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Long Life Corrosion Protection of Steel by Zinc-Aluminium Coating Formed by Thermal Spray Process

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ABSTRACT

Zinc and aluminium coatings have been used as sacrificial anodic coatings since many years to afford protection to the steel structures. Among the various methods available to carry out the coatings of aluminium and zinc, thermal spraying is the most economical and user friendly method. This paper discusses the current status of thermal sprayed zinc and aluminium coatings for corrosion protection. A new development in this field has been the sealing of coatings by powder flame spraying of polymers. The process and advantages of spraying polymers is also discussed.

INTRODUCTION

A material may be given a surface coating to achieve the desired surface property. Most metals, alloys, ceramics plastics & some inter metallic compounds can be applied as coatings either individually or as mixture, but their characteristics often limit the processes which can be used for their deposition. Refractory oxides for e.g. can not be applied by welding processes and carbides require a metal or alloy matrix. The material/process relationship not only identifies where they can be used together but also determines properties that can be expected from the coating, such as density and adhesion to the substrate. Table 1 compares the various surface modification techniques.

BASIC PROCESS OF THERMAL SPRAYING

The basic process of thermal spraying consists of bringing the material to be sprayed or "coated" to its molten form, atomizing it to a fine stream of particles and propelling the fine particles at a high velocity to the substrate or "base" where it gets flattened on striking and finally adheres to it. In more than half a century of its existence there is not much of a change in the basic process although tremendous developments have taken place in respect of the heat source employed, velocities that can be achieved, range of materials & coating properties etc.

Table 1 : Comparison of surfacing Processes and Deposits

	Vapour Deposition	**Electro Deposition**	**Thermal Spraying**	**Spray Fusing**	**Welding**
Thickness (mm)	0.001 – 0.2	0.02 – 0.5	0.1 – 1.0	0.5 – 1.5	1.20 or more
Component Geometry	Versatile	Versatile	Access to internal controlled by size of torch/gun		
Component Size	Limited by chamber size	Limited by plating bath	No limit	Limited by fusing facility	No limit
Substrate Material	Almost limitless	Almost limitless	Almost limitless	Metals or alloys of higher melting point than coating	
Substrate Temperature (C)	30 - 1000	100	200	1050	1400
Pre-treatment	PVD – ion Bombardment CVD - Various	Chemical cleaning & etching	Clean and roughen surface		Mechanical cleaning
Post-treatment	None / stress relief	None / stress relief	None	Nil	Nil
Coating Porosity	Nil to small	Nil to small	1 – 15 %	Nil	Nil
Bond Strength (MPa)	High	100	20 - 140	High	High
Bond Mechanism	Atomic surface force	Surface force	Mechanical	Metallurgical	Metallurgical
Control of deposit thickness	Good	Good	Fairly good	Moderate	Manual – variable mechanized – good
Distortion of substrate	Low	Low	Low	Moderate	Can be high depending on substrate geometry

THERMAL SPRAYING OF ZINC & ALUMINIUM

Thermal spray coatings of zinc and aluminium for corrosion protection are usually applied by the twin wire arc process or the wire flame spray process.

Twin Wire Arc Spraying

In this system arc is struck between two wires and the heat generated by the arc melts the wire tip, this molten wire tip is atomized by a high pressure airjet and these atomized particles form a coating on the substrate kept in front of it. In the twin wire arc spraying two dissimilar wires (e.g. Cu & Zn) can be used to form pseudo alloy coatings.

Wire Flame Spraying

In this system a single wire is fed into an oxygen - fuel flame wherein the wire tip melts. This molten droplet is atomized by a high-pressure gasjet. The wire flame spray system has got higher operating costs than the twin wire arc spray system. However the wire flame spray system is portable and it is amenable to on site spraying of zinc and aluminium.

Thermal spray coatings are regularly applied on to steel structures like Bridges, TV Towers, Ship Hulls, Windmill Structures, Pipe Lines, Off Shore Oil rigs etc. In fact the entire North Sea oilrig in UK is coated with aluminium to protect against marine corrosion. Recently Zinc coatings on reinforced concrete have been used for offering corrosion protection to steel rebars. Zinc and Aluminium coatings are usually sealed to offer corrosion protection ability for a period of 40-45 years. Unsealed coatings can offer corrosion protection for 25 to 30 years.

ZINC & ALUMINIUM COATINGS

Thermal spraying of zinc and aluminium for corrosion protection applications is a well-established technique. Thermal spray coatings of zinc and aluminium provide corrosion protection for over 30 years by cathodic protection. Moreover, the products of corrosion close the open porosity in the coating thus inhibiting further corrosion. Thermal spraying offers the following benefits over galvanizing of steel.

