Spotless arc activated high-rate deposition using novel dual crucible technology for titanium dioxide coatings

Bert Scheffel, Thomas Modes, Christoph Metzner,
Fraunhofer Institute for Electron Beam and Plasma Technology (FEP)

Introduction

For deposition of thin oxide coatings there are a lot of qualified PVD processes today. If high productivity or large-area coating is necessary for economic reasons processes with high deposition rate are reasonable. Using electron beam (EB) evaporation all inorganic materials can be evaporated with high rates. Microstructure of coatings deposited by EB-evaporation depends on substrate temperature during layer growth and melting temperature of coating material. Particularly in case of high melting materials columnar and porous microstructure is obtained. For large area coating several plasma sources have been developed in order to enhance energy of condensing particles and to get denser layer microstructure [1].

Spotless arc Activated Deposition (SAD) combines electron beam high-rate evaporation using axial gun and a spotless arc discharge burning in metal vapor on hot evaporating cathode [2]. The SAD process is suitable for evaporation of high-melting metals like titanium, zirconium or tantalum providing high deposition rate up to 2000 nm/s. Moreover plasma-activation enables reactive mode of operation and deposition of oxides, nitrides or other compounds with a high rate in the range of 20 to 100 nm/s. A Spotless arc is an arc discharge burning in metal vapor which is obtained if the cathode temperature is high enough to enable high thermionic electron emission current density. Spotless mode results in relatively low cathodic arc current density and droplets known from arc evaporators with cold cathode are completely avoided [3]. Nevertheless high DC arc current up to 2000 A is possible.

Recent work has shown that SAD process is well suited for deposition of titanium dioxide coatings based on evaporation of titanium and reactive processing in oxygen atmosphere [4]. TiO_2 layers were deposited at very high deposition rates between 40 and 70 nm/s. Depending on process conditions amorphous coatings or crystalline phases were obtained. Coatings consisting of anatase phase show very good properties concerning photoinduced superhydrophilicity and photocatalysis. Transparent layers with high refractive indexes in the range of 2.30 and 2.58 could be reached.

SAD processing with dual crucible

High current arc discharge burning in metal vapor needs a good contact of vapor cloud to an anode. In case of titania deposition anode needs to be coated with understoichiometric titanium oxide coatings in order to maintain electrical conductivity. Therefore anode has to be positioned in the near of evaporation source. A water-cooled anode is well qualified to meet the requirements regarding high arc current, vapor condensation and thermal load during EB and plasma process. However, it has been found that coatings deposited on water-cooled anode will peel off from the anode after some hours of operation time. Therefore long-term stability of SAD process with water-cooled anode is limited. Some industrial applications demand long-term stability of high-rate and large-area coating processes over 100 h.

Limitation of long-term stability of SAD process caused by coatings deposited at anode equipment could be overcome by introduction of a novel dual crucible technology. The process has been

engineered for high-rate electron beam evaporation and is well matched to large area coating. For homogeneous coatings over wide strip width two or several dual crucibles have to be used.

The new process is based on two evaporating electrodes. While evaporating metal within the first crucible acts as cathode, evaporating metal of the second crucible forms the anode of the arc discharge. Both electrodes are in a good contact to vapor and reactive gas but plasma process can't be disturbed by coating of electrodes anymore. In figure 1 schematic of the process and electrical circuitry as well as a picture of plasma process with a laboratory type of dual crucible are shown.

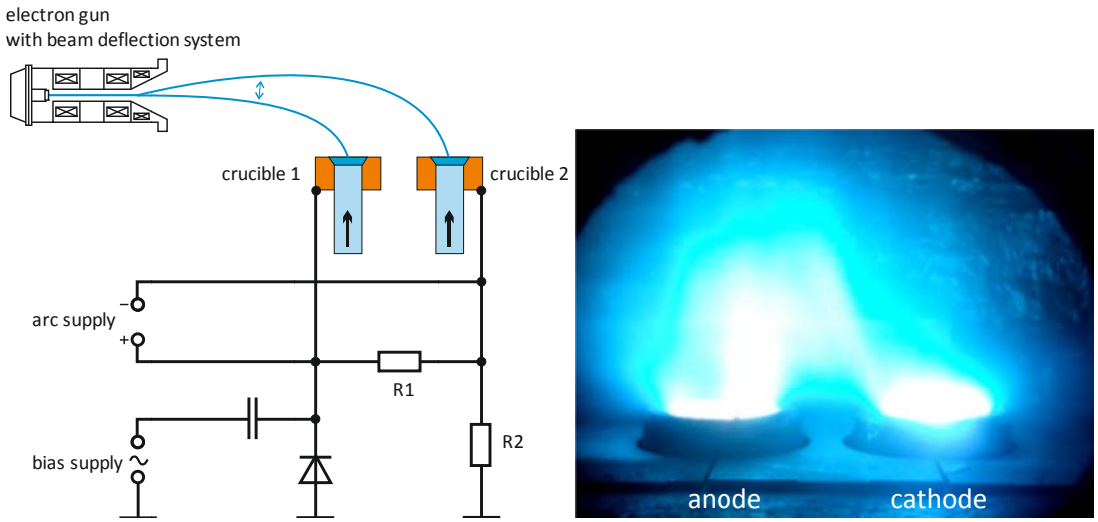

Figure 1 Schematic of SAD process with dual crucible and electrical circuitry for biasing (left)
Dual crucible during SAD process with titanium ingots, arc current 250 A DC (right)

