the sample. Run 3 produced a very thick coating which remained molten on the substrate due to high substrate preheating. In all four cases, the surface of the coating displayed many large splats on the surface. These large blobs of tin, presumed to be unatomized, were often only partially bonded to the rest of the coating and formed easy initiation sites for peeling of the coating. All of these coatings could be peeled easily from the substrate.

Starting with run 5, at which point the slit size was reduced and the use of blasted substrates began, the coatings all took on a similar appearance, as demonstrated by Figure 3, a photo of the as-coated sheet. The bright spots which can be seen are from large, unatomized droplets of tin splatting on the substrate. The rest of the surface is micro-rough, due to the nature of the particle buildup during spray deposition, but smoothness on a macro scale is achievable with sufficiently small atomized particles. Figure 4, showing the results of run 10, demonstrates the effects of increased gas pressure in reducing the number of unatomized droplets and increasing the smoothness and uniformity of the coating. Figure 5 shows the as-coated surface of run 14, which had a longer flight distance and smaller tin charge. This resulted in a thinner and not completely continuous coating, but one with even better smoothness and uniformity. It should also be noted that peeling the as-coated tin from such a sample is nearly impossible.

4.1.2 Profile Measurements

Table 5 shows the profiles of the tin coatings. There are no profile measurements for several runs. Runs 1 and 4 had no adhesion at all (the deposit slid off the substrate when it was picked up). In run 9, the substrate was blown out of position by the atomizing gas before the tin was poured, so no deposit was formed. Run 15 was rolled as a complete piece and no other testing was done. The gas was shut off prematurely in run 16, resulting in an unusable deposit. Run 18 was set aside for use as a demonstration piece and never tested. Two profile lines are given for run 3, due to a large molten blob

which fell on the substrate, causing the measured profile of one edge of the coating to be much higher (this section was not used in any mechanical testing).

4.1.3 Metallography

Photomicrographs of several samples were taken. Most are in the unetched state, but some have been etched in 1% nital, which lightly etches the tin grains. For the as-coated samples, these cross-sections show the tin-steel interface, the degree of porosity and irregularity in the tin coating, and the interparticle boundaries in the tin coating, which also can be used to determine that some of the tin particles were completely solidified when they impacted.

Several representative photos have been included. Figures 6 and 7 show the coating from run 3, etched in 1% nital to reveal the grain structure. Figure 6 shows the molten section where the substrate was above the melting point of tin. The grain structure is columnar, with solidification beginning at the outer surface. Figure 7 shows the outer

Run #	Position on the sample (distance from one side)									avg	std
	0.25"	0.75"	1.25"	1.75"	2.25"	2.75"	3.25"	3.75"	4.25"		
1	---	---	---	---	---	---	---	---	---	---	---
2*	480	770	1011	759	810	770	579	691	511	709	156
3	414	470	255	254	209	203	397	1324	891	491	356
omit 2	414	470	255	254	209	203	397	---	---	315	101
4	---	---	---	---	---	---	---	---	---	---	---
5	250	250	330	440	500	660	480	510	440	430	125
6	180	300	270	360	370	350	320	260	300	300	56
7	190	270	290	340	450	490	460	330	230	340	101
8	50	110	120	120	100	90	80	50	40	80	30
9	---	---	---	---	---	---	---	---	---	---	---
10	229	298	345	418	543	668	666	520	477	463	146
11	408	408	442	284	209	137	149	91	91	247	135
12	282	394	461	442	351	287	229	157	180	309	104
13	147	176	241	296	362	295	250	193	121	231	74
14	51	86	105	125	122	149	194	192	203	136	50
15	---	---	---	---	---	---	---	---	---	---	---
16	---	---	---	---	---	---	---	---	---	---	---
17	85	95	114	125	119	106	118	100	73	104	16
18	---	---	---	---	---	---	---	---	---	---	---
19	148	56	100	114	129	108	110	94	91	106	24

Table 5: Tin coating profile measurements, in μm . The measurements were taken every half inch along a line transverse to the direction of substrate motion during coating, starting 1/4" from one edge. Average and standard deviation are provided for each coating.

* Several such profiles were taken for coating #2. The values given here are the averages of data points taken along several different lines across the sample.

edge of the sample, where the tin coating was much thinner and the substrate temperature was lower; it can be seen that the tin solidified immediately on impact or was already solidified at impact, leading to a structure with large porosity and readily visible particle boundaries. The subsequent as-deposited photos are unetched. Figure 8 is a section from run 6, showing the irregular surface produced from a higher gas-to-metal ratio and less melt enthalpy at impact than in previous runs. The thickness varies from 30 to 300 μm within the frame of the photo, and one of the particles is overhanging the rest of the deposit. Figure 9, from run 7, again shows what are either prior particle boundaries or cracks from shrinkage stresses. The photo also gives a good view of the roughness of the blasted substrate and the irregular bonding between the steel base and the deposited tin. In most places the tin appears well bonded to the steel, but there are a few widowed spots which the initial particles failed to cover and which subsequent particles could not reach. Figure 10, from run 8, one of the best, shows that it is possible to achieve a fairly even and continuous coating less than 100 μm thick which has good adhesion.

In no case did any of the etched, as-coated samples show any evidence of an FeSn_2 layer.

4.1.4 Bend Testing

The bend test results for all as-coated samples are shown in Table 6. Samples 1, 2, 4, 9, and 16 had insufficient adhesion to be tested. Samples 15 and 18 were reserved for other uses and not tested. Most other samples were tested around all three mandrels; separate samples were used for each test. For each sample, the strain (based on sample thickness) is shown, along with the damage, if any, caused on bending and straightening. It should be noted that strains for sample 3 are calculated from the profile omitting the thick tin mass, which was outside the area of deformation in the test. The sample 6 test marked "both sheared" indicates that the test coupon was rotated in the shear so that the tin was deformed on both long sides of the piece.

Figures 11-13 show bent test samples. Figure 11 is a slightly cracked piece from run 5. Figure 12 shows a piece from run 7 on which the coating has cracked and peeled severely, nearly totally delaminated; failures this spectacular were rare. Figure 13 shows two undamaged bent coatings from run 8. In all cases, the photographs were taken from a side in which the piece was sheared on the steel side so that there was no deformation of the tin coating; the damage to the steel base from the shear can be seen on the uncoated edges.

4.1.5 Examination of Overspray Powder

The overspray powder size distributions for the first 14 runs are shown in Table 7. Powders were not collected from runs 4, 9, and 15-19. Because much of the overspray was a result of firing after the substrate and carrier had passed completely under the spray, the overspray powder is characteristic of the material which actually impacted on the substrate. For many runs, no attempt was made to sieve the powders below 38 μm .

Mandrel: Run #	1.75"			0.875"			0.437"		
	strain	bend	straight	strain	bend	straight	strain	bend	straight
1	---	---	---	---	---	---	---	---	---
2	---	---	---	---	---	---	---	---	---
3	3.36*	none	peeled	6.48*	peeled	peeled	12.12	peeled	peeled
4	---	---	---	---	---	---	---	---	---
5	3.87	cracked & peeled	peeled	7.45	cracked & peeled	peeled	13.86	cracked & peeled	peeled
6	3.32	cracked & peeled	peeled	6.40	cracked & peeled	peeled	11.96	cracked & peeled	peeled
6, both sheared				3.32	cracked	none			
7	3.49	cracked & peeled	n/a	6.72	cracked & peeled	n/a	12.42	cracked & peeled	n/a
8	2.37	none	none	4.60	none	none	8.66	none	peeled
9	---	---	---	---	---	---	---	---	---
10	4.01	cracked & peeled	peeled	7.71	cracked & peeled	peeled	14.32	cracked & peeled	n/a
11	3.09	none	peeled	5.97	cracked & peeled	peeled	11.12	cracked & peeled	peeled
12	3.35	cracked & peeled	peeled	6.47	cracked & peeled	none	12.11	cracked & peeled	peeled
13	3.03	cracked & peeled	peeled	5.85	cracked	peeled	10.95	cracked & peeled	peeled
14	2.62	none	none	5.07	none	none	9.53	none	none
15	---	---	---	---	---	---	---	---	---
16	---	---	---	---	---	---	---	---	---
17				4.81	none	none	9.04	none	none
18	---	---	---	---	---	---	---	---	---
19				4.82	cracked & peeled	none	9.07	cracked	none

Table 6: Results of bend testing of as-coated samples.

Run #	Percentages (by mass) of powder by particle size			
	-125 μm	-63 μm	-53 μm	-38 μm
1	53.26%	13.14%	7.42%	n/a
2	50.47%	10.92%	4.86%	n/a
3	51.81%	13.35%	7.15%	n/a
4	-----	-----	-----	-----
5	61.93%	24.25%	13.55%	0.0%
6	65.76%	20.13%	11.50%	n/a
7	86.54%	46.51%	29.44%	0.0%
8	92.94%	60.61%	43.77%	0.0%
9	-----	-----	-----	-----
10	65.27%	20.79%	12.16%	n/a
11	86.67%	55.53%	43.23%	0.0%
12	94.59%	55.30%	40.89%	0.0%
13	93.12%	59.85%	43.50%	0.0%
14	90.65%	55.21%	38.77%	n/a

Table 7: Overspray powder size distributions.

Figures 14-16 show the -53 μm overspray powders from three runs, numbers 2, 5, and 8 respectively. Run 2 represents the lowest gas to metal ratio, with a 1.0 mm slit, a 400 g charge, and only 70 psi atomization pressure. Run 8 had the highest gas to metal ratio, the slit width and charge size having been reduced to 0.7 mm and 245 g and the atomization pressure having been increased to 120 psi. Run 5 lies between, with a 0.7 mm slit, but a 400 g charge and only 70 psi gas pressure. It can be seen that the particles become more uniform and spherical as the gas to metal ratio increases.

4.2 Reflowed Samples

4.2.1 Physical Appearance

The three different types of reflowed samples, argon cover remelted, hydrogen cover remelted, and induction remelted, showed very different surfaces after the reflowing operation. Examples of pieces reflowed under argon are shown in Figures 17 and 18. On all such samples, the surfaces of both the tin and steel were heavily oxidized. Although some spreading of tin occurred, resulting in thin, continuous coatings, over limited parts of a few samples, the tin which spread in that manner was also oxidized and had poor aesthetic quality. More commonly, the tin clumped into oxide-coated ridges or even balls which were poorly adhered to the steel. This was particularly true in sparsely covered areas, where it was hoped that reflowing would have the greatest beneficial

effect. Some samples were also reflowed after rolling. Figure 19 shows a picture of these samples. Two of the coatings showed severe clumping, while the third appeared not to have completely melted. The clumping of tin is further demonstrated by the fact that the tin coatings actually became thicker during reflowing (refer to Tables 8, 5, and 10).

The samples reflowed under hydrogen cover looked better, but still had problems. Again, the tin appeared to have clumped up in regions, although it did not completely peel from the substrate. Also, the surface of the tin appears slightly oxidized, off-white rather than bright, but not covered with the heavy yellow and brown oxides characteristic of the inert atmosphere reflowing work. Figures 20 and 21 show SEM photos of a sample reflowed under hydrogen. Both shots show the same area at the same magnification, but Figure 21 is in backscattered imaging mode, which highlights the tin. It can be seen that some flowing of the tin has occurred, but some balls or prior particles are still visible, and the tin has not spread over the bare steel.

Three samples were reflowed using the induction coil, all three without special protective atmosphere. The first was remelted without any kind of flux. This sample oxidized slightly and showed local clumping of the tin coating. There was no spreading. Figure 22 is an SEM shot of this sample; although the tin clearly melted, it did not form a smooth surface and did not spread. The second was covered with a ZnCl-based soldering flux before heating. In this case, the tin was bright and shiny, apparently unoxidized; however, the tin coating still clumped slightly. Figure 23 shows an SEM shot of this piece. The apparently poor tin coverage largely resulted from incomplete coating prior to reflowing, but clearly the tin did not spread. Note the improved surface smoothness of the tin as compared to the unfluxed piece. Finally, a sample prepared by the hot dipping method and fluxed for heating showed no signs of oxidation and no clumping; however, the very thick tin coating did run under the influence of gravity, resulting in a wavy coating surface. Figure 24 is an SEM photo of the hot dipped and reflowed piece. Note the much better smoothness of this piece. The dark spots are not bare steel, of which there is none, but rather inclusions from the flux.

4.2.2 Profile Measurements

Because most of the reflowed samples had very irregular surfaces, no profile measurements were taken on any of them except for spot measurements for bending test strain calculations.

4.2.3 Metallography

Figure 25 shows a cross-section of the coating from run 5 after reflowing for 20 minutes under argon cover. This section is from the region of the smooth coating which can be seen in the lower piece in Figure 17. The tin coating is smooth, continuous, and well-adhered, but there is no evidence of formation of FeSn₂ at the interface.

4.2.4 Bend Testing

Only two reflowed samples were bend tested, both from run 5 and both reflowed under an argon cover at 230°C, one for 20 minutes and one for 12. The 12 minute sample was tested twice, at two different places. Thickness values for these pieces were determined by measurement in the area of the bend and are listed in Table 9. Table 10 shows the bend test results. In addition, three rolled and then reflowed samples were bent, including one (#3) twice in the same place. These results are also shown in table 10. Note that the extremely high strains are due to the very thick tin coatings.

None of the other inert atmosphere reflowed samples had sufficient continuity of the tin layer to bend test. Although samples from the hydrogen reflowing and induction reflowing experiments could have been tested, they were not, as the effort was geared more towards improving surface quality and coating continuity than towards improvement of mechanical properties.

Sample	Total Thickness	standard dev.	Substrate	Tin Thickness
5, rf20m	936	19	906	30
5, rf12m	1254	337	913	341
5, roll1&reflow	1597	268	903	694
5, roll2&reflow	1364	141	871	493
5, roll3&reflow	1008	13	824	184

Table 8: Tin coating thicknesses for reflowed bend test samples. Values in μm .

Mandrel:	1.75"			0.875"			0.437"		
	strain	bend	straight	strain	bend	straight	strain	bend	straight
5, rf20m				4.09	peeled	none			
5, rf12m				6.67	none	none	12.46	none	peeled
5, roll#1 + reflow				9.45	none	peeled			
5, roll#2 + reflow				9.58	none	none			
5, roll#3 + reflow				5.04	none	none	9.52	none	none

Table 9: Bend test results for reflowed samples.

4.3 Rolled Samples

4.3.1 Physical Appearance

The rolled tin strips had a shiny surface, usually smooth, but occasionally lined along prior particle boundaries, particularly on the samples with thinner tin coatings. The lining got worse toward the ends of the sample (which were the edges of the substrate during coating and thus received a thinner tin coating) and in some cases deteriorated to individual rolled particles. Figures 26 and 27 show rolled strips from runs 7 and 8, respectively. In some cases, a heavier tin coating was rolled over the side of the steel substrate. This only occurred on unsheared edges (i.e., sides where the shearing action had been on the steel instead of the tin). Figure 28 shows an example of this. This effect was detrimental to properties, as the smeared tin was often cracked and could be easily peeled from the substrate. It was also noted that samples rolled in several passes at the same roll gap had a better surface finish and less variation in thickness than samples given the same deformation in a single pass.

One set of rolled and reflowed samples was rolled a second time. As the reflowing had created distinct blobs of tin on the surface, the rolled coating was non-continuous. Also, the very thick reflowed coatings tended to become folded over on themselves during rolling. Even the relatively thin sections did not flow well, developing a wavy surface with periodic peaks and troughs.

4.3.2 Profile Measurements

Table 10 lists the thicknesses of each rolled sample before and after rolling, the total reduction, and the estimated reduction of the steel substrate. Total thicknesses were measured, steel substrate thicknesses before rolling were taken from the as-coated profile measurements, and steel substrate thicknesses after rolling were estimated from elongation of the steel strip. It should be noted that in a few cases the estimated thickness of the steel after rolling is greater than the total thickness. While it is recognized that these numbers are in error, they are reported as calculated. It is likely that all such estimated values are too high.

