Fabrication of superhydrophobic nanostructured films by Physical Vapour Deposition

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ABSTRACT

This work reports on recent advances in the deposition of non-wettable coatings with high water contact angles (WCAs). We propose a simple and easily-controlled method for fabricating different types of nanoestructured films of Al_2O_3 with hydrophobic properties by Physical Vapour Deposition (PVD).

The films have been deposited over three types of hydrophilic substrates with very different values of roughness and free surface energy. The results of this study showed that the hydrophobicity of the Al_2O_3 coatings do not depend on the starting conditions of the substrate.

GD-OES and FESEM showed a 50-250 nm surface flake structure of Al_2O_3. This surface flake structure, which is responsible of the hydrophobic effects, is optimized in thicker films.

These Al_2O_3 hydrophobic films presented similar values of contact angle in water to the classic polymeric films based on methyl and fluorocarbons groups.

Keywords: Superhydrophobic surface, nanostructured films, aluminum oxide, Physical Vapour Deposition, wettability

1 INTRODUCTION

The wettability of a solid surface is a very important property that depends not only on the surface energy but also on the geometry structures on the surface. When the contact angle (CA) is smaller than 90º, the surface is hydrophilic; when it is higher than 90º, the surface is hydrophobic. Superhydrophilic surfaces (CA smaller than 5º) and superhydrophobic surfaces (CA higher than 150º) present very interesting properties not only in fundamental research but also in many practical applications, such as surfaces for satellite dishes, solar energy panels, photovoltaics, exterior architectural glass and green houses or heat transfer surfaces in air conditioning equipment.

Due to the small contact area between the surface and water, chemical reactions or bond formation with water are limited on a hydrophobic surface. Because of that, non-wettable surface prevent the adherence of frost or snow, the deposition of dust, oxidation processes or electrical conduction.

Many surfaces in nature exhibit superhydrophobic properties, such as the winds of butterflies [1] or the leaves of some plants [2]. Moreover, the best-known example of a non-wettable surface is the lotus plant [4]. Electron microscopy of the surface of lotus leaves shows a micrometer structure covered with nanocrystallites. Several studies conclude that this combination of micrometer-scale and nanometer-scale roughness is responsible for the hydrophobic properties [5]. However, other natural examples do not exhibit two-length scales and many studies calling into a question this requirement [6, 7].

To obtain superhydrophobic surfaces, surface energy and surface roughness are two dominant factors. When surface energy is lowered, by adding methyl or fluorocarbons groups, the hydrophobicity property is enhanced. On the other side, the ability to control the morphology of a surface on micron and nanometer scale is the key to achieve non-wetting effect [8, 9, 10].

Most of the superhydrophobic surfaces that are described in the literature are based on activated polymeric compounds [11]. Although good results have been obtained with this type of coatings, the surface energy of these coatings increases with time and the hydrophobic properties of the material fade. The main objective of this study is to prepare inorganic films with low free surface energy, low hysteresis and low tilt angle, which present highly and permanent hydrophobic properties. As the tribological properties play an important role in many applications requiring water-repellent properties, another important objective is to analyze the adhesion and the friction properties of these coatings.

2 EXPERIMENTAL

Three different types of ceramic substrates have been used: S06, S12 and S13. Before coating, the roughness of the substrates was determined by optical interferometry, using a WYKO RST 500 interferometric profilometer. Five measures were developed along each sample to determine the averaged roughness, R_a.

The hydrophilic character of these substrates was quantified by determining the contact angle of the surfaces in water, using as EASY DROOP equipment [13]. Ten measures were developed along each sample, five on the left side and five on the right one, to determine the contact angle.

Before coating, the substrates were cleaned with absolute ethanol.

The polymeric fluorine-based coatings were developed by a plasma polymerization (PP) process, using an

EUROPLASMA equipment. Two different procedures were applied, which are denoted as PP1 and PP2.

The Al_2O_3 coatings were prepared by Physical Vapour Deposition (PVD) in a commercial METAPLAS MZR 323 PVD chamber equipped with 3 magnetron sputtening sources. The characteristic parameters of the PVD process (dose, bias, temperature, pressure, flow of O_2) have been studied and optimized to obtain films of Al_2O_3 with the desire combination of micro- and nanostructure. The optimization of these parameters of control allows obtaining different effects on the final film properties, from hydrophobic to superhydrophobic. Once these parameters of control were optimized, two different processes were studied depending on the time of deposition, in order to study the influence of the thickness in the micro- and nanostructure of the final surface. They are denoted PVD1 and PVD2.

Table 1 summarizes the nomenclature used to denote the samples.

