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Arc and Plasma Spraying Today and in the 90th

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Abstract  
In view of continually increasing construction material requirements and the increasing expense of materials with special properties such as high resistance to corrosion and wear, thermal spraying methods, in particular plasma and arc spraying, are becoming more and more important. In this paper, the operating principles, current and future application fields as well as the latest operational variants of these two methods will be presented.

KEY WORDS: (Plasma Spraying) (Arc Spraying) (New developments in processing) (New developments in materials)

1. Introduction

In recent years, thermal spraying has increasingly gained importance by satisfying industrial demands for the economical and competitive production of layer composites. Owing to the broad range of applications of the materials available to be processed, thermal spraying excels as the coating method of the future in almost all areas of industry (ref.1).

Recent developments of methods, equipment and spraying filler metals are characterized above all by higher quality requirements, new applications and problems, as well as by the demand for improved coating properties, higher deposition efficiency, and mechanisation and automatisation of the spraying process.

2. Plasma Spraying

2.1 Atmospheric Plasma Spraying

Industrially the most common and technically the most important use of non-transmitted plasma generators (so-called indirect plasmatrons, in technical terms plasma burner or torch) is atmospheric plasma spraying. More than 2,000 plants are estimated to be in use world-wide.
Fig. 1: Scheme of a plasma gun; cross section

Fig. 1 schematically illustrates a plasma spray-gun. For plasma spraying, a pilot arc is produced by means of a high-frequency ignition between an anodic, water-cooled plasma exit nozzle (generally copper) and a thoriated tungsten cathode. A gas mixture or pure gases, so-called plasma gases (Ar, He, N₂, H₂), flow tangentially around or through this pilot arc. In consequence of the heating, excitation, dissociation and partial ionisation of these gases, a free plasma jet of about 4 to 5 cm length results. The respective plasma gases are chosen principally according to their heat content and their reactivity. The higher enthalpy of a diatomic gas is generally used when refractory materials are to be processed. In contrast to other thermal spraying methods, plasma spraying allows refractory materials to be processed at high deposition rates because of the high temperature of the plasma flame (about 6,000 to 15,000°C (ref.2)). In addition to metallic materials, oxide ceramic additives, carbides, borides, nitrides, silicides, cermets and some plastics are now plasma-sprayed. The prerequisite for the process of these materials is however the molten-liquid state of the spraying materials. Materials that thermally decompose or sublime such as SiC or Si₃N₄ can not be processed in pure form. The main applications of thermally sprayed coatings at present are wear and corrosion protection.

A further field of application of atmospheric plasma spraying with a promising future is the coating of turbine or engine parts subject to high thermal loads with ceramic heat insulation systems (ref.3).

Thermal barrier coatings are currently subdivided into three types, cf. Fig. 2 (ref.5):

- duplex coatings
- three or multiple layer coatings
- graded coatings
Fig. 2: Thermal barrier coatings - schematically (ref.5)

Fig. 3: Plasma-sprayed segmented thermal barrier coating

These different coating systems have in common that a so-called bond coat is always applied as the first layer to the component. This metallic layer of NiCr, NiCrAl or MCrAlY alloys ("M" stands for Ni, Co, Fe or their blends) is intended both to give improved adhesion of the following ceramic layers and to protect the base material from hot gas corrosion (ref.6). The adhesive layer is then followed either by further metal layers, cermet or graduate metal ceramic layers or by purely ceramic top layers. Plasma-sprayed thermal-barrier-
coatings based on zirconia are preferred at present (Fig. 3).

A further and likewise extensive application field of plasma spraying could in future be the production of fibre-reinforced materials. Plasma spraying is especially suitable for the direct production of fibre-reinforced materials in view of the high flexibility of the materials to be processed. Recent studies have demonstrated this (ref.7). Fig. 4 shows a monotape produced in this way. More complex reinforced components could for example be manufactured by binding several monotapes by means of hot isostatic pressing.

![Monotape](image)

**Fig 4: Plasma-sprayed Monotape**

2.2 Vacuum Plasma Spraying (VPS)

A second industrially-employed variant of plasma spraying is vacuum plasma spraying. The significant element of a vacuum plasma spraying system (VPS) is the vacuum chamber that is evacuated to about $5 \times 10^{-2}$ mbar prior to spraying (Fig. 5).
Fig. 5: Scheme of a vacuum plasma spraying system (VPS)

Heat exchanger and filter are in front of the pump. Within the receptacle, sample holder and burner are mounted on a multiple-axis carriage. During spraying an operating pressure between 30 and 150 mbar is maintained. The pressure conditions within the work chamber lead to considerable expansion of the plasma beam during vacuum plasma spraying (Fig.6).

