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Functional coatings – a look into the state of the art of hard and decorative coatings

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Coatings for decorative purposes have a long tradition that remounts to ancient Egypt where could be found leaf gold plating. In more recent times, the coatings were produced by electrochemical deposition, anodising and lacquer coating, but the progress in vacuum and plasma technologies allowed developing vapour deposition processes: physical vapour deposition processes (PVD) and chemical vapour deposition processes (CVD). This work will show short reviews of the possibilities of some of surface treatment methods, but is mainly focused in PVD deposition processes.

1. INTRODUCTION

Thin film science is a major research area. In recent years, thin film production has been one of the most important fields in the synthesis of new materials. The evolution of the processing technology is connected to the development of materials with applications in microelectronics, optics and nano-technology, but the production of thin films for optical and magnetic devices, electrochemistry, catalysis, protective and decorative coatings as grown significantly during last decade. The market asks for new materials with new physical properties. The development of processing technologies allows material scientists to have the possibility of tailoring the microstructure of the thin films in order to optimise their performance. In this work we intend to write about hard and decorative functional coatings produced by PVD techniques.

2. DEPOSITION TECHNIQUES

There are several methods of depositing thin films. Pure chemical or pure physical processes, but more and more the combination of different processes is used. Each process has its advantages and disadvantages.

2.1. Non-vapour phase techniques

Non-vapour phase techniques are actually dominating the market. They are essentially chemical processes.

Electroplating uses the substrate as a cathode immerged in an aqueous solution of an electrolyte. The metal ions are deposited on the substrate. Commercially only some metallic elements, alloys and oxides are actually deposited (Cr, Ni, Zn, Sn, In, Ag, Cd, Au, Pb, Rh, brass, bronze, Pb-Sn, Au-Co, Sn-Ni, Ni-Fe, Ni-P, Co-P, PbO_2, Cr_2O_3) [1].

Electroless plating doesn't need an external voltage or current source. To produce a coating by this process, a reduction reaction of positive metallic ions is promoted on the surface of the substrate, catalysed by boron or phosphorous. The materials usually deposited by this process are Ni, Cu, Au, Pd, Pt Ag, Co and Ni-Fe alloys [1].

Major advantages of these plating techniques are to produce wear and corrosion resistant coatings and being very well known techniques, and consequently not too expensive and easy to control. In terms of decorative coatings, the range of possible colours is limited. Usually it is achieved the typical metallic colour (bright or matt appearance), but is also possible to produce black coatings, like black chrome. The main disadvantage of these techniques is related with the production of ecological hazardous chemical agents as cyanides and hexavalent Cr compounds.

Electrophoretic deposition corresponds to the migration of charged particles in an electric field. With this technique particles not soluble in water (glass, organic molecules, paint globules) can be deposited [1].

Another possibility is anodising. It is typically associated to Al and its alloys, but may also be applied to other metals (Mg, Ti, Zn). The purpose is to create a layer of porous metal oxide. The advantages of these coatings are corrosion and abrasion resistance, good adhesion, electrical insulation and allowing the possibility of subsequent plating. In terms of decorative coatings, an important advantage is the possibility of having a wide range of decorative colours, obtained by absorption of organic dyes or mineral pigments in the pores.

2.2 – Vapour phase techniques

Vapour deposition techniques are essentially CVD and PVD. These technologies don't dominate the market but the interest in using them increased significantly in last decades. There is the possibility of depositing a large number of compound materials, namely the important group of the ceramics. In terms of decorative coatings, transition metal nitrides give us a large possibility of having coloured coatings. With oxides it is obtained transparent films and with C-containing materials, black or dark grey coatings are produced. In addition these ceramic coatings have excellent mechanical and tribological properties and are corrosion and thermal shock resistant.

In CVD a chemical process occurs at the surface to be coated. Classical CVD needs high temperature in the reactor in order to promote reduction or decomposition of the vapour precursor, which contains the material to be deposited. This requirement is not compatible with some substrate materials. A great advantage of this technique is the homogeneity of coating thickness for large and tri-dimensional parts. Today, plasma enhanced CVD (PECVD) allows the possibility of having the advantages of conventional CVD with lower deposition temperatures.

In last decades, PVD processes have been used to produce decorative coatings. During the fifties the dominant technique, mainly to perform aluminium metallization of automobile parts, reflectors, or household parts, was the thermal evaporation. The following decade introduced e-beam and arc evaporation, but also magnetron sputtering in the metallization of materials. Titanium nitride (TiN) began to be produced by reactive magnetron sputtering in the eighties. The golden colour of this ceramic would allow replace electroplated gold with the advantage of being not expensive and being wear resistant. The nineties brought the reactive arc evaporation to produce hard coatings to coat door hardware, faucets, etc.

