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The High Temperature Erosion/Corrosion Behavior of Industrial Thermally Sprayed Coatings

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Abstract

There are numerous industrial applications where materials are subjected to simultaneous high temperature oxidation/corrosion and wear (such as erosion). This combination often leads to accelerated degradation. Specific industries include: chemical, waste incineration, power generation and paper/pulp with typical applications including boilers and cyclones. Previous studies have established wrought material compositions and microstructures which can resist these environments. In searching for cost-effective industrial solutions, surface coating via thermal spray becomes attractive. However, the microstructural complexity of such coatings can make the simple extrapolation of bulk material behavior to these coatings dangerous. If these coatings are to be used more widely, a greater understanding of their high temperature erosion/corrosion behavior and the influence of coating process is required.

A range of Fe-and Ni-based alloys and thermal spray techniques were studied under various high temperature erosion/corrosion conditions. The critical erosion parameters of impact angle (30° to 90°) and temperature (up to 550°C in air) have been studied in an atmospheric fluidized bed test rig environment, using Al_2O_3 erodent at a typical impact velocity of 4m/sec and conventional high temperature erosion test equipment.

The important microstructural and mechanical features of the coatings and the effect of the thermal spray process are discussed in terms of their high temperature degradation mechanisms.

HIGH WASTAGE RATES OF BULK, WROUGHT alloys have been reported in many elevated temperature erosion environments which include coal and oil conversion industries. In some cases, the formation of a protective oxide scale at high temperature on a particular alloy can inhibit erosion; in other cases it can enhance it (1-2). Increasingly, the use of a tailored coating may be the only possible route to minimising erosion and they are finding increasing acceptance in coal-fired boilers (3).

Thermally sprayed coatings offer some potential in reducing erosion in such conditions because of the ability to combine hard particles with a matrix possessing good oxidation resistance. One problem is spalling due to differences in properties between substrate and coating (hardness, modulus, thermal expansion coefficient, etc.). In addition, a material's erosion rate depends on a wide variety of parameters (properties of the particle, target, temperature and the environment, etc.). The effects of such parameters are not completely understood for bulk materials and are more complex with a coating material. In this case, the coating microstructure is determined not only by its chemistry but the thermal spray process and the parameters used.

There exists a wide range of thermal spray techniques which could produce potential coatings for these environments. The range includes Air-Plasma, Electric Arc-Wire, High Velocity Oxy-Fuel (HVOF) and Spray and Fuse (S&F). In the coating of large industrial components a practical, cost effective solution is sought. Therefore, in addition to the coating performance there are issues such as on-site or off-site spraying, spray-rates, equipment mobility, ease of use, investment cost, etc. to take into account. This may determine that only one type of thermal spray technique is possible, but the alloy choice is open. Alternatively, the temperatures and corrosion environments may dictate that only a particular alloy class can be used and the thermal spray technique choice is open.

The effect of temperature and erodent impact angle for Fe-Cr bulk, wrought alloys in erosion conditions have been documented (1-2). However, for the unique microstructures of thermally sprayed coatings these effects have not been widely investigated to date. There has also been little or no work performed on the influence of the thermal spray technique on the high temperature erosion performance of one particular alloy.

One route to improving high temperature erosion performance of bulk and coating materials is to add inert hard particles. Previous high temperature erosion studies of hard particle containing coatings have shown the strong influence of hard particle volume fraction and temperature (4,5).

The purpose of this study was to investigate the combined effects of erosion impact angle, temperature and microstructure of thermally sprayed coatings on their high temperature erosion behaviour. Key issues addressed were the influence of spraying technique and the role of the coating microstructure and reinforcement rather than chemistry.

Experimental Details

Alloys and Thermal Spray Processes. All consumables (wires and powder) were manufactured within the Eutectic + Castolin Group. All arc-spraying was with metal-cored wires (1.6 mm ∅). Powders were gas and water atomized. All consumables were sprayed with standard equipment and recommended spray parameters on arc-wire, air-plasma and HVOF units.

For the UMIST testing all substrates were 316 stainless, with dimensions 30 mm x 110 mm x 3 mm. Preparation involved grit blasting and mechanically attaching the substrates to a metal block (to reduce overheating). Coating thickness for all materials was 0.7 mm and the maximum substrate temperature was held at 120 ˚C. All samples required for erosion testing were cut from the centre of one specimen by water jet cutting (to include coating and substrate). For the Tampere testing, coatings were applied to a tube substrate of 17 mm diameter and 32 mm length.

