"High-rate electron beam deposition – the possibility of high-quality coating of large areas"

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High-rate electron beam deposition is one of the most effective PVD technologies. The very high productivity of this technology makes it predestined to coat large areas like metal strips and webs. Some features such as very dense and pure layers, different layers on both sides of the strip, wide range of possible layer material and environmental friendly processing enable the technology to overcome limitations known from electroplating. Well adapted powerful plasma activation processes developed at FEP extend the possibilities of electron beam deposition additional. Considering coating of copper as an example the paper will present new developments at FEP.

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1. Current status of the surface finishing of metallic sheets and strips

The use of metallic sheets and strips is growing rapidly, due to their outstanding characteristics. However metals do have a fundamental disadvantage: their resistance to corrosion is often insufficient. Enormous quantities of materials are wasted annually. On the other hand metals with outstanding body properties are useless in many cases because of their insufficient surface properties. Historically there has always been a struggle to finish metal surfaces.

The coating of metal 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 metallic 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.

For other functional coatings of metals like electrical contact surface, enhancement of solderability, tribological functions and decorative coatings electroplating is a well established technology.

In principle **PVD** processes (**P**hysical **V**apour **D**eposition) are suitable for depositing corrosion protection and other functional layers onto metallic 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.

2. 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.

For the PVD process these requirements are best met by vacuum evaporation, in many cases by **EBHD** (**E**lectron **B**eam **H**igh-rate **D**eposition). This offers comparably high deposition rates (up to 20 µm/s [800 µin./sec]) and is outstandingly well suited to deposition on large areas (area of evaporator up to 0.3 m²; [3.3 ft²]). 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[1].

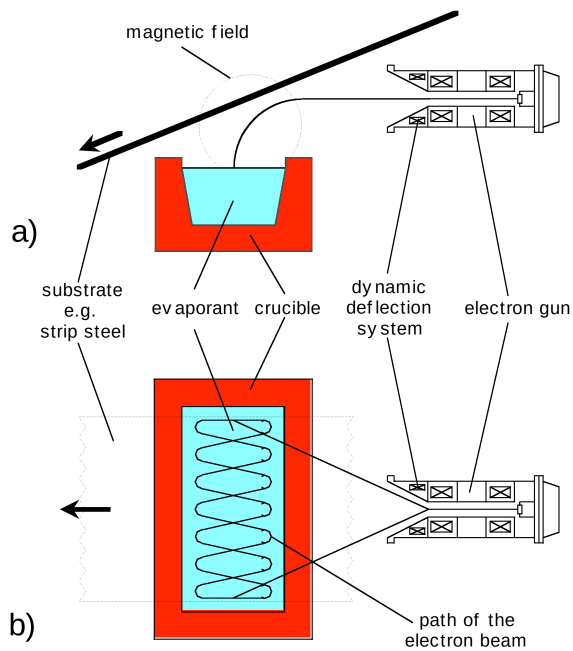


Figure 1: Large-area high-rate electron beam evaporator with dynamic beam deflection; a) side view, b) top view

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 - 60 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.

For special application cases, in particular for the deposition of very thin layers (<100 nm [4 μin.]) 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 [130 ft]) at relatively high deposition rates (up to 10 nm/s [0.4 μin./sec])[2].

Substrate pretreatment in a vacuum is an important prerequisite when using EBHD for metallic 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 pretreatment:

- desorption of gas and water films,
- removal of oxides and other contaminants,
- generation of free valencies at the metal surface by breaking chemical bonds and
- formation of special intermediate layers, known as IFL (Interfacial Layers)[3].

The type and intensity of the substrate pretreatment 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 pretreatment 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.

3. 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[4]. 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.

