Coatings and applications produced by "Purecoat$_{TM}$" an improved shrouding technique.

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Abstract

Arc spraying has always been the most cost-effective way of thermal spraying metal alloys but oxide content and degradation of the alloy by loss of particular alloying elements have limited quality of the coatings. In this paper a process is described which greatly reduces degradation and improves coating density and oxide content. Corrosion behaviour both in aqueous and high temperature environments is markedly improved.

For aqueous applications coatings of Inconel 625 were tested in a potentio-dynamic cell and by salt spray testing to evaluate both the inherent properties and the permeability of the coating and significantly improved behaviour was found in both cases.

For high temperature corrosion, samples of FeCrAl were tested in air and in a sulphidising environment with and without thermal cycling. Coatings of NiCrAl and NiCrTi were also examined. The coating types and test regimes were aimed at specific practical applications such as fireside corrosion in boilers and waste incinerators, hot oxidation of flare stack burners etc. In the aqueous situation valves and process vessels are being examined as candidate applications for Inconel 625 coatings.

Introduction

Thermal spraying is by no means a new technique. Invented in 1912 in Switzerland, it is well established and widespread with coatings produced in this manner being used in all manner of industries. However, so varied are the possibilities afforded by the process that it is continually evolving and growing with new methods and applications. One such evolution is the Purecoat$_{TM}$ process.

A little over three years ago a group of seven interested companies set up a European Economic Community funded BRITE project to find a ways of improving the coating quality of existing spraying techniques, without significantly raising the operating cost. The starting point for such an exercise is to analyse the problems with existing technologies and to do that one has to understand something of the structure of a metal-sprayed coating.

All forms of thermal spraying involve the projection of small heated particles of material at a prepared substrate. Upon impact, the particles spread and freeze, adhering to asperities on the surface as they do so. As more and more particles follow, they land on each other and together form a continuous coating. Upon the properties of each of those particles depends the quality of the final coating. For instance a cold particle will not deform properly at the surface and will lead to porosity around it and a poor cohesive strength. On the other hand if the particle is too hot and exposed to oxygen it will oxidise and the coating will contain a large amount of oxides as well as the desired metal. How can we avoid these problems?

Arc spraying is a process that uses a wire feedstock melted by an arc. Because of this it is not possible to produce unmelted particles. This solves the first problem of ensuring that all the particles are melted. Now the question remains as to how to stop the oxidation.

The obvious answer is to spray using an inert gas in an inert gas chamber. This has been done on various occasions since the 1950's by Metallisation and by others and it works. Even coatings of Titanium can be produced with almost no oxidation. Figure 1 shows and inert chamber arcspray coating of Titanium enveloping Silicon Carbide fibres intended as reinforcement. However, the use of a chamber means that the components are limited in size and fixed in location and one of the great benefits of thermal spraying may be lost. How much better would it be to be able to shroud the spray in inert gas so as to have a truly portable inert environment for spraying.

This idea is also not new. Patents and papers for shrouding of plasma spray systems go back to the 1960's and varying levels of success have been achieved because it is not as easy as it would at first appear

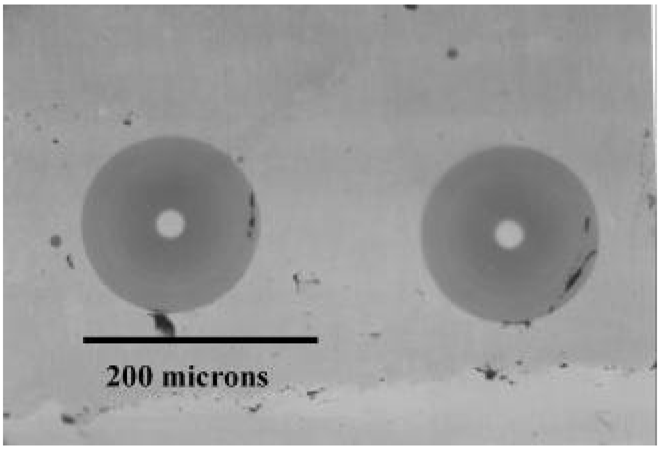

Figure 1: Strengthening fibres embedded in a titanium matrix Arcsprayed under argon atmosphere in a chamber

If one just puts the spray head into a plain tube and uses inert gas as the propellant then the divergence of the spraystream within the tube tends to coat the inside with molten material, which builds up and finally obstructs the spray. Furthermore, as the fast moving jet of gas exits the tube it creates a region of low pressure and the surrounding air is sucked into the inert gas diluting it to the point of uselessness within a short distance. Houben and Zaat described such problems in the seventies (1). How can these problems of spray divergence and oxygen entrainment be overcome?

The problem was attacked on two fronts. On the one hand Metallisation experimented with various designs of head to cause the spray to be more concentrated. This was a conventional iterative process making components and doing static spot spray trials to evaluate the particle mass distribution radially across the spraystream. The outcome was a compound spray concentrating arrangement, which will not be discussed further in this paper.

