A COMPARATIVE STUDY OF NON-FERROUS COATINGS ON STEEL

A. N. KAPOOR, A. B. CHATTERJEA & B. R. NIJHAWAN
National Metallurgical Laboratory, Jamshedpur

Abstract

Considerable tonnages of zinc and tin are imported annually to meet the demands of galvanizing and tinning industries. Keeping in view the availability of raw materials in India, the possibilities of using aluminized steel are discussed. A comparison of the micro-structures obtained in different hot-dip processes for protection of steel surfaces and of the resistance of the coated products to corrosion is given. Points in favour of aluminium-coated steel have been brought out.

Introduction

The annual consumption of zinc and tin in India amounts to nearly 30,000 and 60,000 tons respectively, though their indigenous production is almost negligible. The only source of zinc in India is the Zawar Mines, Udaipur. Deposits, however, are not very extensive. The zinc concentrate produced at Zawar is exported to Belgium for the extraction of zinc, half of which is returned. About 40 per cent of the imported zinc goes to feed the galvanizing industry of India. Tinning and tin-plating industries consume nearly 50 per cent of the imported tin. Substantial proportions of these metals would be eliminated if some other metal abundantly available in India could be used for coating steel.

Although the actual production of aluminium is not high at present, its reserves in the form of bauxite are extensive. The Lohardaga area in Ranchi district alone is estimated to contain sufficient ore to meet the indigenous requirements for several decades to come. Further workable deposits are available in Madhya Pradesh, Jammu and Salem districts. With the development of hydro-electric projects and especially the setting up of the proposed 16,000 tons aluminium reduction plant at Hirakud, large quantities of commercial aluminium should be available, and much interest therefore applies to the suitability of aluminium for coating steel.

It has already been established that a coating of aluminium on steel makes the metal more resistant to heat and to atmospheric corrosion. Under many conditions, an aluminium coating on steel, like a zinc coating, affords galvanic or electrolytic protection on bare spots, that is, through anodic sacrificial attack reduces the corrosive attack of the exposed steel base metal which acts as the cathode. Zinc coatings, at high ambient temperatures and humidities, e.g. in the tropics, corrode readily with the formation of bulky, unsightly white coatings, usually of basic zinc carbonate. Aluminium coatings, on the other hand, form a thin film of impervious aluminium oxide and this prevents further corrosion. Aluminium coatings have also superior resistance to sulphurous atmospheres in which zinc coatings are adversely affected.

In the electrochemical series, tin is electropositive to iron, so that no sacrificial protection is involved. Tin plate very often shows pin holes in the tin coating given to the steel base. Tin plate is, therefore, not used for outdoor applications. Tin is also extremely costly and restrictions on its use are justified. Tin plate is consumed mainly by the canning industry. The tin coating in contact with canned food does not give rise to any products harmful for human consumption. Aluminium, like tin, is not affected on
contact with most foods and it is, therefore, likely that aluminized steel sheets, possessing all the surface properties of aluminium but being much cheaper than aluminium sheets, could replace tin plate in the canning industry. For this purpose it would, of course, be essential for the coating to be at least as perfect as that on good tin plate. Aluminized steel sheet is said to lend itself to various fabricating processes, including shearing and forming on a press brake, and can be moderately drawn as also moderately stamped. It can also be welded by conventional welding methods.

The difficulty associated with hot-dip aluminizing is the high melting point of aluminium, coupled with its rapid oxidation at aluminizing temperature, necessitating the use of suitable fluxes for the protection of the aluminium bath.

**Coating Processes**

In principle, the hot-dipping process is very simple. The steel article to be coated must be properly cleaned, fully immersed in the molten metal bath and withdrawn after an optimum thickness of coating has been obtained. But in practice the process is not so simple. Cleaning of the surface of the molten metal bath, regulation of the bath temperature and the use of additive agents thereto are important factors each of which exercises marked influence on the quality of the resultant coating.

Galvanizing and tinning are relatively easy operations because of low operating temperatures. The higher melting point of aluminium makes aluminizing processes more difficult. At these high operating temperatures, steel tends to get oxidized before it comes into contact with the molten aluminium bath. Secondly, the tenacious film of aluminium oxide, which forms so readily in the bath, tends to cover the steel in the dipping operation and hinders good adhesion. Two precautions are, therefore, necessary. First, the base metal must be protected from oxidation either by bright annealing or by suitable treatment in a molten flux bath. Secondly, the aluminium bath must be protected from oxidation either by covering it with suitable flux or by surrounding it by an inert or reducing atmosphere. Many patents have been based on these ideas. Fink has suggested the use of hydrogen as a reducing atmosphere, both for the molten aluminium and the base metal. Alferieff's method uses an atmosphere containing hydrogen, nitrogen and a quantity of water vapour, mixed in suitable proportion so that the gas is oxidizing at low and reducing at high temperatures. The material, after bright annealing, directly enters the molten bath of aluminium maintained under a reducing atmosphere. The water vapour effects some decarburization of steel surface and promotes the quick formation of the Fe-Al alloy layer. Fig. 1 shows the layout of the process patented by Sendzimir. It shows how wire can be aluminized under controlled atmospheres.