Sample	Total Thickness		Reduction	
	Before	After	Steel	Total
Run 3	1070	870	7.9%	18.7%
Run 5, #1	1320	1074	2.9%	18.6%
Run 5, #2	1390	1015	6.3%	27.0%
Run 5, #3	1340	890	11.4%	33.6%
Run 5, #1+rf	1597	1056	3.5%	33.9%
Run 5, #2+rf	1364	1054	1.2%	22.7%
Run 5, #3+rf	1008	807	13.1%	19.9%
Run 6, A	1300	970	8.4%	25.4%
Run 6, B	1220	970	5.1%	20.5%
Run 6, C	1350	980	5.1%	27.4%
Run 6, D	1240	970	4.7%	21.8%
Run 7, A	1370	1020	6.9%	25.5%
Run 7, B	1340	1060	5.5%	20.9%
Run 7, C	1260	1050	4.3%	16.7%
Run 7, D	1370	1070	5.5%	21.9%
Run 8, A	1040	730	21.4%	29.8%
Run 8, B	1060	710	22.7%	33.0%
Run 8, C	1020	730	20.7%	28.4%
Run 8, D	1040	720	21.0%	30.8%
Run 10, A	1602	821	25.5%	48.8%
Run 10, B	1489	1077	5.5%	27.7%
Run 10, C	1545	1081	7.1%	30.0%
Run 10, D	1403	1053	4.6%	24.9%
Run 11, A	1149	862	16.0%	25.0%
Run 11, B	1129	844	16.0%	25.2%
Run 11, C	1115	826	17.0%	25.9%
Run 11, D	1125	818	17.7%	27.3%
Run 12, A	1364	899	17.5%	34.1%
Run 12, B	1349	1001	11.4%	25.8%
Run 12, C	1370	993	12.5%	27.5%
Run 12, D	1300	976	12.2%	24.9%
Run 13, A	1182	976	2.7%	17.4%
Run 13, B	1191	967	4.3%	18.8%
Run 13, C	1211	958	6.2%	20.9%
Run 13, D	1256	961	7.7%	23.5%
Run 14, A	1187	818	12.6%	24.7%
Run 14, B	1084	786	15.7%	27.5%
Run 14, C	1093	772	17.8%	29.4%
Run 14, D	1076	755	18.3%	29.8%
Run 17, A	1051	791	15.3%	24.7%
Run 17, B	1046	797	14.3%	23.8%
Run 17, C	1039	816	12.5%	21.5%
Run 17, D	1035	820	12.5%	20.8%
Run 19, A	1039	856	8.7%	17.6%
Run 19, B	1030	795	15.4%	22.8%
Run 19, C	1037	721	22.5%	30.5%
Run 19, D	1036	781	16.4%	24.6%

Table 10: Thickness and reduction of rolled samples. All thicknesses in μm .

4.3.3 Metallography

Limited optical metallography was done on rolled samples. Figures 29 and 30 show rolled coatings from run 7 and run 8 respectively. Note that in both cases, the coating-substrate interface is continuous and appears to show good adhesion. Both coatings show some surface flaws; in particular, the photo from run 8 shows what appears to be porosity from prior particle boundaries which was not completely removed by rolling. However, the overall quality of the rolled tin appears good. Etching in 1% nital revealed what appeared to be recrystallized, equiaxed grains in the rolled specimens.

4.3.4 Bend Testing

Bend tests were performed on most rolled samples. It rapidly became apparent that very few, if any, of the rolled coatings had poor enough adhesion to fail on the 1.75" mandrel, so only the .875" and .437" mandrels were used for most runs. In cases where a single strip was tested on two mandrels, different spots were used so that the regions of deformation did not overlap. Table 11 shows the results of the bend testing of rolled samples.

4.4 Miscellaneous

4.4.1 Rolled As-coated Sheet

A single sheet (run #15) was rolled as-coated as a single piece. The rolling direction was the same as the direction of substrate motion during deposition, to simulate an in-line process. The sheet warped badly to the greater elongation of the center section where the tin was thicker; and this warping caused the tin coating to delaminate in the center section. Test bars were cut from the less warped ends of the piece for bend testing. Table 12 shows the thickness of the leading and trailing edges before and after rolling as well as the deformation of the steel substrate in the center and at the sides.

Three strips sheared from the rolled sheet were bend tested. Table 13 shows the results. Due to the uneven deformation of the substrate, the strains listed are only estimates.

4.4.2 Spray Coating of Ceramics

For several of the experiments, a large ceramic tray was placed underneath the substrate support to catch the liquid tin which poured out of the tundish after the atomizing gas was shut off. It was noted the on those occasions that the atomized spray

Mandrel:	1.75"			0.875"			0.437"		
	strain	bend	straight	strain	bend	straight	strain	bend	straight
3, rolled							7.43	none	peeled
5, roll#1				5.24	cracked	none			
5, roll#2				4.90	none	none			
5, #1 + rf + roll				5.23	peeled	n/a			
5, #2 + rf + roll				5.26	peeled	n/a			
5, #3 + rf + roll				3.84	none	peeled			
6, rolled	2.37	none	none	4.56	none	none	8.42	cracked & peeled	none
7, rolled	2.60	none	none	5.18	cracked & peeled	buckled & peeled	10.16	cracked & peeled	buckled
8, rolled	1.60	none	none	3.10	none	none	5.78	none	none
10, roll A				4.07	none	none			
10, roll B				5.38	none	peeled			
10, roll C				5.48	cracked	none			
10, roll D				5.15	none	peeled			
11, roll A				4.05	none	none			
11, roll B				3.90	cracked	none			
11, roll C				3.79	none	none	7.20	lined	none
11, roll D							7.13	lined	none
12, roll A				4.38	none	peeled			
12, roll B				4.98	none	none			
12, roll C				4.95	cracked	peeled			
12, roll D				4.80	none	none	9.08	cracked	peeled
13, roll A				4.42	none	peeled			
13, roll B				4.41	none	peeled			
13, roll C				4.41	none	none			
13, roll D				4.50	lined	none	8.50	lined	peeled
14, roll A				3.50	none	none	6.66	lined	none
14, roll B							6.40	lined	none
14, roll C							6.35	lined	none
14, roll D							6.12	none	none
17, roll A				3.39	none	peeled			
17, roll B							6.46	lined	none
19, roll A				3.66	none	none			
19, roll B							6.53	cracked	none

Table 11: Bend test results for rolled samples.

struck the ceramic tray, a thin and extremely adherent tin coating was formed on the tray. This coating could not be peeled off and could only be removed by melting or filing of the tin.

4.5 Summary of Bend Test Results

Table 14 shows a summary of all successful bend tests in order of increasing strain. Table 15 shows the minimum strain at which coatings failed and the maximum strain which coatings survived for each of the conditions (as coated, reflowed, rolled, and rolled + reflowed). Note that samples which developed lining on bending were considered to have been successful in the bend test, as the damage was purely aesthetic.

Sample	Total Thickness		Reduction	
	Before	After	Steel	Total
15, front	1090	926		15.3%
15, back	1024	876		14.4%
15, center			6.2%	
15, edge			4.5%	

Table 12: Rolling reductions of as-coated rolled sheet, run 15.

Mandrel:	1.75"			0.875"			0.437"		
	strain	bend	straight	strain	bend	straight	strain	bend	straight
15, rolled	1.92	none	none	3.73	none	none	7.07	none	none

Table 13: Bend test results from as-coated rolled sheet, run 15.

Maximum True Strain	Run #	Condition
1.60	8	rolled
1.92	15	rolled
2.37	6	rolled
2.37	8	as coated
2.60	7	rolled
2.62	14	as coated
3.10	8	rolled
3.50	14	rolled
3.66	19	rolled
3.73	15	rolled
3.79	11	rolled
4.05	11	rolled
4.07	10	rolled
4.41	13	rolled
4.50 (lined)	13	rolled
4.56	6	rolled
4.60	8	as coated
4.80	12	rolled
4.81	17	as coated
4.90	5	rolled
4.98	12	rolled
5.04	5	rolled + reflowed
5.07	14	as coated
5.24	5	rolled
5.78	8	rolled
6.12	14	rolled
6.35 (lined)	14	rolled
6.40 (lined)	14	rolled
6.46 (lined)	17	rolled
6.66 (lined)	14	rolled
6.67	5	reflowed
7.07	15	rolled
7.13 (lined)	11	rolled
7.20 (lined)	11	rolled
9.04	17	as coated
9.52	5	rolled + reflowed
9.53	14	as coated
9.58	5	rolled + reflowed

Table 14: Successful bend tests.

condition	minimum strain to failure	maximum strain survived
as coated	3.03	9.53
reflowed	4.09*	6.67†
rolled	3.39	7.07 (7.20 lined)
rolled + reflowed	9.45	9.58†

Table 15: Minimum strain to failure and maximum strain survived in bend testing.

* smallest strain tested in this condition

† largest strain tested in this condition

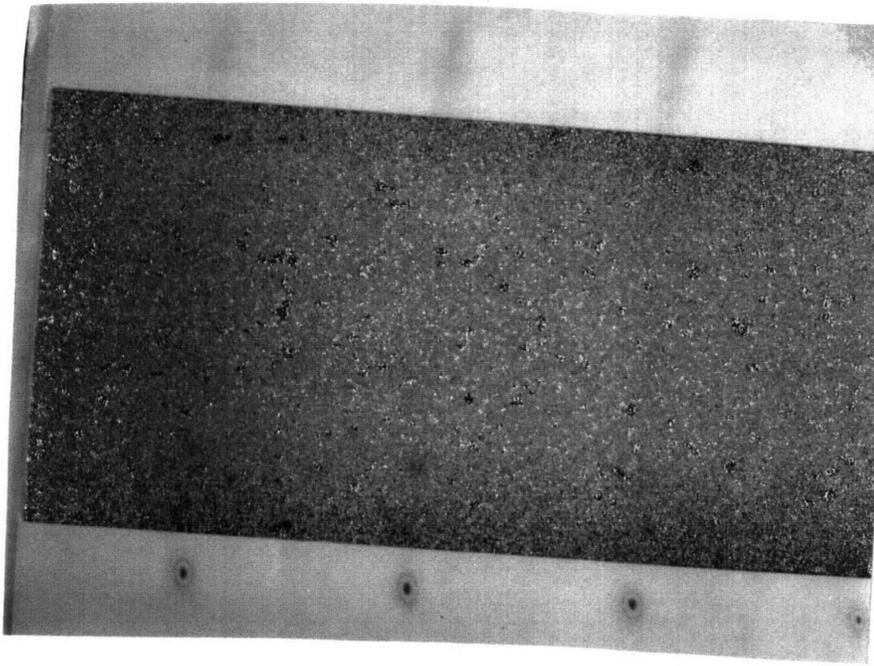


Figure 3: Surface of coating #6, as coated (sample size is 9" x 4.5").

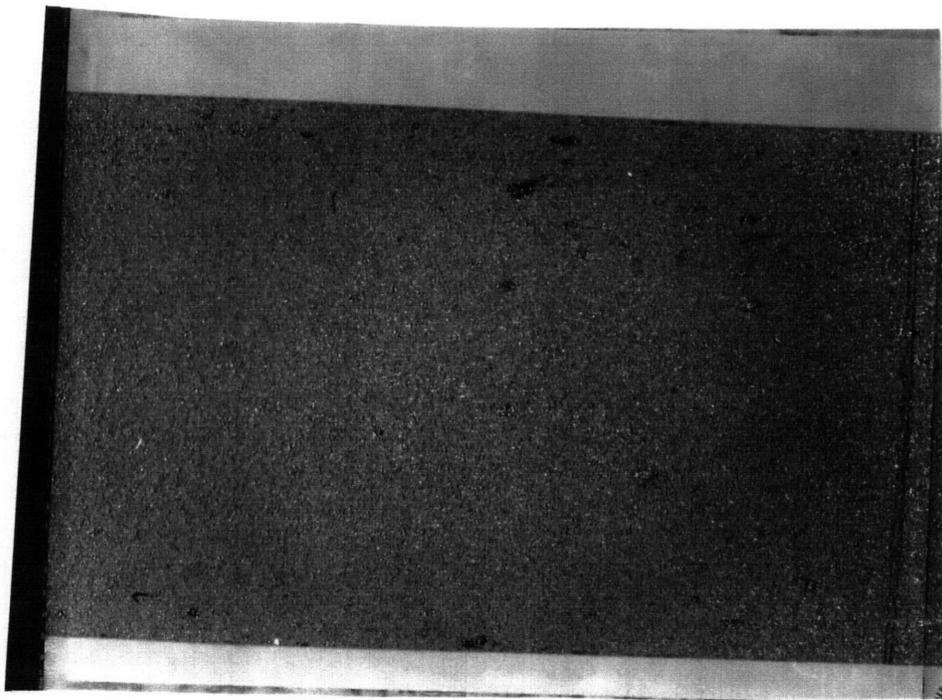


Figure 4: Surface of coating #10, as coated (sample size is 9" x 4.5").

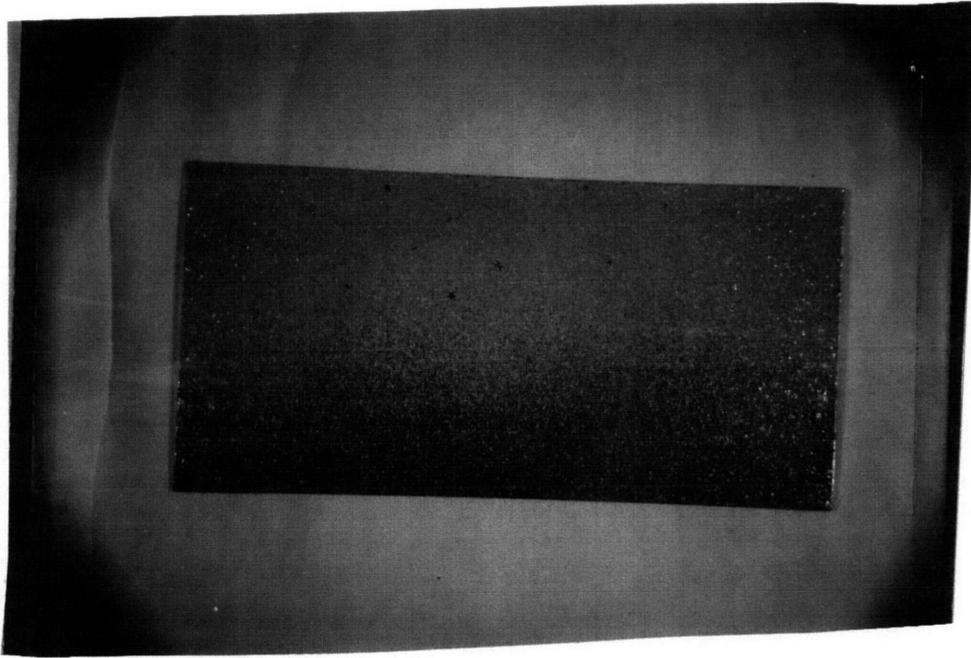
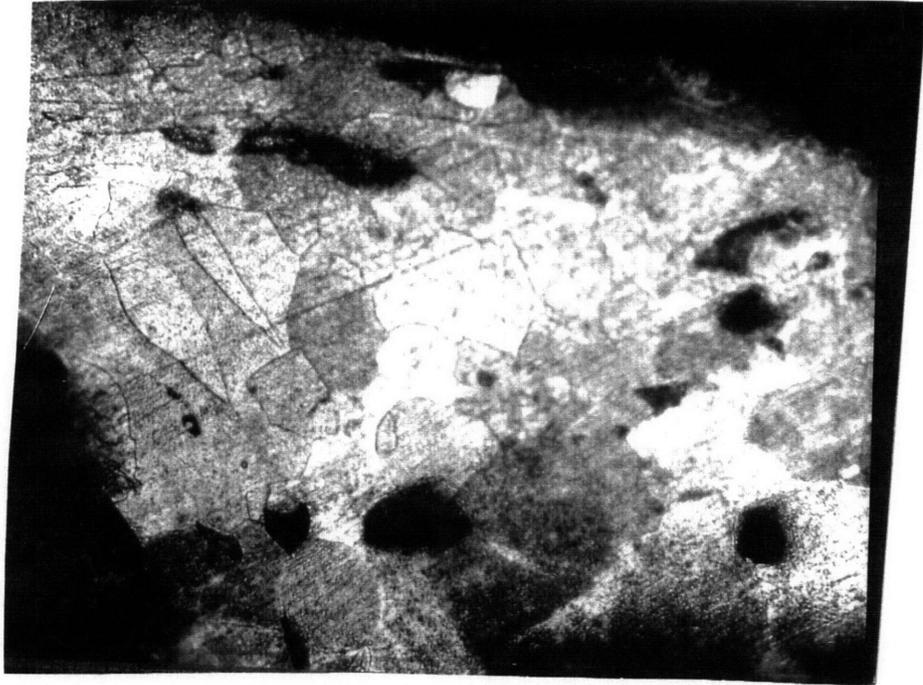


Figure 5: Surface of coating #14, as coated (sample size is 9" x 4.5").



|-----| 100 μ m

Figure 6: Coating #3, as coated cross-section, center section, etched in 1% nital.