Dual crucible consists of two water-cooled crucibles each equipped with an independently motor-driven rod-feed system from below. Titanium rods of a diameter of 65 mm can be moved with constant speed into the titanium melt heated by electron beam. A static magnetic field bends the electron beam from beam generation direction to the titanium surfaces. Electron beam is generated by an electron gun of axial type and is deflected by an integrated fast magnetic beam deflection system. Deflection pattern on surface, jumping beam frequency and duty cycle can be defined within wide ranges and define power density distribution and mean power for each crucible. Both crucibles are electrically insulating fastened from each other and from ground potential. Resistors R1 and R2 were dimensioned so that losses of arc and bias current are negligible but crucible potentials are shifted towards ground potential.

A bias supply delivers a sinus ac current in mid-frequency range (25 kHz) for pulsed plasma biasing method. The alternating voltage is rectified by a Villard circuit. Resulting pulsed positive voltage is applied to one of the crucibles with respect to ground potential. In this way plasma potential can be periodically shifted with respect to substrate potential if substrate is at ground potential. For large area coating of metal substrates, e.g. metal strip, it is a big advantage if substrate can be kept at ground potential. Nevertheless positively charged ions will be accelerated to high energy in the plasma sheath near the substrate surface.

The arc discharge burns between the two evaporating titanium melts. There are several possibilities for arrangement of crucibles and electron gun and for circuitry of arc supply: with or without magnetic beam bending, parallel or perpendicular arrangement of crucibles related to magnetic field lines, DC or AC arc supply, Cathode of DC arc discharge = crucible 1 or crucible 2. Moreover jumping beam

frequency and arc AC frequency can be synchronized or not. Also phase relation plays a role if same frequencies are used (e.g. deflected EB always meets cathode or EB always meets anode).

All main options have been approved. Favorable option is an arrangement of crucibles as shown in figure 1 - at which a line linking the crucibles is perpendicular to field lines of magnetic bending field (not shown) - and DC arc discharge with crucible 2 acting as cathode. Low energy plasma electrons have to drift perpendicularly to the magnetic field resulting in increased arc voltage and ionization rate. In this configuration plasma is not only generated at cathode (as in case of water-cooled anode) but also at the anode. Moreover plasma jets are formed in the region between anode and cathode having their roots at the electrodes. Anodic and inter-electrode phenomena of the magnetized plasma are not well understood up to now. Additional plasma generation at the anode is a very welcome effect compensating the loss of ionization degree that can be expected if a water cooled anode is replaced by an evaporating anode. Arc discharge can be sustained in a wide range of evaporation of anode. The arc discharge extinguishes if heating of anode or cathode is switched off. Degree of flux ionization calculated by relation of ion saturation current density (assuming singly charged ions) and deposition rate is in the range of 10 to 30 %.

High-rate deposition of titanium dioxide coatings

An oxygen flow in the range of 3000 to 6000 sccm was necessary to obtain stoichiometric and transparent titanium dioxide layers. Coating thickness was measured in situ using light reflection spectroscopy. Dynamic deposition rate of oxide layers was between 500 and 1000 nm m/min corresponding to a stationary deposition rate between 40 and 80 nm/s. Optical properties concerning absorption and refractive index of the TiO_2 coatings were investigated by ellipsometry, analysis of phase composition phase was done by x-ray diffraction. The layers are practically free of absorption in the visible range of spectrum. The refractive index is drastically influenced by substrate temperature and plasma parameters. Layers deposited with plasma activation have a significant higher refractive index between 2.30 and 2.58, even at low substrate temperature.

