PVD COATING OF STEEL STRIPS

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ABSTRACT

Coatings deposited by Physical Vapour Deposition (PVD) are a promising alternative for the corrosion protection of super-high strength steels. PVD is an environment-friendly technology and is famous for the nearly unlimited material variety. Meanwhile PVD coatings obtained by evaporation or sputtering are discussed and used in different branches for many years. Electron beam high-rate deposition (EBHD) with deposition rates up to some micrometers per second is the most powerful PVD technology for low cost coating on steel strips. Recently developed technologies, especially plasma activated processes, opened a fresh ground to think about new applications. The new layer stacks produced by PVD represent an outstanding supplement to existing products. It could be verified that the deposition cost are low enough in comparison to competitive technologies. The combination of evaporation with powerful plasma is an efficient possibility to influence the layer properties in a wide range. In the paper an overview about such emergent PVD technologies will be presented. The influence of the plasma on the layer properties will be demonstrated. On this ground we developed some new PVD processes and layer stacks. The new process technologies and available equipment's are depicted. Finally the paper gives an overview about new trends and developments in large area PVD coating of steel strips.

KEYWORDS

PVD, vacuum coating, evaporation, plasma activated high rate electron beam evaporation, corrosion protection

INTRODUCTION

The use of super-high strength steels is growing rapidly, due to their outstanding characteristics. However most steels do have a fundamental disadvantage: their resistance to corrosion is often insufficient. The coating of steel sheets and strips has developed to a high level, with corrosion protection layers based on zinc and tin playing a particularly important role. These layers are manufactured mainly by either hot-dip coating or electrolytic deposition and there are a large number of these high-productivity plants in operation world-wide. Another technology important for the surface finishing of steel sheets and strips is the use of organic coatings such as varnishes. High-loaded metal components, e.g. automobile bodies, are protected from corrosion with a multilayer system combining various coating technologies. Nowadays strips of starting material are firstly galvanized either electrolytically or by hot-dip coating. A further coating then follows to ensure that the zinc coating is temporarily resistant to corrosion and forms a good foundation for the varnish. Chromium or phosphate compounds are deposited by dipping, spraying or rinsing processes, followed by a coating of multilayered varnish. In principle PVD processes (Physical Vapour Deposition) are suitable for depositing corrosion protection and other functional layers onto steel sheets and strips. This technology offers two deciding advantages:

- a wide variety of coating materials can be deposited (metals, alloys, compounds, also metastable and gradient layers) and
- it is environmentally-friendly.

The main obstacles to widening the industrial application of PVD technology for coating metallic sheets and strips are:

- the high status of conventional finishing,
- the extremely large investment demanded by this type of plant and
- the often unsatisfactory properties of the deposited PVD coating.

To further complicate matters, up until now it has been difficult to give precise information regarding coating costs and the long-term stability of the PVD process for many applications.

1 USE OF THE PVD PROCESS

The coating costs and the quality of the deposited layers for PVD coatings must be compared with other conventional surface finishing processes, particularly those that permit the coating of large areas at high speed. Comparatively low finishing costs can be achieved when the coating plant runs continuously with high productivity and the deposited layers are relatively thin [1].

For the PVD process these requirements are best met by vacuum evaporation, in many cases by EBHD (Electron Beam High-rate Deposition). This offers comparably high deposition rates (up to 20 µm/s) and is outstandingly well suited to deposition on large areas (area of evaporator up to 0.3 m²) [2]. Moving sheets and strips can be coated in widths of more than a metre and at speeds of up to hundreds of metres per minute. Continuous operation lasting over one week is possible [3]. Figure 1 shows the layout of a large-area high-rate electron beam evaporator with dynamic beam deflection. The electrons are generated by thermionic emission from a cathode and accelerated by voltages of 20 - 50 kV in an electric field. After passing through a ring anode they are formed into an electron beam and focussed. At the exit of the so-called electron gun is an electromagnetic dynamic deflection system capable of rapidly deflecting the electron beam at frequencies in the kHz range. Further electromagnetic deflection fields guide the electron beam onto the surface of material contained in a crucible. The ensuing heat causes the material to vaporize and the vapour thus formed condenses as a coating on the substrate. These types of evaporator configuration are currently available with outputs up to 800 kW and deposition widths of more than one metre.