Another of the partners in the project, ESIL in Dublin, modelled the arcspraying process by finite element techniques using a Cray Supercomputer. This in itself is not easy, bearing in mind the random nature of the particle production in arcspraying and the asymmetry of the spray head. In addition to a simplified geometric design of the head, information such as gas mass flows, metal mass flow and typical particle size distributions had to be input into the model. The outcome of each run of the model was a series of charts showing the velocity and trajectory of the particles, the gas velocities and vectors and the concentration of oxygen present at various positions in front of the shroud. The predicted recirculation of the surrounding air could be seen clearly at the exit of the shroud. The models clearly predicted that no practical amount of shrouding gas fed through the atomising system of the sprayhead could prevent the ingress of air from around the shroud. Indeed the more gas was supplied to the nozzle the worse the air entrainment.

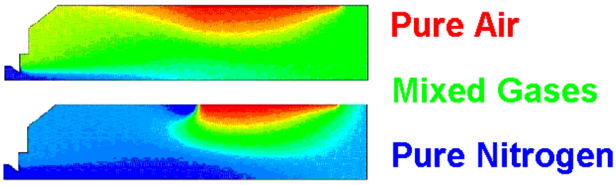

Figure 2. Colour coded predictions of Air concentration. The figure above is effectively a plain tube and that below an optimised shroud

The computer model produced by was able to predict the levels of oxygen in the gas stream at various distances downstream and radial distances from the spray centreline. At the laboratories of CISE in Milan, these results were confirmed by physical measurements of the oxygen concentrations at a variety of positions in front of the shroud. There was a remarkable consistency between the theoretical and experimental results

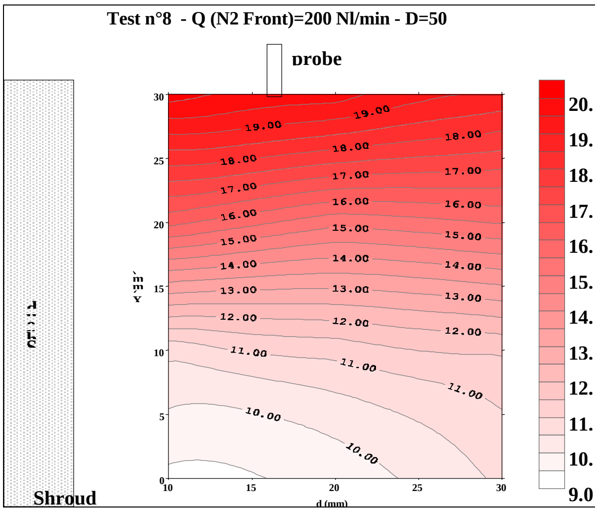

Figure 3. Map of measured oxygen concentration from a real system

From these results and knowing from our measurements of divergence that almost all the spray fell within the low oxygen region, we were able to predict that the coating material would not be heavily oxidised in flight.

In parallel with the results from the modelling, prototypes were built to test the divergence and the patterns of flow.

APPLICATIONS

From the very outset of the project, it was intended to target the results towards specific application areas, which were of interest to the end-user members of the consortium. ENEL, the largest of these, is the Italian State owned power generation utility. It therefore operates a multitude of different types of power generation plant including coal-fired boilers, gas turbines and hydroelectric plant. Because of this, coating testing was done on specific alloy systems directed at solving particular real problems. These could be defined as High temperature oxidation and corrosion and wet corrosion. For other smaller end users matters such as coating conductivity and ductility were also investigated.

High temperature oxidation and sulphidation.

The same factors arise in the protection of components against high temperature oxidation and sulphidation. In this case alloys high chromium alloys or alloys with chromium and aluminium such as Metallisation 78E 86E and 88E are used. The chromium and aluminium form an adherent oxide scale, which inhibits further corrosion. Where the coating is already oxidised the corrosive species migrate along the boundaries and allow the coating to be corroded internally as well as from the surface. All of these materials rely on providing a dense resistant barrier of an alloy, which is not degraded by the spraying process. Normal coatings fail due to degradation of the alloy and penetration through the coating. The Purecoat process minimises these deleterious effects leading to better performance and longer life.

Wet Corrosion Resistant Alloys e.g. Inconel 625

These alloys provide corrosion protection by providing a resistant barrier layer. They offer protection by readily forming an adherent oxide film, usually of chromium oxide, on their surface, which inhibits further corrosion. However, this readiness to form oxides mean that normally sprayed coatings will contain oxidised particles, which are therefore depleted in chromium. If the material is depleted in chromium, it is clearly no longer the intended material and cannot be expected to perform as expected. The fact that a conventional coating comprises depleted and non depleted zones means that it is no longer homogeneous and internal electrolytic cells can be set up causing dissimilar metal corrosion. Research has also shown that these oxide layers around the particles and chromium depleted regions are prematurely attacked. Therefore, they can act as a path for further oxidation and penetration of the oxidising medium to the substrate. Hence, the lower the degradation and oxide content of the coating the better. Coating density is also very important in reducing the paths along which the corrosive medium can migrate.