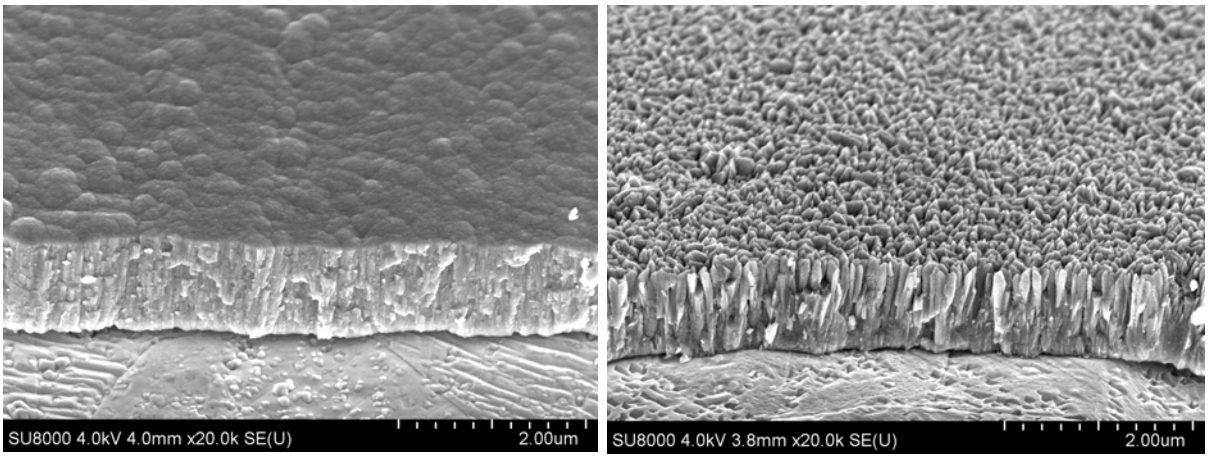

Figure 2 Titanium dioxide coatings on steel strip, SEM images of cross fracture, amorphous (left) and anatase phase (right)

Depending on substrate temperature, oxygen partial pressure and plasma parameters amorphous, anatase-phase or rutile-phase can be obtained. Amorphous and anatase-phase coatings were deposited at a substrate temperature below 150°C and above 200°C respectively. SEM images of cross fractures of such coatings are shown in figure 2. Associated XRD diagrams are given in figure 3. XRD diagram of anatase layer does not show any traces of rutile phase crystallites.

In order to check long-term stability of the process titanium dioxide coatings were deposited on continuously moved 250 mm wide stainless steel strip. Liquid titanium level was kept constant by adapted speed of rod feed of each crucible. Process and coating parameters could be kept constant without problems over many hours. The process stability was only limited by the length of the titanium rods of 230 mm. Total process duration of 30 h was achieved by some process interruptions and re-load titanium rods.

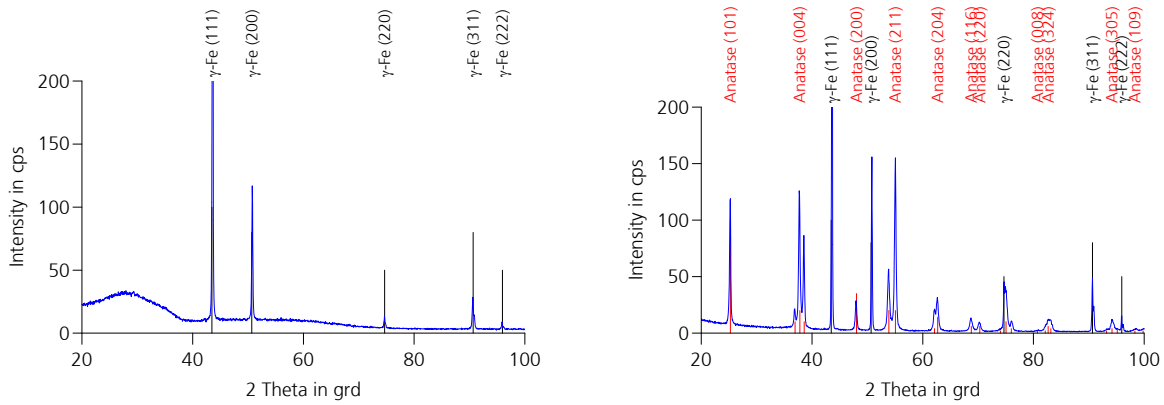

Figure 3 Titanium dioxide coatings on steel strip, XRD diagrams, amorphous (left) and anatase phase (right)

Acknowledgement

The project was funded by the European Union and the Free State of Saxony (funding reference 14274/2473). We gratefully acknowledge co-operational research with the company Von Ardenne Anlagentechnik GmbH.

Literature

[1] A. Anders, Surface & Coatings Technology 200 (2005) 1893 – 1906

[2] K. Goedicke, B. Scheffel, S. Schiller, Surface & Coatings Technology 68/69 (1994) 799-803

[3] A. I. Vasin, A. M. Dorodnov, V. A. Petrosov, Sov. Tech. Phys. Lett. 5 (12) (1979), 634-636

[4] T. Modes, B. Scheffel, C. Metzner, O. Zywitzki, E. Reinhold, Surface & Coatings Technology 200 (2005) 306– 309