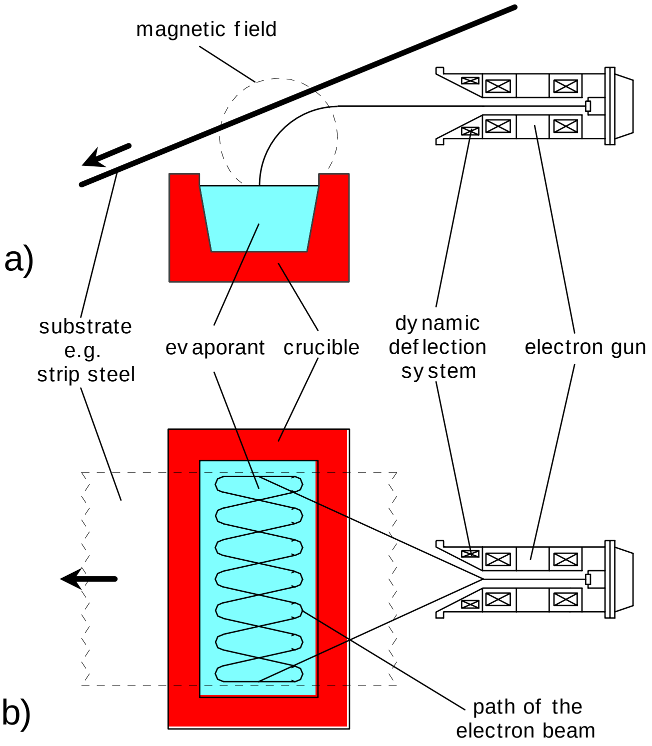

Fig. 1: Large-area high-rate electron beam evaporator with dynamic beam deflection; a) side view, b) top view

For special application cases, in particular for the deposition of very thin layers (<100 nm) with high specifications of layer quality and coating uniformity (layer thickness deviation < ± 5%), magnetron sputtering is used. Applying pulse techniques in the middle frequency range (10-50 kHz) allows the deposition of highly insulating layers of aluminium or silicon oxide over large coating widths (up to 4 m) at relatively high deposition rates (up to 10 nm/s) [4].

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Substrate pre-treatment in vacuum is an important prerequisite when using PVD coating for steel sheets and strips, being much more than just a physical cleaning under vacuum. Additional advantageous surface effects are achieved particularly as a result of plasma pre-treatment:

- desorption of gas and water films,
- removal of oxides and other contaminants,
- generation of free valences at the metal surface by breaking chemical bonds and
- formation of special intermediate layers, known as IFL (Interfacial Layers) [5].

The type and intensity of the substrate pre-treatment must be matched to both the condition of the substrate surface to be coated and the requirements of the deposited layers, with particular attention to adhesion. The process speed of the vacuum pre-treatment governs the speed and thus the economy of the entire process. Therefore dense plasmas are necessary for these process steps, in order to guarantee the mentioned high strip speeds during coating.

2 NEW PVD PROCESSES

The route to ever higher coating speeds, particularly for EBHD, is complicated in that layers coated at high rates have a marked columnar structure [6]. This makes them unsuitable for many applications, including protection from corrosion. The effect is caused by the low energy of the vapour particles with EBHD - the condensing particles have neither enough time nor energy to form a dense microstructure by atomic exchange. Particle energy can be increased in two main ways:

- deposition at very high substrate temperatures and
- plasma activation during deposition.

The temperature of the substrate cannot usually be increased because of its properties. Raising the temperature would drastically alter the mechanical properties of the steel sheets and strips. If the substrate has been pre-finished, e.g. galvanized, tinned or varnished, then these pre-treatment will determine the maximum applicable substrate temperature. Zinc exhibits an elevated vapour pressure under vacuum at raised temperatures, evaporating at a rate of about 30 nm/s even at 300 °C and at 1.5 µm/s at 400 °C [7]. These effects would be intolerable in many applications.

The principle of plasma activated deposition has been known for a long time [8]. Until the 1990s however there were no high-powered sources for dense plasmas that were suited to high coating rates and large-area coating. German firms and the Fraunhofer-Institut für Elektronenstrahl- und Plasmatechnik (FEP) devoted themselves to the task of developing such sources. The most effective plasmas are generated by arc discharge. At FEP some processes were developed on the basis of combining EBHD with different controlled arc discharges.