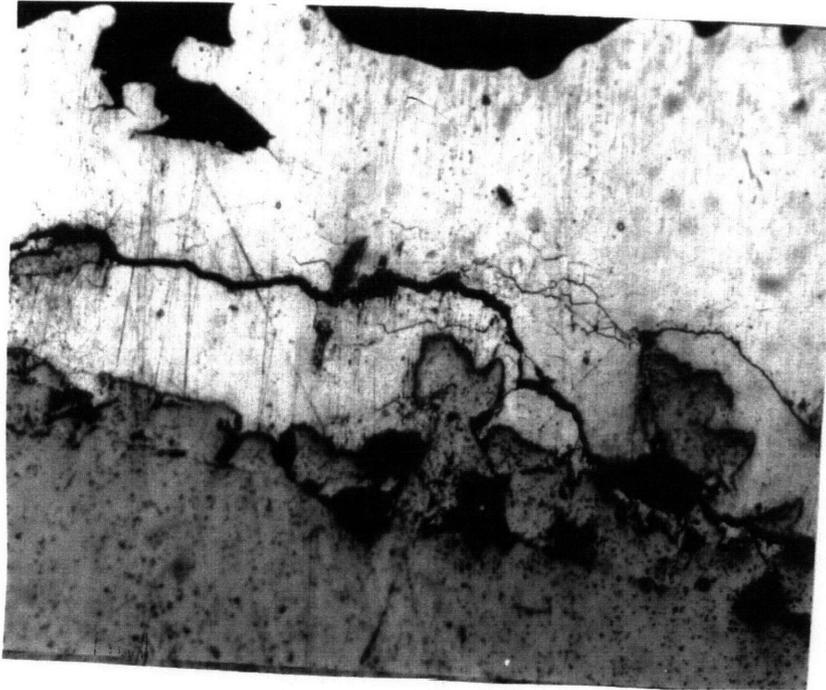
|-----| 100 μ m

Figure 7: Coating #3, as coated cross-section, edge, etched in 1% nital.



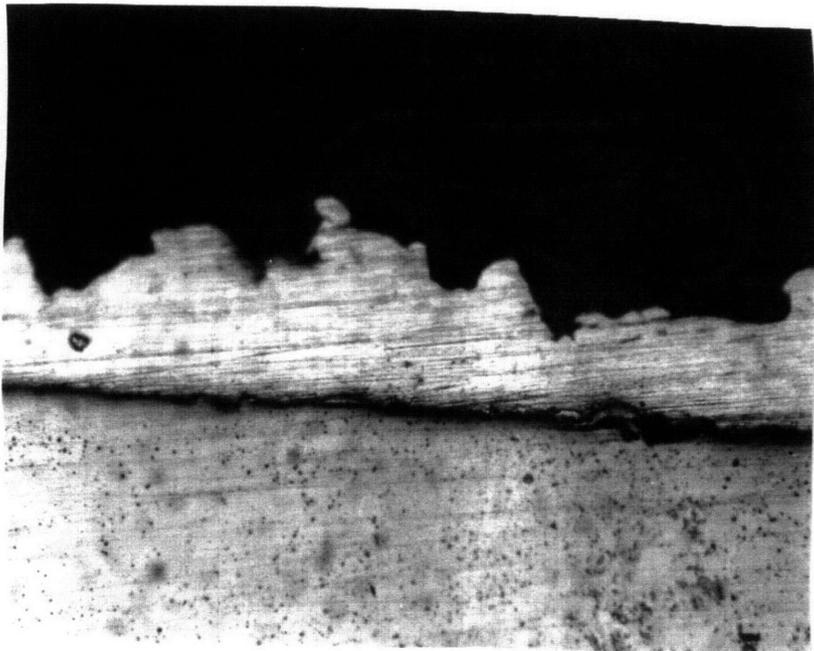
|-----| 200 μ m

Figure 8: Coating #6, as coated cross-section, unetched.



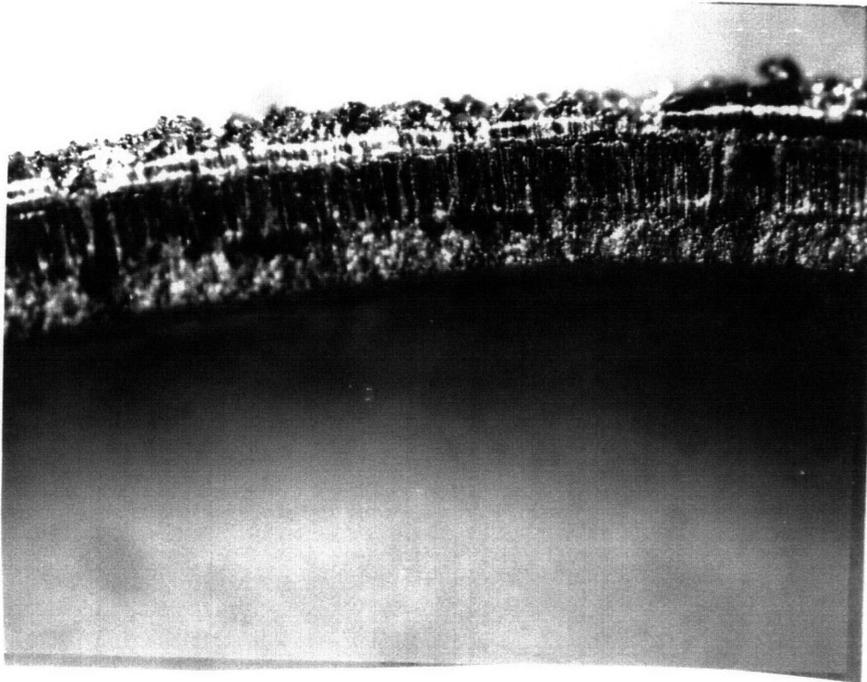
|-----| 100 μ m

Figure 9: Coating #7, as coated cross-section, unetched.



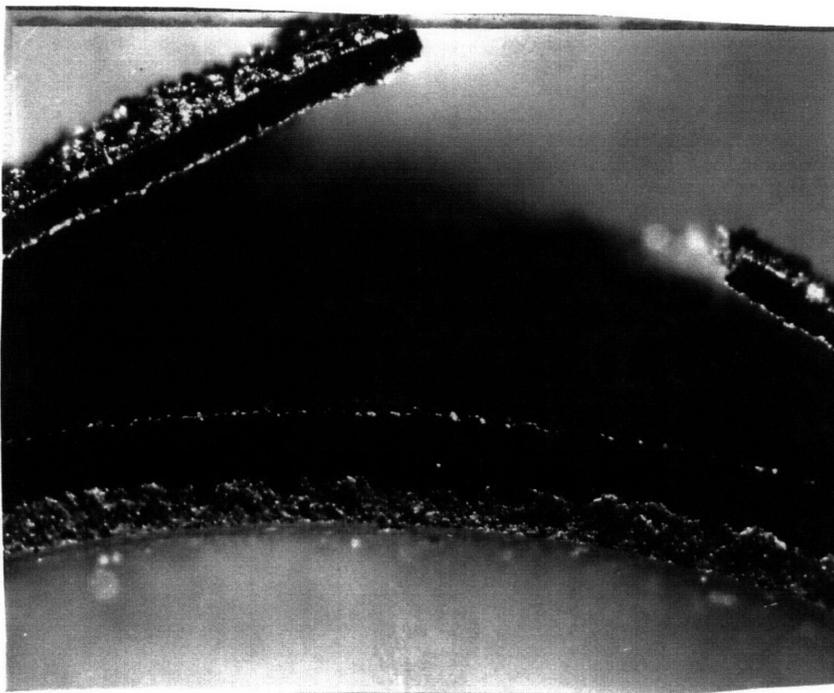
|-----| 100 μ m

Figure 10: Coating #8, as coated cross-section, unetched.



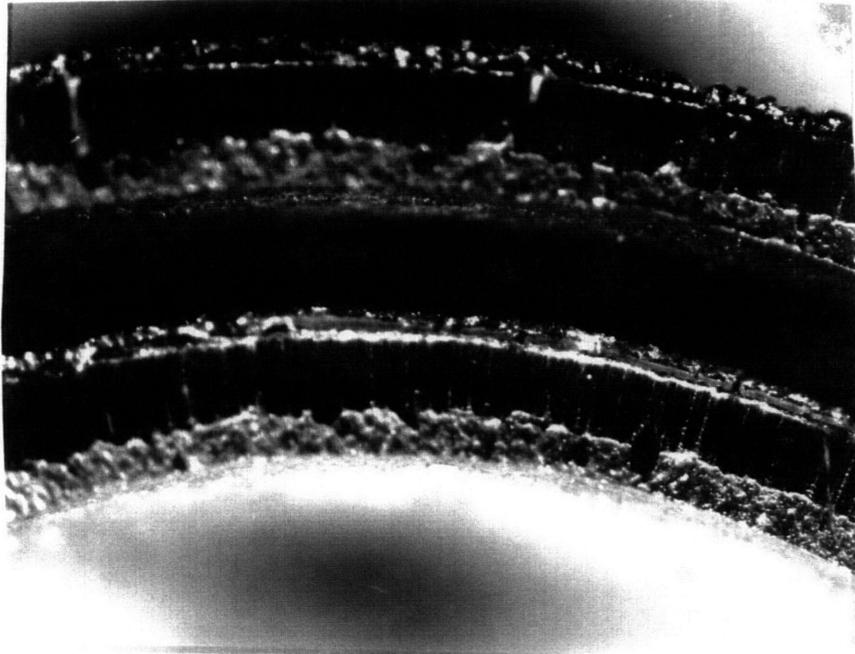
|-----| 1 mm

Figure 11: Coating #5, cracked in bend test around 1.75" mandrel.



|-----| 1 mm

Figure 12: Coating #7, cracked and peeled in bend test around 0.875" mandrel.



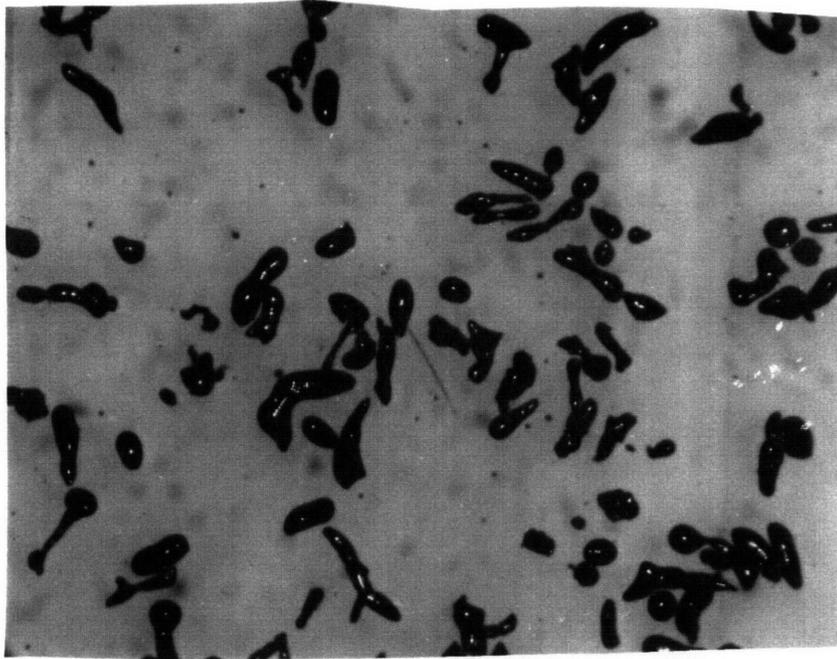
|-----| 1 mm

Figure 13: Coating #8, two undamaged bent strips. Top: 0.875" mandrel, bottom: 0.437" mandrel.



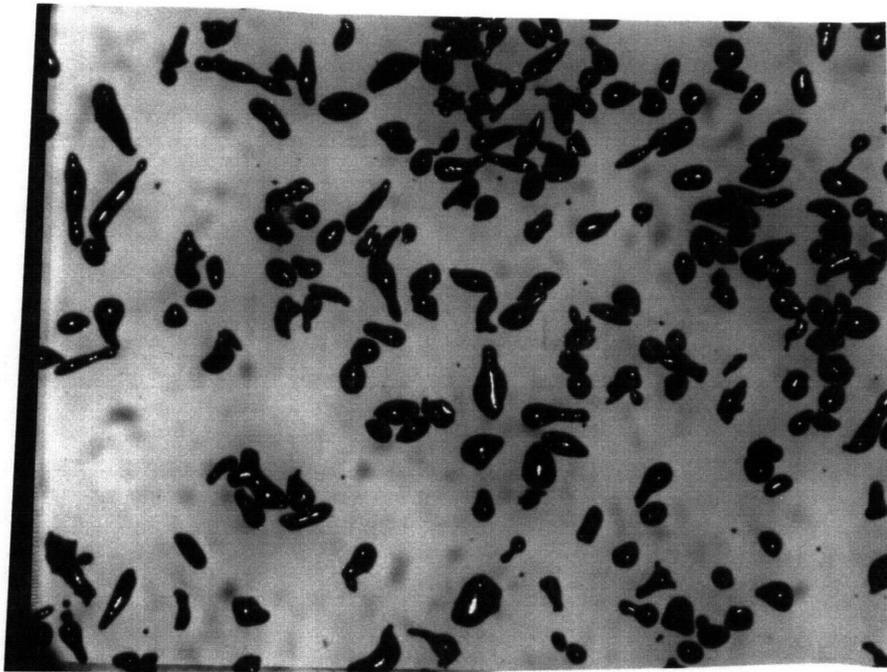
|-----| 100 μm

Figure 14: -53 μm overspray powder, run #2.



|-----| 100 μm

Figure 15: -53 μm overspray powder, run #5.



|-----| 100 μm

Figure 16: -53 μm overspray powder, run #8.

