HEXAMETILDISSILOXANE PLASMA DEPOSITION ON AL_2O_3 CERAMIC: WATERPROOFING EFFECT

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Abstract. Polymeric HMDSO plasma deposition was performed on two Al_2O_3 ceramic surfaces. The purpose of this deposition was to verify possible changes on ceramics wetability due to the HMDSO film. Al_2O_3 ceramic samples were obtained from A-S5G and A-1000 commercial powders, in order to attain opened and closed pores on the surface, respectively. Samples were obtained at 40 MPa uniaxial pressure and then through sintering process at 1600^0 C for two hours. HMDSO plasma polymerization was made with a 13.56 MHz RF source at 25 and 50 W for different periods of time. Surface characterization was made with a contact angle meter device. Results showed (a) reduction on ceramics wetability on A-1.000 Al_2O_3 samples, and (b) total ceramics waterproofing gain on A-S5G Al_2O_3 samples. These results may be interesting from a bacteriological point of view.

1. Introduction

Al_2O_3 is a large spectrum application material for ceramic devices, with analytical purity or commercial options with specific dopants or impurities, and with specific granulometry. Such dopants and granulometry result on ceramic characterization like mechanical strength, porosity, wetability and densification.

The surface of the sintered ceramic samples depends on the granulometry and powder purity. Its wetability and porosity determine applications. Porosity is an important factor if the ceramic device is exposed to bacteria colonies that can migrate into subsurface layers. Another important factor to be considered is wetability which value can affect bacteria fixing on ceramic surface. Vitreous and enameled layers or polymeric sealants have been used to cover the ceramic surface or modify wetability, but such coatings need new thermal steps or "maturation periods". In addition, solvents can remove some polymeric sealants.

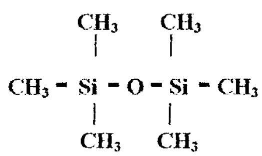
On the other hand, plasma technology has got the possibility to produce chemically stable polymers from molecules without chemical catalytic process (D'Agostino, 1990, Lamendola and D'Agostino, 1998). These polymers do not dissolve by solvents action. The plasma process is based on vapor monomer introduction into a vacuum chamber where cold glow plasma breaks monomer molecules, and their ionized parts are recombined on cold surfaces.

HMDSO (hexamethyldisiloxane) is a typical stable monomer used by industry to improve plasma-polymerized films on semiconductors, or to apply anti-reflective films on vitreous lenses. Vapor pressure of HMDSO is nearly 8 Torr at room temperature, and it is not difficult to produce HMDSO ions under RF action at low pressure (10^{-3} Torr - 10^{-1} Torr). Through recombination of ions by random processes, a polymeric film is obtained as presented in fig. 1 (Tajima and Yamamoto, 1985). The recombination of free radicals does not stop at the end of plasma deposition, but some hours later. Final polymeric film thickness may vary from hundreds of angstroms to one or two microns, and bear small residual tensile stress (Nery *et al*, 1996, 2000). Layer thickness homogeneity is inherent to plasma deposition process, where there are no electric field concentration points as occurs in electroplating galvanic processes. The topography of the substratum is reproduced on the polymeric surface with micrometric resolution (Teixeira, 2003). HMDSO polymeric films do not display any color or opacity. Some visual color effects on the surface occur exclusively from optical interferometric patterns. Chemical composition and hardness of HMDSO polymeric layer depend on plasma parameters such as vacuum pressure, RF power, reactor and electrodes geometry, and substrate temperature.

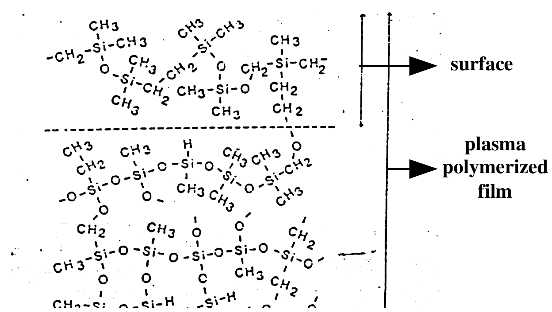
In this work, polymeric HMDSO plasma deposition process was tested on ceramic surfaces for the purpose of modifying their wetability characteristics, or obtaining waterproof surfaces.

