Sprayed Metal Coatings for Corrosion Prevention

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Introduction :

Since the time metals were first known, the phenomenon of metallic corrosion has always engaged the attention of mankind. With the almost explosive increase that has taken place in the manufacture and use of metals in the last few decades, this problem has naturally assumed much greater importance and there are now a variety of highly developed processes in use which help in reducing the rate of corrosion and in increasing the useful life of metallic articles. Iron and steel, the most commonly used metals, are usually protected by the application of coatings on their surface, which can be metallic or non-metallic in nature and which have better resistance to the corrosive media than the iron or steel itself. To mention only a few, there are the paints which are usually brushed on or sprayed on and metal coatings which are electro-deposited or flame sprayed or put on by hot dipping. This paper is concerned with flame sprayed metal coatings and the criteria for choosing the types of coatings to suit specific conditions of service. Before going into the criteria, however, it is necessary to discuss albeit briefly, the process of flame spraying, the nature and special properties of metal coatings so applied and the general principles of corrosion theory.

Flame Spraying :

Basically in metal spraying, the molten metal is atomised and projected on to the surface to be treated by a high velocity stream of compressed air. There are three established systems in use, classified by the form in which the metal is used in the spraying tool.

The first is the molten metal system in which the metal is melted externally to the tool and poured into a receptacle provided in the tool before it is atomised and sprayed. This method is not, however, suitable for any but the lowest melting metals or alloys and hence has limited special uses only.

In the second system, the metal in fine powder form, is passed through an intensely hot flame and the molten particles are then projected on to the surface to be sprayed at a high velocity by a compressed air jet. The widest application of powder spraying is in spraying of zinc for anti-corrosion work although even high melting point metals such as those used for hard-facing can be sprayed by this process.

The third system of wire spraying is by far the most popular one as it can be used for spraying a wide variety of metals and alloys and the equipment is compact and convenient to handle. In the tool used, the wire to be sprayed is fed, at controlled rates, into a high temperature flame where it is melted and, as in the other two systems, a stream of compressed air is employed for atomising and spraying the molten metal.

It must be appreciated that in all these methods of spraying, the bond between the coating metal and the base metal is a mechanical one and is dependent on the condition of the receiving surface (special cleaning and roughening procedures are employed to enable the atomised particles to 'lock' on to the surface) and the velocity of the particles when they reach the surface to be sprayed. During their passage through the pro-

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pelling air stream, the particles lose heat rapidly and are not usually in a molten condition when they reach the work to be treated. The mechanism of the bond on the surface is complex and many theories have been advanced to explain it. It is known however that, on impact, the particles flatten out and the coating is formed by these locking on to the prepared roughtened surface and by interlocking with other spray particles also flattening out on impact. A sprayed metal coating consisting, as it does, of a number of individual particles is porous in nature and not continuous as is the case with a galvanised or electro-plated surface. The coatings as sprayed are not impervious to fluids and, where it is desired, special treatment is required to seal the pores.

The scope for metal spraying for anti-corrosion work is greatest in the protection of structures and large fabrications in steel which cannot be economically or effectively tackled by methods such as hot dipping or electro-deposition and where a greater degree of protection than can be offered by paint coatings alone is desired. The useful areas of the metal coating processes overlap very little indeed and the use of sprayed metal coating--paint coating combinations is accepted practice now.

The Phenomenon of Corrosion :

In general, the corrosive attack on iron and steel is electro-chemical in nature and occurs in the presence of moisture and oxygen. The ability of metals to resist corrosion is largely dependent on their position in the electro-chemical series (Table 1) in which metals are arranged in an order by comparing their equilibrium voltages against standard hydrogen electrode :

TABLE 1

Electro-chemical Series

(*Hydrogen potential* = **0.00**)

Metal	*Electrode potential (volts)*
Platinum	+ 0.86
Silver	+ 0.80
Copper	+ 0.35
Lead	+ 0.13
Tin	+ 0.15
Nickel	+ 0.20
Iron (ferrous)	+ 0.34
Cadmium	+ 0.42
Zinc	+ 0.77
Aluminium	— 1.34
Magnesium	— 1.80
Sodium	— 2.72

The further apart two metals are in this series, the more powerful is the electric current produced by their contact in the presence of an electrolyte. In general, when two metals are in contact in an electrolyte, the greater the rate of attack on the metal in the lower (negative) position, the greater is the protection given to the other by the presence of the dissolving member. Much care, therefore, has to be exercised in choosing the coating metal as conditions such as these may well occur in practice.

