NEW GENERATION COATINGS - A COMBINATION OF THERMAL SPRAY AND ORGANIC PAINT COATINGS TO GIVE ENHANCED CORROSION PROTECTION IN AGGRESSIVE ENVIRONMENTS

A.S.Khanna
Corrosion Science & Engineering,
Indian Institute of Technology, Bombay

Abstract

There is a great concern about the frequent replenishment of paint coatings on certain specific structures and installations, especially erected in aggressive marine environments. Various analysis have shown that a best paint coating with best surface finish and pre-treatment cannot guaranty a life more than 5 years. Hence alternative methods of protecting such structures in aggressive environment is really the need of the hour. Metal coatings using thermal spray is becoming very popular. There are of course some limitations of thermal spray coatings which can either be overcome by modification of the process or by combining thermal spray with organic paint coatings. Such new generation coatings are now guarantying a life of more than 20 years to 40 years. Principal of thermal spray coatings and their application to structures in highly aggressive environments is discussed in this paper.

Introduction

For aggressive environments such as marine, especially for the onshore and offshore structures, many steel components are protected by either high performance coatings, cathodic protection (CP)or by a combination of the two. A combination of paint coating and CP is not possible for structures which are not immersed. Hence for such structures, the protection is restricted by high performance paint coatings only. Deterioration of paint coatings is a continuous process. Depending upon how systematically it is applied the life of a paint coated surface needs 3- 7 years of replenishment. Replenishment of the paint coatings is not only a costly affair, it also results in plant shut down, carrying out surface finishing once again and sometimes it is difficult to have accessibility of the already pained surface for repainting. Hence many industrial houses often ask a question, "What is the way of enhancing the life of the paint coating of a structure by 10 years, 20 years or even more?" Is it possible? Answer is no if we restrict only to paint based coatings. Answer is yes if we combine paint coatings with metal thermal spray coatings, which can assure a life of the structure from a minimum of 20 years to 40-45 years. In this paper an attempt has been made to describe the process and cite examples where such coatings have enhanced the life of structures to very long.

An ordinary paint coating if applied with all care of best surface finish, pre-treatment with a Zinc based primer followed by best epoxy paint and a final paint of polyurethane or acrylic would not assure a life of more than a maximum 5-7 years. Generally in the 4th to 6th year, one must carry out replenishment in order to save the structure. In thermal spray coatings, the structure is first cleaned to a specific surface finish and then sprayed with a metal coating. Basically it is a two step process which itself will assure a life equivalent to the best coated paint coating. In order to enhance the life of such paint coatings, this is further treated with a seal coat and can be followed by any other paint coat of desired colour and property. Such a coated surface can assure a life of more than 20-40 years.

THERMAL SPRAY TECHNIQUES

Thermal spray is usually carried out by one of the four following processes
The main difference between the various thermal spray techniques, namely flame spray, arc spray and detonation gun is the source of heat. Flame spray uses the acetylene oxygen flame, where temperature of only 2500 - 3000°C can be achieved. In arc, the temperature of 3500°C can be achieved. Higher temperature improves the quality of coating, e.g. increases in homogeneity. Second factor is the speed at which the particles are injected on the surface. Both in flame and arc spray, compressed air is used to force the melted particles to reach the substrate surface. In detonation gun, the shock created enhances the speed of melted particles to around 1000 m/sec. Hence the bond strength is highest and porosity is lowest. Different properties achieved by various coating methods are summarised in Table 1.

The schematic of the three set-up is shown in Fig. 1. In the flame spray (Fig.1a), fine powder is carried in a gas stream and is passed through an intense combustion flame where it melts. In this method, the coating material can be fed as wire also. The gas stream expanding rapidly because of heating then sprays the molten droplets on to the substrate where it solidifies. The fuel used is generally acetylene and hydrogen. The carrier gas may be oxygen, air or some inert gas. The quality of the coating depends upon the spray parameters : choice of the gas, geometry of the spray head, gas and powder flow rates, etc..

Table 1: Comparison of various thermal spray coatings

	Flame Spray	Arc Gun	Detonation Gun
Porosity	High	High	Low
Hardness (VPN)	500 - 700	500 - 700	1300
Bond Strength/ Adherence (N/mm^2)	21	30	81-150
Uniformity	Poor	Fair	Good
Structure	in-homogenous	in-homogenous	Dense
Impurity	Large	Quite	Less

Flame spraying process is cold process as the temperature rise of the substrate is hardly 200°C. Since, the coatings are not very dense and have poor mechanical bond, they are usually subjected to fusing operation, i.e. heating the coated material upto 950-1100°C. A particular group of alloys so called self fusing alloys are generally coated with this method. These are Ni-Cr alloys with Boron and Silicon as fluxing agents. After fusing the coating is more homogenous and dense, however, distortion of substrate is usual problem.

Arc Coatings (Fig.1b)use the metal in wire form. This process does not use any external heat source. Heating and melting takes place when a arc is struck between two electrically opposed charged wires. One of the wire is the metal to be coated. The molten metal on the wire tips is atomised and propelled onto the substrate by a stream of compressed air or other gas.