Fig. 6: Shape of plasma jet at different pressures
Whereas the plasma beam reaches a length from 4 to 5 cm at normal atmosphere, it extends 40 to 50 cm in a low-pressure atmosphere. The greater extent of the plasma beam leads to considerable expansion of the coated area, so, minor changes in the spray distance do not significantly affect the coating quality.

The decisive advantage of vacuum spraying is seen in the strongly reduced interaction of the spray particles with the surrounding atmosphere. Through this, processes arising from gas/metal reactions such as alloy ablation, oxidation and nitride formation during vacuum plasma spraying can only be caused by impurities in the plasma gases, the residual gas content of the working chamber, or by impure spray powder.

The main application area of vacuum plasma spraying continues to be the spraying of MCrAlY alloys onto turbine blades made of superalloys (ref.1, 8). The purpose of these protective layers is to protect the base material from hot gas corrosion during the design life.

![CoCrAlY-Coating vacuum-plasma-sprayed (on In 738 LC)](image)

Fig. 7 shows a vacuum plasma-sprayed CoCrAlY layer. It can be recognized that the lamellar structure typical of conventionally-sprayed coatings is completely absent. The etched cross-section reveals a homogeneous distribution of fine cobalt aluminium precipitations (dark) in a CoCr matrix (light). The mean hardness of the coating is 560 HV 0.02 and corresponds approximately to that of the base material (ref.8).

There are recent endeavours to find further applications for this method. Apart from the spraying of ablation-sensitive materials such as nitrides, carbides, etc., these include the spraying of reactive materials such as titanium and tantalum (ref. 9 - 13). With conventional spraying techniques, it is impossible to produce corrosion-resistant coatings of such reactive materials under atmospheric conditions, due to the high reactivity and high gas absorption at increased temperatures (ref.12).
2.3 New Plasma Spraying Concepts

Recently, the methods of thermal spraying have increasingly been employed in component manufacture. Especially parts required in large quantities allow the possibility of automatic production. In addition to high geometric accuracy, the mechanisation and particularly the automation of the spraying process have the advantage that the spraying parameters can almost all nearly completely be detected and held constant to an extent hardly possible in individual manufacture (ref.14, 15).

At present, industrial robots are on the market offering almost unlimited possibilities in the flexible, automatic and reproducible coating of components with complex geometry.

There are worldwide endeavours to develop new plasma burner concepts for industrial production. The adhesion and homogeneity of plasma-sprayed coatings can both be improved by increased particle velocities, leading to development of high-velocity plasma spray guns in recent years. Owing to the extremely short residence time of the particles in the plasma (ref.2), the electrical power must be very high if the sprayed particles are to melt completely.

Recently, water-stabilized plasma generators in particular are used for plasma-spraying large-area workpieces such as plates, sheets and pipes (Fig. 8b). These plasma torches, consisting of a rotating, water-cooled anode and a slowly-consumed graphite cathode have electrical input powers up to 200 kW and permit for example spraying rates of up to 50 kg/h with Al₂O₃ (ref.16). Because of the water plasma used here, this variant is however, suitable for oxide ceramic spraying only.

![Diagram of plasma spraying concepts]

Fig. 8: Various types of plasmatrons shown schematically

At present, magnetic-field stabilized, pulsed and high-frequency plasma torches (Fig. 8d) are under development, aiming at higher energy introduction into the plasma, reduction of electrode erosion, longer residence times of the sprayed particles in the plasma as well as better bundling of the plasma jet. Further methods to be mentioned are: tube plasma spraying (ref.17) and underwater plasma spraying (ref.16). In tube plasma spraying, the plasma beam is
protected by an inert gas stream axially surrounding the plasma, simulating
the influence of ambient air. In contrast, underwater plasma spraying trans-
fers the complete coating process into a water atmosphere. Applications of
this new method include the offshore area.

3. Arc Spraying

In arc spraying, two identical or differing metallic wires are melted
down within an arc, and are thrown onto the prepared workpiece surface by
means of atomizing gas, e.g. compressed air (Fig. 9) (ref.19).

![Diagram of arc spraying process]

Fig. 9: Principle of arc-spraying

Coatings produced by arc spraying possess a lamellar, finecrystalline
structure, but sprayed lamellae vary strongly in size. High-speed motion-
pictures taken at the University of Dortmund demonstrate that molten liquid
material accumulates on the wire ends at irregular intervals, and is then ato-
mized (Fig. 10) (ref.20).

The particle size distribution shows a broad spectrum, which has a nega-
tive effect on the coating quality. Arc-sprayed coatings must therefore in
general be sealed afterwards for special corrosion protection applications.