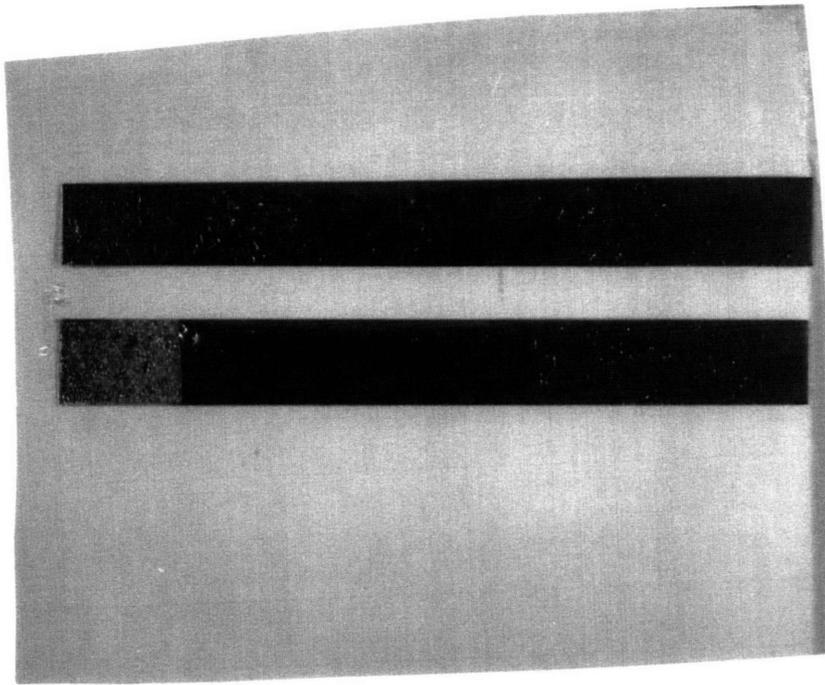


Figure 17: Reflow samples from run #5 (240-250°C in Ar). Top: 12 min, bottom: 20 min.

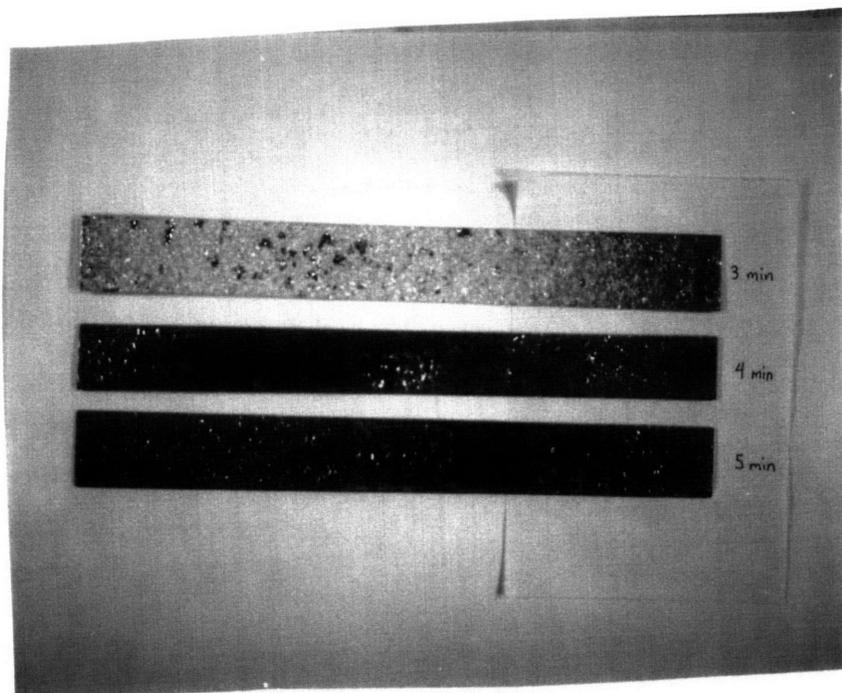


Figure 18: Reflowed samples from run #5. From the top: #2, #3, #1.

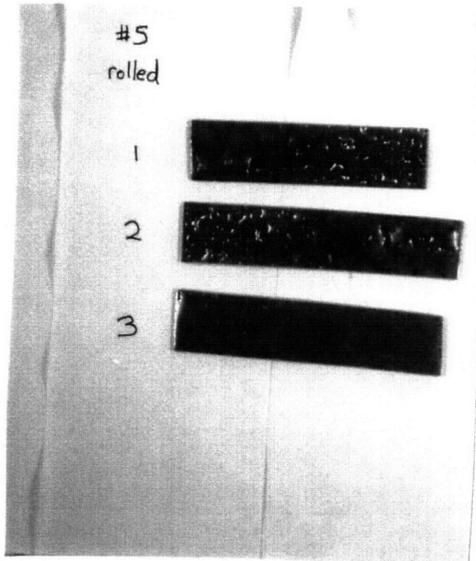


Figure 19: Rolled then reflowed samples from run #5.

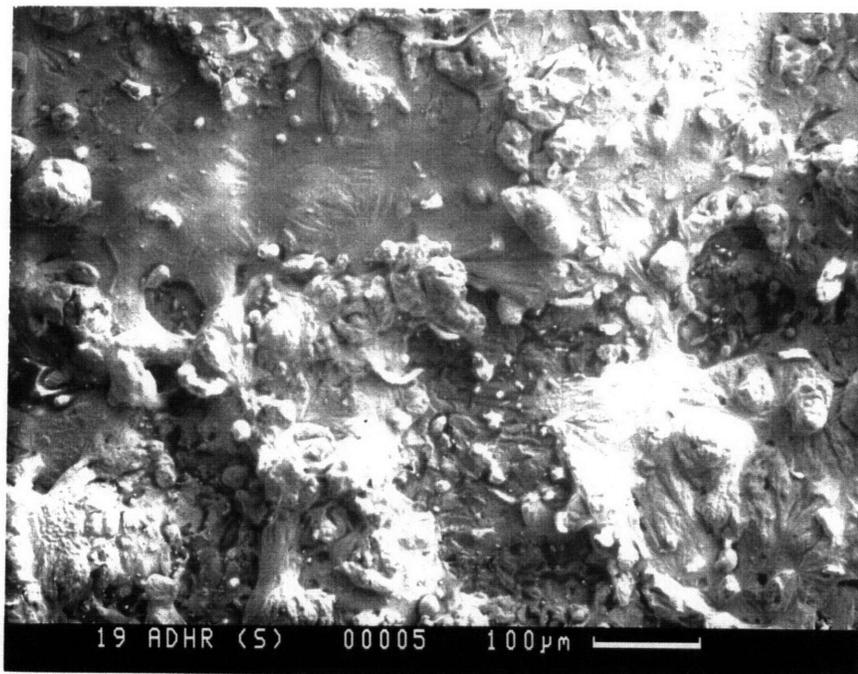


Figure 20: SEM photo of hydrogen reflowed sample.

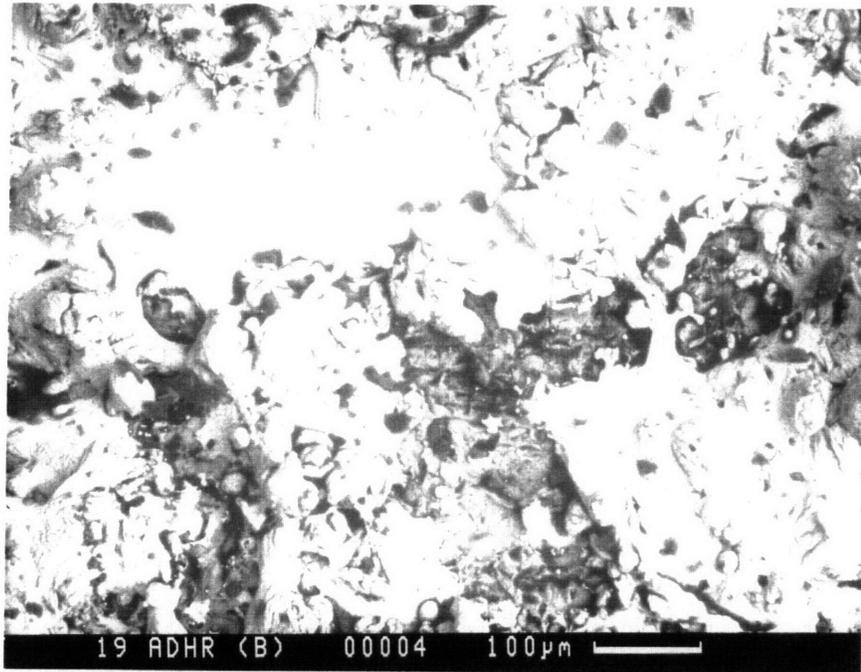


Figure 21: SEM photo of hydrogen reflowed sample, backscattered image.

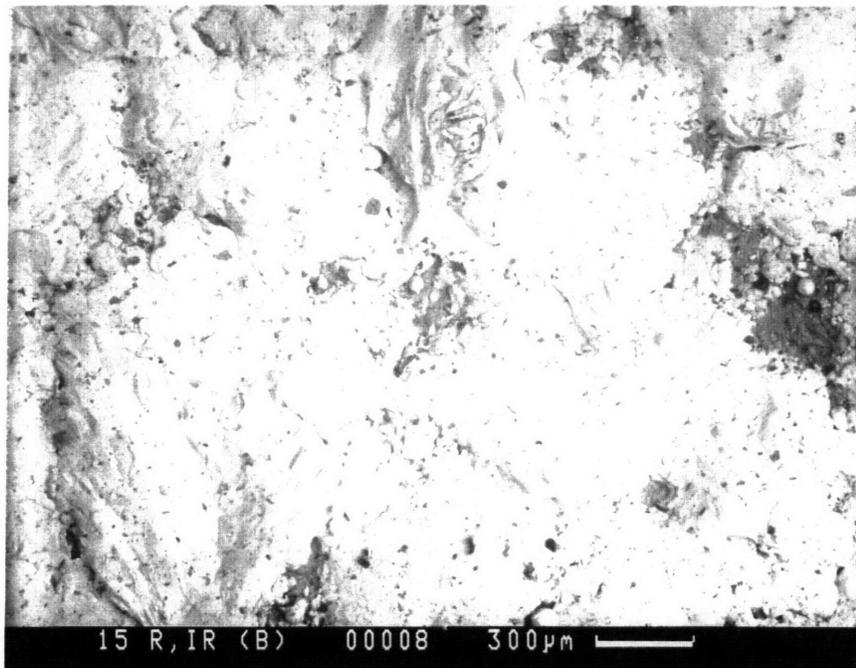


Figure 22: SEM photo of induction reflowed sample (no flux).

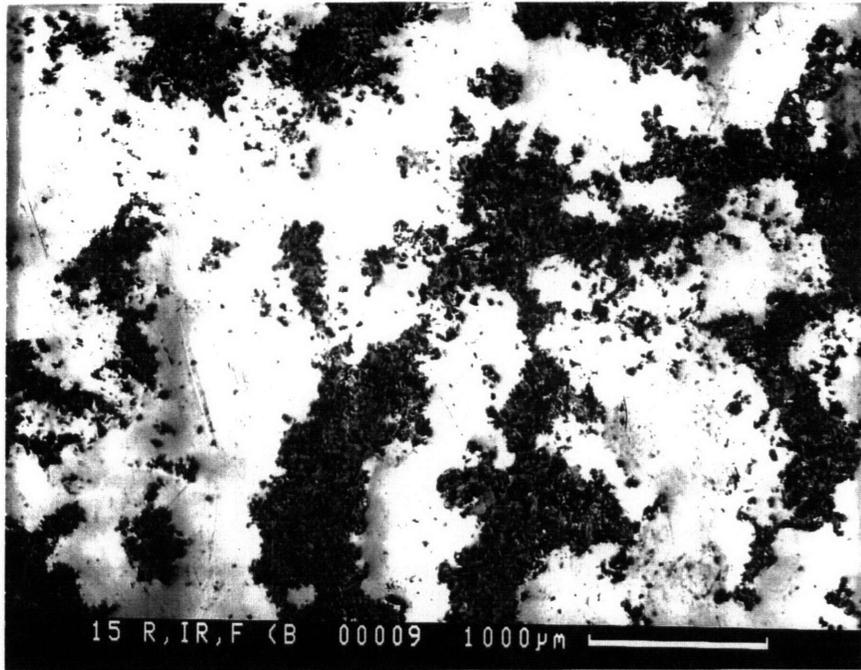


Figure 23: SEM photo of induction reflowed sample (fluxed).

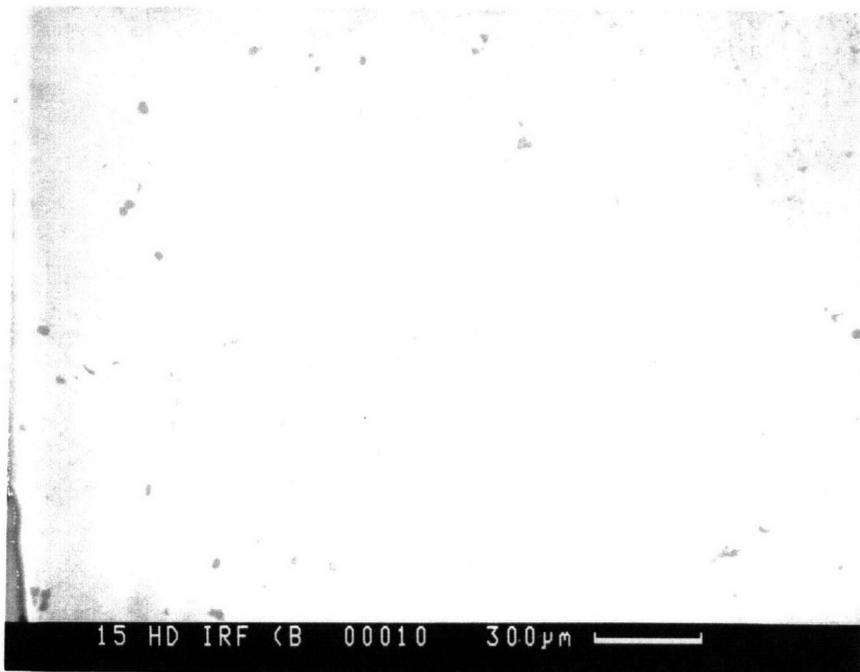
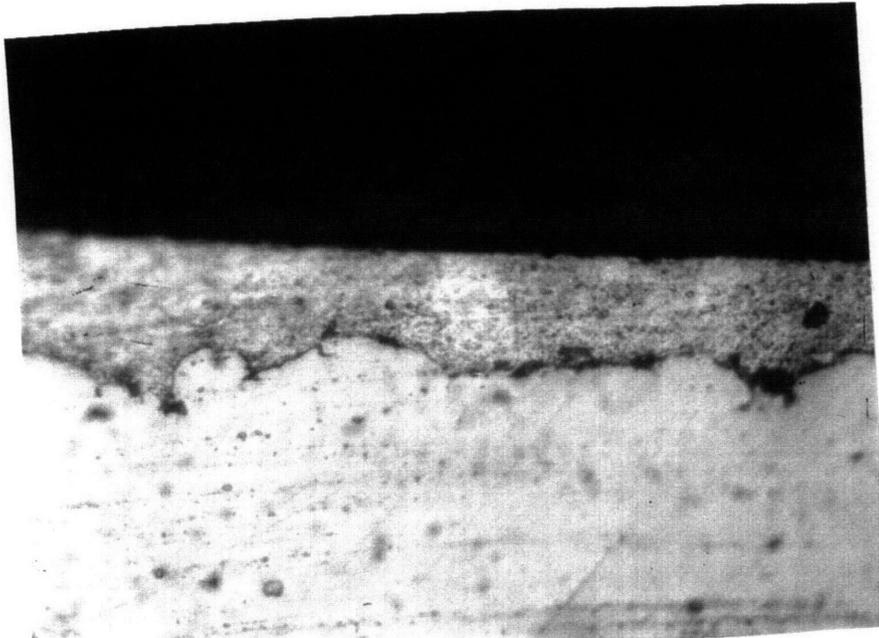


Figure 24: SEM photo of hot dipped and induction reflowed (fluxed) sample.



|-----| 50 μm

Figure 25: Coating #5, reflowed 20 minutes (Ar), cross-section.