Coating Ductility

Some coatings are applied to rolls in the printing industry. These rolls are subsequently mechanically embossed to produce a suitable texture for the carriage of ink , glue or water for various processes. The mechanical embossing process is akin to knurling and severely strains the metal surface. Hence conventional coatings, being full of defects and not at all strain tolerant, break up and are not suitable. Indeed cracks often appear in the surface of electroplated copper rolls of this type at the roots of the embossed forms. If it were possible to obtain a sufficiently ductile copper coating it may be possible to replace electroplating and to bring the refurbishment process within the reach of more general engineering workshops.

General coating trials

Coatings of these types were examined within the laboratories of CISE and ENEL. The following tests were carried out in general

- Optical and or SEM metallography
- Bend tests 180° over a 12 mm bar
- Adhesion tests to EN 582
- Macro and Micro hardness tests

As part of the metallography, quantitative evaluations of porosity and oxide content were carried out using image analysis.

General results

Micrographs (Further Micrographs can be found in the appendix)

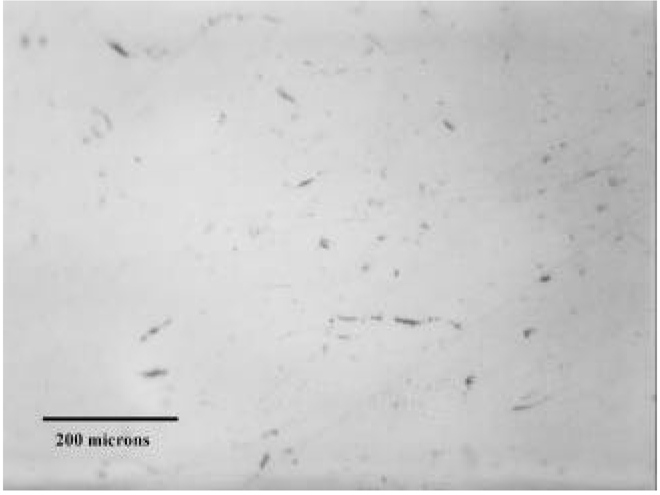

Figure 4a: 86E, a Nickel Chromium Aluminium alloy showing extremely low levels of oxide and porosity.

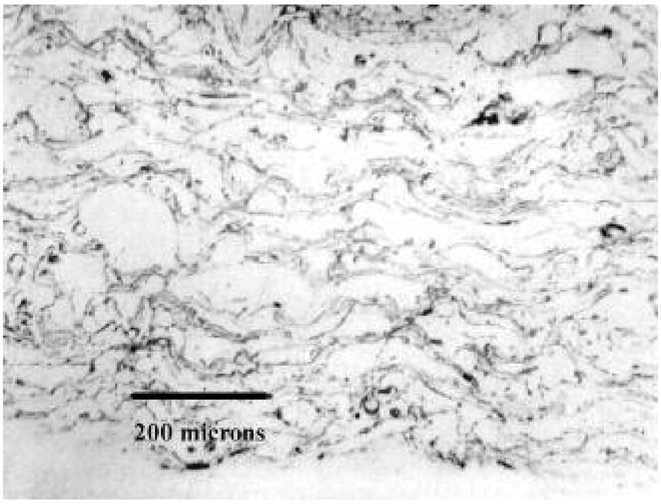

Figure 4b: a similar alloy conventionally sprayed showing significant levels of oxide and porosity.

Oxides and Porosity measurements
The results of these measurements are to be found in Table 2 in the Appendix. In all cases except that of Boron containing alloys the oxide levels and porosity are much reduced.

Hardness trials
The results of both macro and micro hardness trials can be found in Table 3 in the appendix. Hardness values were not unusual being not much changed for the alloys compared to those sprayed in air.

Bend Tests
Satisfactory bend tests for all the tested materials could be obtained. Some coatings such as Stellite 6 exhibited considerably higher residual stress, presumably as a result of improved particle cohesion and substrate preparation was critical to achieving a sound result.

Adhesion tests
Adhesion tests to EN582 were carried out on several materials as shown in Table 4 in the appendix. The adhesion levels found were very similar to those of conventionally arc sprayed counterparts.

Application Testing

Having made the device and seen that the microstructures were promising, the coatings were tested in the laboratory but in realistic environments. Three application areas were chosen, high temperature sulphidation as is found in boilers burning low-grade coal and orimulsion, wet corrosion such as would be encountered in sea water valves or chemical plant and ductility such as is required in the manufacture of inking rolls. For the hot sulphidation tests coatings were made on the entire surface of cylindrical samples and subjected to a thousand hours of testing under a controlled atmosphere in a specially designed furnace. The pieces were examined at 250-hour intervals and weighed to discover the weight gain due to sulphide formation.

Thermal Fatigue can be a problem in coated materials and so 50mm diameter tubes were coated on one side only and thermally cycled for 1000 hours.