Microstructural Analysis and Mechanical Property Testing. The coating was characterized by sectioning, polishing and Optical Microscopy examination with a Leica DM RM connected to a Leica Quantimet 600 Image Analysis unit.

The microhardness (Vickers $HV_{0.3}$) was measured on the polished cross-section of the coated parts. This was performed automatically using a Qualimatest MultiMicro Station with automated X-Y table and Image Analysis. All hardness values are an average of 10 measurements.

The chemical analysis of the powder and coating was performed by Induction Coupled Plasma together with combustion methods for the light elements such as oxygen. For analysis of the coating, samples were spalled off the substrate by mechanical means.

Erosion Wear Apparatus. Two different units were used, one of the Corrosion and Protection Centre, University of Manchester Institute of Science and Technology (UMIST) in England and one of Tampere University in Finland. The UMIST erosion-corrosion apparatus, described elsewhere (1), consisted of a fluidized bed of erodent particles, a heating system and a specimen holder (cross piece on a rotating axle). The specimens and axle can rotate at a range of angular velocities vertically through the fluidized bed of particles (Fig. 1). The atmosphere is air.

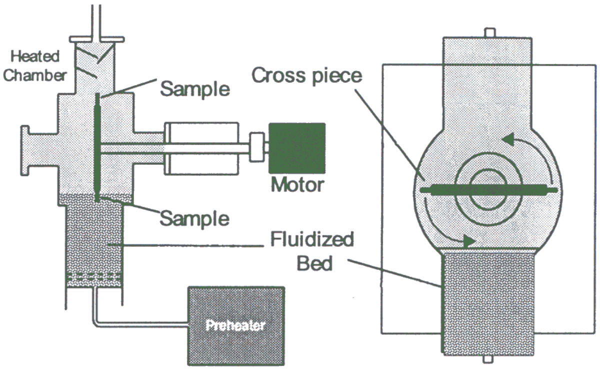


Fig. 1-Schematic of High-Temperature Fluidized Bed Erosion Testing Facility at UMIST, England.

The specimens were rectangular (thickness 4 mm, width 6 mm and length 10 mm with the coating on the outer surface) and were secured flush to the surface of the cross piece to give an impact angle of 90˚ between the particles and the main coating face. In addition, one end of the cross-piece was modified in order to have the surface of the specimen at a 30˚ angle to the erodent, whilst rotating. Where possible the same material was tested simultaneously at 30˚ and 90˚. (It should be noted that the particle concentration at the changing angles is difficult to keep constant).

The bed erodent was alumina (average particle diameters 200 μm and 600 μm). Due to degradation, the erodent was replaced at regular intervals. The experimental run was 20 hrs. and the velocity between the specimens and particles was 4 $m.s^{-1}$. Following the tests, the specimens were cooled to room temperature, degreased in acetone, and thickness loss measurements were made using a digital micrometer, with a precision of 1 μm. Measurements were taken across the surface to avoid edge effects. The eroded surface was examined by Scanning Electron Microscopy (SEM) and Optical Microscopy in cross-section.

In addition to this erosion method, an alternative unit at Tampere University in Finland was used which consists essentially of a static coated tube being eroded in a steam of parallel flowing erodent (quartz of grain size between 100-600 μm) which is shown in Fig. 2 and described in more detail elsewhere (6).

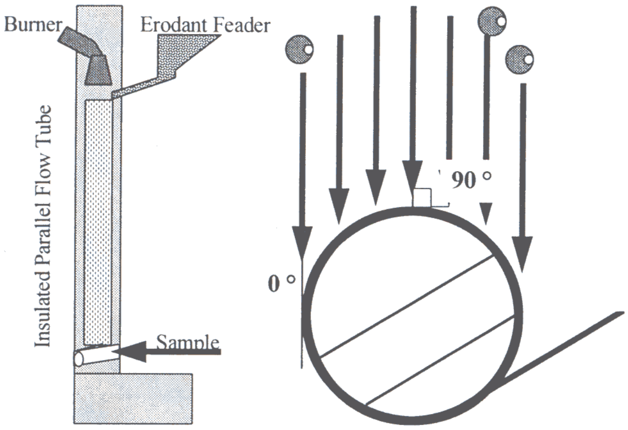


Fig. 2-Schematic of High Temperature Erosion Testing Facility at Tampere University, Finland.