2. Experimental

Disk shaped ceramic samples were made with 20 mm diameter from A-1000 and A-S5G Al_2O_3 commercial powders, both formed at 40 MPa uniaxial mechanical pressures. A-1000 Al_2O_3 powder was used for the purpose of obtaining waterproof ceramic surfaces. A-S5G Al_2O_3 powder was used to obtain porous ceramic surfaces. In both cases, powder was prepared by adding PVal solution, 1wt% MgO, and 10 wt% H_2O. Samples were pre-sintered at 1,000 ^OC for one hour, and then sintered at 1,600 ^0C for two hours. A heating rate of 3^0C / min was used.



(a)



(b)

Figure 1(a). HMDSO monomer. Figure 1(b). Plasma polymerized HMDSO (Tajima and Yamamoto, 1985).

After sintering, samples were cleaned with detergent and acetone baths under ultrasonic agitation, and dried at 120 ^0C for six hours. Then, apparent porosity, H_2O absorption and apparent specific mass were measured by Archimedes method (in accordance with ASTM C20-00). Roughness measurements were made with a Mitutoyo Surfset 301 rugosimeter.

After that, samples wetability was evaluated with a contact angle meter (Kinloch, 1995) as shown in Figs. 2a, 2b, and 2c. Image Tool version 3.00 software was used to measure contact angles. One sample of each type of Al_2O_3 ceramic was polished with sandpaper (granulometry 300) to verify eventual changes on contact angle due to roughness reduction.

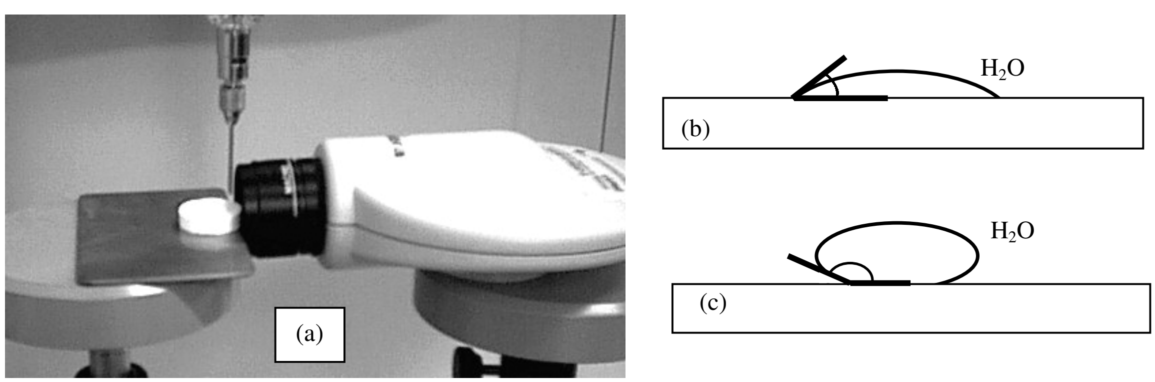


Figure 2. (a) Contact angle meter. (b) Hydrophilic behavior and (c) hydrophobic behavior of ceramic surface.

After the observation of hydrophilic or hydrophobic behavior on the surfaces, samples were taken to plasma deposition system, as shown in fig. 3. A first cleaning of the deposition chamber was performed with a diffusion pump (nearly 3.10^{-4} Torr), to reduce water, nitrogen and oxygen contamination. Then, a precision valve controlled HMDSO vapor introduction. At the desired pressure, vacuum meter gauges were turned off, 13.56 MHz RF source was turned on, and adjusted to better impedance coupling between RF source and plasma. During deposition, total ambient darkness was necessary to guarantee plasma stability monitoring. Plasma process was characterized by parameters shown in Tab.1.