In the SAD process (Spotless arc Activated Deposition) the EBHD is combined with a special vacuum arc discharge (Fig. 2, [9]). The hottest point of the material being evaporated is the cathode foot point of the discharge. For selected metals, especially those with high melting points, the cathode foot point is diffuse at evaporation temperatures rather than being limited to less than 1 mm² as for known arc discharges. This „diffuse foot point“ occupies an area of many cm² and does not emit any droplets. Because the discharge comes from the hottest point of the evaporator and thus follows the deflection of the electron beam, a plasma activated large-area evaporation can be realised without high additional expenditure. With arc currents of many thousand amps it is possible to achieve e.g. for deposition with titanium at a rate of 1 µm/s, ion current densities up to 400 mA/cm² at the substrate [10].

The combination of EBHD with a hollow cathode arc discharge forms the basis of the HAD process (Hollow cathode arc Activated Deposition) (Fig. 3, [11]). For large-area evaporation some hollow cathodes are installed side by side directly under the substrate, and their discharges penetrate the vapour cloud. This process is particularly suitable for reactive deposition with insulating compounds such as silicon and aluminium oxides. A feature of hollow cathode arc discharge is the directed part of the electrons in the plasma. These electrons have an average energy of 10 - 15 eV.

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A correspondingly high self-bias voltage at insulating substrates results from the high electron temperature in the plasma. A special arrangement of the electrodes allows the long-term faultless deposition of highly insulating materials. Typical discharge currents are of the order of 200 A per hollow cathode. With this type of arrangement, Al_2O_3 layers can be deposited at rates of 50 - 120 nm/s and ion current densities of 30 - 50 mA/cm² at the substrate.

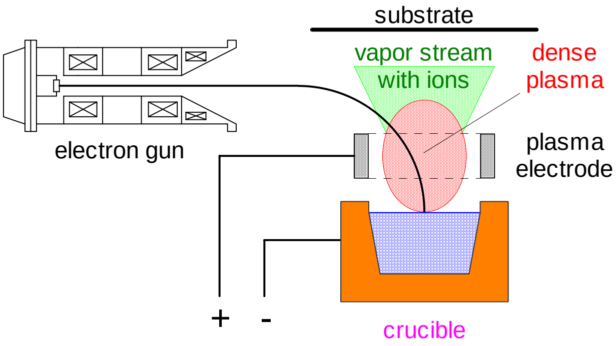

Fig. 2: Schema of the SAD process
(Spotless arc Activated Deposition)

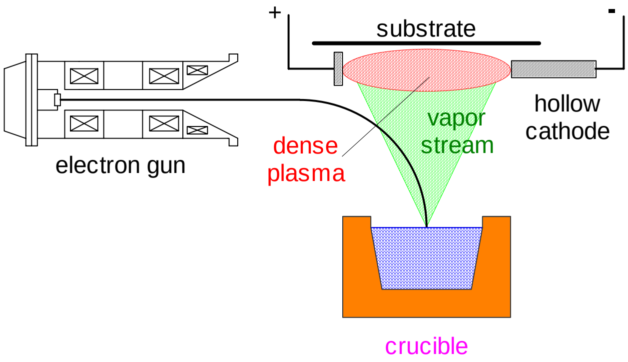

Fig. 3: Schema of the HAD process
(Hollow cathode arc Activated Deposition)

Great efforts have been made in recent years at FEP to lay down the basis for effective plasma pretreatment of metallic sheets and strips. The main aims are:

- high-rate etching of large areas,
- matching pre-treatment speed to the high substrate speed that can be achieved with EBHD,
- to operate continuously in a stable and protracted operation.

At present the use of pulsed magnetron discharges to meet these aims is being investigated. The process is known as the PAT process (Pulse plasma Activated Treatment) [12]. Figure 4 shows an arrangement and a picture of the current pre-treatment of metallic sheets and strips. A magnetic field in the form of an annular gap is installed behind the earthed substrate as is already known from magnetron discharge. This magnetic field penetrates the metal strip. On the opposite side is a screened hollow anode that limits the discharge. The power feed for the discharge pulses unipolar from the anode at pulse frequencies in the range 10 - 30 kHz. First results show that such an arrangement for large strip widths permit etching rates of around 15 nm/s, stable over a protracted period of time, can be achieved.