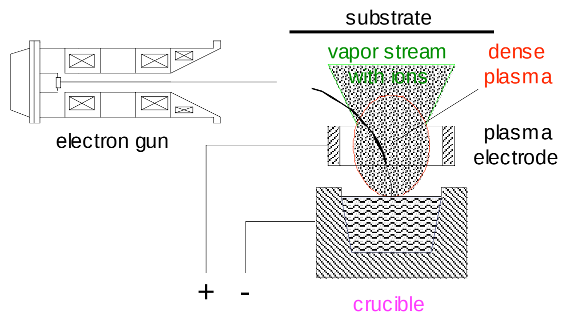
The temperature of the substrate cannot usually be increased because of its properties. Raising the temperature would drastically alter the mechanical properties of the sheets and strips. If the substrate has been prefinished, e.g. galvanized, tinned or varnished, then these pretreatments will determine the maximum applicable substrate temperature. These effects would be intolerable in many applications.

The principle of plasma activated deposition has been known for a long time[5]. 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 Institute for Electron Beam and Plasma Technology (FEP) devoted themselves to the task of developing such sources. The most effective plasmas are generated by arc discharge. At FEP three processes were developed on the basis of combining EBHD with different controlled arc discharges.

In the SAD process (<u>S</u>potless arc <u>A</u>ctivated <u>D</u>eposition) the EBHD is combined with a special vacuum arc discharge (Figure 2, [6]). 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 mm^2 (1550 mil^2) as for known arc discharges. This „diffuse foot point" occupies an area of many cm^2 (many $in.^2$) 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 (40 μin./sec), ion current densities up to 400 mA/cm^2 (2.6 $A/in.^2$) at the substrate[7].

The combination of EBHD with a hollow cathode arc discharge forms the basis of the HAD process (<u>H</u>ollow cathode arc <u>A</u>ctivated <u>D</u>eposition) (Figure 3, [8]). 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.

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 (2 – 48 μin./sec) and ion current densities of 30 - 50 mA/cm^2 (195 – 325 $mA/in.^2$) at the substrate.



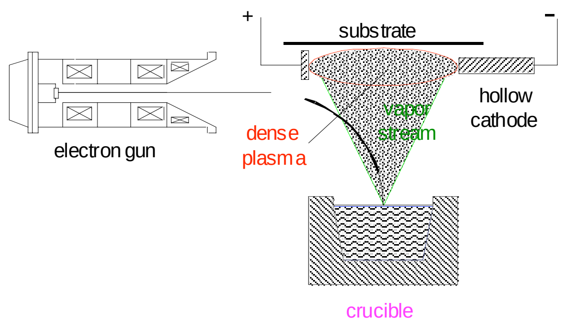


Figure 2: Schema of the SAD process (Spotless arc Activated Deposition)

Figure 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 pre-treatment 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)[9]. 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 (0.6 µin./sec), stable over a protracted period of time, can be achieved.