- Low heat input during spraying eliminates the risk of thermal distortion and metallurgical degradation.
- The process is not limited to zinc. The coating material may be selected specifically for the environment.
- There is no limit to the size of article, which can be treated.
- Articles can be treated on site.
- There is no effluent disposal problem.

Thermal spray coatings have following benefits over paint / epoxy coatings.

- Use on any surface.
- Minimum environmental & safety concerns.
- No mixing, set up or pot life limitations.
- Higher production rates.
- Easier to use
- Harder, better adhesion can be used for high temperature applications.

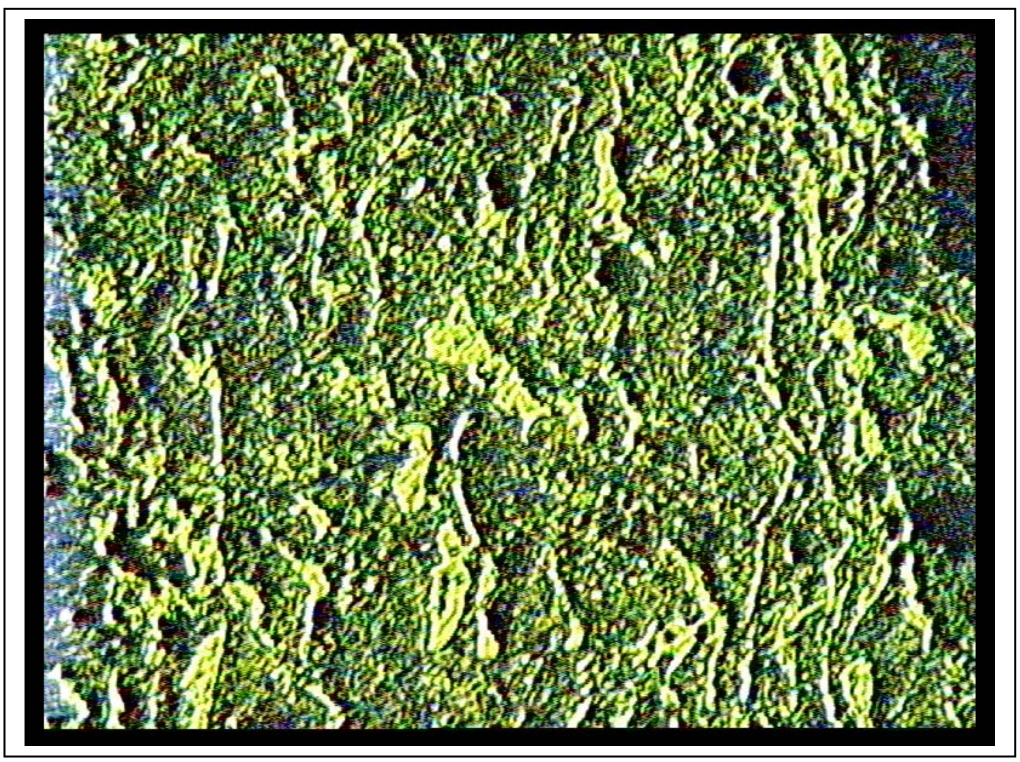
Exotic epoxy and paint systems offer a maximum lifetime of 7 years. Moreover the three-coat epoxy system takes three days to apply due to re-coat window and cure time between coats. Thermal spraying has got no such limitations. Zinc and aluminium coatings are used for corrosion protection of steel structure like TV Towers, bridges, radar, telemetry, command, tanks, barrages, above ground pipe line, exhaust stacks, miscellaneous shop items and reinforced concrete (to provide cathodic protection to the rebar).

PSEUDO ALLOY

Pseudo alloys is the structure formed in the coating when two dissimilar wires are sprayed simultaneously in a twin wire arc spray system. For e.g. Zn & Cu can be sprayed to form pseudo alloy brass coatings. In the present experiment Al and Zn wires were sprayed to form the Al-Zn pseudo alloy coatings.

The pseudo alloy coating consists of the discrete particles of zinc and aluminium plus the stochiometric and non-stochiometric alloy phases of zinc and aluminium. Fig. 1 shows the microstructure of zinc and aluminium pseudo alloy coatings.

Fig. 1 (Arc Sprayed Zinc-Aluminium Pseudo Alloy Coating)



Chemical analysis of the pseudo alloy coating was carried out. The coating formed on the MS substrate was chipped out and the chips were analyzed for the amount of Al and Zinc in the coatings and were compared to the aluminium and zinc content derived from the original wire stock. The result of this analysis is shown in table 2

Table 2 : % of Zinc & Aluminium In The Original Wire Stock & Pseudo Alloy

	Wire Stock	Pseudo Alloy
% Al	99.5%	29.8%
% Zn	99.9%	Balance

Table 3 shows the result of Chemical analysis of Al 15% - Zn alloy wire & its arc sprayed coating

Table 3 : % of Zinc & Aluminium In Alloy Wire & The Alloy Wire Coating.