PVD techniques are, in general, environmental clean, but they need line-of-sight deposition process, with the consequent difficulties in terms of homogeneous thickness coatings. To coat tri-dimensional substrates it is needed a complex system of sample movements. With ion plating appears the possibility of coating parts with complex geometry. This technique presents the advantages of thermal evaporation and sputtering, allowing the production thicker and more compact films.Ion beam assisted deposition (IBAD) is a PVD process with simultaneous ion bombardment. The coatings produced by IBAD have higher adhesion and higher compactness. In research, pulsed laser deposition (PLD) is a technique that enables the synthesis of complex thin film materials. It is an environmental clean technique but it is only possible to coat small areas.

3. HARD AND DECORATIVE COATINGS PRODUCED BY PVD PROCESSES

PVD allows metals to have good adhesion on plastic surfaces. Al, Cr, but also Ag and Au have been deposited by these techniques, but wear and the corrosion resistance of the metallic coatings it is usually not good. To protect them, a transparent lacquer is applied on the top of the coatings. This layer also has a decorative role by granting a coloured tone reflecting a metallic lustre. However, electroplating and electroless processes far dominate the market of metallic coatings.

There is a family of materials that simultaneously presents decorative properties and excellent mechanical and chemical properties: the ceramics. The progress achieved of the deposition techniques led to the production of new materials and great advances have been made in the synthesis of hard coatings bases on ceramic materials. In the hard coating category, titanium nitride is the most studied and used material [2], but we can find hard carbon films and transition metal carbides, nitrides, borides, and silicides. TiN is chemically stable, highly resistant to corrosion by strong acids, and exhibits low friction and wear. Due to these properties, it is extensively used in a wide range of applications, from protective coating of machine parts and cutting tools [2] to applications as diffusion barriers in semiconductor technology [3]. TiN is also very popular as a decorative coating material, due to its golden colour. TiN coatings are obtained by a variety of PVD and CVD processes. Nevertheless due to the relatively low oxidation resistance of TiN, its use in some applications is limited. This fact and the search for harder materials, increased the interest of studying other ceramic coatings, such as chromium nitride (CrN) titanium aluminium nitride (TiAlN), titanium silicon nitride (TiSiN), titanium aluminium silicon nitride (TiAlSiN). Super hard coatings ($H \geq 40$ GPa) like Ti-B-N, reaching 45 GPa, have been produced [4], but theoretical calculations predict that α- and β-C_3N_4 may have hardness and bulk modulus similar of diamond's (70 GPa $< H <$ 100 GPa) [5]. Anyway the synthesis of crystalline carbon nitride is difficult to achieve. The incorporation of some silicon in the growth of carbon nitride films by microwave plasma-enhanced CVD promoted the formation of crystallites [6], although an excess of Si incorporation led to the formation of amorphous phase in PVD process [7]. Silicon nitride (Si_3N_4) is a well-known material: high hardness, high fracture toughness, wear resistance, high thermal stability, chemical inertness and good insulating properties. It is a good material for applications in which wear resistance at high temperature is required and in corrosive environments. In consequence of its dielectric properties, Si_3N_4 is also used for optical and electronic industry. The dielectric properties are strongly dependent on composition. The optical band-gap in SiN_X changes from 1.8 to 5 eV when x changes from 0 to 1.7. Silicon carbide (SiC) has also interesting properties: hard ceramic, resistant to chemically aggressive environments, wear resistant, presents high thermal conductivity [9] and low thermal expansion. SiC is also an indirect semiconductor with wide energy band-gap (2.4 to 3.4 eV depending on polytype) [8].

In films containing C, the increase of the hardness is strongly correlated with the sp^3 (only σ bonds) concentration in the film [9]. Besides hardness, low surface energy is also important in order to avoid sticking effects, mainly in plastic processing. To achieve this effect, low surface energy is required. In the case of C, low surface energy may be achieved by promoting sp^3 bonding states, reducing the amount of unsatured bonds. The production of ternary system Si-C-N could exhibit interesting properties, in combining the characteristics of binary compounds - C_3N_4, Si_3N_4 and SiC, but Si-C-N systems have not been extensively studied. Most of the published work about production of Si-C-N refers to high temperatures deposition processes (CVD). Only few works has been published about the synthesis of Si-C-N at low growth temperatures. Pulsed Laser Deposition (PLD) was used by some authors [10], but there is some work published with ion sputtered deposition of C and Si in a N_2 atmosphere, with simultaneous N ion bombardment of substrates [11] and reactive magnetron sputtering [12]. Research on new ceramic materials in order to be used as hard and decorative coatings is still increasing. The range of colours obtained goes from golden tones (TiN, TiNbN, TiZrN, ZrC_xN_{1-x} (x=0.2)), metallic grey (CrN), light-dark grey (TiC), yellow brown-grey violet-grey (TiAlCN), lilac-bronze (TiCN), black (TiCO, C, Ti/C:H, SiCN), Black-anthracite-aubergine (TiAlN), red-gold (TiC_xN_{1-x} (x<0.2)).These compounds may present variations in physical properties and colours due to variations on composition and microstructure. That is the case of the recent research field in decorative coatings: the production and characterisation of transition metal oxinitrides.

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