Electric arc spray offers several advantages over the flame spray process : higher bond strength, higher deposition rates and lower substrate heating. It is less expensive process as power requirements are generally low. No expensive gas such as Ar, Hydrogen is required. One requires generally ductile, electrically conductive wire of about 1.5 mm diameter. Although, electric arc process for oxides, nitrides and carbides coatings is currently not possible, recent developments of cored wires permits the deposition of some composite coatings containing carbides and oxides. Pseudo-alloy coatings can be made by using dis-similar metal wires. Electric arc coatings are being used for many corrosion resistant coatings such as Zn base, Aluminium and stainless steel coatings.

In **detonation gun method** (Fig.1c), measured amount of powder is injected into the gun along with controlled mixture of oxygen and acetylene. The mixture is ignited and a shock wave is generated, which lasts for microseconds and attains a velocity of 3000 m/s . the high velocity of the gas stream imparts energy to the powder which reach the substrate with a velocity of 800 m/s. During the short duration of particle acceleration, heat is also generated which melts the particles. The coating process is repeated several times in a second depending upon the type of coating. The coating structure is built up from a series of such detonations. The particle impact on the surface flatness or splatter into thin overlapping platelets such that the diameter is many times greater than their thickness. The high kinetic energy of the particles (about 25 times that of flame spray) converted to additional heat . This additional heat keeps the particle in molten form and completely wets the substrate surface. The result is a continuous coating with very high bond strength.

High Velocity Oxyfuel Coating (HVOF)

An alternative of detonation gun technique is High Velocity Oxy flame technique (HVOF). A schematic of a HVOF device is as shown in Fig.2. Fuel, usually propane, propylene or hydrogen is mixed with oxygen and burned in a chamber. In some cases liquid kerosene may be used as fuel and air as oxidiser. The products of combustion are allowed to expand through a nozzle where the gas velocities may become supersonic. Powder is introduced usually axially in the nozzle and is heated and accelerated. The powder is usually fully or partially melted and achieves velocities upto about 550 m/s. Because the powder is exposed to the product of combustion, they may be melted in either an oxidising or reducing environment and significant oxidation of metallic and carbides is possible.

With appropriate equipment, operating parameters and choice of powder, coatings with high density and with bond strengths frequently exceeding 69 MPa (10,000 psi) can be achieved. Coating thickness are usually in the range of 0.05- 0.50 mm, but substantially thicker coatings can occasionally be used when necessary with some materials. HVOF coating can produce coatings of virtually any metallic or cermet material and for some HVOF processes most ceramics, e.g. zirconia coating can be applied by acetylene as fuel

The thermal spray is usually a two step process :

1. Surface finishing which is usually obtained by shot blasting or sand blasting the surface to SA2.5 or 3 finish.
2. This is then blasted with the metal coating with one of the above mentioned techniques which are chosen either on the basis of cost,

surface roughens or on the basis of the job type, whether it is factory owned job or site job.

One of the serious limitations of thermal spray process is the porous surface morphology which is not sufficient to resist corrosion in the aggressive environment. As shown in Fig. 3(a), the surface is not only rough but also has strong pores which if left as such can help aggressive environment to penetrate through the coating and reach base metal and hence corrode it. The cross-section of the coating (Fig. 3(b)) shows uneven surface and inter-connected pores and voids. The minimum porosity is obtained by detonation gun method or HVOF method. In order to prevent this, sealers are needed. The sealers are nothing but epoxy resins which when applied on these surfaces can seal these pores and hence prevent penetration of the aggressive environment. This can then further be painted with a top epoxy or polyurethane or acrylic paint to give smooth, glossy surface of desired colour.

Applications

Structures

Application of thermal spray coatings for corrosion protection of concrete rebars is quite recent. Pure zinc or a coating of Zn-Al alloy is made using arc thermal spray process. It must be recalled that galvanised bars were banned in USA as Zn dissolves in both acids and strong alkali media. However, Zn-Al spray coating has shown a life beyond 27 years [1]. In USA, the Zn thermal spraying has been made on entire bridge. The Frankland Bridge in Florida was coated by zinc spray. The deteriorated concrete was not patched. The aim of Zn coating was to stop corrosion of steel rebars. Passive cathodic protection is expected in this system. Also permeation of corrosive environment can be stopped by Zn coating [2].

Kanmon bridge, located between Honshu and Kyushu across the sea is a suspension bridge, built in 1973 (Fig. 4). The environmental conditions are very severe. Sea fog wraps the bridge. The bridge was protected by 75 μm of zinc coating which was followed by 6 layer paint coating. This bridge requires repainting in 6-12 years. The whole bridge is divided into eight sections, each part is repainted after eight years [3].

Now many better coatings are available such as alloy zinc coatings. Zn 55% Al 45%, Zn 85% Al 15%, ZnMg, ZnMgAl caotings which have longer life. If the coating is carried out by arc process and pores of the sprayed coatings are sealed properly using a proper combination of epoxy and other top coats, a life of more than 25 years is guaranteed [4].