The first condition the coating metal has to fulfil is that it should have better resistance to the corrosive media or environment than the iron or steel it is intended to protect. Among the metals listed in Table 1, if the more expensive metals are left out, the choice is limited to (a) copper, lead, tin and nickel, all of which are cathodic to iron and (b) cadmium, zinc and aluminium which are anodic to steel. All these metals are used depending on the particular exigencies of service. It must be remembered, however, that the cathodic metals can protect iron only mechanically by excluding the corroding influence. If the coating is porous or is subject to mechanical damage, attack on the anode, namely steel, occurs and is usually more intense than if the steel had been left unprotected. The accelerated attack will be greater if the potential difference between the two metals is high and the electrolyte is a good conductor. As has been pointed out earlier, the sprayed metal coating is porous in nature and when metals cathodic to steel are left in the sprayed-on condition, they will do more harm than good under corrosive conditions. It is usual, therefore, to limit sprayed cathodic metal coatings only to work where these are considered essential on other considerations and then also only if the pores on the sprayed surface can be sealed by grinding and polishing or by the application of an effective sealant.

The metals anodic to steel, namely, zinc, aluminium and cadmium are, on the other hand, attacked preferentially to the iron base and hence afford protection to the iron if there is a break or damage to the coating. This protection at the discontinuities in the coating is electro-chemical and involves the sacrifice of the anodic metal coating around the discontinuities. The area of damage which can be so protected is governed by the rapidity of attack on the covering metal, i.e., the iron will remain unaffected until the exposed area is so large that the central portion is beyond the zone protected by the sacrificial action of the coating. This effect depends on many factors and especially on the nature of the electrolyte. It is desirable to choose a metal which is corroded just sufficiently quickly to confer cathodic protection on the steel exposed but not more rapidly than is necessary for this purpose.

The foregoing explanation about the phenomenon of corrosion is necessarily somewhat over-simplified and the mechanics of metallic corrosion under practical conditions are far more complicated. This is the reason why it has not so far been possible to prepare standard "quick reference" tables laying down which coating should be used as a protection against specified corrosive conditions. Many attempts have been made in this direction but such information compiled so far can at best be considered as for general guidance only. When in doubt, therefore, it is good practice to expose sample plates with different coatings under consideration to actual conditions of service for obtaining data.

Types of Coatings :

Zinc :

The most common application of sprayed zinc coatings is for the protection of steel from the action of the atmosphere and natural waters. For most purposes, it can be taken that the protection offered by a zinc coating has a direct relation to its thickness.

Atmospheric attack on zinc is usually slow. On exposure, the freshly sprayed zinc tarnishes rapidly, forming a smooth adherent film of zinc oxide, carbonate and hydroxide, which inhibits further attack on the zinc. In industrial atmospheres, sulphate will also be found but this is liable to be washed off by rain.

The British Standards Institution recommends for the protection of wrought iron and steel parts used outdoors, a minimum coating weight of 0.8 oz. of zinc per sq. ft. of surface and, over these, two coats of paint. This represents a zinc coating of approximately 1.5 mil thickness and as, by spraying, it is difficult to ensure an even coating of such thickness, it is usual to apply a minimum of 2 mils when the surface is to be painted subsequently. Where coatings are used in the unpainted condition or where repainting at periodic intervals is not possible, a minimum coating thickness of 4 mils is recommended.

With sprayed zinc, if the conditions of exposure are at all severe, corrosion products known as 'white rust' appear on the surface. These form streaks which are very unsightly and hence, mainly for aesthetic reasons, it is usual to apply paints over sprayed coatings. Sprayed zinc coatings need no further preparation before painting and the undercoat of sprayed metal with its matte finish gives the paint much longer life than would have been possible if the paint had been applied to bare steel. As regards the most suitable type of paint for use with these coatings, work is still going on but it is advisable that lead base paints are avoided.