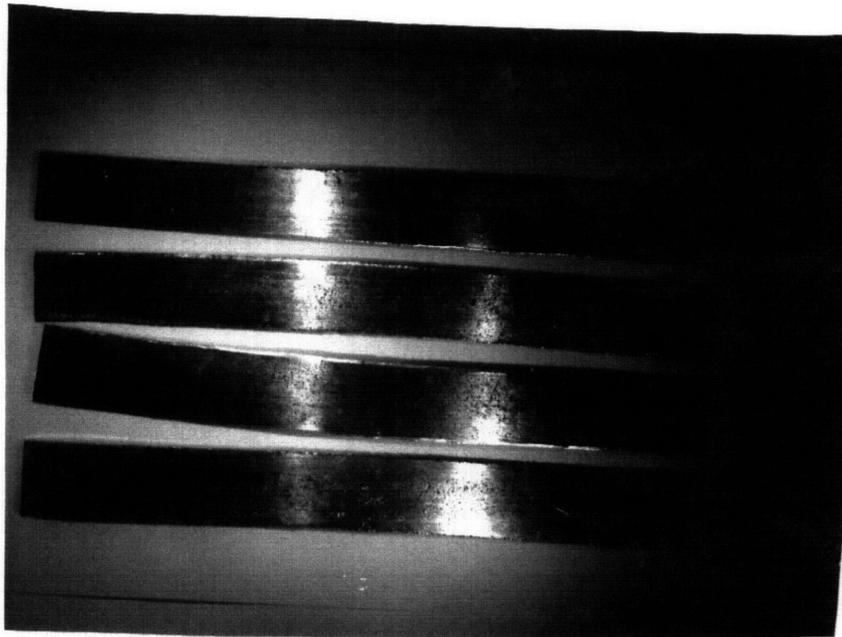


Figure 26: Rolled strips from run #7.

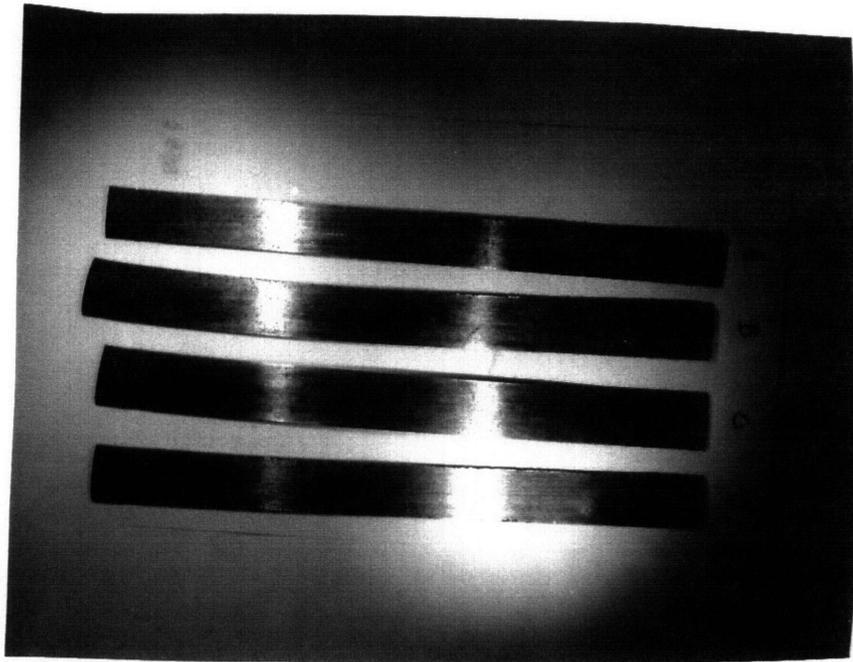
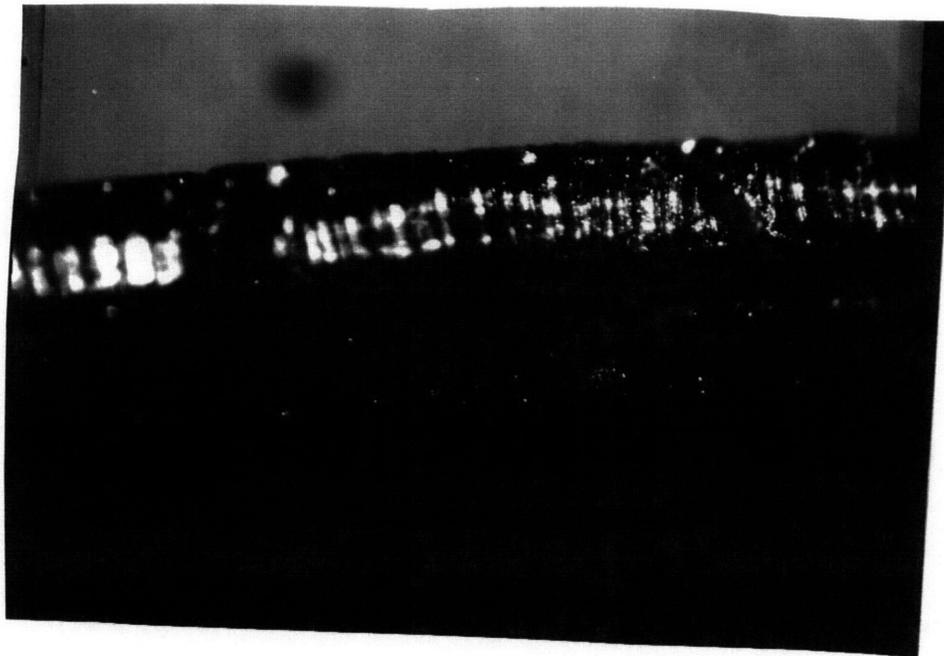
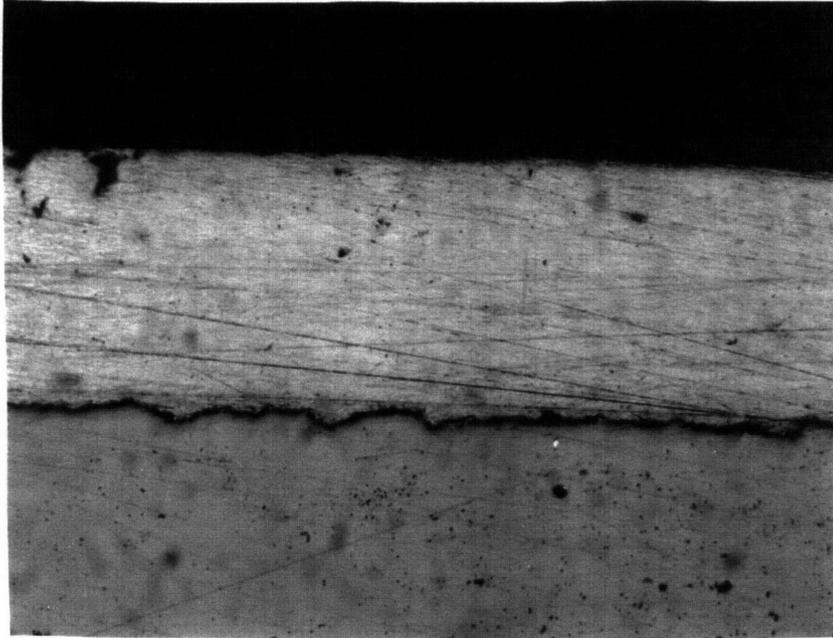


Figure 27: Rolled stips from run #8.



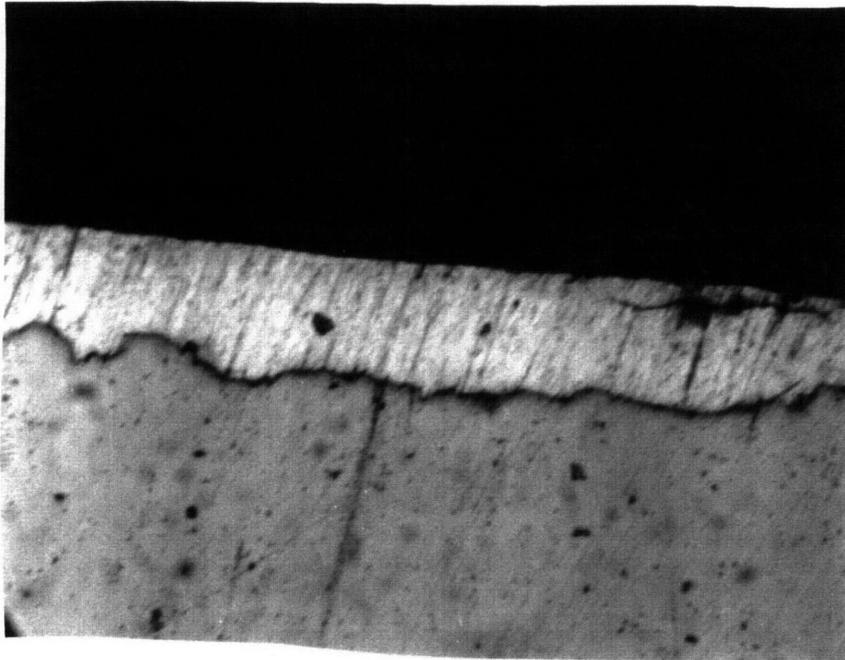
|-----| 0.5 mm

Figure 28: Smearred tin on edge of rolled strip, run #5.



|-----| 200 μm

Figure 29: Tin coating #7, cross-section after rolling, unetched.



|-----| 100 μm

Figure 30: Tin coating #8, cross-section after rolling, unetched.

5. Discussion

In evaluating the coating quality, there are three main factors to consider: adhesion, continuity, and appearance. Good adhesion is crucial so that the coating will stay on the substrate during forming operations and handling during use of the finished part. The coating must be continuous if it is to provide good corrosion protection, although this may be less of an issue for some systems. For most applications, appearance is also an important commercial factor; a coating which is bright and shiny is more pleasing than one which is rough and dull. The most important tests for evaluation of these properties in the tin coatings produced by LDC are the bend tests and the qualitative assessment of coating appearance.

5.1 As-sprayed Coatings

In the case of the as-sprayed coatings, the thinnest coatings produced the best results. Only runs 8, 14, and 17 produced as-coated samples which survived bend testing. At 80, 136, and 104 μm , these were three of the thinnest four coatings; run 19 was the only other run which was below 200 μm in thickness. This trend is expected, as the shrinkage stresses which can predispose the coatings to delaminate grow with the thickness of the coating.

Additionally, all of the good deposits were made on blasted substrates. Again, this is not surprising. Since the mechanism of adhesion for spray coatings is mechanical interlocking of the particles to the substrate and to each other, the roughness of the substrate surface prior to coating will largely determine how well the coating adheres. The amount of roughening needed, however, is likely to be a function of the desired coating thickness, the materials system, and the post-processing to be used. A thinner coating, as mentioned, will be less likely to peel from the effects of shrinkage stresses; thus, it would seem that a thicker coating would require a proportionally rougher substrate than a thinner coating to achieve the same adhesion. The materials used, in the case of coating of systems other than tin/steel, will also have an effect, as the amount of shrinkage stress will increase with the temperature difference between the coating layer and the substrate. Finally, if post-processing of the coating can be done to relieve residual stresses in the coating or to change the bonding from mechanical to metallurgical, the roughness requirements of the substrate can conceivably be lowered to the minimum required to maintain adhesion through post-processing.

The natural problem, in the case of spray deposition, is that a thin coating, good for mechanical properties, will tend to be non-continuous. Because the arrival of particles

from the spray at the substrate is a random process, there is always the possibility of incomplete coverage. However, the fewer layers of particles which, on average, impact the substrate, the more likely bare patches are. Thus, the production of thin coatings requires special care and, below some minimum thickness, makes reliable production of continuous coatings impossible. Some steps can be taken to minimize this problem. A small particle size in the spray, relative to the thickness of the coating, would help. For a given desired coating thickness, more layers would be required for small particles than for large particles, thus reducing the statistical chance of a bare spot. Spherical particles would also be beneficial, as the random orientation of the particles would no longer be a factor.

It can be seen from the overspray analysis and the as-coated micrographs that these conditions were not achieved on the lab scale. Even for the conditions of high gas pressure and low metal flow (small slit and small tin charge), the mass average particle size was in the range of 60-80 μm , with an aspect ratio of approximately 2. From micrographs, we can reasonably expect a final aspect ratio of impacted particles no greater than 5 (for higher melt enthalpies, more compaction of the particles could be achieved). Thus, we expect each layer to be at least 12 μm thick, giving us only 8 layers on average to form a 100 μm thick coating. As can be seen from the micrographs, the variation in thickness of the coating on a small scale is extremely large in some cases; however, as evidenced by the as-coated profile of run 8, it is possible to achieve a fairly even coating by control of the particle size.

On a larger scale of production, more control of these factors is available. A longer atomizing slit will produce a uniform spray over a larger area, leading to more predictable coating of the sample. The ability to pour from the tundish at something near steady-state conditions greatly enhances the ability to control the gas to metal flow ratio, allowing the possibility of finer particle size. Better fixturing of the substrate or simply the use of larger and heavier substrates will allow the flight distance to be reduced, effectively increasing spray enthalpy at impact and thus improving the spread of impacted particles.

Post-processing is another avenue to better continuity. Since coating of the substrate is a random, rather than driven, process, there will always be some chance of non-continuity, which will increase with decreasing coating thickness. A post-processing step which improves the continuity of the deposit could be used to circumvent that problem.

The final issue for the as-sprayed coating is appearance. Unfortunately, random particulate buildup from spray coating will unavoidably result in a surface finish which is, at best, rough on the scale of the spray particle size. This roughness will also cause the

surface to be matte, rather than reflective. While this may be acceptable or even desirable for some applications, most metal-finishing applications call for a bright, smooth surface, mostly for aesthetic value, but also for reduced friction and better wearing of the coating. To the degree that the coating surface can be improved, again a small particle size will reduce the roughness and a high spray enthalpy will yield greater flattening of the particles on impact. For this, a high gas to metal flow rate, a high melt superheat, and, if possible, a short flight distance are necessary.

5.2 Reflowed Coatings

The reflowed coatings examined performed very well in bend testing, but had very poor appearance and continuity. Because of this, despite the mechanical properties, the reflowing process as attempted has to be considered a failure. There are several reasons behind this, some rooted in the coating step and others specific to the three reflowing processes used.

The basic premise of tinplate reflowing is that liquid tin will completely wet a clean low-alloy steel surface. The key point here is that the steel surface must be chemically clean. Tin will not wet iron oxide and will, in fact, ball up on an oxidized surface. The situation is further complicated by the possible presence of tin oxide. In an oxidizing atmosphere, the surface of the molten tin will quickly form an oxide layer which is solid at the melt temperature (stannic oxide melts at 1630°C) and which will pin the melt, preventing it from spreading and also preventing the formation of a smooth surface.

With this in mind, it becomes apparent that simple inert gas cover is insufficient for reflowing. Even assuming the inert gas is completely inert, which will not be achieved in practice, as the oxygen pressure will still be sufficient to at least mildly oxidize metals at elevated temperature, it will not clean the surfaces. The steel will have some oxide on it and the tin coating itself will have a high oxide content from the spraying process.

Hydrogen reflowing offers a slightly better solution. No new oxidation will occur under the reducing cover gas; however, there is still the issue of oxide already present on the steel layer which may prevent spreading of tin and of the effect of trapped oxide in the coating layer, which will presumably rise to the surface when the tin becomes molten. Experimental results showed some oxide on the tin surface, and the tin did not spread.