Recently , metallized coating of Zn-15%Al was carried out on East Washington Avenue bridge in Bridge report. 410 ton bridge required 73000 square foot of metallizing. The metallized coating is expected to provide corrosion protection for the next 50 years [5]. The main advantages of Metallizing are :

- No VOC's
- Long term maintenance free protection.
- Lowest life cycle cost.
- Self sealing characteristics.

A comparison of metallized spray coating with the conventional organic coatings is shown in Fig. 5. The photographs compare the excellent condition of speed coated specimens compared to the as painted specimens.

Cooling Towers

Cooling towers perform a critical function in the process of power generation. Cooling water used in the power cycle for heat exchangers and condensers is cooled in tower structure constructed of steel, reinforced concrete, and other materials. The materials are exposed to corrosive agents present in the cooling water resulting in damage to the structure. Cooling waters systems using brackish water or salt water are exposed to increasing concentration of chlorides which can migrate through the concrete matrix until they reach the level of reinforcing steel. The protective layer which forms on steel in high alkaline concrete breaks down allowing corrosion to occur. As the rebar corrodes and form oxides of iron which are voluminous, resulting in tensile stresses of the order of 50,000 psi. Being weak in tension concrete begins to crack and finally come out.

Metallized cathodic protection is a viable alternative to the corrosion of cooling towers. High purity Zn, thermally sprayed on the surface of concrete acts as anode and discharges a small dc current through the concrete which is picked up by the reinforcing , thus protecting the steel from further corrosion and achieving cathodic protection. Such sprayed anodes can be used as sacrificial anodes or impressed current systems.

Concrete intake structures in a power plant undergo similar corrosion damage as discussed for cooling towers and can be protected in a similar way. Transmission and distribution circuits are essential components of the power grid throughout the world. Most of these circuits consists of current carrying conductors suspended from wood, concrete or steel structures. These structures and hardware are subjected to corrosion attack in the corrosive environment. Corrosion protection usually consists of galvanising, coatings or use of self protecting materials such as weathering steels. These methods are limited in their useful lives and effectiveness. Regular maintenance is required. Thermal spray coatings such as zinc, aluminium and their alloys are effective for long term solution for corrosion control of transmission towers. It has now been proved that only sprayed coatings can provide protection to steel for more than 20 years before the first maintenance cycle in many industrial and marine environments.

Fuel and Bulk Storage Terminals

Corrosion at fuel terminals is a costly problem. Fuel and bulk storage terminal structures exposed to corrosive environments include buried and submerged pipeline, storage tanks, pumps, valves, docks and various other miscellaneous structures and equipment's. Corrosion damage of these structures ranges from aesthetic concerns to leaks and environmental pollution, resulting in constant and costly maintenance to owners and operators.

Corrosion protection of such structures commonly addresses through paints and coatings. Buried and submerged structures are usually cathodically protected. Possibly the greatest corrosion maintenance expense in fuel and bulk storage terminals is paints and coatings. The paint failures generally result from inappropriate surface preparation, intercoat failures, improper curing or exposure to excessive chlorides.

Thermal spray coatings of zinc, aluminium and their alloys are therefore recognised as long term and effective solution to the corrosion problems with a life of more than 3o years and first maintenance cycle not before 20 years. Corrosion Science and Engineering programme at IIT Bombay has already working on the combined coating thermal spray and paint [6].

CONCLUSIONS

A new generation coating which is a metal spray coating in combination with a sealer coat and paint coat enhances the life of structure made of steel, concrete or reinforced steel to atleast five fold. Examples of life extension of about 30-40 years have already been cited with a proper combination of spray parameters and sealer and paint coat. Underground storage tanks, pipelines etc. can also be protected with this technology to make them maintenance free. Many overhead and hanging structures in power plants, chemical and petrochemical plants can be protected using zinc and Zn-Al and other alloys. Ship hulls, ship super structures can be made maintenance free using this technology.

References

1. R.Brousseau, M.Arnott and B.Baldock, J.Thermal Spray Techniques, 5-1 (1996) 49.
2. A.Finkelshtenyn, A.L.Bimman, Proc. NTSC'93, (1993) 679.
3. M.Fukumoto, T.Yamazaki and I.Okane,J. Jp.Thermal Society,30-3, (1993) 108.
4. Tobe S., Proc. 15th ITSC'98, May 25-29, 1998, Nice France (1998) 3.
5. Literature, Corrosion Restoration technologies Inc., USA.
6. P.K.Sharma, 'Thermal spray paint coatings for ship super structures' Ph.D thesis, 1997, IIT Bombay.

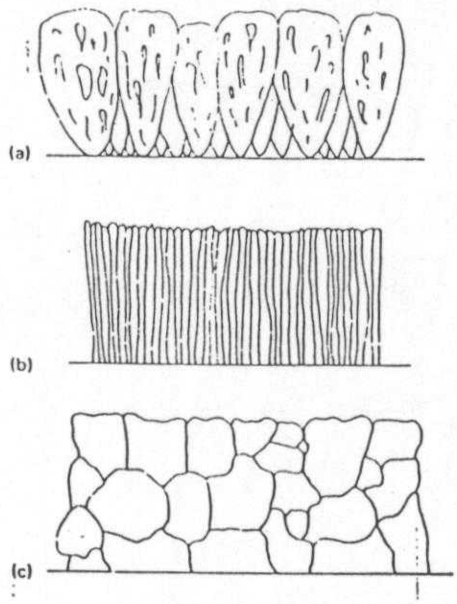


Fig. 1 Effect of temperature on coating structure a) columnar, at substrate temperature less than 0.3 T_M; b) fine columnar, at substrate temperature between 0.3 and 0.5 T_M, c) equiaxed, with substrate temperature above 0.5 T_M.