To use 9.10^{-1} Torr pressure, it was necessary to change electrodes configuration from parallel external circular electrodes to parallel internal plane electrodes, avoiding plasma-triggering and stability problems. At the end of plasma deposition, samples were returned to contact angle measurement.

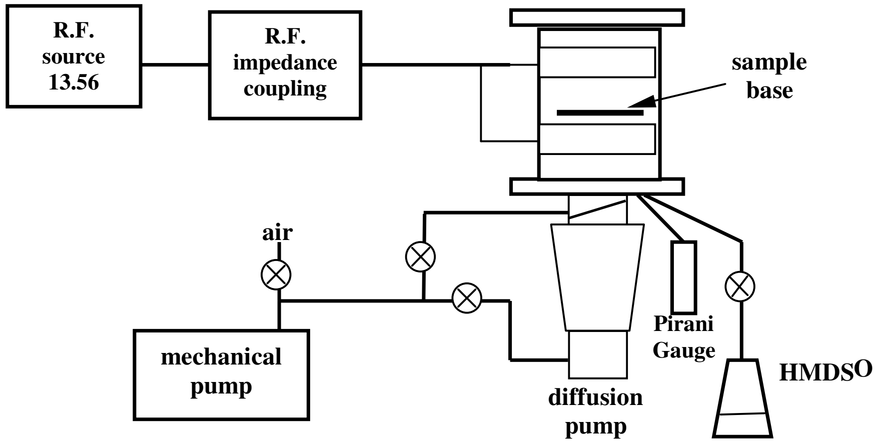


Figure 3. HMDSO plasma deposition system.

Table 1. Plasma parameters used to HMDSO deposition.

	13.56 MHz RF Power (W)	pressure (Torr)	deposition period (minutes)	electrodes configuration
A-S5G Al_2O_3	25	9.10^{-2}	30 – 10 – 5 – 3	external parallel circles
	50	9.10^{-1}	10 – 5 – 3	internal plates
A-1000 Al_2O_3	50	9.10^{-1}	10 – 5 – 3	internal plates

3. Results and discussion

The A-1,000Al_2O_3 samples not treated with plasma showed waterproof surfaces and high resistance to sandpaper action. Samples presented 1.3% apparent porosity, 2.8% H_2O absorption, and 3.37 g/cm^3 apparent specific mass. Roughness measurements result 2.5 µm Ra, 15.7 Rt, and "less peek" R3z (no pores). For the polished sample was obtained 0.8 µm Ra, 5.7 Rt, and "less peek" R3z (no pores). The A - S5G Al_2O_3 samples not treated with plasma showed absorbent surfaces and low resistance to sandpaper action. Samples presented 43.0% apparent porosity, 20.8% H_2O absorption and 2.2 g/cm^3 apparent specific mass. Roughness measurements result 1.3 µm Ra, 11.7 Rt, and 3.8 µm R3z (pores presence) for both cases (with and without sandpaper action). Such different ceramic characteristics allowed observations in how the deposition process interferes on wetability and waterproof gain.

It was not possible to verify any visual difference between ceramic surfaces before and after plasma deposition. Typical ceramic surface roughnesses have much larger peak-vale dimensions than visible light wavelengths, and interferometric effect cannot be observed on such surfaces. Optical microscopic observations on ceramic surfaces are not possible because (a) the several optical levels inherent to roughness condition do not allow any focal adjust and (b) HMDSO is absolutely transparent. SEM technique use is also not possible because electron bean energy is enough to volatize the HMDSO film. The only fast way to distinguish plasma deposited samples from plasma non-deposited samples was to observe surface hydrophobic or hydrophilic behaviors through contact angle measurements. MHDSO film thickness was not measured because smoothed vitreous samples were not prepared to be analyzed with a perfilometer.