To assess the effects upon wet corrosion properties we took one of the most widely used corrosion resistant alloys, Inconel 625, and sprayed it onto carbon steel plates. These plates were tested in two ways. Firstly electro-potential tests were used to compare the new sprayed material with conventionally sprayed Inconel 625. Standard Inconel 625 readily passivates at a certain level. The closer to this level that the sprayed coating passivates the more like the wrought material will be its behaviour.

The mechanical and electrical properties can also be enhanced. Figure 5 shows a gravure cylinder being sprayed with copper. Conventional arcspraying does not produce a surface finish good enough for use with the gravure printing process where a highly polished surface is etched with the image to be printed. Similarly the electrical properties are much improved with the electrical conductivity approaching 80% of that of wrought copper compared to 40% for a conventional sprayed copper. The reason for the difference is clear when the microstructure is examined.

In Figure 6, the layer below is conventionally sprayed and displays large quantities of non conductive oxide around and within the spray particles. In the upper layer sprayed by Purecoat such oxides have almost disappeared.

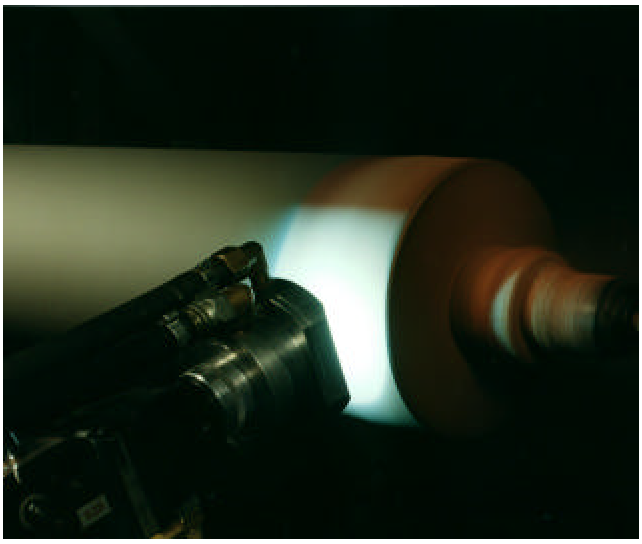

Figure 5. A gravure cylinder being sprayed by the new process

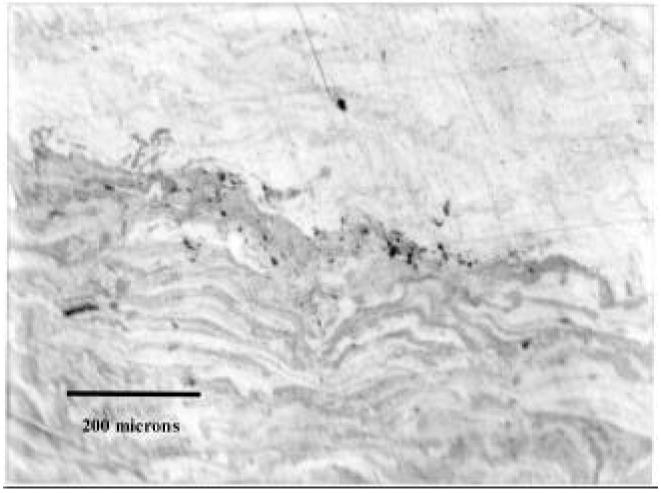

Figure 6 Microstructure of copper(x100) conventional below, Purecoat above

Application test results

High temperature Oxidation

- For Purecoat sprayed 88E NiCrTi corrosion weight gain was still increasing slowly through 6 mg/m2 after 1000 hours
- For Purecoat sprayed 78E FeCrAl corrosion weight gain stabilised at around 3.5 mg/m2
- Samples with smooth surfaces gave better corrosion results than those with rough surfaces
- Spalling did not take place on samples of either 88E or 78E after 100 cycles
- Oxidation can take place at the interface as well as the surface

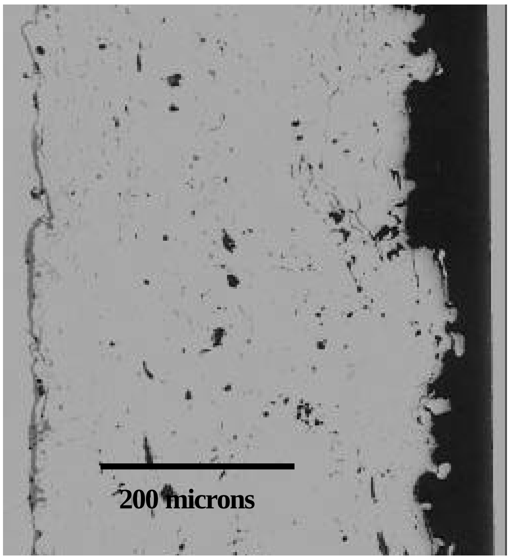

Figure 7 Micrograph (x100) of 78E coating on one side of a tube after 100 thermal cycles Note absence of lifting at interface but growth of an oxide film at this point.

