

VACUUM ARC DEPOSITION OF NANOSTRUCTURED COATINGS

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Vacuum arc deposition is a smart technology allowing to produce dense nanostructured coatings for various applications¹. The main feature is that the vacuum arc discharges in the vapour of the cathode material. The material to be deposited is vaporized under the impact of an electric arc formed between an anode and the target which acts as the cathode. The discharge doesn't require the introduction of a gas like in sputtering. Advantages are low contamination, a high ionization degree of the evaporated species and a high deposition rate. The ionized species fly towards the substrate at much greater energies than in conventional evaporation, thus increasing the quality of the resulting deposited layer. Together with charged species, the arc impact generates microdroplets which prevent the utilization of vacuum arc deposition for the production of optical coatings. However, the high coverage capacity and the low substrate temperature during deposition open a wide range of possibilities.

A high deposition rate for the metals with a low sputter coefficient can be reached (up to 15 n/s for Mo)². The deposition rate decreases rather slow with increasing distance from the cathode and does not depend drastically on the mutual orientation of the cathode and substrate³. Therefore, the vacuum arc deposition is a powerful method for coating of three-dimensional parts of complicated form.

In case if several cathodes are used, the possibility exists to control each discharge independently from the others because no reactive gas is needed which can lead to interrelation among the discharges of individual cathodes. This feature permits an easy fabrication of the multicomponent coatings with the aid of vacuum arc deposition. And more, the deposition rate of each component can be changed during the deposition process *in situ*. It permits to produce gradient coatings. Ti-Ni gradient coatings were deposited by gradually changing the discharge power for both cathodes during the deposition process⁴. Depth-profiling of the produced coatings was made with the aid of secondary ion mass spectroscopy. It was shown that the slope of the Ni and Ti concentration profiles depends on the distance between the substrate and cathodes. Therefore, the concentration gradient in a coating can be influenced not only by changing the discharge power but also by varying the position of the substrate relative to the cathodes.

Due to their attractive properties, TiN coatings have been extensively used in various fields of application. This transition metal nitride has a high melting point, high hardness value, optical properties and metallic conductivity. Coating of cutting tools for increasing wear resistance is probably the best known application^{5,6}. TiN coating on glass is also popular for the production of decorative panel in architecture or solar glass in automotive industry. Reflected

colors are silver, blue and gold whereas transmitted ones are brown and grey⁷. Vacuum arc process is very suitable for the deposition of TiN or TiO₂. Particularly, the low thermally resistant materials like plastics can be coated with metals, nitrides or oxides. Light polymeric masks can also be used for the production of patterned decorative glass. The apparatus "Nikolay" was used for the vacuum arc masked deposition of decorative coatings on large area glass, stainless steel and plastics sheets. Examples of polystyrene mask-coated borosilicate glass with titanium nitride and titanium dioxide are presented.

The industrial scale set up used for the samples production has the following parameters. Size: 6000x3000x3000 mm. Mass: 15500 kg. Maximum power consumed: 75 kW. Ultimate vacuum: 5×10^{-4} Pa. Maximum size of treated glass: 2100x1300x8 mm. Maximum size of roll material: 400x1400 mm. Output capacity for glass: 30 glass sheets 2100x1300x5 mm in a 6 h. Cycle. Output capacity for the roll materials: up to 1 m²/min. A standard procedure for glass decorative coating includes three steps. The glass sheet is precleaned using hot distilled water before being loaded into the machine. After precleaning, glass sheets are mounted on metallic frames and placed in the machine vacuum chamber. Each frame contains two glass sheets, placed back to back. The frame is inserted into a slot (15 slots are available) and allowed to move independently inside the machine, in order to receive the different treatment operations. The displacement velocity of the frame is monitored and can be controlled. Each frame receives in turn a cleaning treatment followed immediately by a coating in order to prevent recontamination.

The complete treatment involves one return of the frame for cleaning and another return for coating. Cleaning is performed using a Hall current accelerator providing high energetic ions which impact and sputter the substrate surface. Though less controllable than Kaufman sources, Hall current accelerator appears better suited to sputter cleaning production requirements⁸. Of greater significance is the lack of any space charge flow limitation on ion current density. Further the reliability in etching is improved through the absence of any delicate structures like cathode or grid optics. The Hall current accelerator requires little maintenance and sputter cleaning can be performed with active gases such as oxygen, nitrogen and carbon dioxide.

A Hall current accelerator is placed on each side of the machine in order to clean the two sheets of the frame in one shot. The sputter dose received by the glass sheet depends mostly on the frame velocity and the distance to the cleaning source. Due to the asymmetry of the frame position relative to the two sources, the cleaning amount differ for the two sheets mounted back to back on a given frame. Nevertheless, the high power provides a sufficient cleaning of both surfaces in any circumstances. Coating in the industrial set up is performed using four circular targets 200 mm diameter. Two targets are placed on each side of the installation. When coating titanium, source tension is 20 V for a 250 A current. A reactive gas may be introduced if oxide coating is to be formed. TiN coating is obtained by introducing nitrogen at 0,05 Pa.