Examples of recorded contact angle measurements are shown in Fig. 4 to Fig. 7. In Fig. 4, A-1000 Al_2O_3 sample presents its hydrophilic behavior before HMDSO plasma deposition. After HMDSO plasma deposition, samples presented radical change on contact angle, from hydrophilic behavior to hydrophobic behavior, as shown in Fig. 5.

For the sandpaper worked samples, the reduction of A-1000 Al_2O_3 surface roughness resulted on drastic change of ceramics wetability, from hydrophilic behavior to hydrophobic behavior, but with lower contact angle than plasma treated A-1000 Al_2O_3 samples (see comparison between Fig. 5 and Fig. 6).

For the A-S5G Al_2O_3 samples not treated with plasma, instantaneous water absorption did not permit contact angle observation. Fig. 7 indicates a special case where after several drips, great amount of water inside sample allowed a fast drop absorption record. In this case, it was possible to observe that instantaneous contact angle was not so different than A-1000 Al_2O_3 samples not treated with plasma (see comparison between Fig. 4 and Fig. 7). To HMDSO plasma treated A-S5G Al_2O_3 samples, all contact angles presented similar values to plasma treated A-1000 Al_2O_3 samples. Tab. 2 sums up contact angle behavior of samples in each step or condition of study.

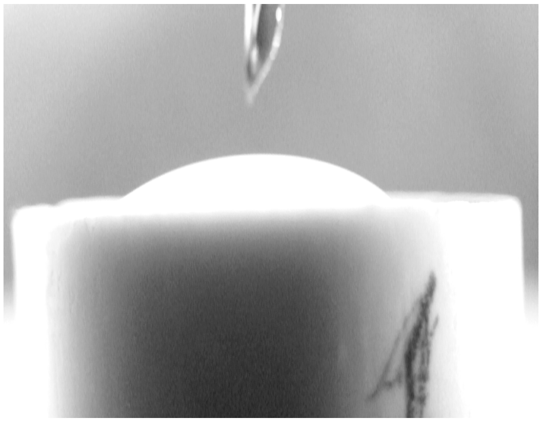


Figure 4. Water drop on A-1000 Al_2O_3 sample not treated with plasma

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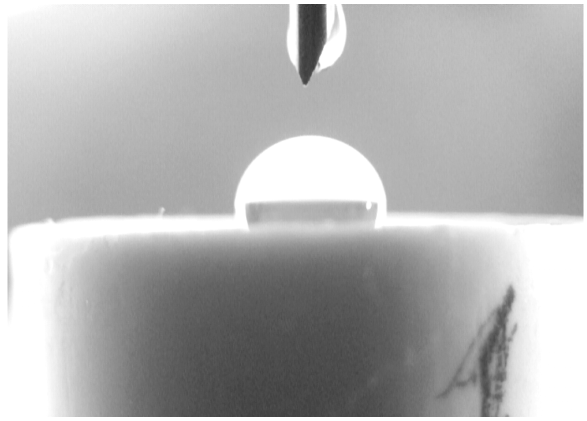

Figure 5. Water drop on A-1000 Al_2O_3 sample treated with HMDSO plasma

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Figure 6. Water drop on sandpaper polished A-1000 sample (not treated with plasma).

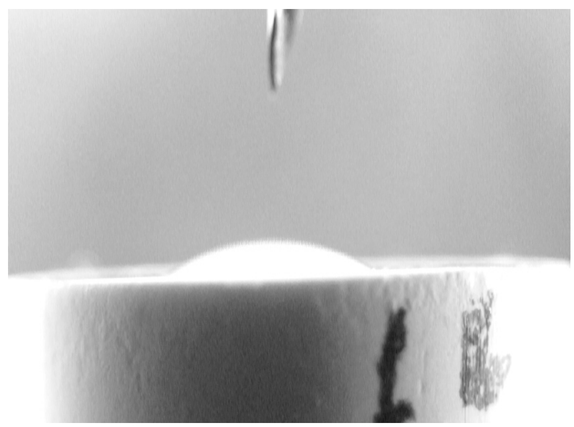

Figure 7. Fast water drop absorption on A-S5G Al_2O_3 surface (not treated with plasma).