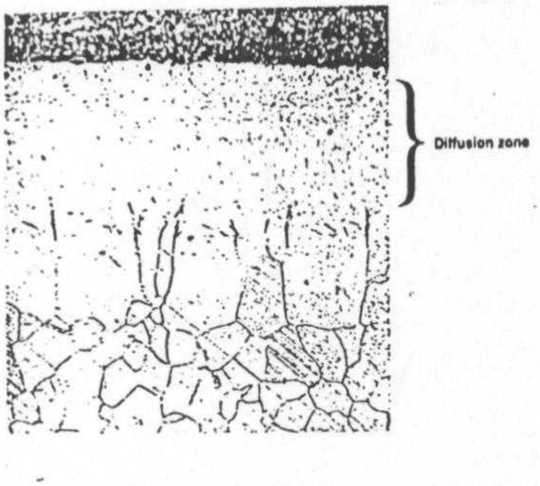


Fig.2 Optical micrograph showing the cross-section of the structure of pack aluminized low-carbon steel

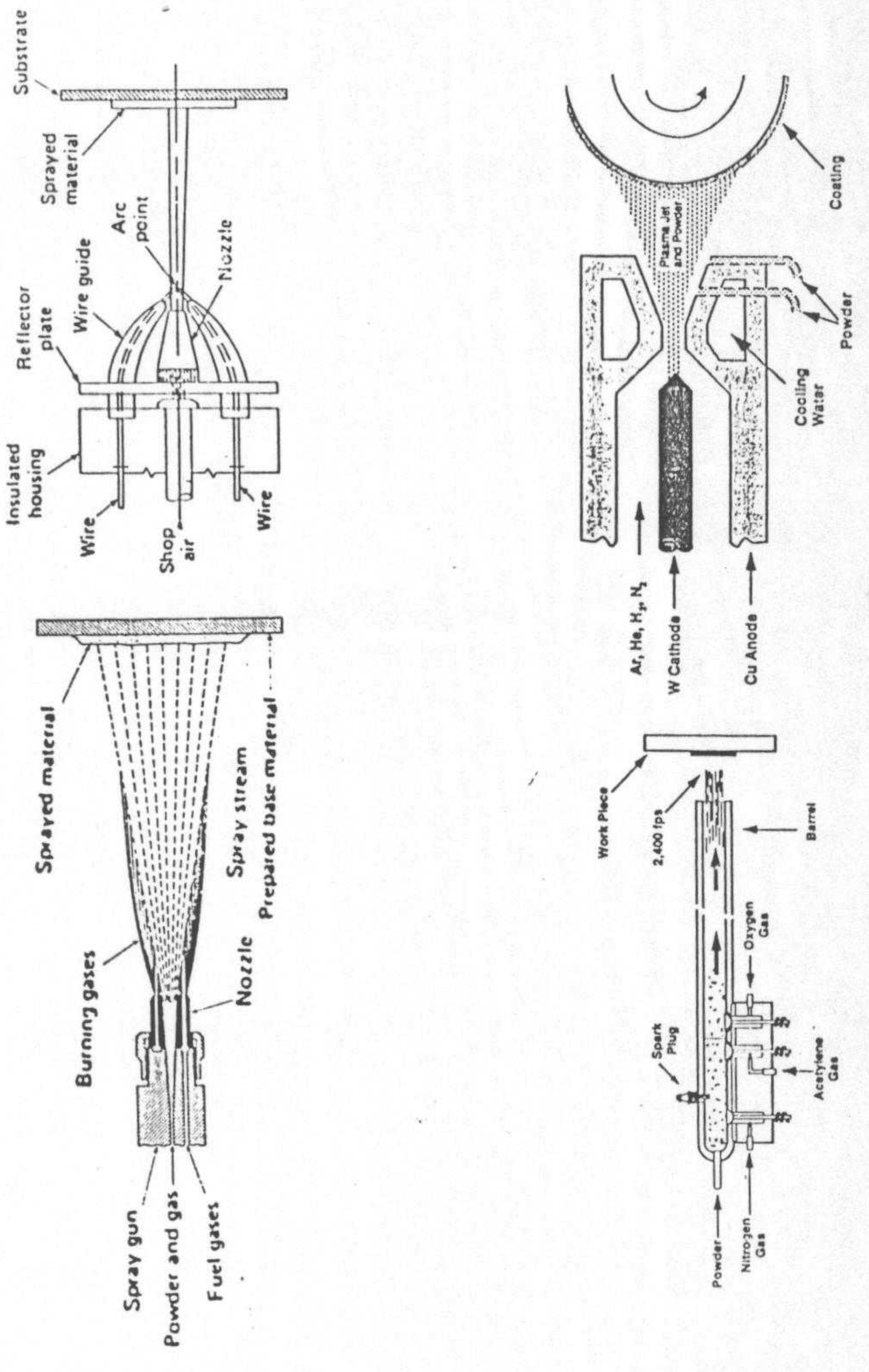


Fig.3 The schematic set-up diagrams for four different thermal spray techniques - a) flame spray gun, b) electric-arc spray, c) detonation gun process and d) plasma spray process