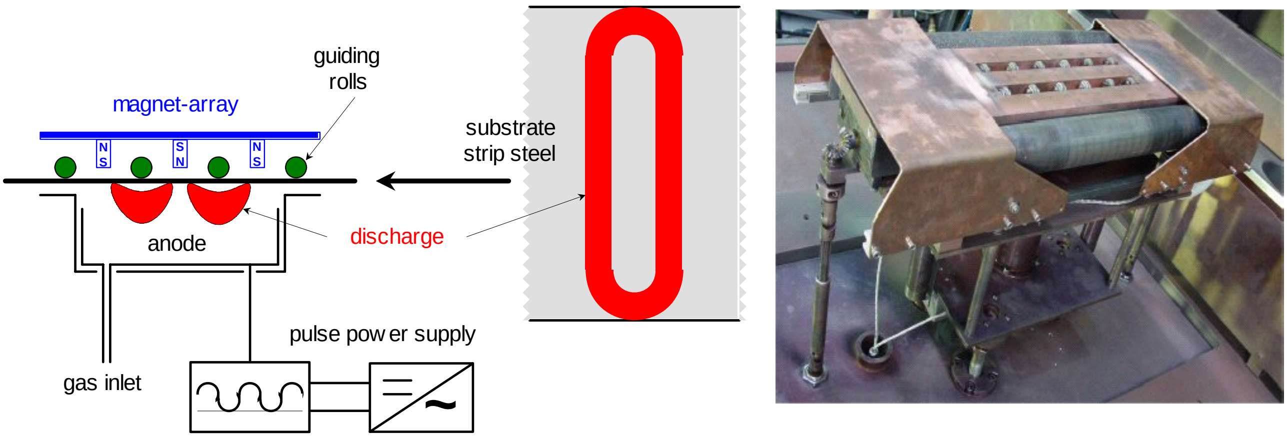

Fig. 4: Arrangement and picture for the pre-treatment of metallic sheets and strips by means of the PAT process (Pulse plasma Activated Treatment)

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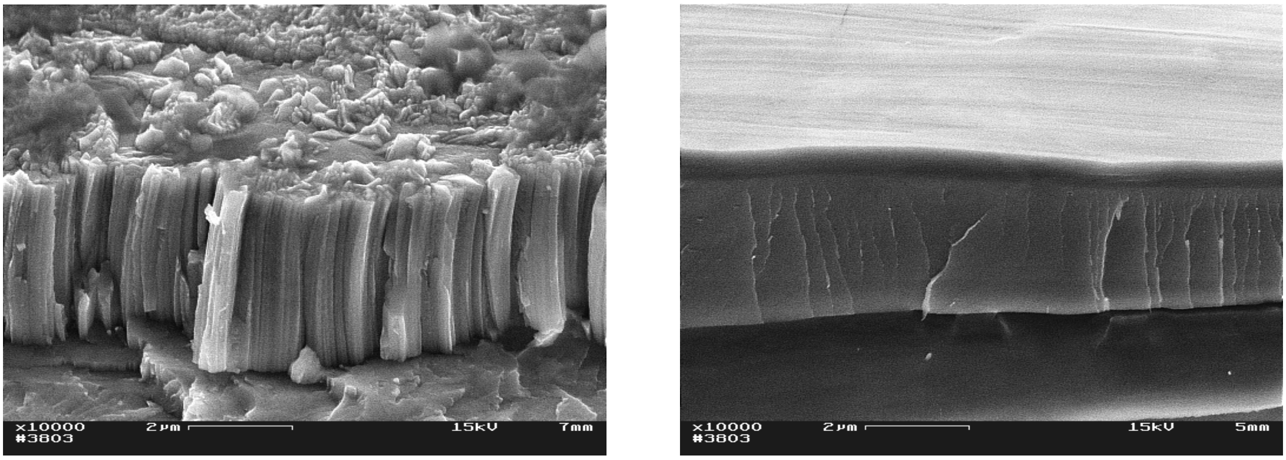
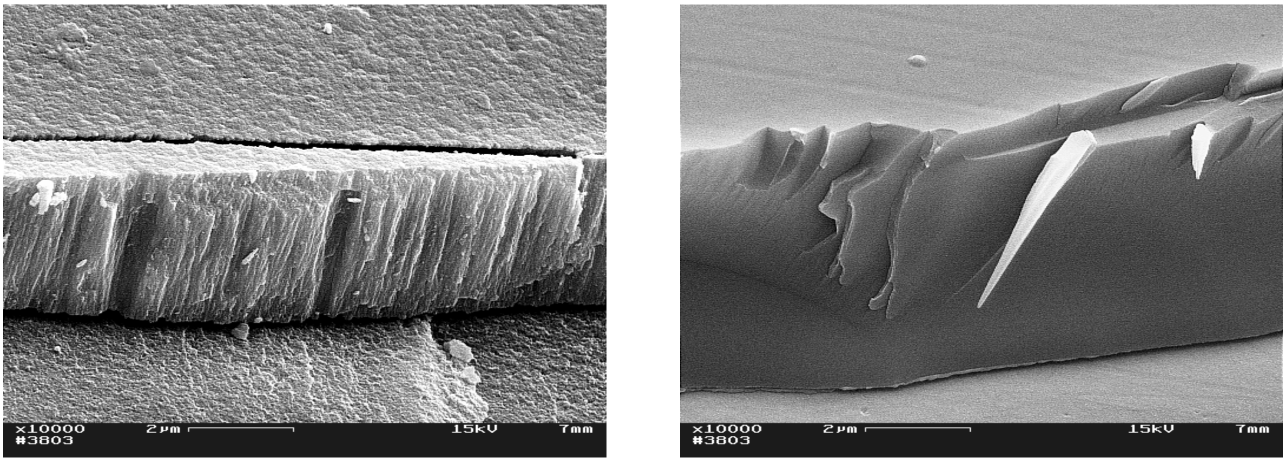
3 SELECTED RESULTS FROM NEW COATING SYSTEMS FOR STEEL STRIPS