Table 2. Contact angle between water and ceramic, before and after HMDSO plasma deposition

	RF Power and pressure	deposition period (min)	contact angle: before deposition (degrees)	contact angle: after deposition (degrees)
A-S5G Al_2O_3	25W / 9.10^{-2} Torr	30 – 10 – 5	not measurable	126 ± 12
		3	not measurable	131 ± 5
	50 W / 9.10^{-1} Torr	10 – 5 – 3	not measurable	135 ± 9
		3 *	not measurable	129 ± 5
A-1000 Al_2O_3	50 W / 9.10^{-1} Torr	10 – 5 – 3	22 ± 7	117 ± 14
		3 *	95 ± 5	133 ± 5

* refer to sandpaper polished samples;

From results and Tab. 2, the comments are as follows:

a) in all cases, hydrophilic and hydrophobic behaviors of ceramic surfaces were well characterized, before and after plasma treatments;
b) before plasma treatment, A-S5G Al_2O_4 samples were absorbent and did not allow contact angle measurements due to instantaneous water absorption;
c) after plasma deposition, all A-S5G Al_2O_4 samples gained an efficient waterproof surface, except for 25 W RF – 9. 10^{-2} Torr – 3 minute deposition samples;
d) for 25 W RF - 9.10^{-2} Torr - 3minute treated A-S5G Al_2O_4 samples, water absorption was slow (a few minutes to total absorption), suggesting small holes existence in HMDSO layer; for 50 W RF - 9.10^{-1} Torr – 3 minute treated A-S5G Al_2O_4 samples, no water absorption was observed, suggesting gain of efficient waterproof HMDSO film; this suggests that higher power RF results in more effective deposition process;
e) in both A-S5G and A-1000 Al_2O_3 ceramics, there was no great difference between contact angle values, suggesting that deposition period does not affect contact angle; because of this, Tab. 2 was arranged without deposition time considerations; if HMDSO film thickness has direct dependence on deposition time, results suggest that HMDSO film thickness does not act on HMDSO hydrophobic behavior; some contact angle differences between plasma treated A-S5G and A-1,000 ceramic samples can be attributed to surface roughness differences;
f) sandpaper polished A-S5G Al_2O_4 sample (treated with plasma) presented contact angle value within other A-S5G Al_2O_4 samples bandwidth; this result suggests that contact angle values depend upon HMDSO hydrophobic behavior rather than surface roughness;
g) in case of A-1000 Al_2O_3 samples (not treated with plasma), standard deviation of contact angle represents 30% of mean value (22 degrees); to sandpaper polished sample (not treated with plasma), contact angle was nearly 330 % greater than that observed for non-polished samples; this result shows that surface roughness is an important factor to determine contact angle of non-treated ceramics;
h) to plasma treated A-1000 Al_2O_3 samples, standard deviation of contact angles of non-polished samples was reduced to 12% of mean value (117 degrees); the polished sample had a contact angle 13% greater than other A-1000 Al_2O_3 treated samples; in same way of A-S5G Al_2O_4 samples case, this results suggest that surface roughness variation is not a very important factor to determine contact angle for the plasma treated ceramics however, HMDSO hydrophobic behavior is the predominant factor.

4. Conclusions

1) Plasma polymerized HMDSO films grant efficient waterproof surface for porous A-S5G Al_2O_3 ceramics; to make it possible it is necessary to use adequate plasma parameters such as 50 W RF, 9.10^{-1} Torr, and at least 3minute deposition;
2) Plasma polymerized HMDSO films show hydrophobic behavior, whatever HMDSO film thickness is;
3) HMDSO films hydrophobic behavior displays negligible variation related to surface roughness;
4) Plasma polymerized HMDSO films do not display any visual aspect changes on treated ceramic surface;
5) Surface contact angle measurement is an effective way to verify that a ceramic surface has received plasma polymerized HMDSO films.

5. Acknowledgements

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