The new Forth Road Bridge in Scotland is an excellent example where sprayed zinc coatings have been used to protect steel exposed to marine atmosphere. The old bridge built in 1890 has required almost continual maintenance by painting and because of the rising labour costs, it was decided that the reduction in periodic maintenance would more than justify the initial cost of metal spraying.

Protective coatings of sprayed zinc have been used successfully on steel boats and ships for many years. The results of Dr. Hudson's experiments with specimens immersed in sea water are summarised in Table 2 below :

TABLE 2

Behaviour of sprayed metal coatings on steel immersed in sea water

Coating		Immersion rust %
Metal or alloy	*Weight per sq. ft. oz.*	*condition after 2 years.*
Aluminium	0.9	0.2
Cadmium	2.1	1
82/18 Cadmium-zinc alloy	1.4	80
Lead	3.8	80
88/12 Lead-tin alloy	1.3	20
Tin	1.5	20
Zinc	1.9	0.1

It may be seen that zinc gives far superior results, with aluminium, the second best.

It has been observed that hulls of boats sprayed with zinc were in excellent condition even after 10 years and the cost of hull maintenance due to corrosion, in the meantime, had been negligible. Although covering the hull with a protective metal coating and overcoats of suitable paint may put up the initial cost of the vessel, the economies as a direct result of this could be considerable. In designing a sea–going vessel, it is usual when selecting the hull material gauge to make certain allowances for loss by corrosion. If effective protective coatings are used, it would be possible to design the ship with lighter gauge material with all the attendant savings in cost. Then again, with life of paint coatings enhanced by the undercoat of metal, the frequency and cost of hull maintenance can be greatly reduced.

Tests have shown that zinc coatings of about 5 mil thickness in the unpainted condition would protect steel in sea water for six years.

In the treatment of hulls of ships and piers, it is often necessary to cover any protective scheme with an antifouling composition. These materials contain salts of copper and mercury which are intended to leach out slowly and so discourage marine organisms. Solutions of these metals attack zinc and hence it is necessary to have at least one good central priming coat such as red oxide between the zinc and the antifouling composition.

There is some evidence to suggest that if prior to putting it in service in sea water, the zinc coating is sprayed or painted with sea water and then allowed to dry, the formation of insoluble zinc oxy chloride on the surface would give the coating an increased life.

Aluminium :

While as a coating for general purposes, zinc remains most popular, aluminium is coming into use to an increasing extent. In the case of aluminium, the formation in the pores of the coating of the insoluble corrosion products of aluminium make the protection more effective ; some of the corrosion products of zinc are soluble and deliquescent, with the result that zinc coatings do not behave well under conditions of marked humidity and pollution, such as, for instance in railway tunnels. Aluminium coatings are much more suitable for such conditions and also in industrial atmospheres where there is usually attack by sulphurous gases. The British Standards Institution's recommendation for aluminium coatings for protection of steel out-of-doors is 2 mils thickness if followed by painting and 3 to 4 mils if left unpainted.

Some years ago, the Abbey works of the Steel Company of Wales decided that all constructional steel work above crane level at this new works would be sprayed with aluminium. The spraying was done by passing the steel sections through specially designed mechanised spraying equipment and spraying at site was limited to touching up only. The coating was covered with one coat of aluminium paint mainly to improve the appearance. Over the years, this additional expenditure has more than paid for itself as maintenance costs had been reduced to a minimum.

Another interesting job undertaken was at the Spanish National Steel Works at Aviles on the North Coast of Spain, where aluminium coatings were used for protecting gas holders, gas mains and even blast furnaces.

Aluminium coating 4 to 8 mils thick are preferred to zinc for service in soft waters (except for Zeolite-softened waters, in which there is usually a small amount of alkali).

In the food industry, sprayed deposits of aluminium up to 10 mils thick have been used successfully for tanks containing edible oils.