Various chloride mixtures have been used as suitable fluxes for cleaning and protection of the base metal before it enters the aluminium bath. Work done by the authors involving flux treatment of steel strip has given satisfactory aluminium coating. The flux used was a mixture containing 10 per cent cryolite, 10 per cent zinc chloride, 25 per cent sodium chloride, 30 per cent potassium chloride, 20 per cent barium chloride and 5 per cent aluminium fluoride. Two separate furnaces were used, one for holding the molten flux mixture and the other for the molten aluminium bath. The temperature of the flux was maintained at about 700°C. and that of the aluminium bath at about 675°C. The steel strip was degreased and pickled prior to treatment in the flux bath. From the flux bath it was quickly transferred to the aluminium bath and removed after 15 to 30 seconds’ dipping. The coatings obtained were good in respect of adhesion and uniform thickness of the coated layer and were of pleasing appearance.
Hughes and Moses\cite{Hughes M. 1953} have reported that they have produced good coatings by using glycerol in place of molten halide flux. The pilot plant of the fluxing processes as used by them is shown in Fig. 2.

Molten halide fluxes are highly reactive and corrode not only steel and stainless steel pots but also many refractory materials including graphite. Mullite containers are resistant to the corrosive action of the flux and may, therefore, be used provided their inherent porosity is low. The melting of aluminium is not possible in steel pots as such pots easily react with the molten metal and go into solution. The difficulty is overcome by the use of special nickel-chrome cast iron containers. Certain refractory materials, such as graphite, are also resistant to molten aluminium.

**Dross Formation**

In galvanizing it is rather difficult to avoid loss of zinc, but it can be reduced to a minimum by adopting suitable precautions. Dross formation is comparatively high, but the percentage of zinc lost in the dross varies very widely from a minimum of 6 per cent to a maximum of 38 per cent. In aluminumizing, dross formation is much less and the dross settles down more readily than in galvanizing, because it is much heavier than the bath itself. In galvanizing, the dross density does not differ more than 3 per cent from that of the bath.

**Nature of Coating**

Microscopic examination of tin, zinc and aluminium coatings does not reveal fundamental structural differences. They all contain one or more alloy layers between the outer pure metal and the steel base. The coatings, however, differ in their characteristics and behaviour.
When steel is immersed in a molten metal bath, reaction occurs and the formation of different alloy layers will depend upon the relevant constitutional diagrams at the temperature level of the bath. At first, the coating metal alloys itself with the base metal to form a solid reaction product. Subsequently, phases are formed as a result of diffusion through this solid phase. It seems probable that the entire complement of diffusion phases is formed in a matter of seconds after the steel attains the temperature of the bath. The growth of the various phases is dependent, primarily, on time and rate of mutual diffusion of iron and the coating metal through the intermediate layers. The outermost layer is that of bath material and has a cast structure over the subsequent alloy layer.

With a galvanizing temperature near 450°C, the sequence of phases expected in iron-zinc alloys, starting at the iron end of the system, should be \( \alpha, \Gamma, \delta, \xi + \eta \) and \( \eta \) as shown in Fig. 3.

Tinning is done at a temperature of 320°-330°C. At this temperature, tin forms an intermediate compound with iron, but iron does not appear to dissolve in tin. This fact is of considerable importance in the manufacture of tin plate. Hot-dipped tin coatings show an alloy layer, immediately adjacent to the iron base, with an outer layer of tin covering it. The alloy layer is exceedingly thin and is difficult to detect. The chief constituent of the alloy layer is FeSn\(_2\) as shown in Fig. 4.