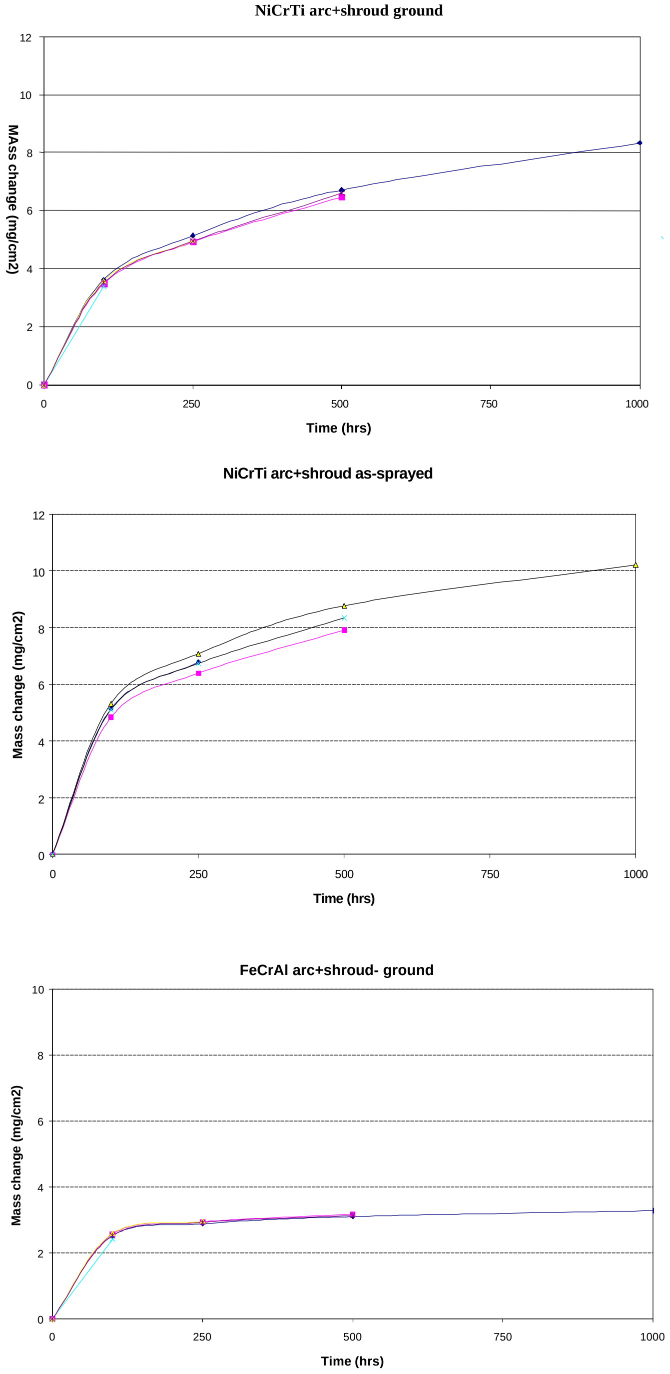

Figure8 Weight gain/time plots for FeCrAl and NiCrTi

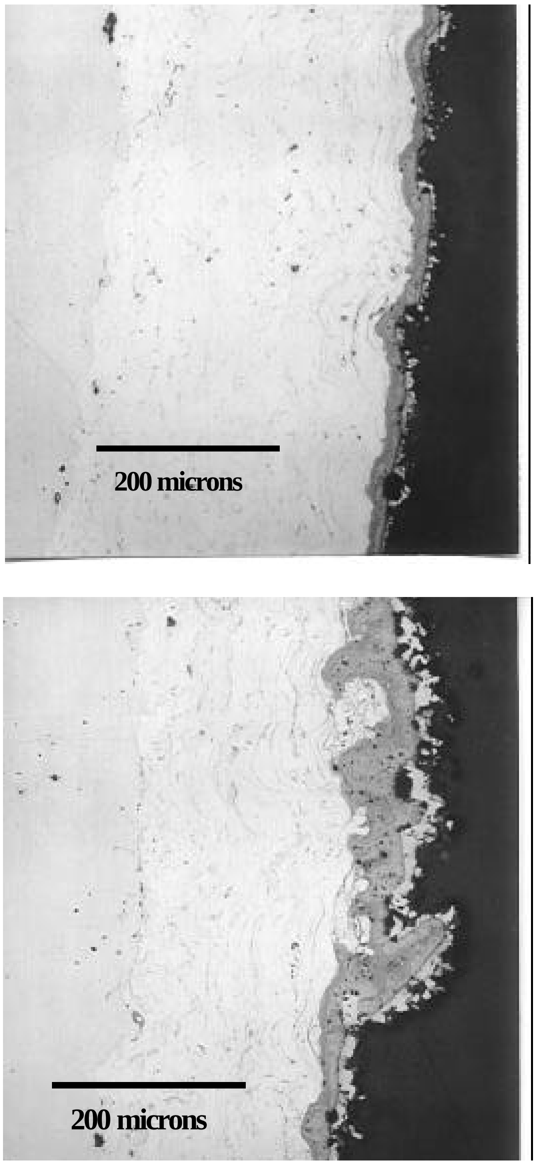

Figure 9 Comparison between the attack morphology of coatings of 88E (NiCrTi 100x), as sprayed (below) and ground (above), all after 1000 hours of exposure in a sulphidising environment.