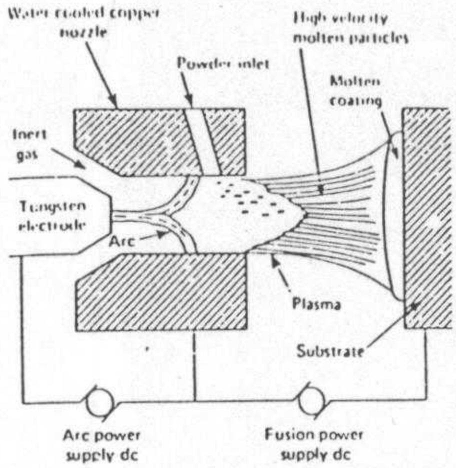


Fig.4 The schematic diagram of transferred plasma arc spraying device

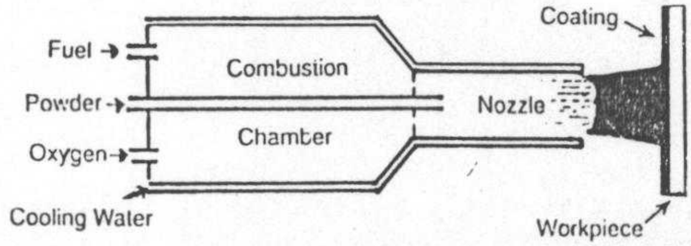


Fig.5 The schematic diagram of high velocity oxyfue. process device

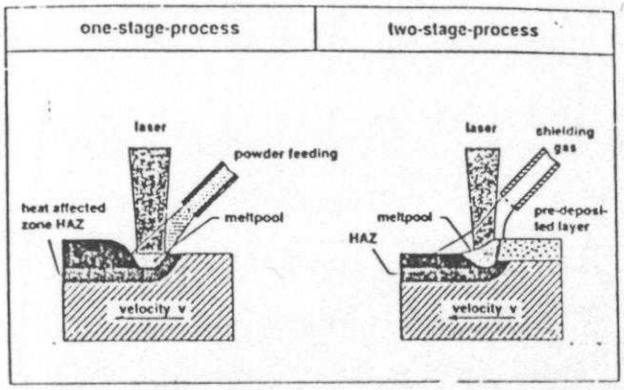


Fig.6 One and two stage processes of laser surface alloying

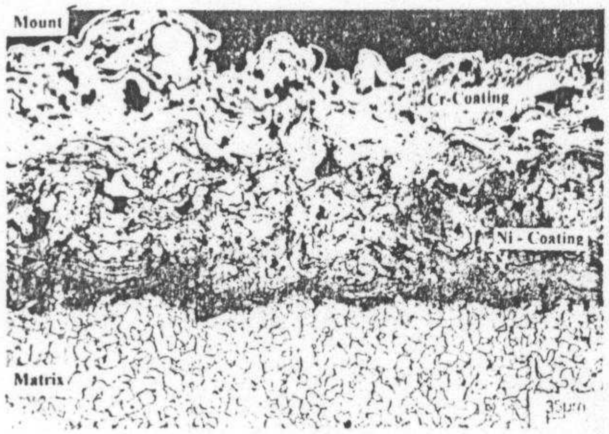


Fig.7 Optical micrograph showing the cross-section of the plasma Ni+Cr coated mild steel