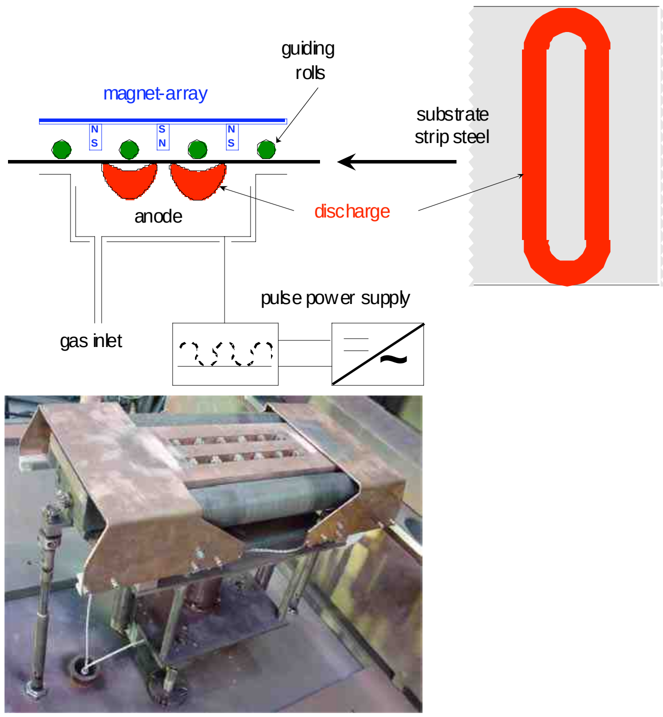
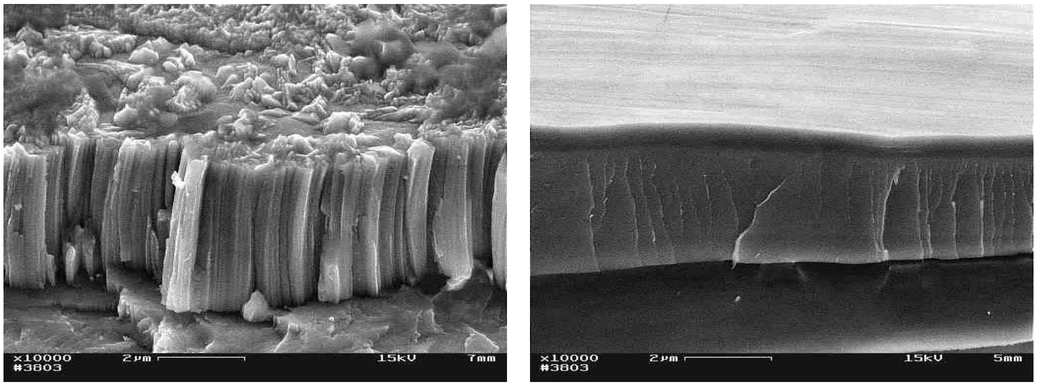


Figure 4: Arrangement and picture for the pre-treatment of metallic sheets and strips by means of the PAT process (Pulse plasma Activated Treatment)

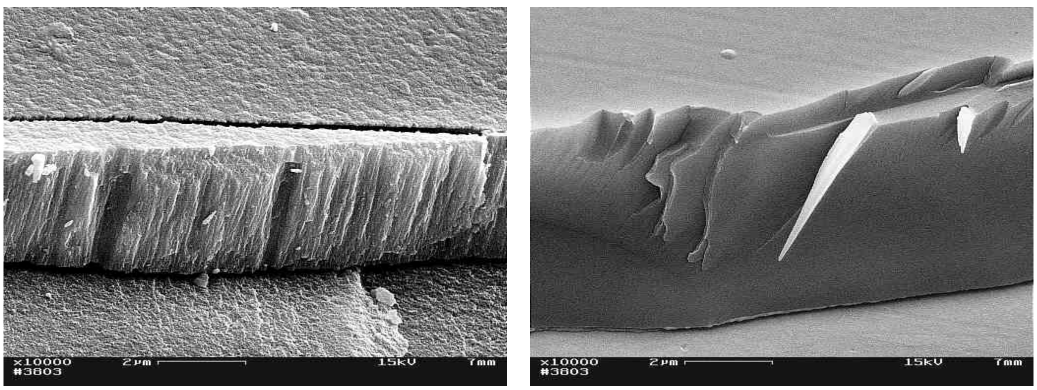
4. Selected results from new coating systems for metallic sheets and strips

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 Figure 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 (160 µin.) thick chromium layer deposited without plasma activation at a rate of 1 µm/s (40 µin./sec). The coating has a porous microstructure with columns and the layer surface is rough. However Figure 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)*

Figure 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)*

Figure 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)

Also for titanium layers deposited by the SAD process[7] 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 (930 °F) (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.

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 (4 μin./sec) 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 steel products with new properties like easy-to-clean and antibacterial 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 (2.8 μin./sec)[10].

This list of results and applications continues to grow, but no further details can be given because of the need to maintain confidentiality.

5. Copper coating by EBHD – effective and high qualitatively

Coating of copper onto steel is the absolute domain of electroplating. But more and more EBHD will be interesting in this field because of some special advantages:

- copper layer with very high purity can be coated
- strips can be coated with different layers on both sides, e.g. one side coated with copper and the other side with nickel
- copper layer can be covered by additional layer without vacuum interruption and therewith without oxidation of copper surface, no additional cleaning is necessary.