Aluminizing is done at a temperature of 675°-680°C. At this temperature iron and aluminium react to form compounds which, starting from the iron end, consist of the three phases, \( \xi, \eta \) and \( \theta \). The alloy layer, according to Alferieff, consists of: (a) a solid solution of aluminium in iron; (b) a layer containing Fe-Al and Fe-Al\(_2\); (c) an unidentified phase probably FeAl\(_2\); and (d) the phase FeAl\(_3\). Rohrig has described hot-dipped aluminium coatings as made up of four layers, including the steel base. The alloy layer is described as FeAl\(_3\) with an alloy solid solution below it. Fig. 5 shows the structure of a hot-dipped aluminium coating as produced by the authors. Three distinct

---

**Fig. 3** - Different phases obtained on galvanizing. \( \times 1000 \) [From D. H. Rowland, *T.A.S.M.*, 40 (1948)]

**Fig. 4** - Compound layer in a tin coating with chief constituents FeSn\(_2\). \( \times 500 \) [From Hoare & Hedges, *Tin Plate*, London, 1946, Edward Arnolds]

**Fig. 5** - Structure of aluminium coating showing steel base, alloy layer and aluminium. \( \times 450 \)
layers are seen. The outermost is the layer of aluminium, the next is the alloy layer and the innermost is the steel base. So far the authors have not been able to observe the different phases in the alloy layer. Hughes and Moses observed more than one phase in the alloy layer developed from a bath containing high silicon as shown in Fig. 6. They also got some evidence for the existence of a thin layer of alloy between the steel and the layer referred to above as shown in Fig. 7.

The alloy layers of most hot-dipped coatings on steel are hard and brittle, which is attributed to the formation of intermetallic compounds at the coating temperatures. The brittleness is in some measure associated with thickness of the layer of the compounds, and as the thickness decreases, the apparent brittleness of the alloy layer diminishes. Some reduction in thickness can be obtained by decreasing the bath temperatures and the time of immersion of the steel in the coating bath, by rapid cooling of the coated sheet after it leaves the bath, or by a combination of these three factors. A substantial reduction in hardness of the brittle layer can be obtained by judicious addition of alloying elements to the bath.

The alloy layer in a tin plate is not very thick and hence no serious attempts have been made to reduce its thickness. Zinc is the only element that is commercially added to the tin bath and this is done to improve the corrosion resistance of tin plate. The presence of small proportions of aluminium in the tin coating makes it more brittle. Although zinc is a soft and ductile metal, it gives big spangled grains which tend to peel off on mechanical working or severe heating. Shannon says, 'The zinc outer layer exists in a brittle form, possibly because of its large crystalline structure, indicated by the spangles themselves, and that wherever there is severe distortion the outer layer itself breaks; further, that this layer is not very adherent to the underlying iron-zinc alloy, consequently the broken pieces of the zinc layer fall away in the characteristic flakes, whereas the iron-zinc alloy frequently remains at the point of flaking.'

The presence of aluminium in a galvanizing bath results in a considerable decrease in the thickness of the galvanized coating and a marked reduction in the thickness of the iron-zinc alloy layer. The mechanism is still a controversial subject. One theory is that an aluminium oxide film or membrane is formed on the surface of the steel. However, when hot-dipped aluminium coatings are obtained on steel, the aluminium oxide film or membrane is not seen on the steel surface.

Additions of silicon, copper and beryllium to the aluminium bath considerably reduce the thickness of the alloy layer in aluminium coatings on steel. Beryllium additions result in a more ductile aluminium layer than obtained by silicon additions, but do not
affect the characteristic brightness of the as-dipped aluminium coatings. Fig. 8 shows the effect of silicon, copper and beryllium additions on the thickness of the alloy layer of the aluminium coatings. The authors have studied the effect of increasing additions of silicon up to 8 per cent and have observed a considerable reduction in the thickness of the alloy layer, as will be evident from Fig. 9 which shows the structure of a coating obtained by hot-dipping in a bath containing 2.5 per cent silicon.

The hardness of an aluminized coating increases gradually with distance from the steel interface. This is quite different from the position with hot-galvanized coatings. The iron-zinc alloy layers differ appreciably in hardness, the hardest layer being adjacent to the steel base. The maximum hardness of aluminized coatings is considerably reduced by the presence of suitable additive elements in the bath.

The aluminium coating behaves very well in the alternating bend test. Aluminium coatings can withstand tension successfully, but appear to fail earlier by buckling as in the compression of thin sheets. Flaking of the coating on the outside of the bend, as encountered in many zinc coatings, does not occur, but cracking may appear around the base of the dome as shown in Fig. 10. A further difference between aluminium and zinc coating is that the plane of failure is seen to be in the alloy layer which is badly

---

**Fig. 8** — The effect of copper, silicon and beryllium additions on the thickness of the alloy layer of the aluminium coatings [From T.A.S.M., 43 (1951)]

**Fig. 9** — Structure of coating obtained from a bath containing 2.5 per cent Si. × 450

**Fig. 10** — Bending behaviour of aluminized strip [Hughes & Moses, Metallurgia (Sept. 1953)]
shattered in the former, whereas flaking in a zinc coating almost always involves a clean separation between the alloy layer and the steel.