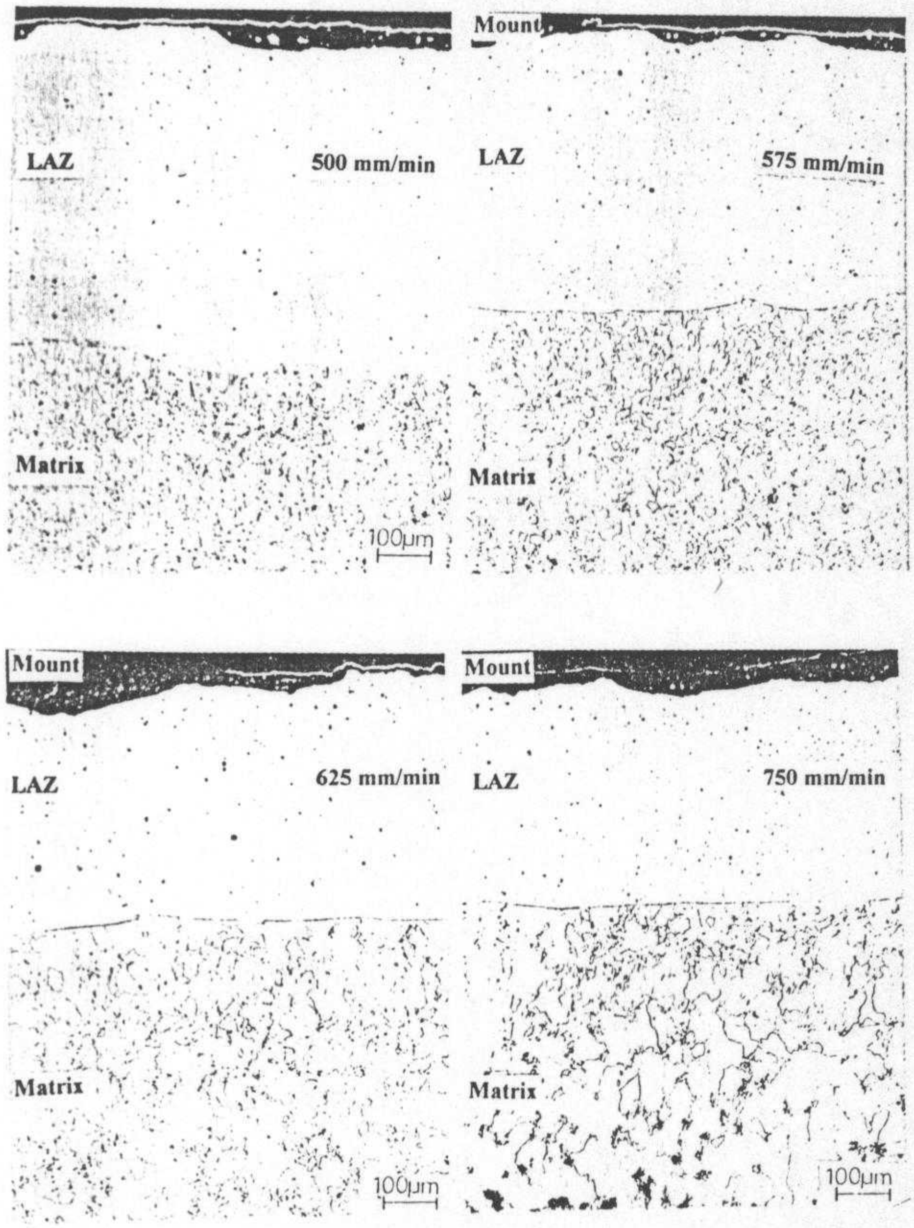


Fig.8 Optical micrographs showing the cross-sections of the laser Ni + Cr alloyed mild steel specimens with varying laser sweep speeds, a)500 mm/min, b)575 mm/min, c)625 mm/min and d)750 mm/min

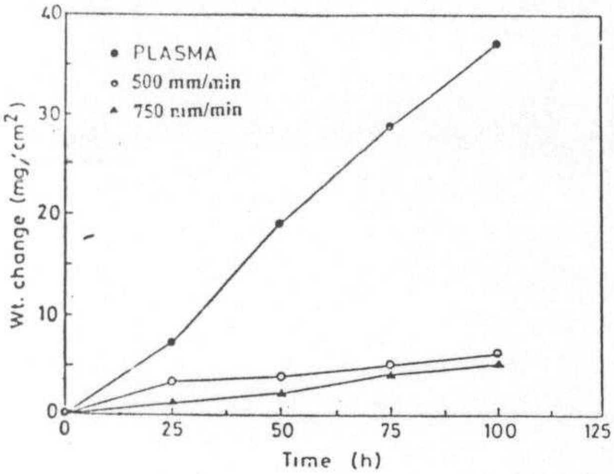


Fig.9 Linear plot of weight gain vs time for the oxidation of Ni + Cr plasma coated and laser treated specimens

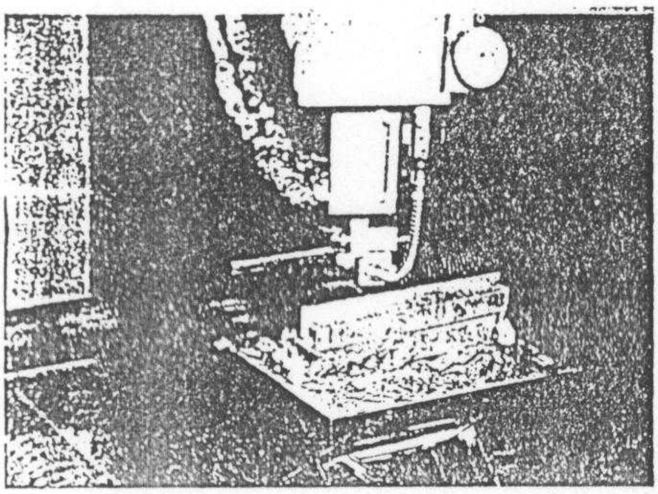
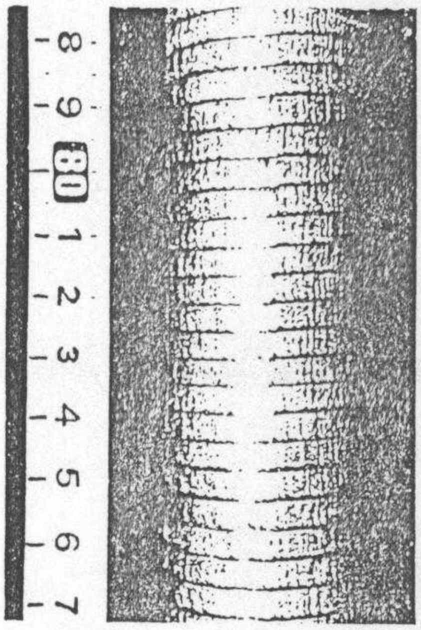
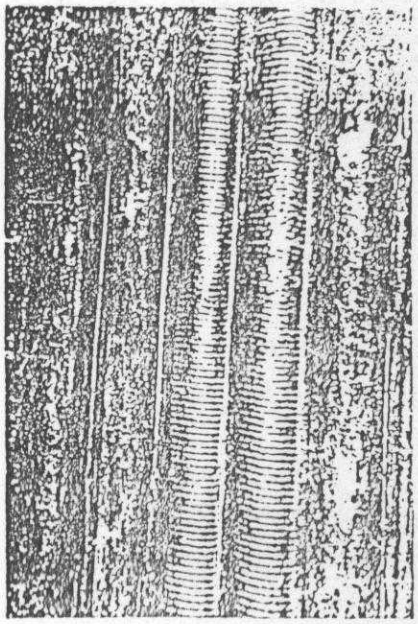