Up to 500°C, aluminium coatings are protective against the attack of sulphurous gases and also for protection of steel work exposed to comparatively high temperatures, such as, the roofs of buildings where industrial processes are carried out.

For temperatures above 500°C, aluminium coatings are used in the heat treated or 'aluminised' conditions.

Cadmium :

While this metal can be satisfactorily sprayed, precautions have to be taken to protect the operator adequately. Except in conditions of total immersion in stagnant water, cadmium coatings show no advantage over zinc. In view of its higher cost and the elaborate arrangements needed to protect the operator, sprayed coatings of cadmium find little application except for very special purposes.

Tin :

Sprayed tin coatings find use mainly in the food industry because the metal is physiologically inactive and in the absence of oxidisers is not attacked by foodstuffs. While it is quite suitable for milk vessels and can resist the attack of distilled or zeolite softened waters, it is unsuitable for hot fruit juices, acetic acid and its solutions.

Tin is very close to iron in its electro-chemical behaviour and it will depend entirely on the conditions of service whether it is anodic or cathodic to the steel base. The pH value of the contents has much effect on this and as a rule, tin is safer in slightly alkaline conditions than in very acid conditions. Tin is usually effective only when applied in thickness of over 10 mils. Heavy scratch brushing finish improves performance.

Lead :

The most obvious application one would think of for sprayed lead coatings would be lining of chemical plant in place of homogeneous or sheet-lead linings. Fortunately, however, in view of the porous nature of sprayed lead deposit, a minimum of 20 mils thickness of coating is necessary for it to be reasonably non-porous. If the associated health hazards are also taken into consideration, the cost of an effective sprayed coating would be no less than that of a homogenous lead lining coating which has certain other desirable qualities as well. As a rule, therefore, sprayed lead coatings are not used for lead lining but in thickness of 5 mils or so, they are useful in slightly acid conditions such as in ductings carrying acid fumes and in areas where splashing from weak sulphuric acid may occur.

Lead coatings have been used with limited success in industrial atmospheres as well but results obtained so far are not quite conclusive. It must be remembered also that as lead is cathodic to steel, if the coating is damaged, it is the steel which is preferentially attacked.

Other Metals & Alloys :

Nickel and its alloys, stainless steel and copper and its alloys are used as sprayed coatings to protect iron and steel in special cases where sufficiently thick coatings can be applied and lend themselves to finishing by grinding and polishing. Unless these are finished this way, the coatings cannot withstand corrosive condition. Nickel and stainless steels are used for building up pump rods and rolls and shafts which may have to run in corrosive conditions. Copper coatings are used for building up large rolls used, for example, in the paper industry.

Conclusion :

The metal spraying process has some significant advantages over alternative methods. It is possible to apply coatings of any metal on any other metal or even on non-metallic surfaces. As the bond is mechanical, complications on account of formation of inter-metallic compounds etc. do not arise. The process is virtually cold and hence it is possible to eliminate problems of distortion such as may come up in hot dipping. Finally, there is no limit to the size of job that can be tackled as the process is quite suitable for site work as well. Under certain conditions, the type of bond could be a limitation and so also would be the porous nature of the coating. A wise engineer should have a good knowledge of the possibilities and limitations of this versatile process, so that he can utilise this knowledge at the right opportunity and to the best advantage.

Bibliography :

1. Evans, U. R.—'Corrosion and Oxidation of Metals', Arnold, London, 1960.

2. Evans, U. R.—'J. Birmingham Met. Soc., 23, No. 4, Dec. 1944'.

3. Hudson, J. C.—'The Corrosion of Iron & Steel', Chapman and Hall Ltd.

4. British Standards Inst.—'Recommendations on methods of protection against corrosion of light gauge steel', PD 420, Nov. 1945.

5. Ballard, W. E.—'Metal Spraying and the flame deposition of Ceramics and Plastics', Griffin, London, 1963.

6. Hudson, J. C. and Stanners, J. F—J. Iron & Steel Inst., 1953, 175.

7. Scott, S. Y.—Second International Metal Spraying Conference, Birmingham, 1958.