In recent years many innovative coating systems using EBHD deposition on metallic sheets and strips have been based on the new PVD processes. At the forefront are the plasma activated processes SAD and HAD process for improving the coating microstructure. As expected, the influence of the plasma on the microstructure of the coated layers is observed for both processes. In Fig. 5 the effect of the SAD process during EBHD on the coating of chromium layers is shown in scanning electron microscope images of the cross-sections. Figure 5a shows a 4 µm thick chromium layer deposited without plasma activation at a rate of 1 µm/s. The coating has a porous microstructure with columns and the layer surface is rough. However Fig. 5b shows that the influence of the diffuse arc discharge in the SAD process combined with a bias voltage of 100 V results in the chromium layer having a denser microstructure and smoother surface. The effect can also be demonstrated in corrosion tests with increased resistance to corrosion for the same layer thickness. Previously such dense layers could only be manufactured at very low coating rates or with magnetron sputtering.



a) b)

Fig. 5: Influence of plasma activation on the microstructure of chromium layers
a) Layer deposited without plasma activation
b) Layer deposited with plasma activation (SAD process)



a) b)

Fig. 6: Influence of plasma activation on the microstructure of aluminium oxide layers
a) Layer deposited without plasma activation
b) Layer deposited with plasma activation (HAD process)

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Also for titanium layers deposited by the SAD process [10] similar effects with respect to improvements in the microstructure of the coating, surface topography and corrosion resistance can be demonstrated.

Figure 6 shows aluminium oxide layers made by reactive deposition by the HAD process on steel sheet at a substrate temperature of 500 °C (a) without and (b) with plasma activation. The clear influence of the plasma activation on the microstructure of the layer is visible. Note also that use of the HAD process doubles the hardness of the deposited layer from 6 to 12 GPa, and reduces the abrasion. With SiO_X layers deposited by the HAD process we could reach a hardness up to 15 GPa overstepping the hardness of bulk SiO_2. Characteristically, the ratio O to Si in at-% decreases to 1.2 for hard layers. A process window exists with absorption coefficient below 0.01 for very hard layers. Such kinds of layers are useful for transparent abrasion resistant and corrosion protective layers onto super-high strength steel sheets.