Fig.10a



Before Exposure

Fig.10b



After 1 year Exposure

Fig.10c

Fig.10 Photographs showing a) CO_2 laser cladding procedure and b) unexposed and exposed 2.25 Cr-1Mo steel cladded with Ni-25Cr specimens in actual heat exchanger conditions for one year.

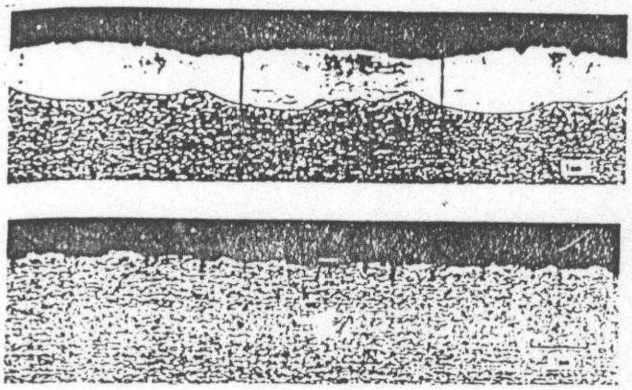


Fig.11 The optical micrographs of the cross-sections of the exposed CO_2 laser cladded 2.25 Cr-1Mo steel with Ni-25Cr specimens in actual heat exchanger conditions for one year

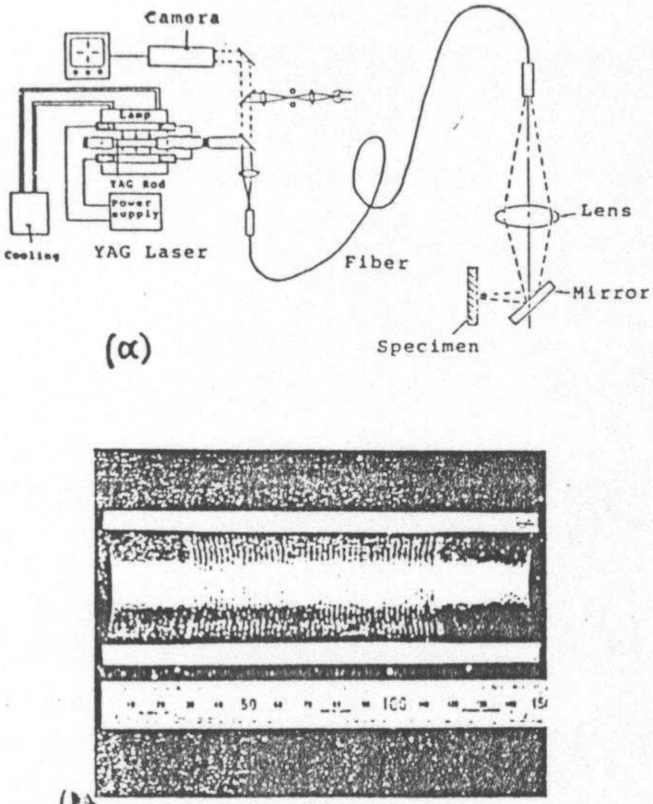


Fig.12 a)The schematic diagram of Nd: YAG laser cladding sytem and b)typical appearance of laser clad pipe