Induction reflowing in air obviously has all of these problems. Although the sample is only at high temperature for a very short time, this is still sufficient for at least the tin to oxidize in air, pinning the coating as described above and damaging the appearance. The use of a flux cover solved part of the problem, but not completely. Even the fluxed

tin did not spread, although it did stay clean and smooth. The issue here is the oxide layer already present on the steel, probably even before coating but certainly after the sample was allowed to sit between coating and reflowing. In order for wetting to occur, the fluxing action must break down the oxide layer at least sufficiently for the tin to penetrate it. However, going back to hot dipping, it may be easily understood why this does not occur in the induction reflowing process.

There are two factors modifying the effectiveness of the flux, the first being the starting condition of the steel and the second being the condition under which the steel and flux are heated. Referring to the practices of the hot dipping industry, we see that the steel used for hot dipping is either abraded or pickled immediately before fluxing or has been pickled and then oiled at some previous point in the strip manufacturing process. This gives a much cleaner steel surface than that which was present in any of the attempts to reflow the LDC tinplate. The fluxing action may simply not be strong enough to clean the steel sufficiently for tin wetting. The second issue, that of the conditions of heating, can be better understood by looking at the experience of hot dipping a sample for reflow testing. The abraded and fluxed steel strip was submerged in a pot of molten tin with a very thin flux cover. The side which entered the tin first was coated fairly evenly and completely for such a clumsy operation; the tin coverage was complete, adhesion was good, and the surface quality was high. On the other hand, on the back side, which was heated by contact with the molten tin, the flux burned off in the air, allowing oxidation of the steel to begin before the tin could spread. Once the surface had become oxidized, it was impossible to immerse it in the tin. When this sample was induction reflowed under flux, the side which was previously tin coated remained well coated and the tin surface remained mostly smooth and shiny (although the very heavy tin layer did run under the influence of gravity) while the side which had not previously been completely covered showed no movement of the tin coating.

Despite all of this, the reflowing process does still offer some opportunities for coating improvement. As a minimum condition, the starting steel base must be clean and all subsequent operations, including the spraying itself and reflowing, must be carried out in an inert, or preferably slightly reducing, atmosphere. The ideal cleaning method would be pickling, although this complicates the processing line and adds an otherwise unnecessary chemical step which we hope to be able to eliminate by use of LDC coating. In any case, none of this was attempted in these experiments, as the batch nature of the laboratory apparatus would not have permitted smooth, clean, and rapid transfer of the part from one step to the next. If these conditions can be met, there is no basic reason why the LDC coated tin cannot be made to reflow; however, the reflowed coating may

still be matte in appearance, due to the roughness of the blasted substrate. Ideally, a reflowing step after coating would allow spraying of thin, non-continuous layers, which were then smoothed to thin, continuous coatings by the reflow process.

5.3 Rolled Coatings

The rolled coatings were in all ways the most successful. Most displayed good to excellent adhesion in the bend test. Surface finishes were smooth, bright, and shiny, although lining of the surfaces was sometimes a problem. Continuity was also improved by rolling, although in cases of incomplete coverage, care must be taken in evaluating the effectiveness of rolling for improving continuity.

The effect of rolling on surface finish is the most obvious. The rolling process, if sufficient reductions are used, will result in a completely flat coating surface which, if clean, will have the properties of smoothness and reflectivity desired in a bright tin coating. Improved adhesion is believed to come from two factors. First, the rolling process fills the tin more completely into the irregularities of the steel surface, improving mechanical bonding. Second, because of the low melting point of tin, it will recrystallize under heavy work even at room temperature. This recrystallization of tin was observed in rolled samples and may serve to eliminate the residual stresses associated with the spray coating process, thus removing the coating's predisposition to peel. By smoothing the tin, the process also spreads it, leading to better uniformity and continuity of the coating. More importantly, it will close up porosity within the coating layer, greatly increasing the effective thickness of the coating with regard to corrosive environments.

It should not be believed, however, the rolling is a cure-all for sprayed coatings. The quality of the part that goes into the rolls has a strong effect on the quality of the part that comes out. The as coated sample must have sufficient adhesion to remain properly attached to the substrate during rolling without warping, peeling, or splitting. The coating must be thin enough that it will not fold over on itself, develop a rippled surface, or smear over the edges of the substrate. A heavily oxidized tin coating is more susceptible to all of these surface flaws due to the restricted flow of the coating caused by the oxide layer. In terms of adhesion, rolling merely improves the mechanical bonding which already exists; it does not create any new forms of bonding and will not cause mechanical bonding where none exists. Also, improvements in coating continuity must be considered suspect. The folding of the tin coating over onto previously exposed steel will provide little protection from corrosion if the oxide layer on the steel is not broken; in fact, the narrow crevice created by this deformation may even prove more damaging than the bare spot which existed prior to rolling.

Overall, the rolling process for LDC coatings appears to give large benefits for a very low cost. In addition to production of coatings typically electrodeposited or hot dipped, the LDC coat plus rolling technique may find application for thickly clad systems currently manufactured by roll-bonding of individually produced sheets. Such a set-up could allow use of a continuous roll-bonding line where the base material would be LDC coated with the a thick layer of cladding and then the entire piece rolled to densify the coating and improve the bond. Such a process would eliminate the need to separately roll the cladding and the problems of properly aligning and affixing the cladding sheet to the base metal for rolling.

5.4 Intermetallic Layer

In all hot dipped tinplate and in reflowed electrolytic tinplate, an intermetallic layer of FeSn_2 is formed between the tin coating and the steel. This layer metallurgically bonds the coating to the substrate and provides improved continuity by promoting wetting, improved adhesion, and improved corrosion resistance. Such an intermetallic layer is also typically formed in other coating systems, including all hot dipped coatings, many CVD coatings, all ion implanted coatings, many plasma sprayed coatings, and even some roll-bonded claddings, and serves much the same purpose. However, no evidence of the formation of such a layer was found in any of the LDC coatings produced.

There are two main reasons why the absence of such a layer is not really surprising. First, the LDC process, regardless of melt temperature, results in rapid quenching of the sprayed particles at the substrate. Such rapid quenching removes the heat from the interface quickly and also rapidly solidifies the coating. Under these circumstances, the time at elevated temperature is insufficient for creation of an intermetallic layer between the coating and the substrate. The absence of intermetallic layers in traditional sprayed coatings is an example of this effect. The second reason comes back to the condition of the substrate surface. Formation of the intermetallic layer requires a chemically clean substrate surface to interact with the hot coating layer. Since a chemically clean surface is not a requirement for mechanical bonding in spray coating, no effort was made to achieve one. Thus, even if the melt hits the substrate with sufficient heat, it cannot interact with the steel base, only with the oxide layer. Attempts at heating the substrate to provide the thermal conditions necessary for formation of an intermetallic layer only exacerbated the oxidation problem, making it impossible to achieve any kind of good bonding. The reflowing step could have helped to develop an intermetallic layer, as occurs in electrolytic tinplate, but evidence from the reflowing work indicates the

presence of an oxide layer between the tin and the substrate which would, again, have prevented the formation of the intermetallic.

If an intermetallic layer is desired in an LDC tinplate, the solution is in the cleanliness of the substrate. As mentioned in the discussion of reflowing, the substrate must be chemically clean prior to coating and remain in a reducing atmosphere until such time as the steel surface is completely covered by tin. It should be noted that in other systems where the coating metal might dissolve the oxide of the base metal at elevated temperatures, it may be possible by post-processing to achieve metallurgical bonding without pickling and special handling of the substrate.

5.5 Ceramic Coating

A brief mention of ceramic coating by LDC should be made. Although no controlled experiments on this subject were done, the evidence from overspray coating of the ceramic crucible indicates potential promise. Here, the ability to mechanically bond a metal to a substrate in a situation where chemical bonding is normally difficult or impossible opens up great possibilities for LDC coating. Although rolling and reflowing are not possible, preventing formation of bright coatings, this method could be useful for metallization of ceramics and even plastics for joining by soldering or brazing. Additionally, it serves as an indicator that many normally incompatible coating/base systems could be coated using the LDC process.

5.6 General Applications

Although this work has been done entirely with tin and steel, the intent of the research was never simply to produce tinplate. The system of tin coated steel was selected as an easy starting point to examine the potential applicability of LDC coating for a wide range of coating applications. The continuous, high-production capabilities of the linear LDC nozzle and its ability to produce coatings of widely varying thicknesses with minimal alteration of the coating apparatus make it ideal for high-production rate coating of sheet and strip material.

Despite the fact that the generally thicker coatings produced by the LDC process make it unlikely that it will ever be economical to replace electrolytic tinplating by this process, many other coating systems not only accept but in fact demand thicker coatings. Heavier coatings of tin, tin and lead (terneplate), lead, and zinc for heavily corrosive environments currently produced by electroplating or hot dipping could be produced by an LDC followed by rolling process. Roll-bonded claddings, particularly for aluminum-clad aluminum alloys, could easily be manufactured by LDC coating. Higher melting

coatings for specialized applications might prove out of reach or uneconomic, but low melting, easily sprayed alloys still account for a large volume of the corrosion resistant coating in wide use today. Finally LDC coating opens the possibilities for rapid production of coated ceramics and plastics and for coating of currently incompatible metal-metal systems.

6. Conclusions

- 1. The LDC process can be used for production of tin coatings on steel. The conditions which produce the best as-sprayed coatings are: a rough substrate surface, a particle size and particle aspect ratio which are small relative to the thickness of coating produced, good spread and rapid quench of the particles on the substrate, and a substrate which is at least moderately oxide-free.**
- 2. Rolling of LDC coated strips can effect large improvements in adhesion, appearance, and coating continuity; however, it must be remembered that rolling cannot salvage a bad piece and that the initial quality of the as-coated sample is important if the finished part is to have the desired appearance and mechanical properties.**
- 3. Reflowing and formation of metallurgical bonding via an intermetallic layer require much higher standards for cleanliness of the substrate and special inert or preferably reducing atmospheres for all handling through the reflowing step, including the atomization itself.**
- 4. Spray coating may potentially be used for a wide variety of coating systems, including some not currently possible due to incompatibility of the coating and substrate materials.**

7. Recommendations for Future Work

Most of the important advances to be made in continuing this work are dependent on the construction of more specialized equipment for coating and for cleaning and handling of the substrate to improve post-processing.

1. The LDC process is typically carried out in an inert atmosphere to severely limit the oxidation of the spray particles and thus promote better wetting between the impacting particles and the previously deposited layers. It is believed that a first step for any continuation of the coating work should be to make some runs in an inert atmosphere to determine the effect this has on coating quality and on the improvements subsequently achieved through post-processing.

2. In order to improve the effectiveness of the LDC coating process for production of thin coatings such as those used in manufacture of tinplate, it will be necessary to improve some variant of the reflowing process to the level that spreading of the coating on the substrate resulting in complete coverage and at least some formation of the intermetallic occurs during the reflowing step. In order to accomplish this, it is believed that some system for cleaning the substrate and then maintaining it in an inert or reducing atmosphere is necessary. However, because of the multiple step process and the need to separate the cleaning, coating, and reflowing steps, this will require specialized equipment to protect the steel surface from oxidation during transport from one step to the next.

3. Since rolling has offered a cheap and easy method of achieving vast improvements in all aspects of coating quality, further work in this area should focus on developing the potential for a truly continuous process of spray coating followed by rolling. The requirement for this would be extension of the linear atomizer to achieve a uniform coating thickness across the substrate.

4. As the original intent of this work was to study the feasibility of LDC spray coating for a variety of applications, it is believed that attempts should be made to spray other metals. Of particular commercial interest and well suited to the process are zinc and aluminum coatings on steel and aluminum cladding on aluminum.

5. One of the advantages of the LDC coating process is the ability to coat systems in which the substrate and coating may normally be incompatible. With this in mind, it is recommended that controlled experiments in the coating of ceramics and plastics be done. Also, there are metal-metal systems, a commercially relevant example being lead coating of steel, where the coating metal will not normally wet the basis metal. Although this may not be the ideal system, as one must hesitate in recommending the atomization of lead without very strict safety precautions, this or another system like it bears examination.

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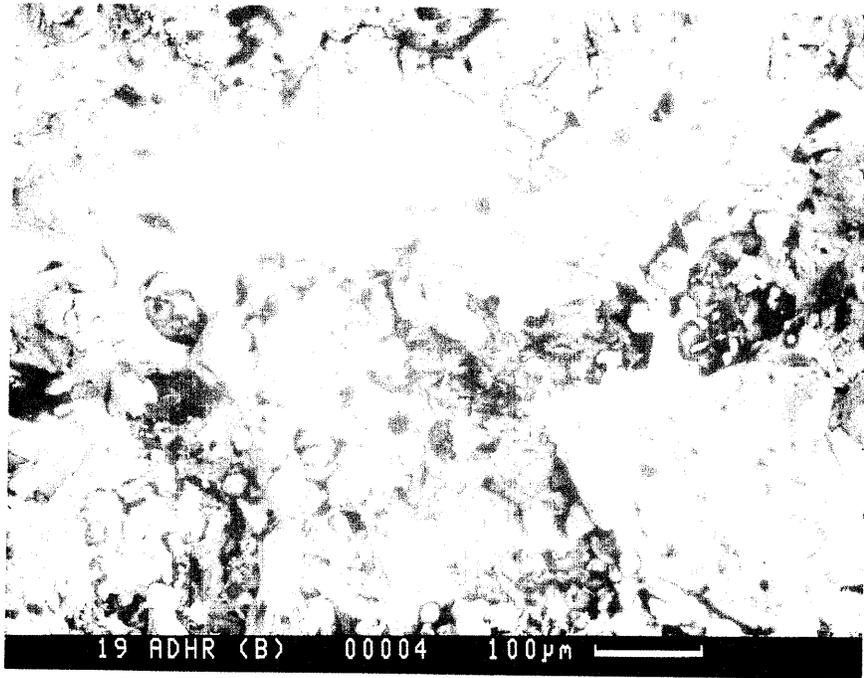


Figure 21: SEM photo of hydrogen reflowed sample, backscattered image.

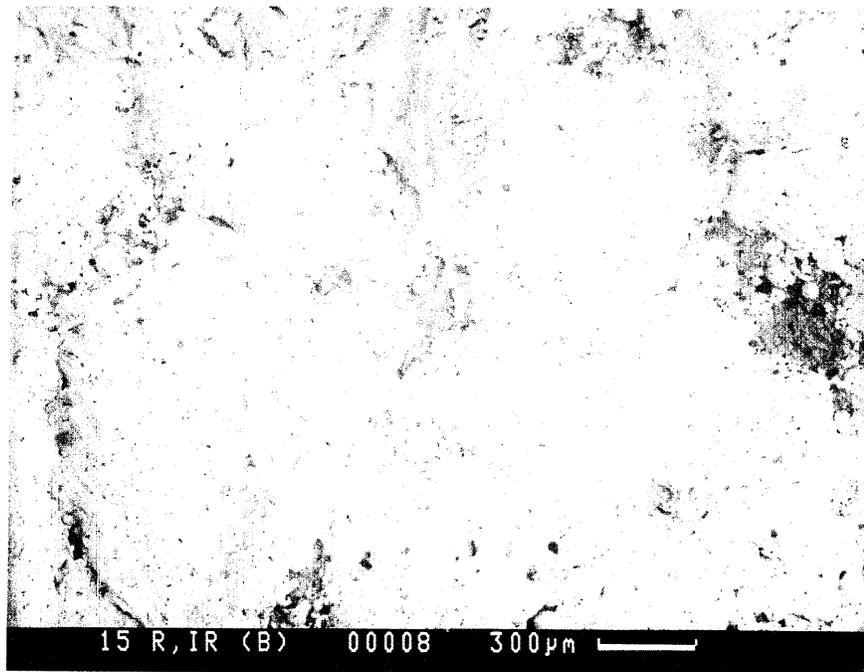


Figure 22: SEM photo of induction reflowed sample (no flux).