Sample	Substrate	Treatment	Procedure	Nomenclature
1	S06	PP	1	S06PP1A
2	S06	PP	1	S06PP1B
3	S06	PP	2	S06PP2A
4	S06	PP	2	S06PP2B
5	S12	PP	1	S12PP1A
6	PVD	PP	1	S12PP1B
7	S12	PP	2	S12PP2A
8	S12	PP	2	S12PP2B
9	S13	PP	1	S13PP1A
10	S13	PP	1	S13PP1B
11	S13	PP	2	S13PP2A
12	S13	PP	2	S13PP2B
13	S06	PVD	1	S06PVD1A
14	S06	PVD	1	S06PVD1B
15	S06	PVD	2	S06PVD2A
16	S06	PVD	2	S06PVD2B
17	S06	PVD	2	S12PVD1A
18	S12	PVD	1	S12PVD1B
19	S12	PVD	1	S12PVD2A
20	S12	PVD	2	S12PVD2B
21	S12	PVD	2	S12PVD1A
22	S13	PVD	1	S13PVD1B
23	S13	PVD	1	S13PVD2A
24	S13	PVD	2	S13PVD2B

Table 1 Nomenclature of the samples

The composition of the films was studied by GD-OES, with a Jobin-Yvon HD1000 Glow Discharge analyzer [14]. Changes in the chemical composition profile of the coatings have been also analyzed. The morphology of these new coatings has been studied by FE-SEM, using a Hitachi S-4800 FE-SEM microscope.

The wettability of the surfaces was studied by determining the angle contact in water with an EASY DROP equipment.

The mechanical and tribological characterization of the coatings includes the determination of the film adhesion (scratch test), thickness, and wear and friction coefficient.

3 RESULTS AND DISCUSSION

Figure 1 shows the roughness and the contact angles in water of the three types of substrates that have been used in this study.

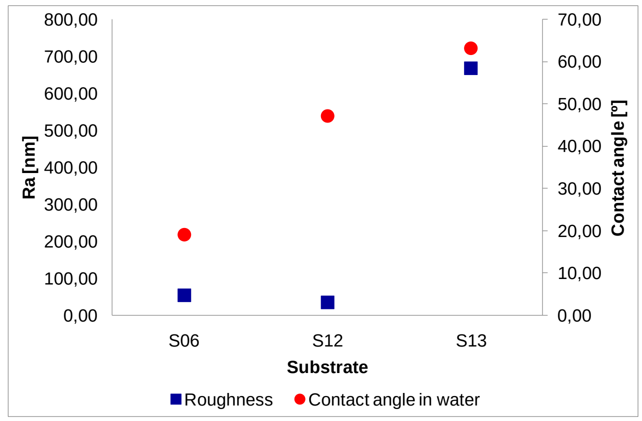

Figure 1: Roughness and contact angles in water of the substrates

This plot shows that surfaces S06 and S12 are smooth, with R_a of 53.61±8.75 nm and 34.75±2.80 nm, respectively. The surface roughness of S13 is one order of magnitude larger, with a R_a of 667.52±192.02 nm. This plot also reveals that S06 is the most hydrophilic substrate, with a contact angle in water of 19.11±4.26º. S12 shows 47.20±1.73º and S13, 63.17±3.27º.

The visual inspection of the samples showed that the PVD coatings, as well as the polymeric films, are transparent.

The scratch tests revealed a good adherence between the PVD coatings and the three types of substrates. No significant differences were observed between them.

GD-OES analysis confirmed that the chemical composition of the PVD coatings is Al_2O_3. The changes in the chemical composition profile allow determining the thickness of the coatings. Al_2O_3 films of 50 nm were observed for the shorter PVD deposition (PVD1) and 250 nm films for the longer process (PVD2)

The investigation by FE-SEM microscopy of cross-sections of the samples revealed the thickness of the coatings. These values were in good agreement with the ones obtained by GD-OES.

Figure 2 shows the averaged contact angles of water of the coatings. It shows that the hydrophobic character of the final surface do not depend on the properties of the substrate, because similar values are obtained for S06, S12 and S13. However, it reveals that PVD2 process is more efficient than PVD1, because thicker Al_2O_3 coatings are more hydrophobic that the thinner ones. FESEM micrographs showed that the surface flake structure, which is responsible for the hydrophobic properties, is optimized in thicker samples. Al_2O_3 coatings prepared by PVD2 process showed similar values of wettability to the polymeric films of reference.

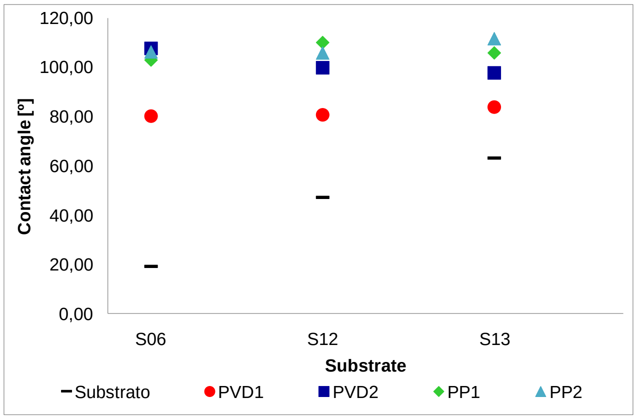

Figure 2: Averaged contact angles in water

FE-SEM micrographs showed a surface flake structure of the PVD coatings. Figure 3 shows the micrograph of a sample prepared by the longer PVD procedure. The thickness of this sample is 300 nm. As it can be observed in figure 3, this flake structure combines a micro and nano scale. According to the bibliography, this micro/nano structure in the surface is supposed to be responsible of the hydrophobic properties [12].