	Al 15% Zn Alloy Wire	Alloy Wire Coating
% Al	15%	15.4%
% Zn	85%	Balance

Table 2 & Table 3 show that during arc spraying there is very little deterioration of the coating species in terms of oxidation of the coating species. The coating species remain more or less unchanged chemically during the coating process. This means that arc spraying can be used to spray aluminium and zinc coatings with very little deterioration of the coating species.

MECHANISM OF CORROSION PROTECTION

Aluminium coating has the structure of aluminium splat, which is surrounded on the outside by aluminium oxide. The thin oxide layer functions as a barrier coating which is liable to pitting and damage by erosion. Such coating can be sealed to prevent further corrosion. Zinc coatings offer cathodic protection to the substrate. The high sacrificial action of zinc provides cathodic protection to the steel surface. Moreover the sacrificial action of zinc produces insoluble corrosion products which blocks the porosity of thermal sprayed coatings thus further restricting corrosion of the substrate by preventing the corrosive media to penetrate the coating and come into contact with metallic substrate. The Al-Zn pseudo alloy coatings contain two phases, one is zinc rich and the other is aluminium rich. The zinc rich phase offers cathodic protection by its sacrificial action while the aluminium rich phase provides protection by barrier action. The porosity of the coating is partially closed by the products of zinc corrosion. Due to these reasons the aluminium -zinc coating offers considerable advantages with respect to corrosion protection vis a vis the conventional zinc and aluminium sprayed coatings. Electro-chemical tests carried out on the coatings (ref. 7) also show that performance of pseudo alloy thermal spray coating is better than pre-alloyed, or purely metallic coating; and; its sealing further yields a synergistic upgradation in the coating performance, both in terms of corrosion behaviour and mechanical strength.

The aluminium zinc coatings formed using the alloy wire as feedstock material has got the limitation that the aluminium percentage in the alloy wire can not be increased above 15% wt. aluminium because of the brittle intermetallic phases that form. This limitation is not there in the pseudo alloy coatings.

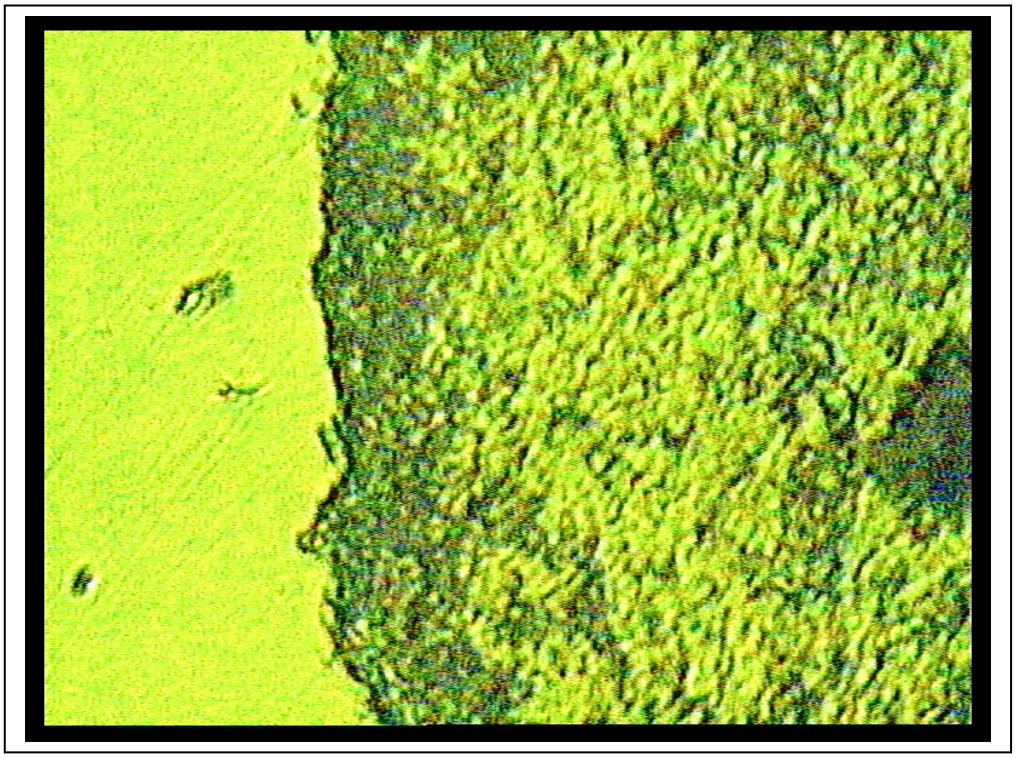
By using the wire feed stock of pure aluminium and zinc the aluminium content of coating formed is 27% wt. The amount of aluminium in the coating can be increased by

- using aluminium wire of larger diameter
- increasing the speed of feeding aluminium versus the speed of zinc wire.