There are other applications in addition to these layer systems that mainly provide metallic sheets and strips with resistance to corrosion and abrasion. To provide temporary protection against corrosion and a good adhesion for varnishes, metallic substrates are usually treated with chromate or phosphate. Typical substrates are sheet metal (galvanized or tinned) and aluminium. The coating is done by dipping, rinsing or spraying. There are increasing health and environmental problems with Cr^{6+} ions in vessels and waste water, so alternative solutions are being sought world-wide. Within a project funded jointly by the German and Austrian governments in conjunction with leading steel manufacturers in both countries, an alternative based on PVD layers has been found. This involves the deposition of thin oxide layers by EBHD [13]. The starting material for these oxides can be silicon, aluminium or chromium. These layers provide similarly satisfactory temporary resistance to corrosion and a good adhesion for varnishes to those achievable with conventional chromate or phosphate treatments. The coated sheets can be processed further e.g. by mechanical deformation, spot welding, cathodic dip varnishing etc. without any problems [14]. The estimated coating costs are of the same order as for conventional processes.

To improve the surface properties e.g. of hot-dip galvanized metal sheets, in particular the stone-blasting resistance, after the hot-dip galvanizing a so-called „galvannealing process“ is often used. During this heat treatment iron diffuses from the substrate into the zinc coating and forms a hard, brittle zinc-iron alloy containing 8 % Fe by weight. However this brittleness can lead to „powdering“, or unwanted high abrasion during further processing. Therefore the development aimed to improve the stone-blasting resistance of hot-dip galvanized sheet metal while keeping the ordinarily low abrasion of this material. This task is achieved by depositing a thin metal layer, e.g. 400 nm Magnesium, followed by a very rapid annealing. An intensive plasma treatment before the coating guarantees unhindered diffusion of the Magnesium layer into the Zinc coating during the rapid annealing. This results in hot-dip galvanized sheet metal where only the thin surface layer of 1 - 2 µm is of a Zinc-Magnesium alloy. The remains of an underlying ductile Zinc layer ensures that these new products have good processing characteristics with low abrasion. The thin surface layer meanwhile improves the surface properties, above all of the stone-blasting resistance. Figure 7 shows (a) the stone-blasting resistance and (b) abrasion of the new product (Z+Zn/Mg) compared to those of hot-dip galvanized starting material (Z) and to galvannealed reference material (ZF) [15]. A further advantage of the new layer system is the drastically improved corrosion resistance of the steel sheets. In the alternating climate test a and in the salt spray test the corrosion resistance could be increased by a factor of 20 and 10 respectively compared to hot dip galvanized steel sheets [16]. For automotive application this advantage can be used in two ways:

- to avoid the additional conservation of hollows and
- to improve the laser weld ability by combination with a reduced Zinc layer thickness.

The developed solution works for electro galvanized steel sheets very well too. A first estimation of the coating costs for this application is also shown, and they are comparable to those of conventional processes.

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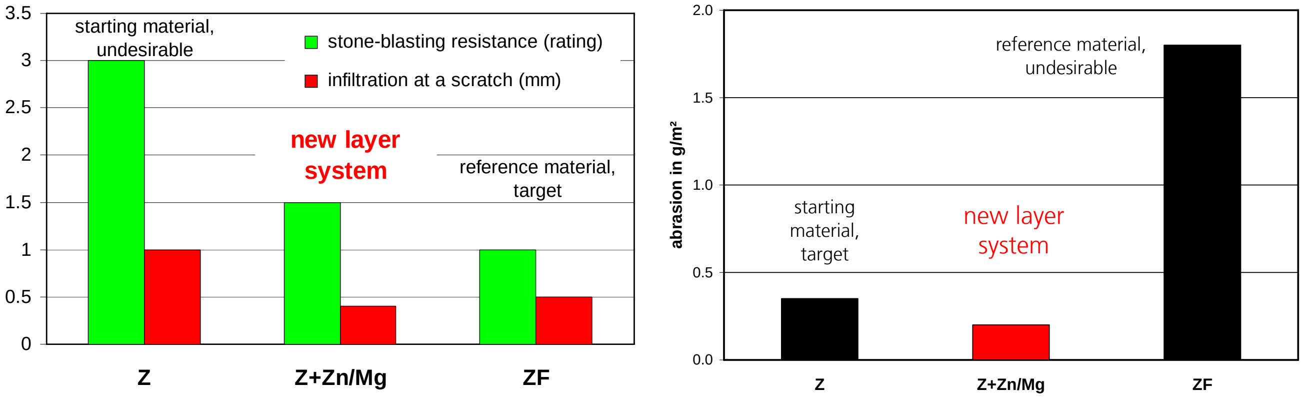

a) b)