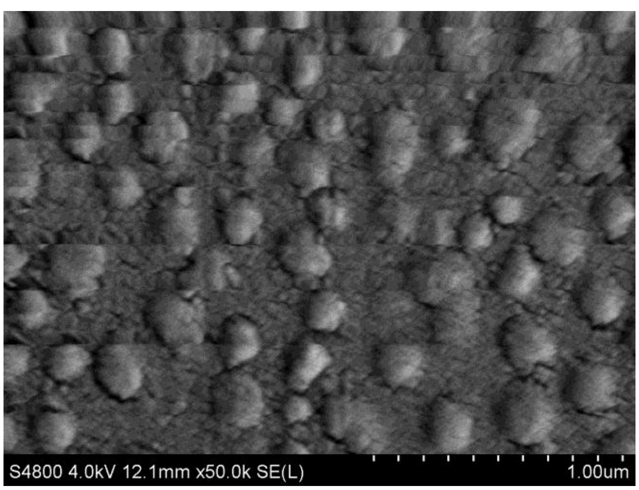

Figure 3: FE-SEM micrograph of sample S06PVD2B

However, this flake structure is not well-defined in all the samples. Figure 4 shows the micrograph of a sample prepared by the shorter PVD procedure. The thickness of the sample is 50 nm.

Comparing figures 3 and 4, we can confirm that the surface flake structure is more defined in thicker samples than in the thinner ones. These results are in good accordance with the contact angles in water that are summarized in figure 2, and explained why thicker Al_2O_3 coatings are more hydrophobic that the thinner ones: as the flake structure of the Al_2O_3 is more defined in thicker coatings, they are more hydrophobic. Compare figure 3 and 4.

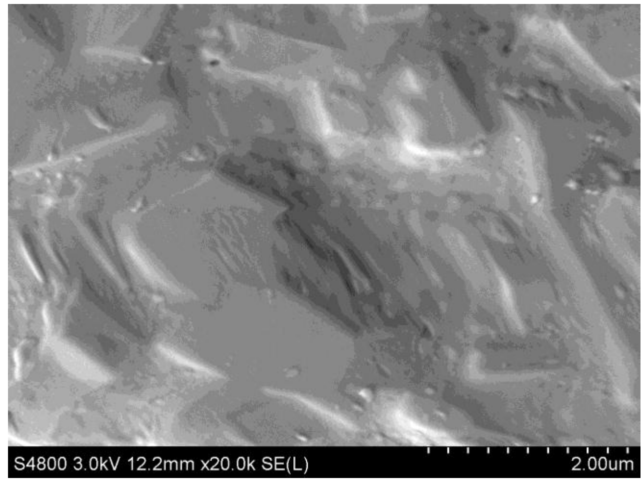

Figure 3: FE-SEM micrograph of sample S06PVD2B

Figure 2 summarized the averaged values of wettability of the samples. However, the samples prepared by PVD process presented an important variation in the values of contact angles in water, up to 140º (see figure 5). The cleaning procedure, the position of the samples in the PVD chamber, the uniformity of the plasma and the rate of O_2 flow during the process should be analyzed in following studies, in other to optimize the wettability of the Al_2O_3 coatings.

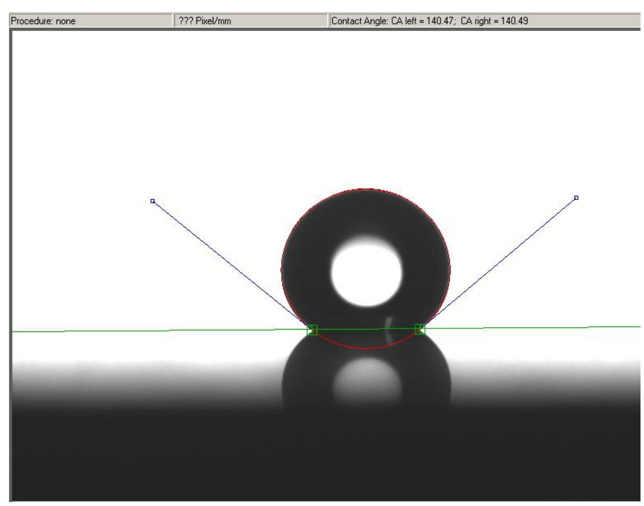

Figure 5: Contact angle in water (sample S13PVD2B)

4 CONCLUSIONS

Hydrophobic Al_2O_3 coatings with contact angles up to 140 º were deposited by PVD over three different types of ceramic substrates.

The contact angles of these Al_2O_3 coatings do not depend either on the roughness neither on the surface energy of the substrates.

These coatings present a surface flake structure which combines a micro and a nanoscale. The quality of this structure determines the hydrophobicity of the coatings, and it is optimized in thicker films.

The results of this study might open a new pathway to the fabrication of superhydrophobic transparent conducting surfaces that can be used in several fields such as engineering, photovoltaic, decorative, among others.

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