Additional to these technological possibilities copper coating by EBHD is very effective for large area deposition. Copper evaporation is done by using graphite crucible without active cooling. That means most of energy input can be used for evaporation with minimized heat loss. This will be beneficial especially for long time coating of strips because of the large volume of heat storage inside of evaporator. In consideration of these facts it is possible to produce dynamic deposition rates of about 2.5 μm/s (100 μin./sec). This enormous high deposition rate allows very high production speed.

Not only copper coating onto steel is field of research but also coating onto plastic sheets and web is very interesting. New developments in EBHD evaporator design allow also high speed copper coating of plastics by reducing of substrate heat load. Industry of printed circuits is very interested in directly structured metallized plastics to save technological steps in printed circuit production. Therefore next development steps will be focused in directly structured deposition.

Other important question for industrial application of copper coating is long term stability and homogenous layer properties because very precise layers allow reducing of necessary layer thicknesses.

Historically electron beam evaporation is not predestined for very precisely layer thickness homogeneity. Therefore at FEP new developments are in process to enhance quality of layer homogeneity over long term operation to combine high rate deposition with high level of preciseness. These new developments base on **APC** (**A**dvanced **P**rocess **C**ontrol) principles[11]. The APC system, well known from large microelectronic FAB's, will be changed into a very flexible tool adaptable to each PVD coating system. The so called Insitu-APC system is the task of our actually development and will be place EBHD in the position to overcome disadvantages in preciseness and long term stability.

6. The "MAXI" inline 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 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 7 and 8). This plant makes it possible to pretreat 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.

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 (20 in.). 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.

Figure 7: In-line PVD coating plant MAXI

Sheets of up to 500 mm x 500 mm (20 in. x 20 in.) 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 (40 in./sec) 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.

Metallic strips can be coated under vacuum at widths up to 300 mm (12 in.) and thicknesses in the range 0.02 to 0.5 mm (0.8 mil to 20 mil). A coil of strip metal weighing up to 1000 kg (2200 lb) 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 (40 in./sec) 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.

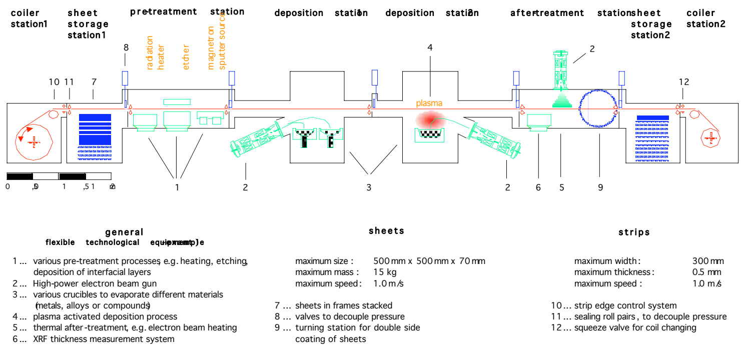


Figure 8: Layout of the in-line PVD coating plant MAXI for metallic sheets and strips

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.

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.

6. Outlook

PVD coating of metallic sheets and strips opens fully new potentials for the manufacture of attractive and innovative products with enhanced surface properties. FEP has analyzed this field and noted development trends. These formed processing wise bases for the plasma acti-vated 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 ap-plications. Thus, high-value articles made from semi finished products such as metallic sheets and strips with average dimensions will play an important role, for example:

- decorative and scratch-resistant layers onto stainless steel,
- sliding and contact layers,
- optical layers (also for solar energy capture) and
- special functional layers of stainless steel, aluminium, copper and magnesium.

It can also be expected that the applications of PVD coating described in section 3 will be introduced for the mass production of items such as galvanized car bodies and household appliances, though this step still needs more development. Table 1 shows selected examples for used coating materials onto steel strip in our institute in the last 5 years.

Acknowledgements

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