**Corrosion Resistance of Aluminized Coatings**

Aluminium, like zinc, is electropositive to iron in the electrochemical series. As such, aluminium coatings will protect steel surfaces provided the film of oxide which forms on the surface of aluminium is broken.

The atmospheric exposure tests carried out by the A.S.T.M. Committee A-5 (Corrosion of Iron and Steel), Sub-Committee VIII (Field Tests of Metallic Coatings), have demonstrated the value of hot-dip aluminizing. These observations showed that the aluminium coatings gave remarkably good results, which in most cases were superior to those given by hot-galvanized coatings even when the latter were thicker and, therefore, much heavier than aluminized coatings. It was also observed that at places where the steel base was exposed to the atmosphere the aluminium could not protect the steel because of the lack of electrochemical protection and that the superiority of the aluminized coatings was less marked in marine locations.

Corrosion tests on Armco aluminized steel samples carried out in several laboratories showed that the coating was quite resistant except at the cut edges. It could withstand the attack of salt spray for eleven months. Localized pitting was observed at exposed areas as the coating failed to provide electrochemical protection.

Finkbone refers to tests which showed that after four years' exposure in a mild industrial atmosphere, hot-dipped aluminium coatings lost approximately one-tenth as much weight as galvanized coatings under identical conditions. Samples exposed for two years in a marine atmosphere lost about one-fifth as much weight as galvanized coatings. Here also the galvanic protection at cut edges was found to be less than with zinc coatings.

If galvanized and aluminized specimens are heated together in steam, the galvanized specimens develop white corrosion products after a few days of exposure while the aluminized specimens remain unchanged. Fig. 11 shows the comparative superior resistance of aluminized coatings over galvanized coatings.

The failure of hot-dip aluminium coating to protect cut edges may be avoided by covering such areas with sprayed aluminium. In the Aeronautical Material Specification for aluminized sheet and strip drawn up by the American Society of Aeronautical Engineers, a salt spray test is included and it is stated that 'corrosion of basis steel at cut edges shall be disregarded'.

**Heat Resistance of Aluminized Coatings**

Aluminium-coated steel has a high resistance to oxidation at moderately elevated temperatures. Exposure to heat up to about 480°C. does not produce discoloration, thus preserving at high value the ability of coating to reflect heat and light. When the temperature is raised above 480°C., however, the alloy layers grow at the expense of the outer aluminium layer by inter-diffusion. Formation of the alloy phases proceeds rapidly above about 650°C. and the coating disintegrates into a whitish oxidized scale at about 1090°C. On account of the heat-resisting properties, aluminized steel has shown superior performance when used for mufflers, combustion chambers of gas-fired warm air heating furnaces and heat exchanger tubes. Galvanized steel or a tinned steel is not able to withstand such elevated temperatures.

**Conclusions**

Aluminium coating on steel appears to have properties superior to those of either
zinc coating or tin coating, both for high temperature work and for exposure to sulphurous atmospheres. The dross formation in aluminizing is comparatively less than in galvanizing or tinning. The structure of the coating includes an intermediate thick and brittle alloy layer. The thickness of this layer may be considerably reduced by the presence of silicon, beryllium and copper in the molten aluminium bath. Aluminium coatings have shown better resistance than zinc coatings on long exposures (except at cut edges, where zinc coating is superior because of its sacrificial nature). In spite of these advantages, aluminium coatings have not been able to replace galvanized coatings or tin coatings because of manufacturing difficulties. Further pilot scale work is needed to make the process simple and easily adaptable.

References

6. Hudson, J. C., Corrosion Committee (Iron & Steel Inst.), Protective Coatings Sub-Committee (February 1946).


18. SHANNON, Sheet Steel and Tinplate, 181.


Discussions

MR. C. H. WATSON (Tinplate Co. of India Ltd., Tatanagar)

A high proportion of the articles made from tin plate depends for their success on some form of soldered seam. Can such soldered seams be successfully produced on aluminized sheets?

Authors’ Reply

As aluminizing of steels is of recent development, much work remains to be done on soldering response of aluminized materials. However, a Belgian patent No. 510,972 taken by J. Bertholet on August 16, 1952 [Chem. Abstract, 48 (1954), 2558], may be referred to for details of the technique. It is stated there that an alloy of 16-6 per cent aluminium, 33-2 per cent zinc and 49 per cent Sn is a suitable solder for aluminium or its alloys in presence of sodium hydroxide with 1 per cent soft soap.