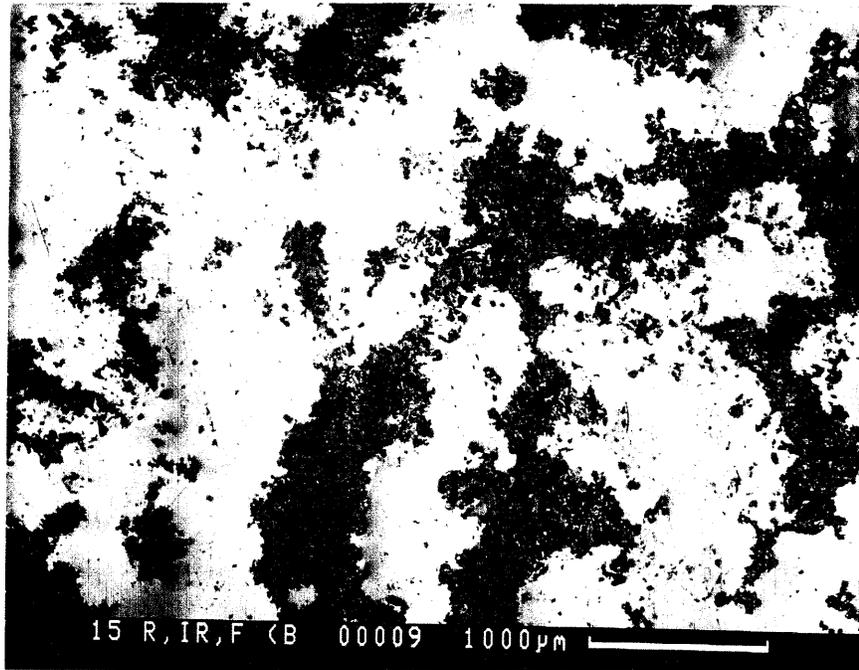


Figure 23: SEM photo of induction reflowed sample (fluxed).

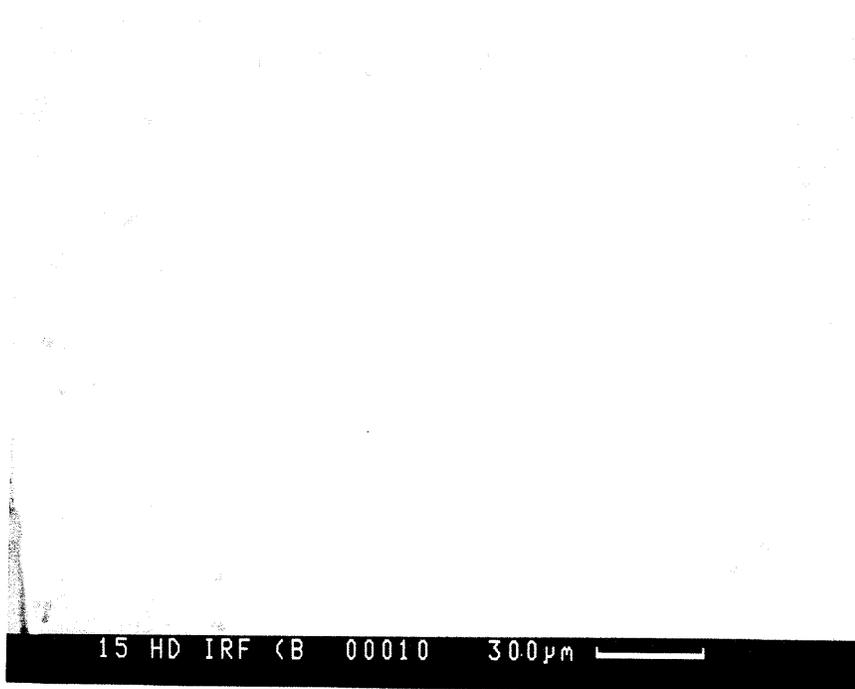


Figure 24: SEM photo of hot dipped and induction reflowed (fluxed) sample.



|-----| 50 μm

Figure 25: Coating #5, reflowed 20 minutes (Ar), cross-section.

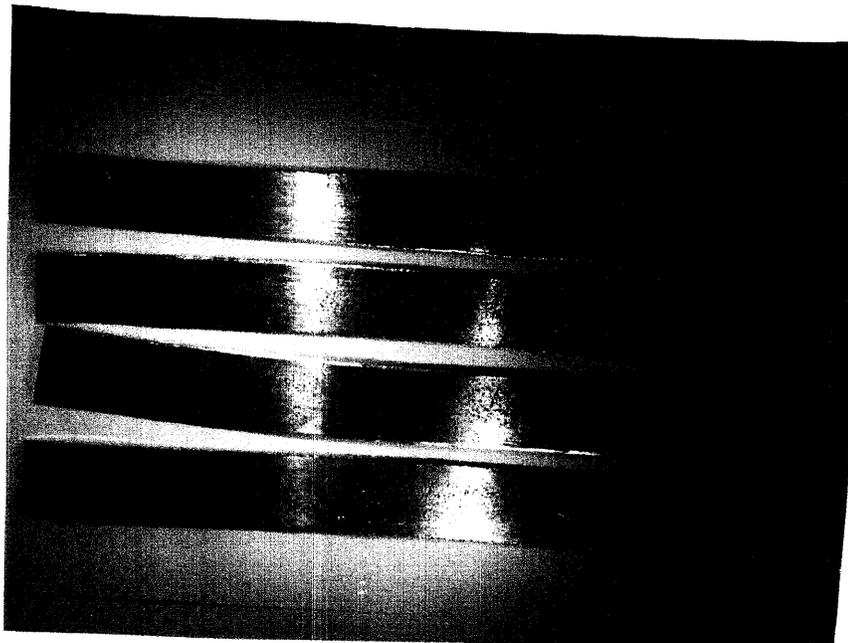


Figure 26: Rolled strips from run #7.

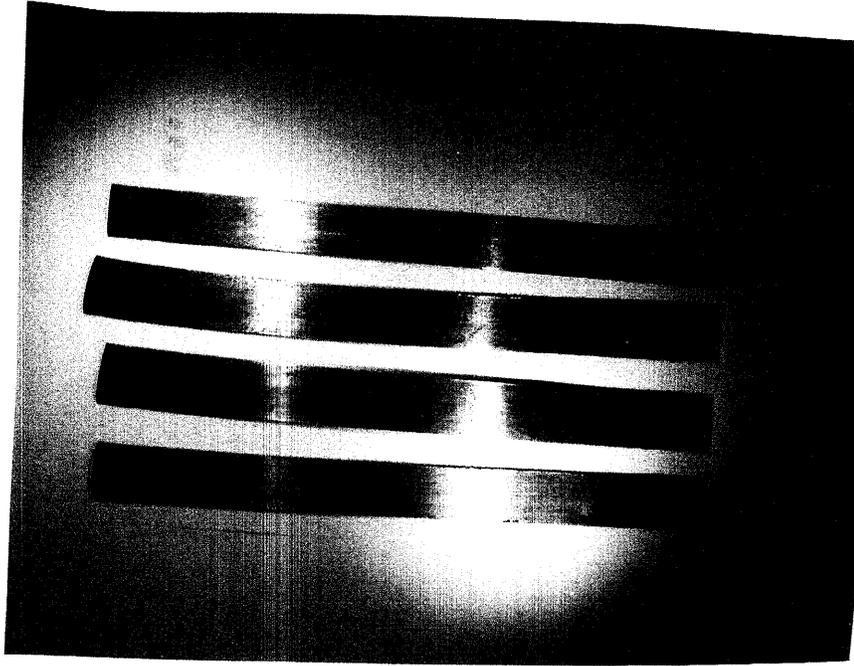
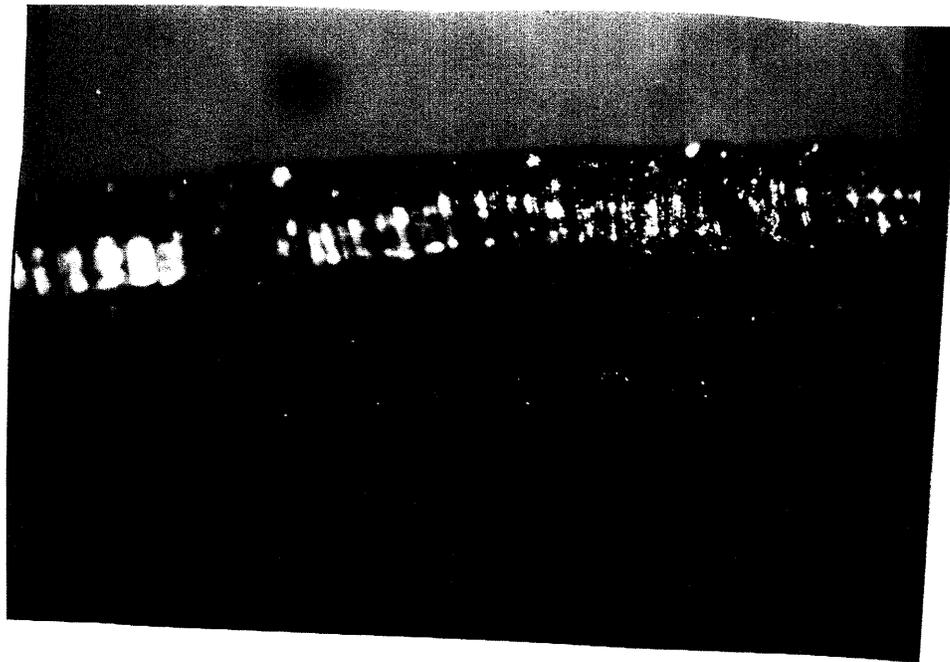
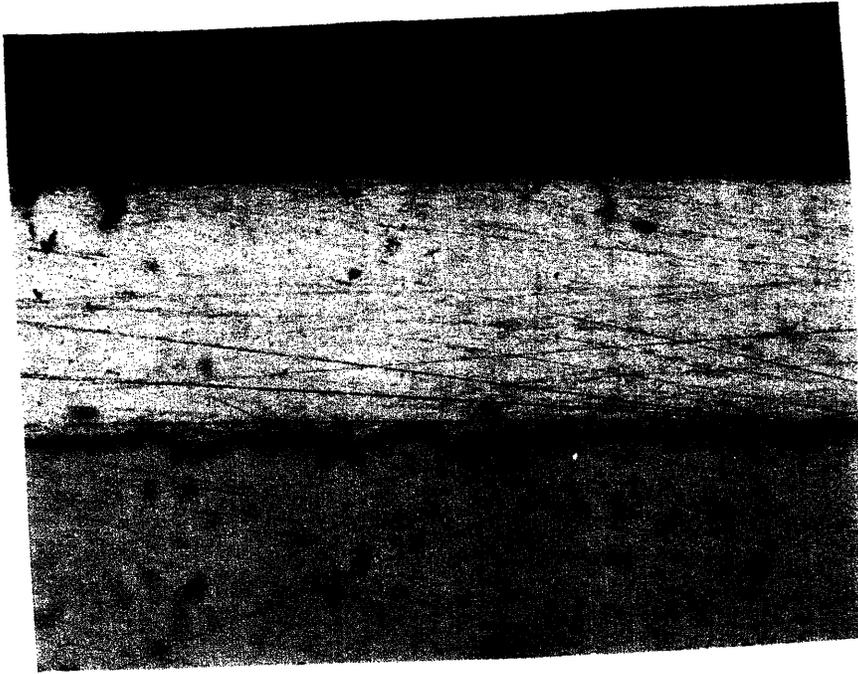


Figure 27: Rolled strips from run #8.



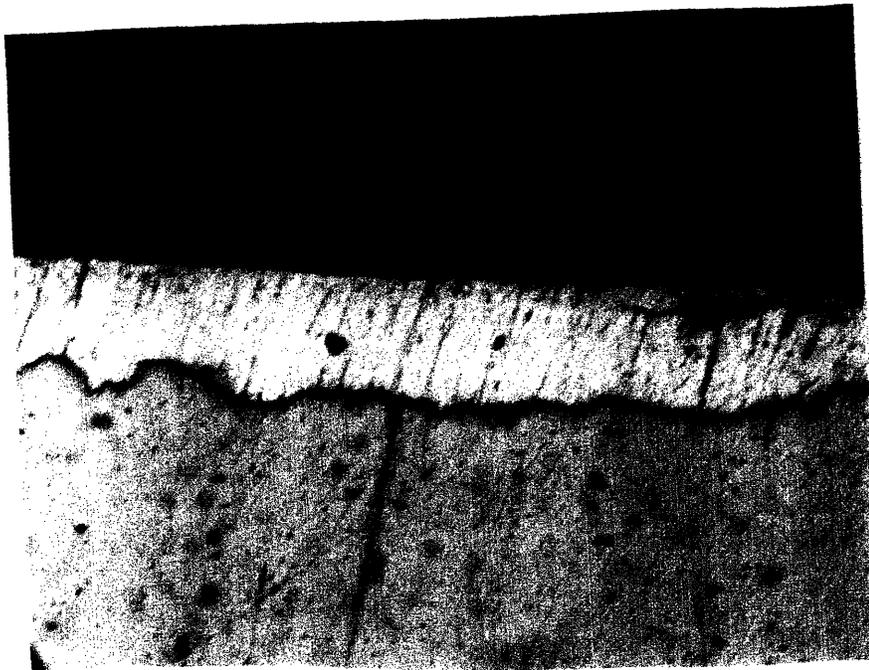
|-----| 0.5 mm

Figure 28: Smearred tin on edge of rolled strip, run #5.



|-----| 200 μ m

Figure 29: Tin coating #7, cross-section after rolling, unetched.



|-----| 100 μ m

Figure 30: Tin coating #8, cross-section after rolling, unetched.

5. Discussion

In evaluating the coating quality, there are three main factors to consider: adhesion, continuity, and appearance. Good adhesion is crucial so that the coating will stay on the substrate during forming operations and handling during use of the finished part. The coating must be continuous if it is to provide good corrosion protection, although this may be less of an issue for some systems. For most applications, appearance is also an important commercial factor; a coating which is bright and shiny is more pleasing than one which is rough and dull. The most important tests for evaluation of these properties in the tin coatings produced by LDC are the bend tests and the qualitative assessment of coating appearance.

5.1 As-sprayed Coatings

In the case of the as-sprayed coatings, the thinnest coatings produced the best results. Only runs 8, 14, and 17 produced as-coated samples which survived bend testing. At 80, 136, and 104 μm , these were three of the thinnest four coatings; run 19 was the only other run which was below 200 μm in thickness. This trend is expected, as the shrinkage stresses which can predispose the coatings to delaminate grow with the thickness of the coating.

Additionally, all of the good deposits were made on blasted substrates. Again, this is not surprising. Since the mechanism of adhesion for spray coatings is mechanical interlocking of the particles to the substrate and to each other, the roughness of the substrate surface prior to coating will largely determine how well the coating adheres. The amount of roughening needed, however, is likely to be a function of the desired coating thickness, the materials system, and the post-processing to be used. A thinner coating, as mentioned, will be less likely to peel from the effects of shrinkage stresses; thus, it would seem that a thicker coating would require a proportionally rougher substrate than a thinner coating to achieve the same adhesion. The materials used, in the case of coating of systems other than tin/steel, will also have an effect, as the amount of shrinkage stress will increase with the temperature difference between the coating layer and the substrate. Finally, if post-processing of the coating can be done to relieve residual stresses in the coating or to change the bonding from mechanical to metallurgical, the roughness requirements of the substrate can conceivably be lowered to the minimum required to maintain adhesion through post-processing.

The natural problem, in the case of spray deposition, is that a thin coating, good for mechanical properties, will tend to be non-continuous. Because the arrival of particles

from the spray at the substrate is a random process, there is always the possibility of incomplete coverage. However, the fewer layers of particles which, on average, impact the substrate, the more likely bare patches are. Thus, the production of thin coatings requires special care and, below some minimum thickness, makes reliable production of continuous coatings impossible. Some steps can be taken to minimize this problem. A small particle size in the spray, relative to the thickness of the coating, would help. For a given desired coating thickness, more layers would be required for small particles than for large particles, thus reducing the statistical chance of a bare spot. Spherical particles would also be beneficial, as the random orientation of the particles would no longer be a factor.