Here the particle velocity is 25 m.s.$^{-1}$ and the tube sees the whole range of impact angles. The erosion loss is determined from the weight change of the whole coated tube after a set test period (16 hours) and is consequently an average loss at all angles. The testing was at 3 temperatures 20 ˚C, 300 ˚C and 500 ˚C. The alloys tested are detailed in Table 1.

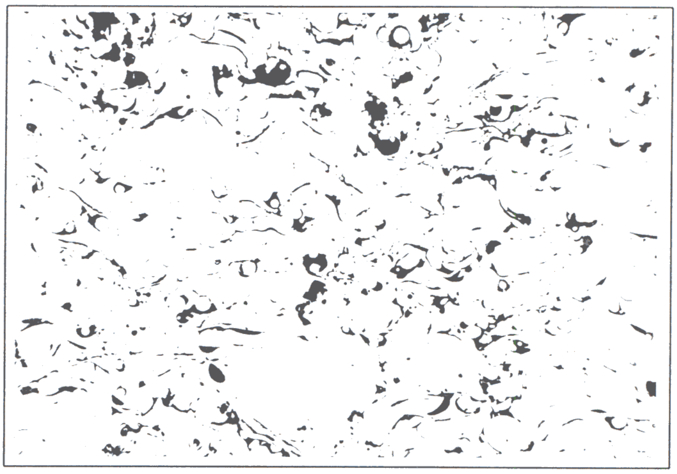
Table 1. Details of Coatings Studied

Code	Form	Spraying	Chemistry	HV0.3	Testing
A	Wire	Arc-Wire	Fe-Cr-Ti	553	Tampere
B	Wire	Arc-Wire	Fe-Cr-Al	264	Tampere
C	Wire	Arc-Wire	Fe-Cr-Al+20% Hard particles	446	Tampere
D	Wire	Arc-Wire	Fe-Cr-Ti	553	UMIST
E	Wire	Arc-Wire	Fe-Cr-Al	264	UMIST
F	Wire	Arc-Wire	Ni-Cr	281	UMIST
G	Powder	Plasma	Fe-Cr-Al	348	UMIST
H	Powder	HVOF	Fe-Cr-Al	383	UMIST
I	Powder	HVOF	Fe-Cr-Al+30% Hard particles	470	UMIST
J	Powder	Plasma	Fe-Cr-Al+50% Hard particles	433	UMIST

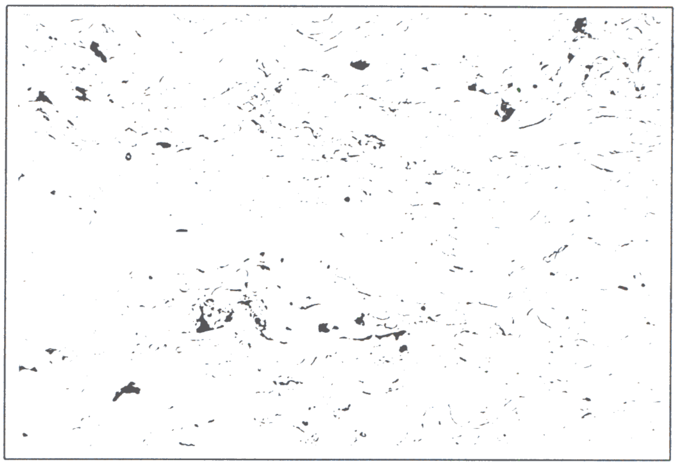
Results and Discussion

Coating Microstructures. The microstructures of typical sprayed coatings are shown in Fig. 3. Image analysis was used to estimate the volume fractions of porosity and oxide. This proved extremely difficult to accurately quantify due to the variation in the nature of the coatings.