The reverse of the above steps will lead to reduced aluminium content in the coating.

The microstructure of the aluminium - zinc alloy coating is shown in the figure 2.

Fig. 2 - Arc Sprayed Zinc-Aluminium Alloy Wire Coating



SEALING OF THERMAL SPRAY COATINGS

Thermal spray coatings of zinc and aluminium offer corrosion protection upto 25 years without any sealing, and, sealing the coating increase the component life upto nearly forty years (for general atmospheric corrosion). The sealants generally used for sealing thermal sprayed coatings are varnish based, epoxy based, phenolic of polymer based. More of the sealant in the market are proprietary products. The sealer is applied to the coated component immediately after spraying, using, either a brush or a paint spray gun. The component after sealing is put into oven for drying or it can be dried in bright sunlight. The sealer enters the pores of the coating and closes the porosity, which restricts the entry of the corrosive media to the coating and the substrate.

Sealing thermal spray coatings using polymer materials offers nearly lifelong protection from corrosion. The polymer materials are applied for sealing using a powder flame spray system.

CASE STUDY

The major problem faced in the desert regions of Rajasthan (India) is that of the availability of clean drinking water. The underground water in large areas of Rajasthan is unfit for human consumption as it contains too high salt content. A Govt. of India R&D Organization in Jodhpur (India) has developed a water desalinization plant to soften the brackish water available in the wells of the desert region.

The well water has a salt content of 5000 ppm, which was reduced by the water desalinization plant to the level of 1500 ppm. A small quantity of water, in this process, collected at the anode with salt content of 5000 ppm. This water was thrown away. However, during the operation of the plant the high salt content of the water caused the problem of corrosion of the plant steel structure, which consisted of top and bottom frame and tie rods to hold these frames. A filter assembly was also part of this system. The coating function requirement apart from offering corrosion protection to the substrate, was to have electrical insulation properties in the case of tie rods. To provide electrical insulation to the tie rods it was decided to coat it with the ceramic powder having the composition of aluminium oxide 85% (wt) and titanium oxide 15% (w). This powder is prepared by blending and mixing the aluminium oxide and titanium oxide powder. The aluminium oxide powder offers the best electrical insulation properties, however, pure aluminium oxide powder can not be sprayed by the flame spray system because of its high melting temperature coupled with low thermal conductivity. Mixing titanium oxide with the aluminium oxide renders the powder blend sprayable by the powder flame spray system.

The top and bottom frame of the structure and the filter body of the desalinization plant were coated with a pseudo alloy of aluminium and zinc using the twin wire arc spray system.

The tie rods and frames were sealed by spraying LLDPE Powder on it (linear low-density polyethylene). The LLDPE Powder was sprayed using the powder flame spray gun. An external powder feeder was attached to feed the powder to the gun. The gun was initially operated using an oxy-acetylene flame but it was observed that the flame temperature of the oxy-acetylene flame was very high (3100°C), this caused the LLDPE Powder particles to evaporate leading to reduction in the deposit efficiency. The oxy-acetylene flame also caused the overheating of the substrate if proper precautions were not taken while spraying LLDPE. For this reason, the spray gun was later set up on the air-acetylene flame. The air-acetylene flame is much cooler as compared to the oxy-acetylene flame, as nearly 80% of air consists of nitrogen, which takes no part in the combustion of acetylene. The powder feeder was operated using air as the carrier gas and the feed rate of LLDPE Powder was kept at 18 gm/min.

The plant was coated as above and it was tested in laboratory of the Govt. of India Enterprise.

The coating on the plant proved to be more than adequate in its response as a corrosion protection coating. The coating was approved and the MEC R&D, subsequently received a repeat order for coating the water desalinization plant.

CONCLUSIONS

The arc sprayed aluminium-zinc pseudo alloy coatings offer us a better alternative to the conventional aluminium and zinc coatings for corrosion protection of steel structures. However, the coatings must be sealed to give the longest life of the steel structure. The LLDPE spray-sealing process carried out on the tie rods and frames and the filter body shows very good corrosion resistance to the brackish water encountered. The arc spray coatings of zinc-aluminium alloy wire and the zinc-aluminium pseudo alloy show good microstructure with low levels of porosity and well-integrated splat structure. The cost of operation of the arc spray system is lower than the operating cost of powder flame spray system because gases like oxygen and acetylene are not used in arc spraying.

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