Fig. 7: Comparison of the new product (Z+Zn/Mg) with hot-dip galvanized starting material (Z) and galvannealed reference material (ZF);

a) Corrosion and stone-blasting resistance, tested in accordance with automotive standards of pre-treatment, KT-varnishing, corrosion-testing after stone-blasting (VDA 621 - 415)

b) Abrasion by mechanical deformation in the draw-bead test,
oiled samples (2 g/m²), strain: 15 %, draw speed: 200 mm/min

With the new PVD technology a lot of further application could be made like decorative coatings based on body coloured layers or interference layers. For instance golden coloured TiN coatings can be deposited by plasma activated electron beam evaporation with rates up to 100 nm/s onto large areas. The powerful colour of thin interference layers base on the light reflection at top and bottom of very thin transparent oxide layers like TiO_2 or Cr_2O_3. The colour can be adjusted by the layer thickness over a wide colour range. Because of the very high demands concerning the layer homogeneity the oxide layers will be deposited by Pulse Magnetron Sputtering (PMS).
The photo induced hydrophilic and photo catalytic behaviour of TiO_2 films with the anatase phase allows creating super-high strength steel products with new properties like easy-to-clean and anti-bacterial surfaces. We can use two PVD methods for high rate deposition of crystalline TiO_2 films: reactive medium frequency pulse magnetron sputtering (PMS) and plasma-activated evaporation by the SAD process. With this process we could produce anatase TiO_2 layers with promising photo induced superhydrophilicity at deposition rates up to 70 nm/s [17].
This list of results and applications continues to grow, but no further details can be given because of the need to maintain confidentiality.

4 THE “MAXI” IN-LINE PVD COATING PLANT

The aim of these newly developed PVD technologies, layer systems and applications is to enable the manufacture and marketing of new innovative products in industrial quantities. Preliminary investigations using large-area samples under conditions well suited to scaling-up, particularly with respect to coating rate, mean that there are good preconditions for passing over the results into industrial production. A major problem in this research and development work was the need to use batch processing, which is unsuited to coating systems requiring a sequence of single processes to be performed without interrupting the vacuum. The Z+Zn/Mg system consisting of the steps „vacuum pre-treatment – evaporation with Magnesium – rapid annealing under inert gas” is an example of this sequence. A further disadvantage is that sample size is often limited to letter format.
In order to continue this research ”MAXI”, a special in-line coating plant for flat metal substrates, was built at FEP (see Figures 8 and 9). This plant makes it possible to preterit steel sheets and strips under conditions comparable to actual production without breaking the vacuum, to coat various materials by high-rate PVD processes, and also to carry out after treatments when desired.

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In the four „technology chambers“ (pre-treatment station, coating stations 1 and 2, after treatment station) different PVD processes can be installed flexibly. For pre- and after treatment there are for example many different ion etchers plus a radiation and electron beam heater available. Magnetron sources, capable of pulse operation if desired, can be installed to deposit interfacial layers (IFL). Both coating stations are envisaged as being suitable for high-rate electron beam deposition. The installed electron guns of up to 300 kW permit metals, alloys and compounds be coated at high coating rates using the plasma activation processes SAD and HAD for widths up to 500 mm. Other evaporation sources (e.g. the so-called jet-evaporator for zinc or magnesium) or other plasma activation processes (e.g. with microwave excitation) can be installed.

Sheets of up to 500 mm x 500 mm are inserted into substrate frames for coating – up to 20 frames can be held at one time. Since vacuum valves separate the individual chambers, they can be run at different operating pressures. The substrate can be accelerated and braked at up to 60 m/min for the “dynamic” plasma treatment and coating in each chamber. The installation of the sheet turnover mechanism in the after treatment chamber permits the double-sided coating of sheets without breaking the vacuum.