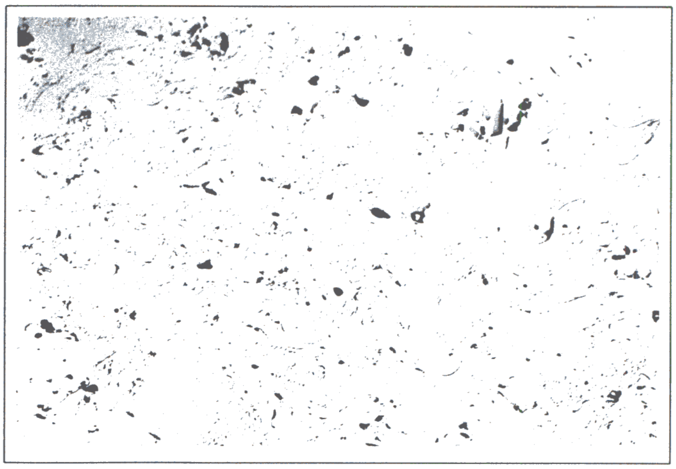
Fig. 3a, 3b and 3c represent coatings produced via plasma, arc-wire and HVOF respectively and illustrate not only the large variation in the type of microstructure, but also the variation in coating density for the same alloy composition. Fig. 3d represents a microstructure typical of that reinforced with a hard phase.



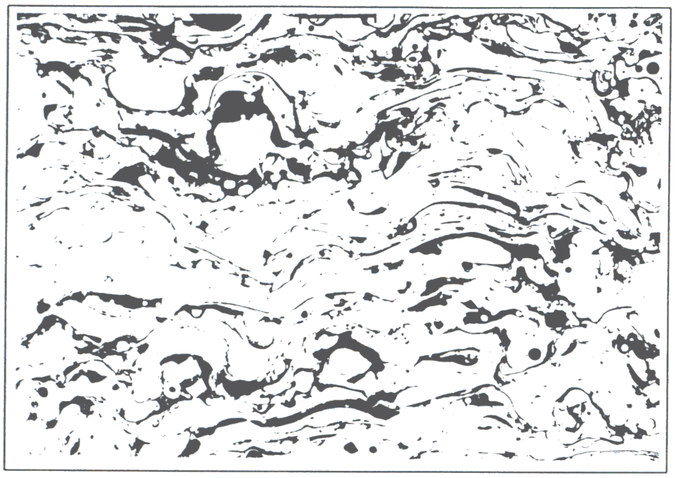
a) Plasma Sprayed Coating G



b) Arc-Wire Sprayed Coating E



c) HVOF Sprayed Coating H



d) Arc Sprayed Containing Hard Particles Coating C

Fig. 3-Optical Micrographs of FeCrAl Coatings Produced with Different Thermal Spray Methods. (Magnification is 100 x).

Coating Mechanical Properties. The mean Vickers hardness of 10 measurements at HV 0.3 are given in Table 1. The variation in the coating microstructure and the presence of pores and hard particles (either as oxides or as an intentional second phase) complicate the hardness measurements.

Effect of Impact Angle and Temperature on Material Erosion Rate. Coating E was tested at a range of impact angles and temperatures with the results shown in Figure 4.

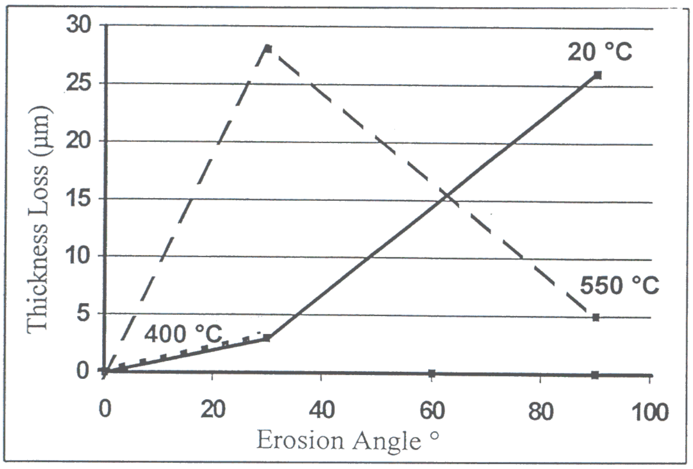


Fig. 4- Impact Angle and Temperature Effects on Erosion of Arc-Sprayed Coating E.