Wet Corrosion

- Electro-potential tests in 5% Sulphuric acid showed significant difference between Purecoat$_{TM}$ and conventional spray with the former behaviour being closer to that of wrought material
- Salt spray tests give significantly better results. The only through attack arose near unsealed edges rather than through the body of the coating

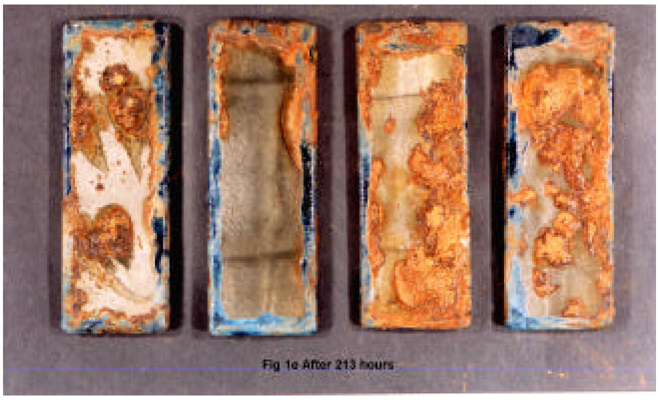

Figure 10.Carbon steel plates coated with Inconel 625 (not sealed). The coating one from the left is applied using the new technique and the others are conventional. The plates have been exposed to Salt spray at 35ºC for 213 hours

Print Roll Trials

The coating is more ductile and can as sprayed be knurled in some areas. However, this is unreliable and so far impractical. Heat treatment resolves the cohesion problems but adds complexity and cost. This is the subject of continuing trials on parameters such as traverse and throughput rates to provide a consistent result.

Discussion

High Temperature Corrosion.

For similar levels of chromium content Iron based alloys are known to give better sulphidation resistance than Nickel based alloys but even so this result is surprising since the FeCrAl only contains 25% Chromium compared to 45% in the Nickel alloy. There is an enormous cost differential between the Iron and Nickel based alloys and hence more serious attention should be paid to the FeCrAl.alloy. There have been concerns about thermal fatigue in the past and there are always concerns about the ability to achieve adequate substrate preparation on site. However it looks possible to overcome these difficulties. The cycling tests show that, with reasonable substrate preparation, spalling does not seem to be an issue.

HPHVOF 50/50 Nickel Chromium coatings actually gave higher corrosion rates than the new process FeCrAl so that the new process is not only attractive because of cost but is genuinely at the forefront of performance.

Wet Corrosion

There is clearly a difference in the behaviour of Purecoat Inconel 625. This is now being explored for the internal protection of vessels in petrochemical installations.

Print Roll Trials

Whilst progress has been made in this area further work needs to be done to obtain a consistently satisfactory result.

Costs

With the use of relatively large quantities of Nitrogen (~1.5m^3 per minute), it may sound as if this is an expensive system to operate. However if all the costs are analysed this is found not to be so. The capital cost of a system is around 25% more than for a conventional Arcspray system but these are already relatively inexpensive compared to other spraying techniques. The only added running cost of such a system is the use of relatively large volumes of Nitrogen. However, if we discount such inexpensive materials as zinc or aluminium, probably the most costly element of the total coating cost is the spray material. Taking a whole job cost approach and including labour, electricity and materials as well as consumable gases, the cost burden is much reduced.

For example, using a material such as a Nickel alloy costing £14.00 per kg ($9.52/lb), to spray a shaft 2 metres long by 200mm diameter to a thickness of 1mm would cost:

- £492.00 by HPHVOF
- £231.88 by conventional Arcspray
- £255.28 by the Purecoat$_{TM}$ spray process.

In other words it costs around 10% more to apply a coating by Purecoat$_{TM}$ than by Arcspray and about half as much as by HVOF.

Conclusions

1. A reliable and effective system now exists to produce low oxide and porosity coatings with the simplicity of operation normally associated with Arcspray.
2. In high temperature sulphidation trials such a coating performed better than an HVOF coating costing several times as much to apply.
3. Coating production costs are typically around ten per cent more than for conventional arcspray.
4. A wide range of materials can be sprayed and in general there is no loss of other properties such as adhesive strength etc.when compared to conventional coatings.