It can be seen from the overspray analysis and the as-coated micrographs that these conditions were not achieved on the lab scale. Even for the conditions of high gas pressure and low metal flow (small slit and small tin charge), the mass average particle size was in the range of 60-80 μm , with an aspect ratio of approximately 2. From micrographs, we can reasonably expect a final aspect ratio of impacted particles no greater than 5 (for higher melt enthalpies, more compaction of the particles could be achieved). Thus, we expect each layer to be at least 12 μm thick, giving us only 8 layers on average to form a 100 μm thick coating. As can be seen from the micrographs, the variation in thickness of the coating on a small scale is extremely large in some cases; however, as evidenced by the as-coated profile of run 8, it is possible to achieve a fairly even coating by control of the particle size.

On a larger scale of production, more control of these factors is available. A longer atomizing slit will produce a uniform spray over a larger area, leading to more predictable coating of the sample. The ability to pour from the tundish at something near steady-state conditions greatly enhances the ability to control the gas to metal flow ratio, allowing the possibility of finer particle size. Better fixturing of the substrate or simply the use of larger and heavier substrates will allow the flight distance to be reduced, effectively increasing spray enthalpy at impact and thus improving the spread of impacted particles.

Post-processing is another avenue to better continuity. Since coating of the substrate is a random, rather than driven, process, there will always be some chance of non-continuity, which will increase with decreasing coating thickness. A post-processing step which improves the continuity of the deposit could be used to circumvent that problem.

The final issue for the as-sprayed coating is appearance. Unfortunately, random particulate buildup from spray coating will unavoidably result in a surface finish which is, at best, rough on the scale of the spray particle size. This roughness will also cause the

surface to be matte, rather than reflective. While this may be acceptable or even desirable for some applications, most metal-finishing applications call for a bright, smooth surface, mostly for aesthetic value, but also for reduced friction and better wearing of the coating. To the degree that the coating surface can be improved, again a small particle size will reduce the roughness and a high spray enthalpy will yield greater flattening of the particles on impact. For this, a high gas to metal flow rate, a high melt superheat, and, if possible, a short flight distance are necessary.

5.2 Reflowed Coatings

The reflowed coatings examined performed very well in bend testing, but had very poor appearance and continuity. Because of this, despite the mechanical properties, the reflowing process as attempted has to be considered a failure. There are several reasons behind this, some rooted in the coating step and others specific to the three reflowing processes used.

The basic premise of tinplate reflowing is that liquid tin will completely wet a clean low-alloy steel surface. The key point here is that the steel surface must be chemically clean. Tin will not wet iron oxide and will, in fact, ball up on an oxidized surface. The situation is further complicated by the possible presence of tin oxide. In an oxidizing atmosphere, the surface of the molten tin will quickly form an oxide layer which is solid at the melt temperature (stannic oxide melts at 1630°C) and which will pin the melt, preventing it from spreading and also preventing the formation of a smooth surface.

With this in mind, it becomes apparent that simple inert gas cover is insufficient for reflowing. Even assuming the inert gas is completely inert, which will not be achieved in practice, as the oxygen pressure will still be sufficient to at least mildly oxidize metals at elevated temperature, it will not clean the surfaces. The steel will have some oxide on it and the tin coating itself will have a high oxide content from the spraying process.

Hydrogen reflowing offers a slightly better solution. No new oxidation will occur under the reducing cover gas; however, there is still the issue of oxide already present on the steel layer which may prevent spreading of tin and of the effect of trapped oxide in the coating layer, which will presumably rise to the surface when the tin becomes molten. Experimental results showed some oxide on the tin surface, and the tin did not spread.

Induction reflowing in air obviously has all of these problems. Although the sample is only at high temperature for a very short time, this is still sufficient for at least the tin to oxidize in air, pinning the coating as described above and damaging the appearance. The use of a flux cover solved part of the problem, but not completely. Even the fluxed

tin did not spread, although it did stay clean and smooth. The issue here is the oxide layer already present on the steel, probably even before coating but certainly after the sample was allowed to sit between coating and reflowing. In order for wetting to occur, the fluxing action must break down the oxide layer at least sufficiently for the tin to penetrate it. However, going back to hot dipping, it may be easily understood why this does not occur in the induction reflowing process.

There are two factors modifying the effectiveness of the flux, the first being the starting condition of the steel and the second being the condition under which the steel and flux are heated. Referring to the practices of the hot dipping industry, we see that the steel used for hot dipping is either abraded or pickled immediately before fluxing or has been pickled and then oiled at some previous point in the strip manufacturing process. This gives a much cleaner steel surface than that which was present in any of the attempts to reflow the LDC tinplate. The fluxing action may simply not be strong enough to clean the steel sufficiently for tin wetting. The second issue, that of the conditions of heating, can be better understood by looking at the experience of hot dipping a sample for reflow testing. The abraded and fluxed steel strip was submerged in a pot of molten tin with a very thin flux cover. The side which entered the tin first was coated fairly evenly and completely for such a clumsy operation; the tin coverage was complete, adhesion was good, and the surface quality was high. On the other hand, on the back side, which was heated by contact with the molten tin, the flux burned off in the air, allowing oxidation of the steel to begin before the tin could spread. Once the surface had become oxidized, it was impossible to immerse it in the tin. When this sample was induction reflowed under flux, the side which was previously tin coated remained well coated and the tin surface remained mostly smooth and shiny (although the very heavy tin layer did run under the influence of gravity) while the side which had not previously been completely covered showed no movement of the tin coating.

Despite all of this, the reflowing process does still offer some opportunities for coating improvement. As a minimum condition, the starting steel base must be clean and all subsequent operations, including the spraying itself and reflowing, must be carried out in an inert, or preferably slightly reducing, atmosphere. The ideal cleaning method would be pickling, although this complicates the processing line and adds an otherwise unnecessary chemical step which we hope to be able to eliminate by use of LDC coating. In any case, none of this was attempted in these experiments, as the batch nature of the laboratory apparatus would not have permitted smooth, clean, and rapid transfer of the part from one step to the next. If these conditions can be met, there is no basic reason why the LDC coated tin cannot be made to reflow; however, the reflowed coating may

still be matte in appearance, due to the roughness of the blasted substrate. Ideally, a reflowing step after coating would allow spraying of thin, non-continuous layers, which were then smoothed to thin, continuous coatings by the reflow process.

5.3 Rolled Coatings

The rolled coatings were in all ways the most successful. Most displayed good to excellent adhesion in the bend test. Surface finishes were smooth, bright, and shiny, although lining of the surfaces was sometimes a problem. Continuity was also improved by rolling, although in cases of incomplete coverage, care must be taken in evaluating the effectiveness of rolling for improving continuity.

The effect of rolling on surface finish is the most obvious. The rolling process, if sufficient reductions are used, will result in a completely flat coating surface which, if clean, will have the properties of smoothness and reflectivity desired in a bright tin coating. Improved adhesion is believed to come from two factors. First, the rolling process fills the tin more completely into the irregularities of the steel surface, improving mechanical bonding. Second, because of the low melting point of tin, it will recrystallize under heavy work even at room temperature. This recrystallization of tin was observed in rolled samples and may serve to eliminate the residual stresses associated with the spray coating process, thus removing the coating's predisposition to peel. By smoothing the tin, the process also spreads it, leading to better uniformity and continuity of the coating. More importantly, it will close up porosity within the coating layer, greatly increasing the effective thickness of the coating with regard to corrosive environments.

It should not be believed, however, the rolling is a cure-all for sprayed coatings. The quality of the part that goes into the rolls has a strong effect on the quality of the part that comes out. The as coated sample must have sufficient adhesion to remain properly attached to the substrate during rolling without warping, peeling, or splitting. The coating must be thin enough that it will not fold over on itself, develop a rippled surface, or smear over the edges of the substrate. A heavily oxidized tin coating is more susceptible to all of these surface flaws due to the restricted flow of the coating caused by the oxide layer. In terms of adhesion, rolling merely improves the mechanical bonding which already exists; it does not create any new forms of bonding and will not cause mechanical bonding where none exists. Also, improvements in coating continuity must be considered suspect. The folding of the tin coating over onto previously exposed steel will provide little protection from corrosion if the oxide layer on the steel is not broken; in fact, the narrow crevice created by this deformation may even prove more damaging than the bare spot which existed prior to rolling.

Overall, the rolling process for LDC coatings appears to give large benefits for a very low cost. In addition to production of coatings typically electrodeposited or hot dipped, the LDC coat plus rolling technique may find application for thickly clad systems currently manufactured by roll-bonding of individually produced sheets. Such a set-up could allow use of a continuous roll-bonding line where the base material would be LDC coated with the a thick layer of cladding and then the entire piece rolled to densify the coating and improve the bond. Such a process would eliminate the need to separately roll the cladding and the problems of properly aligning and affixing the cladding sheet to the base metal for rolling.

5.4 Intermetallic Layer

In all hot dipped tinplate and in reflowed electrolytic tinplate, an intermetallic layer of FeSn_2 is formed between the tin coating and the steel. This layer metallurgically bonds the coating to the substrate and provides improved continuity by promoting wetting, improved adhesion, and improved corrosion resistance. Such an intermetallic layer is also typically formed in other coating systems, including all hot dipped coatings, many CVD coatings, all ion implanted coatings, many plasma sprayed coatings, and even some roll-bonded claddings, and serves much the same purpose. However, no evidence of the formation of such a layer was found in any of the LDC coatings produced.

There are two main reasons why the absence of such a layer is not really surprising. First, the LDC process, regardless of melt temperature, results in rapid quenching of the sprayed particles at the substrate. Such rapid quenching removes the heat from the interface quickly and also rapidly solidifies the coating. Under these circumstances, the time at elevated temperature is insufficient for creation of an intermetallic layer between the coating and the substrate. The absence of intermetallic layers in traditional sprayed coatings is an example of this effect. The second reason comes back to the condition of the substrate surface. Formation of the intermetallic layer requires a chemically clean substrate surface to interact with the hot coating layer. Since a chemically clean surface is not a requirement for mechanical bonding in spray coating, no effort was made to achieve one. Thus, even if the melt hits the substrate with sufficient heat, it cannot interact with the steel base, only with the oxide layer. Attempts at heating the substrate to provide the thermal conditions necessary for formation of an intermetallic layer only exacerbated the oxidation problem, making it impossible to achieve any kind of good bonding. The reflowing step could have helped to develop an intermetallic layer, as occurs in electrolytic tinplate, but evidence from the reflowing work indicates the

presence of an oxide layer between the tin and the substrate which would, again, have prevented the formation of the intermetallic.

If an intermetallic layer is desired in an LDC tinplate, the solution is in the cleanliness of the substrate. As mentioned in the discussion of reflowing, the substrate must be chemically clean prior to coating and remain in a reducing atmosphere until such time as the steel surface is completely covered by tin. It should be noted that in other systems where the coating metal might dissolve the oxide of the base metal at elevated temperatures, it may be possible by post-processing to achieve metallurgical bonding without pickling and special handling of the substrate.

5.5 Ceramic Coating

A brief mention of ceramic coating by LDC should be made. Although no controlled experiments on this subject were done, the evidence from overspray coating of the ceramic crucible indicates potential promise. Here, the ability to mechanically bond a metal to a substrate in a situation where chemical bonding is normally difficult or impossible opens up great possibilities for LDC coating. Although rolling and reflowing are not possible, preventing formation of bright coatings, this method could be useful for metallization of ceramics and even plastics for joining by soldering or brazing. Additionally, it serves as an indicator that many normally incompatible coating/base systems could be coated using the LDC process.

5.6 General Applications

Although this work has been done entirely with tin and steel, the intent of the research was never simply to produce tinplate. The system of tin coated steel was selected as an easy starting point to examine the potential applicability of LDC coating for a wide range of coating applications. The continuous, high-production capabilities of the linear LDC nozzle and its ability to produce coatings of widely varying thicknesses with minimal alteration of the coating apparatus make it ideal for high-production rate coating of sheet and strip material.

Despite the fact that the generally thicker coatings produced by the LDC process make it unlikely that it will ever be economical to replace electrolytic tinplating by this process, many other coating systems not only accept but in fact demand thicker coatings. Heavier coatings of tin, tin and lead (terneplate), lead, and zinc for heavily corrosive environments currently produced by electroplating or hot dipping could be produced by an LDC followed by rolling process. Roll-bonded claddings, particularly for aluminum-clad aluminum alloys, could easily be manufactured by LDC coating. Higher melting

coatings for specialized applications might prove out of reach or uneconomic, but low melting, easily sprayed alloys still account for a large volume of the corrosion resistant coating in wide use today. Finally LDC coating opens the possibilities for rapid production of coated ceramics and plastics and for coating of currently incompatible metal-metal systems.

6. Conclusions

1. The LDC process can be used for production of tin coatings on steel. The conditions which produce the best as-sprayed coatings are: a rough substrate surface, a particle size and particle aspect ratio which are small relative to the thickness of coating produced, good spread and rapid quench of the particles on the substrate, and a substrate which is at least moderately oxide-free.
2. Rolling of LDC coated strips can effect large improvements in adhesion, appearance, and coating continuity; however, it must be remembered that rolling cannot salvage a bad piece and that the initial quality of the as-coated sample is important if the finished part is to have the desired appearance and mechanical properties.
3. Reflowing and formation of metallurgical bonding via an intermetallic layer require much higher standards for cleanliness of the substrate and special inert or preferably reducing atmospheres for all handling through the reflowing step, including the atomization itself.
4. Spray coating may potentially be used for a wide variety of coating systems, including some not currently possible due to incompatibility of the coating and substrate materials.

7. Recommendations for Future Work

Most of the important advances to be made in continuing this work are dependent on the construction of more specialized equipment for coating and for cleaning and handling of the substrate to improve post-processing.

1. The LDC process is typically carried out in an inert atmosphere to severely limit the oxidation of the spray particles and thus promote better wetting between the impacting particles and the previously deposited layers. It is believed that a first step for any continuation of the coating work should be to make some runs in an inert atmosphere to determine the effect this has on coating quality and on the improvements subsequently achieved through post-processing.

2. In order to improve the effectiveness of the LDC coating process for production of thin coatings such as those used in manufacture of tinplate, it will be necessary to improve some variant of the reflowing process to the level that spreading of the coating on the substrate resulting in complete coverage and at least some formation of the intermetallic occurs during the reflowing step. In order to accomplish this, it is believed that some system for cleaning the substrate and then maintaining it in an inert or reducing atmosphere is necessary. However, because of the multiple step process and the need to separate the cleaning, coating, and reflowing steps, this will require specialized equipment to protect the steel surface from oxidation during transport from one step to the next.

3. Since rolling has offered a cheap and easy method of achieving vast improvements in all aspects of coating quality, further work in this area should focus on developing the potential for a truly continuous process of spray coating followed by rolling. The requirement for this would be extension of the linear atomizer to achieve a uniform coating thickness across the substrate.

4. As the original intent of this work was to study the feasibility of LDC spray coating for a variety of applications, it is believed that attempts should be made to spray other metals. Of particular commercial interest and well suited to the process are zinc and aluminum coatings on steel and aluminum cladding on aluminum.

5. One of the advantages of the LDC coating process is the ability to coat systems in which the substrate and coating may normally be incompatible. With this in mind, it is recommended that controlled experiments in the coating of ceramics and plastics be done. Also, there are metal-metal systems, a commercially relevant example being lead coating of steel, where the coating metal will not normally wet the basis metal. Although this may not be the ideal system, as one must hesitate in recommending the atomization of lead without very strict safety precautions, this or another system like it bears examination.

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