It is observed that at 20 °C the erosion rate increases steadily with impact angle up to 90°, behaviour typical of a brittle material reported elsewhere (4,5). With increasing temperature there is an increase in erosion loss, but only above 400 °C. From 20 °C to 400 °C at low angles, erosion loss is minimal. An increase of 150° C above 400 °C increases erosion loss by an order of magnitude. The erosion of brittle materials is observed to be a maximum, and that of ductile materials a minimum, at impact angles of 90° (4,5). Although this relationship can reverse depending on the erosion conditions (i.e. particle shape (5), velocity (7)), it is observed that for the erosion with angular particles, brittle materials exhibit highest erosion rates at 90° (5). This points to a transition to another wear mechanism between 400 °C and 550 °C. At 550 °C, with increasing angle the wear rate rapidly falls. At 90°, an increase in temperature has reduced the erosion loss, exactly the reverse of than recorded at 30°. Further, the form of the 550 °C curve is now typical of a ductile material (5). In conclusion, Coating E is showing a brittle to ductile transition in erosive wear behaviour above a critical temperature between 400 °C and 550 °C.

The thickness loss relationships with impact angle in Fig. 4 demonstrate that arc-wire sprayed materials (even if they have low microhardness) behave as brittle materials under erosive wear conditions at low temperatures (below the transition temperature). This is surprising considering the low microhardness values and is most probably due to the particular microstructure of the coating. It has a lamella structure, is highly strained, has a small crystalline size with inter-droplet particle interface defects and contains oxides and pores. All of which reduce the coating's ability to plastically deform on a macroscopic scale under erosion at intermediate temperatures. This would suggest that the erosion rate at 90° should show a decrease with increasing plasticity of the target represented by a reduction in the volume percentage of oxides, pores and other defects.

The influence of temperature on the 30° impact angle erosion rate of the 3 arc-wire sprayed coatings (D, E and F) is presented in Fig. 5.

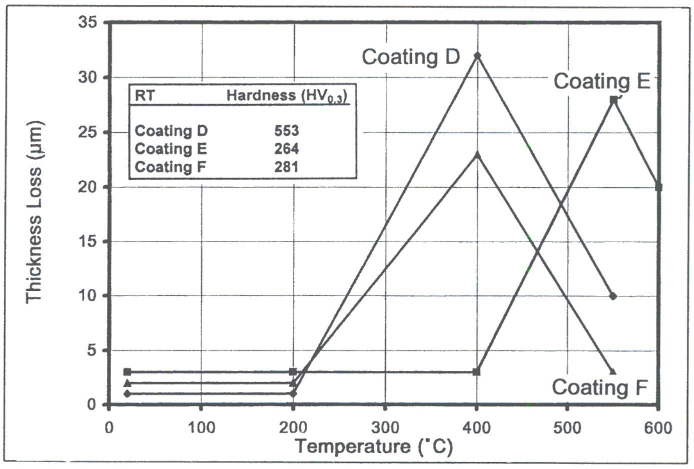


Fig. 5-Temperature Effect on 30° Impact Angle Erosion Rate of Arc-Sprayed Coatings D, E and F.

The form of the relationship is similar for all 3 coatings in having a characteristic peak at an intermediate temperature. A second observation is that this peak temperature varies with coating composition. A similar temperature/erosion relationship has been observed in bulk, wrought alloys where the erosion rate also shows a maximum at some intermediate temperature (1, 2, 8). The explanation for bulk alloys is that as the erosion temperature increased the material loss mechanism goes through 4 stages; 1). Erosion Dominated, 2). Erosion-Corrosion Dominated, 3). Corrosion Dominated 1 and 4). Corrosion Dominated 2. Stages 1 and 2 are characterised by an increase in material loss with temperature. Here, the substrate is losing metal by corrosion (and removal of corrosion product by erosion) and by direct erosion of the softer substrate metal. In stages 3 and 4 there is a reduction in weight loss with temperature. Here, the oxide phase is harder than the substrate metal and also adheres well so that the erodent sees the oxide rather than the softer metal during erosion.