Refernces

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3. H. Kayser, "Spraying under Argon Atmosphere" Proc. 8th International Thermal Spray Conference, p123 - 130, Miami FLA USA Sept.27th – Oct 1st 1976

4. W. Milewski and M. Sartowski "Some Properties of Coatings Arc-sprayed in Nitrogen or Argon Atmosphere" Proc. 11th International Thermal Spray Conference, p467 – 474, Montreal, Sept. 8th – 12th 1986

5. E. Erturk and H-D Steffens "Low Pressure Arc Spraying in Comparison with Low Pressure Plasma Spraying" Proc. 11th International Thermal Spray Conference, p83 - 92, Montreal, Sept. 8th – 12th, 1986.

6. M. Vardelle, A. Vardelle, Ph. Roumilhac, P. Fauchais "Influence of the Surrounding Atmosphere under Plasma Spraying Conditions, Proceedings of the 9th National Thermal Spraying Conference, p117 – 122, Cincinnati OH USA Oct 24-27th 1988

7. S. Jamais, M. Creaven, C Rinaldi "Calculated and measured oxygen contents in the gas flows of a shrouded thermal spray process", in these Proceedings

8. C. Rinaldi, L. Ferravante, F.Uberti, P.Bianchi,"Extensive Characterisation of Dense and Corrosion Resistant Coatings Produced by Improved Shrouded Techniques",.in these Proceedings.

Appendix 1
Tables of Results

Table 1: Coating Material analysis.

WIRE	Fe	Cr	Ni	Co	Mn	Si	Al	Ti	W/Mo	C	B
60E	Bal	13.25	-	-	0.33	-	-	-	-	0.35	-
78E	Bal	25	-	-	-	-	5	-			
86E	-	20	Bal	-	-	-	3	-			
88E	-	45	Bal	-	-	-	-	3			
103T	Bal	28	-	-	1	-	-	-	-	0.3	3
100T	-	14	-	-	-	5	-	-	-	0.7	3
101T*			Bal				5		5		
Stellite 6	2.5	27	2.5	Bal	1	1		-	5W	1	-

Table 2: Coating Porosity and Oxide levels.

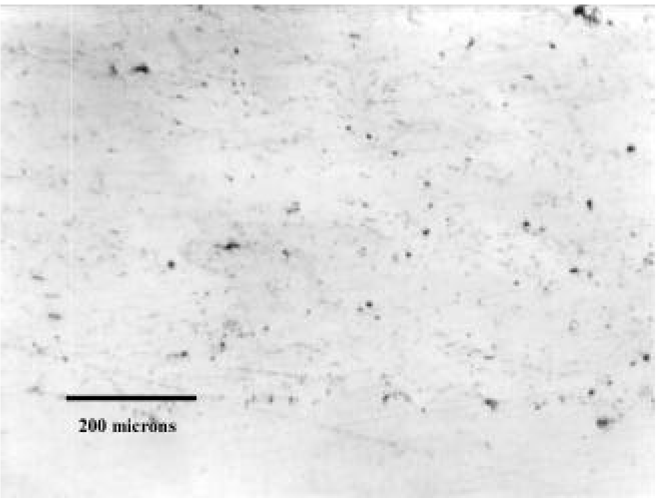
Coatings	86E	78E	88E	60E	St6	100T	103T	101T
Oxide (%)	5	4	2	0.8	3.5	0.7	3	2
Porosity (%)	0.5	0.4	0.6	0.4	0.3	1.7	3	0.6

Table 3: Coating Macro & Micro hardness values.

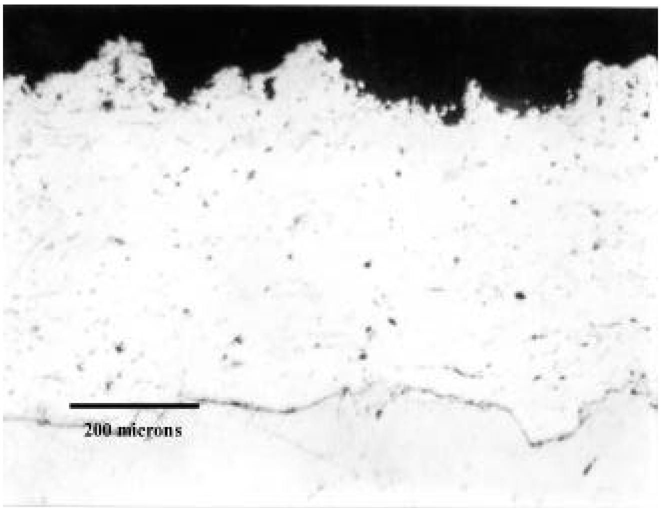
Coatings	86E	78E	88E	60E	St6	100T	103T	101T
Hardness HV 5Kg				257 ± 61		742 ± 30	866 ± 41	175 ± 10
Microhardness (300g)	215 ± 51	274 ± 51	283 ± 33	385 ± 47	440 ± 90	971 ± 71	981 ± 228	185 ± 26

Table 4: Adhesion Values to EN582 (Similar to ASTM 633).