Fig. 8: In-line PVD coating plant MAXI

Metallic strips can be coated under vacuum at widths up to 300 mm and thicknesses in the range 0.02 to 0.5 mm. A coil of strip metal weighing up to 1000 kg is inserted in one of the winding stations and moved through the whole plant using modern processes for strip tension, strip speed and strip edge control. The strip speed can be preset up to 60 m/min in a stepless manner. To work at different pressures in the individual „technology chambers“, they are separated by a strip lock system with sealing roll pair that allow pressure decoupling of at least one order of size.

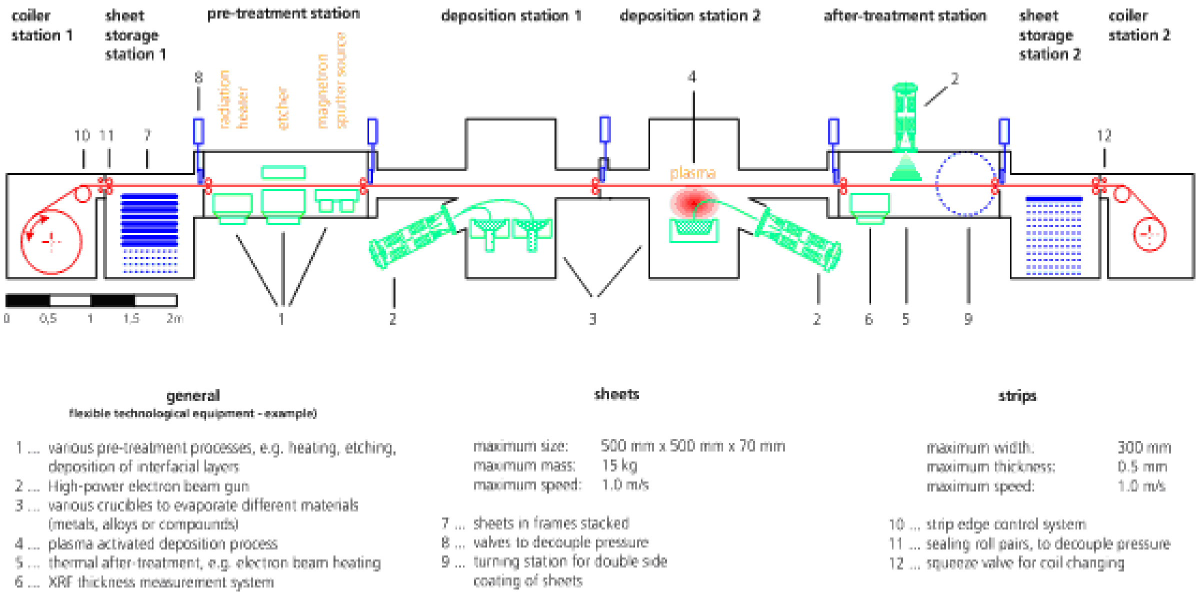

Fig. 9: Layout of the in-line PVD coating plant MAXI for metallic sheets and strips

Since 2000, all the new PVD processes, layer systems and applications for steel sheets and strips described in the paper are be realised in the MAXI coating plant. After work on layer and process development, scaling-up the PVD processes for industrial use is crucial. Product development, pilot and sample production are ongoing prior to the introduction of products into the market.

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At the same time this quasi-continuous operation can test the long-term stability of the processes and allow the coating costs to be estimated with great reliability. The MAXI in-line coating plant for metallic sheets and strips is thus an important link to industrial research and production. It should help to minimise the risks of introducing PVD technologies for coating metallic sheets and strips for FEP's industrial partners.

5 OUTLOOK

PVD coating of super-high strength steel and other metallic strips and sheets opens fully new potentials for the manufacture of attractive and innovative products with enhanced surface properties. FEP has analysed this field and noted development trends. These formed processingwise bases for the plasma activated high-rate electron beam deposition. In cooperation with many partners competency is bundled and the fundamentals of the plant technique have been established. FEP expects a great innovative thrust in this area, with the technology being used first of all for special applications. Thus, high-value articles made from semifinished products such as metallic sheets and strips with average dimensions will play an important role. It can also be expected that the applications of PVD coating described in section 4 will be introduced for the mass production of items such as galvanized car bodies and household appliances next years.

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