Coatings D and F have similar transition temperatures and wear losses at the various temperatures. This is in spite of the fact that there is a large difference in hardness (HV 553 cf HV 281) and a different alloy base. The Fe-based alloy E is more alloyed than its related alloy D with respect to high temperature alloying elements and has only 50% of the hardness. These observations suggest that it is the corrosion effect rather than a material softening which is giving rise to the wear increase at intermediate temperatures. One important observation from Fig. 5 is that at an operating temperature of 500 °C, the lower alloyed materials (with lower temperature wear peaks) is suggested to outperform the higher alloyed coating. An explanation is that the alloys D and F are in an erosion/corrosion regime where the corrosion rate is greater than the rate of corrosion product removed by erosion. Essentially the corrosive product (which is normally an oxide and harder than substrate metal) becomes the surface seen by the erodent. Alloy E is in an erosion dominated regime where material is lost by oxidation and erosion of both the soft substrate and the slowly forming corrosive product.

Effect of Thermal Spray Process on Coating Erosion Behaviour. The effect on high temperature erosion of changing thermal spray technique for the same alloy is illustrated in Fig. 6. Here the erosion impact angle was 30° for the 3 Coatings E, G and H. Testing for Coatings H and G was only to 550 °C. Coating E was tested to 600 °C and shows a reduction in erosion rate and thus the bell-curve relationship. Analysis of the results is initially confusing. At any temperature the ranking order of coating performance changes completely, e.g. compare 20 °C, 400 °C and 550 °C values. This change in performance is far greater than for the alloy changes with the same spray technique as in Fig. 5. This suggests an enormous effect (order of magnitude) of the coating technique on performance. Once again, a comparison of the room temperature hardnesses give very little indication of the performance variations (Fig. 6).

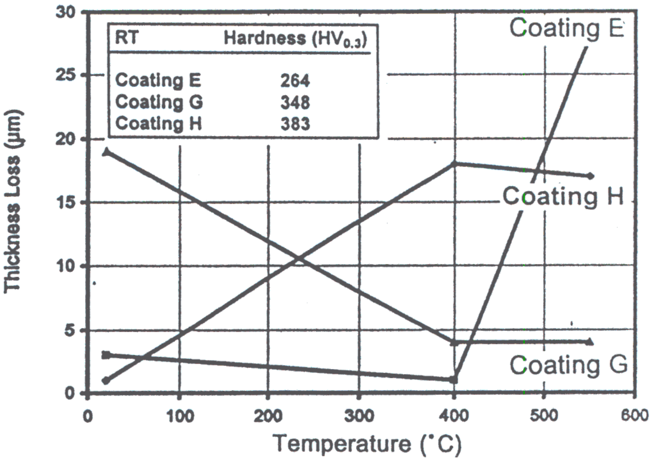


Fig. 6- The Erosion Rates at 30° Impact Angle at Different Temperatures for the same FeCrAl Alloy Sprayed with Different Thermal Spray Techniques.

Such complex results for materials sprayed with differing techniques have also been reported in the literature (18) but there has been little discussion as to the possible reasons and consequences. In the present study it is felt that the data is too limited to give a complete picture, but that there are strong indications which should be explored. From the previous work on these coatings and the results for Coating E in Fig. 6 it is proposed that the coatings could be behaving as described schematically in Fig. 7.

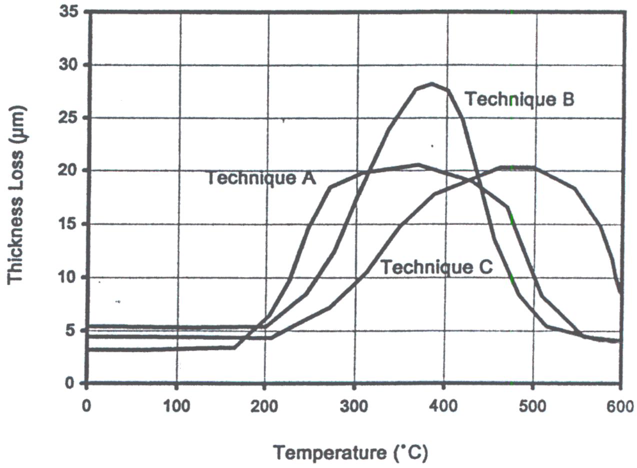


Fig. 7- Schematic of the Effect of Thermal Spray Method on the Erosion Rate/Temperature Relationship.

The bell-curve relationship is presumed with the characteristic peak erosion rate height and temperature varying with spray technique. This is comparable to Fig. 5 with the conclusion that the degree of flexibility demonstrated with changing alloy is as great as with a fixed alloy and changing spray technique. Such a conclusion suggests that for any coating solution