The arc generation is continuous and random. Targets are enclosed 800 mm away from the glass sheets path. As the microdroplets are ejected at small angles⁹ with

respect to the target surface, this configuration provides shielding and enables to increase the charged particles component of the beam. As for cleaning, the thickness of the deposited layer is controlled by varying the translation speed of the frame. Glass, metal and plastic sheets have been successfully coated with TiN. When decorative patterns have to be produced, light polymer sheets are used to provide masking. An example is shown of pattern on TiN decorative glass masked with a textile material. Various colors can be produced depending on the gas and deposition parameters used.

The Hall current accelerator has a shape of a very elongated loop. The large aperture (1400 mm in the vertical direction) allows one to use it for deposition on large area glass and plastic sheets by vacuum arc deposition and magnetron sputtering. The source cleaning profile was determined. 200 mm wide samples were sputter cleaned fixed to the source for different exposition times. Before cleaning, pen marks lines were drawn at a regular spacing interval on the sample surface. Pen marks provide masking against sputter cleaning of the sample surface. After cleaning treatment, they were removed with alcohol leaving a step between the sputtered and non sputtered parts. Step height was measured using a Taylor-Hobson profilometer. Measures along the width of the sample give the cleaning distribution of the source for a given exposition time.

Such experiments were carried out on borosilicate glass and poly(methyl metacrylate) samples. The profile depends on the material cleaned because borosilicate glass and poly(methyl metacrylate) have different behaviours towards sputtering. Poly(methyl metacrylate) has a lower thermal resistance compared to borosilicate glass. Sputtering times beyond five minutes lead to poly(methyl metacrylate) deterioration. Below this value, material is sputtered at a maximum rate of a 100 nm/min. Cleaning distribution for organic glass is not simple because a combined physical and thermal sputtering seems to take place. As time is increased, the band of maximum sputtering is getting narrower down to around 20 mm. Borosilicate glass has more reproducible cleaning profile with time. The main difference is the appearance of two distinct peaks in the distribution. The twin construction of the source can hence be resolved when sputter cleaning borosilicate glass. In the region of maximum sputter cleaning (corresponding to the two peaks), sputter rate for glass is 7.5 nm/min. For borosilicate glass, longer times are needed to obtain significant and measurable steps. Sputter cleaning of two materials of interest showed that the source cleaning profile is highly non uniform and material dependent. Source profile for organic glass is difficult to interpret as the ion bombardment produces a combined effect of physical and thermal sputtering on the low thermal resistance polymer. Material deterioration similar to the damage induced by ionizing radiation can be expected.

Composition of the combined TiN/TiO₂ coating was derived by Auger electron spectroscopy. The corrosion behaviour of both TiN and TiO₂ coatings on borosilicate glass was characterized. The standard accelerated tests on atmospheric corrosion were carried out. The accelerated test in 3.5% NaCl solution at 22–25 °C under both full and partial immersion was also carried out. The polarization behavior was measured potentiodynamically. Before potentiodynamic measurements, the corrosion potential E_c was monitored for 1.5 h. The

measurement was carried out in an electrolyte of 3.5% NaCl solution with pH = 7 and pH = 3.

After 3 months of tests in atmospheric corrosion with conditions which correspond to the most aggressive part of the industrial atmosphere, no changes of mass and appearance in the characterized samples was monitored. It demonstrates the high resistance against atmospheric corrosion of the characterized TiN and TiO₂ coatings on borosilicate glass. The corrosion tests carried out in the NaCl solution during 3 months also showed no changes in the mass and appearance of the samples both by full immersion and by partial immersion in the zone of contact between solution and air. The data of electrochemical tests show that). For both TiN and TiO₂ no active peaks are present and the coatings are in the self-passivated state. The corrosion potentials E_c versus the Ag/AgCl electrode are E_c (TiN) = 0.12 V and E_c (TiO₂) = 0.25 V for pH = 7. In acidic solution the difference between TiN and TiO₂ coatings is more pronounced. For pH = 3 E_c (TiN) = 0.47 V and E_c (TiO₂) = 0.17 V. The corrosion potential E_c of the TiN in the neutral NaCl solution in our work is about 0.15 mV more positive than E_c reported in ¹⁰ for the same electrochemical conditions. In ¹¹ the data are given for pH = 1 ($E_c = -0.23$ V, recalculated for the Ag/AgCl electrode) and pH = 12 ($E_c = -0.33$ V) which is much lower than both values obtained in this work. The pronounced anodic peak is present in all potentiodynamic curves presented in ¹¹. In this work no active peak is present and the coatings are in the self-passivated state. Therefore, the corrosion resistance of TiN deposited by the vacuum arc process is definitely higher than this of TiN coatings deposited by reactive d.c. sputtering ¹⁰ and on Al₂O₃ by plasma-assisted chemical vapor deposition ¹¹.

The vacuum arc deposition process proved to be an industrially viable technique to provide a wide range of decorative coatings on large area substrates. The low substrate temperature and the coverage efficiency of vacuum arc deposition make it possible to coat plastics or use them as mask to create patterns. Because of its attractive properties, titanium has been deposited alone or in presence of a reactive gas (nitrogen, oxygen) to produce various colored coatings. TiN and TiO₂ layers deposited on borosilicate glass have been investigated. TiN showed carbon and oxygen impurity content. Both coatings exhibited relevant corrosion resistance compared to values found in the literature.

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