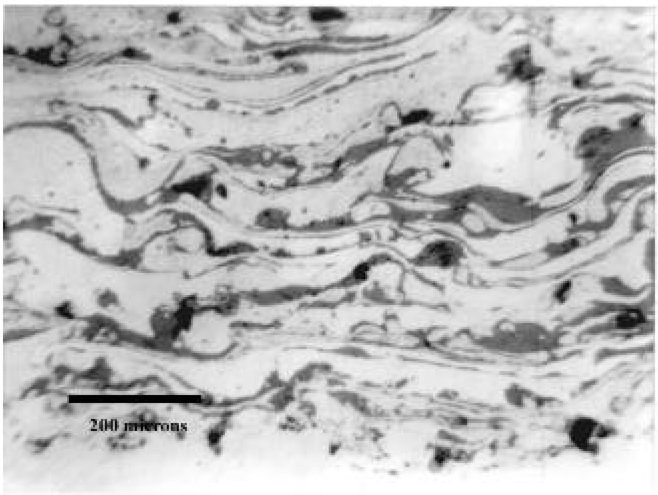
Coating / substrate	Spraying technique	Number	Adhesion (MPa)	Fracture
NiCrAl (86E)/A105steel	Purecoat$_{TM}$	4 of 5	41+/-2	Cohesive*
FeCrAl (78E)/A105steel	Purecoat$_{TM}$	4 of 5	39+/-5	Cohesive
NiCrB (100T)/AISI304steel	Purecoat$_{TM}$	4 of 5	38+/-7	Mixed
Stellite 6 / AISI403steel	Purecoat$_{TM}$	4 of 5	40+/-4	Cohesive



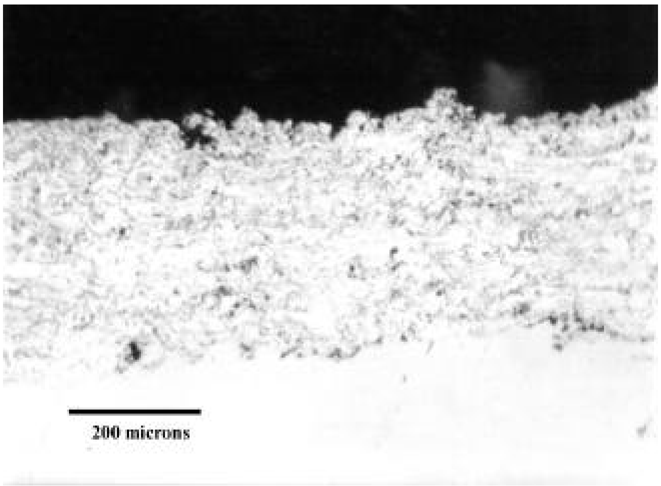
Purecoat 60E



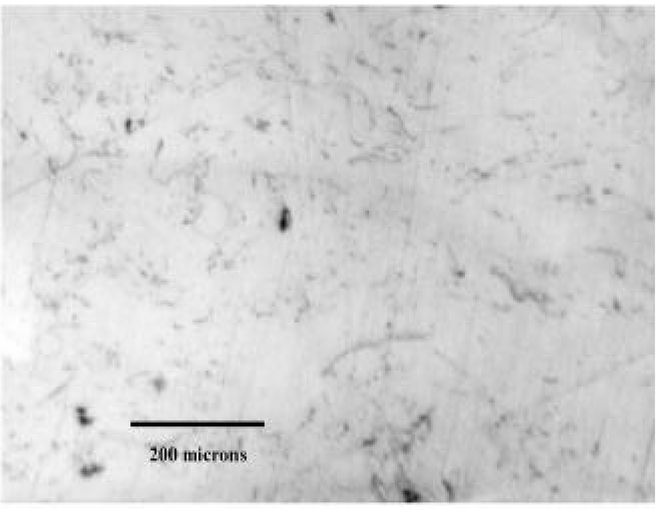
Purecoat Stellite 6



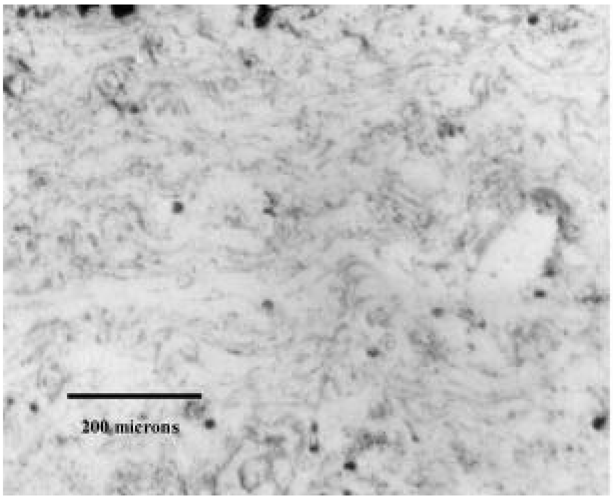
Conventional 60E



Conventional Stellite 6



Purecoat Inconel 625



Conventional Inconel 625