It is to be expected that the melting conditions will be improved by spe-
cific influences on the flow behaviour or by pulsed current sources. Another
possibility of positively influencing particle formation during arc spraying
is provided by so-called "closed nozzle systems". The result is a finer spray
as well as a more strongly bundled spray jet, whereby the porosity of the
sprayed coatings can be reduced.
Fig. 10: Melt-off wire-electrodes by arc-spraying (ref.20)

3.1 Development in Materials

The functional principle of arc spraying means that the spraying materials must be in wire form and must be electrically conductive. By using cored wires, hard materials can also be sprayed in addition to conventional metals and alloys. This, in turn, permits completely new applications of arc spraying as concerns protection against corrosion and wear. The development of new cored wires is in principle based on two basic concepts (ref.21):

- the use of filler metals in the form of pure, precipitated hard phases in the cores
- the use of composites in the case from which new phases are precipitated during the spraying process.

The microstructure of a coating produced by spraying a cored wire (composition as in Table 1) is shown in Fig. 11 (ref.22).
Fig. 11: Arc-sprayed coating produced with a cored wire (ref. 22)

The microstructure consisted of a light coloured "carbide" phase containing mainly FeCrC, Cr$_2$C$_3$ and Cr$_3$C$_2$ (as determined by microprobe analysis), in a mild steel matrix. The micro-hardness of these carbides was found to range from 605 to 1854 HV 0.1. Metallographic preparation of these micro-hardness specimens resulted in the preferential wear of some of these carbides giving rise to the "cratering" shown in Fig. 11.

Another important problem in arc spraying is the ablation of alloyed elements during the spraying process (ref.23). In sprayed coatings of stainless chromium nickel steels, for example, rust seams can occur, in consequence of the chromium depletion. The use of active gases like CH$_4$ (added to the atomizing compressed air), however, substantially reduces the alloy ablation.

Fig. 13 (bottom) shows the microstructure obtained from an arc sprayed steel wire (LSD-110 MnCrTi 8) containing 0.216 wt.% Ti sprayed with a methane-containing atomizing gas. The microstructure showed a large reduction in oxide content when compared with the same wire sprayed without a methane-containing atomizing gas (Fig. 12, top). The composition of the wire may be found in Table 1.
Fig. 12: Arc-sprayed steel coating with/without CH₄ (ref. 22)

Tab. 1: Composition of the wires applied

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<th>C</th>
<th>P</th>
<th>S</th>
<th>N</th>
<th>bal.</th>
<th>O</th>
<th>Cr</th>
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*as per manufacturer
3.3 Vacuum Arc Spraying

Arc spraying within a inert gas chamber at atmospheric pressure admittedly enables reactive materials to be processed, but the unavoidable uptake of gas leads to unwanted porosity (ref. 23). A further step towards the production of highly pure, dense and corrosion-resistant protective coatings is the reduction of the pressure within the process chamber. Process-technical problems require a corresponding modification of the arc spraying head in order to prevent the arc attacking the contact nozzles and thus destroying the spray head. By increasing the pressure at the short-circuit point, i.e. the arc burns in an antechamber pressurized relative to spray chamber (Fig. 13), a stable arc could be attained.

![Scheme of a vacuum-arc-spraying-unit with a closed nozzle-system](image)

Fig. 13: Scheme of a vacuum-arc-spraying-unit with a closed nozzle-system

Fig. 14 (ref. 12) shows a Ti coating produced by this method, though it has been shown that this arrangement is characterized by very short operating lives. A modified variant based on this principle is at present under development at the University of Dortmund (ref. 24). This system enables continuous operation at low pressure. High-Quality coatings of manganese-alloyed steel, chrome-nickel steel as well as titanium have already been achieved. Problems still arise from the unfavourable melting conditions. The deposition of very dense, pure and corrosion-resistant coatings of reactive materials for use in chemical apparatus construction is the main area application of vacuum arc
spraying. The method has the advantage over low pressure plasma spraying of reduced plant costs as well as of higher deposition efficiency. In contrast to powders, wire-shaped spraying filler metals have process-technical advantages because of the higher purity associated with the smaller specific surface.

![Structure diagram](image)

**Structure**

unetched, DIC

![Etched diagram](image)

etched, according to Kroll, DIC

- gas contents:
  - $\text{H}_2$: 23ppm
  - $\text{N}_2$: 100ppm
  - $\text{O}_2$: 1000ppm

  (vacuum hot extraction in platinum bath at 1500°C)

- hardness of the coating:
  - 179 HV 0.1

  chamber pressure: 182 - 296 mbar

Fig. 14: Vacuum-arc-sprayed Ti-coating

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