MR. I. M. PAI (Indian Steel & Wire Products Ltd., Jamshedpur)

The heating pan used for holding zinc is kept continuously at a temperature of below 500°C, and in spite of the low temperature these pans do not last very long. In the aluminizing process, we have to keep the pan full of molten aluminium at 675°C, and at this temperature the pan life will be reduced, so much so that replacement costs of the pans may render the process rather expensive.

Authors’ Reply

The authors have used alloy cast iron pots for melting and holding aluminium. However, if outer mild steel pots are used, their life can be substantially increased by ramming a sufficiently thick layer of graphite or high-alumina bricks so as to avoid direct contact of the mild steel pots with molten aluminium.

MR. I. M. PAI (Indian Steel & Wire Products Ltd., Jamshedpur)

In the bulk production of galvanized wire which we manufacture, a large quantity is hard quality with tensile strength of 40 to 45 tons per sq. in. In aluminizing process we have to pass the wire through temperatures of 675°C which may make the wire soft. Is there any way to aluminize hard wire?

Authors’ Reply

We feel that a slight cold-drawing of wire after hot-dip aluminizing can bring up the tensile strength
of the wire effectively. Final cold-drawing is usually done to improve the surface coating. To improve the tensile strength further, the base metal could be of low-alloy high-strength steel. These will also get annealed during the process of aluminizing, but the effect will not be as severe as in the case of mild-drawn steel wire. Even though desired tensile strength could be had with aluminized wire up to some extent, some softening in the case of aluminized high tensile steel wire was to be expected.

MR. S. S. GILL (Hindustan Motors Ltd., Uttarpura)

1. I also suggest a slight cold-drawing of wire after hot-dip aluminizing, to bring up the tensile strength of the wire.

2. Is it essential to have an atmosphere control in the cooling chamber after the hot-dip aluminizing?

3. How did the authors take the hardness of the coating? I believe it was through micro-hardness.

4. I just want to bring to the authors' notice that some work is being done on galvanizing steel after copper or Ni-plating. This process has greatly improved the galvanized coating.

5. The authors have not discussed electro-galvanizing in comparative study of protective coatings.

Authors' Reply

1 & 2. In some plants, aluminizing is done under atmospheric control to avoid oxidation of the surface both before and after aluminizing and it furnishes a product of very pleasing appearance. In cases where salt fluxes are used and coating is done without atmospheric control, the coated product is quenched in water or oil, or air-cooled. The air-cooled aluminized product will have a dull surface due to the oxide film adhering to the surface.

3. Yes—the hardness values of the layers of aluminized products were obtained through micro-hardness.

4. The authors thank Mr. Gill for information on galvanizing, where pre-plating of Ni or Cu is adopted, resulting in an improved galvanized coating. In aluminizing, too, the pre-plating has been tried and good coatings obtained; but these pre-coatings usually dissolve in the aluminium bath, thus contaminating the latter except in the case of sprayed aluminium coating supplemented on the pre-plated coat.

5. The authors have confined themselves to an investigation of different non-ferrous coatings obtained on hot-dipping, electro-galvanizing has not been discussed. However, a paper on electrodeposition presented elsewhere in this symposium may be referred to.

MR. R. A. P. MISRA (Indian Wild Barfield Co. Ltd., Bombay)

Could the authors give some details of the protective atmosphere used in the aluminizing plant? Has any work been done on the weldability of aluminized steel?

To elaborate further the point raised by Mr. Watson it should be borne in mind that the solderability of aluminized sheet should be as good as that of tin plate if it were to compete in the food-canning field. Some of the can-making mechanics solder seams at the rate of hundreds per minute. Any large-scale changes of plant in the can-making industry required by aluminized sheet may not be practical.

Authors' Reply

Protective atmosphere in aluminizing plant can be had by passing cracked ammonia as adopted by Armco. Water vapour along with hydrogen may be used—nitrogen mixed with water vapour causes decarburization of the surface at higher temperatures.

For details on weldability of aluminized steel an article in Materials and Methods, 24 (1946), 90-94, may be referred to.

As regards soldering of seams, it may be pointed out that researches on soldering of aluminium are being done at many centres especially in U.S.A. and the outcome of their results will apply to aluminized steel as well. More so, it has been seen that if a sheet is shaped in the form of a tube and the two edges are in close contact, the aluminizing of such a steel gives a self-soldering effect as well, i.e. aluminium penetrates between the edges and the alloy layer formed keeps the two edges together in much the same way as soldering. Also overall advantages of aluminizing steel may outweigh cost considerations involved in plant modification thereby required.