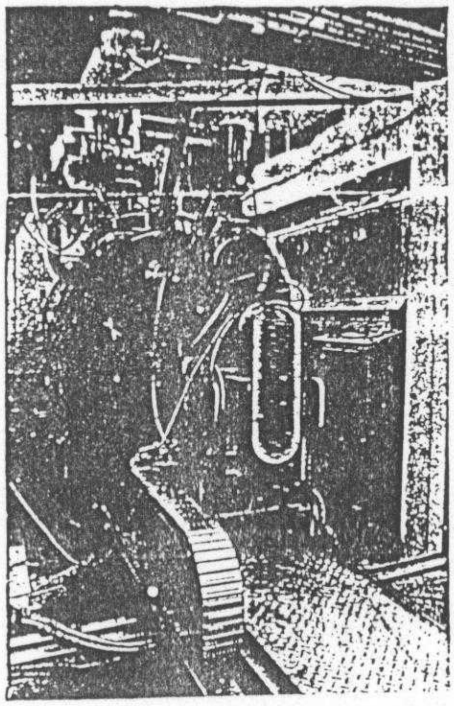


Fig.13 Photograph showing the set-up of LPC plasma laser hybrid thermal spray apparatus

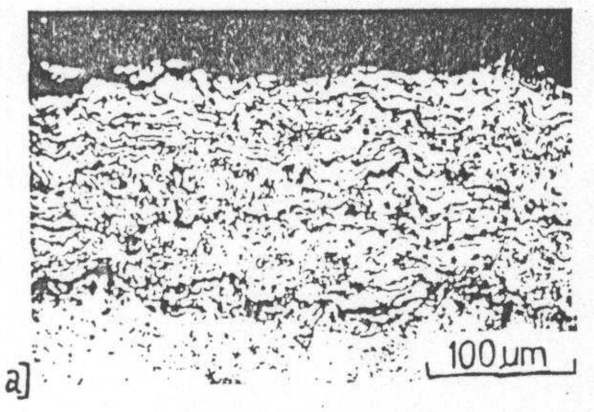


Fig.14 Optical micrographs showing, a) TiN(Ti) coating sprayed by N_2 plasma in N_2 atmosphere, and b)laser irradiated TiN coating in N_2 atmosphere

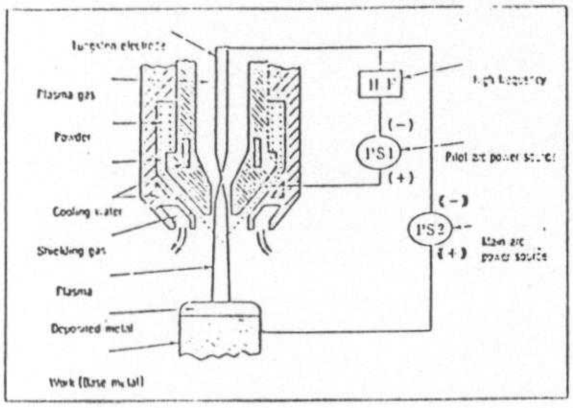


Fig.15 The schematic diagram of plasma powder welding process device

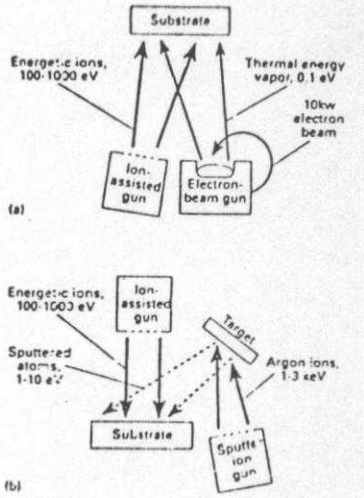


Fig.16 Two common ion-beam processing techniques: a) Ion-beam-assisted deposition (IBAD), and b) Dual-ion beam sputtering (DIBS)

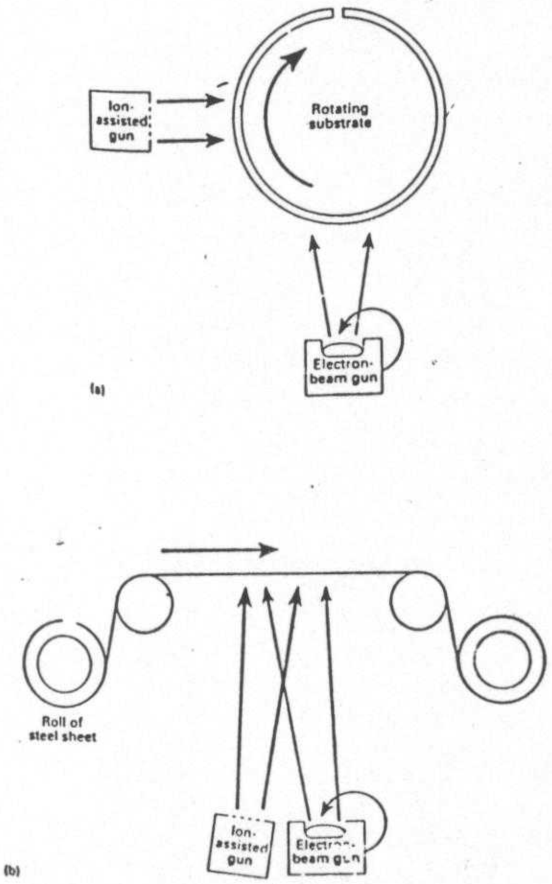


Fig.17 Two methods used for large area, high volume implementation of ion-beam-assisted-deposition, a) for optical films and b) for steel sheet