

Superficial Modifications in TiO₂ and Al₂O₃ Ceramics

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The properties of hydrophilicity or hydrophobicity of materials are defined mainly, though not exclusively, by their composition, morphology and surface energy. In this work, titanium dioxide (TiO₂) and aluminum oxide-alumina (Al₂O₃) ceramics prepared by uniaxial pressing were studied in terms of surface energy. The surfaces of these ceramics were treated with nitrogen plasma, using a stainless steel reactor excited by a 13,6 MHz radio frequency operating at 50 W input power and 13 Pa nitrogen pressure. The surface morphology was investigated by scanning electron microscopy (SEM) analysis. Surface energy and contact angle measurements were taken using a RAMÉ-HART goniometer. These measurements were taken as function of time, over a 21-day period. The contact angle and surface energy values were found to change by almost 34% in comparison to their initial values immediately following plasma treatment. Nonetheless, the hydrophilic character of the Al₂O₃ and TiO₂ remained constant throughout the test period.

Keywords: titanium dioxide, alumina, surface energy, contact angle

1. Introduction

Kingery¹ defined *Ceramics* as the art, science or technology of manufacturing and using solid pieces composed essentially and mostly of non-metallic inorganic materials called *ceramic materials*.

The scientific study of ceramic materials gained greater momentum from the 1940's on, with the emergence of *advanced ceramics* such as barium titanate capacitors (BaTiO₃) and alumina (Al₂O₃) ignition plugs² for automobiles. These ceramics are applied in the high tech electronic, aerospace and automotive industries³.

Although ceramics have reportedly been employed as *biomaterials* for bone repairs since the late 19th century, the modern era of bioceramics is considered to have begun in 1963 with the study of *cerosium*, composed of an aluminate impregnated with epoxy resin, which was also used to replace bone parts, starting in 1963⁴. The late 1970's saw a considerably heightened focus on the study and use of bioceramics, mainly in the areas of Orthopedics and Dentistry, including removable prosthetic applications.

The study of biomaterials involves investigations into the relevant characteristics of these materials, i.e., their mechanical, thermal, electrical and especially their surface properties, for the surface is in contact with living tissue. Thus, the study of these materials' surfaces is crucial to determine their biocompatibility and to evaluate their hydrophobic or hydrophilic character⁵.

Among the materials that are applicable as biomaterials, titanium dioxide (TiO₂) constitutes an alternative material, mainly because it is sterilizable when properly stimulated by ultraviolet radiation with a wavelength similar to the Sun's radiation⁶.

The use of alumina (Al₂O₃) as a biomaterial offers the advantage of bio-inertness⁷, although it is not as sterilizable as TiO₂. However, when alumina is mixed with titanium dioxide, it allows the degree of porosity of the ceramic to be controlled, ensuring new potential applications as filters and selective membranes⁸.

This work deals with the production of TiO₂ and Al₂O₃ ceramics subjected to plasma treatments in a nitrogen at-

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mosphere. The materials' wettability was verified by investigating their surface energies and contact angles before and after the plasma treatments. The mechanical properties, i.e., rupture strain, apparent specific density, porosity levels, percentile of water absorption and superficial roughness, were also verified.

2. Methods and Processes

TiO₂ and Al₂O₃ samples were prepared from powder with the addition of 0,5% in mass of a polyvinyl alcohol solution (PVal) and 10% in mass of distilled water. The mixtures were then ball milled for 30 min to homogenize them completely, sifted through a 10-mesh sieve, placed in a non-porous metallic mold and uniaxially pressed under a pressure of 40 MPa to shape them into 22 mm diameter, 3 mm thick disk-shaped test specimens. Other samples were shaped into 45 mm long, 4 mm wide, 3 mm thick bars. After pressing, the TiO₂ samples were sintered for one hour at 1450 °C and the Al₂O₃ samples at 1650 °C in an electric EDG7000-EDGCOM3P furnace, using a heating rate of 5 °C/min.

The ceramic's mechanical strength was evaluated by three-point flexural testing, following the ASTM C1161/94 standard, using an EMIC testing machine at a speed of 0,5 mm/min. The results were analyzed based on Weibull's statistical method to verify the material's characteristic rupture strain (σ_0) and mean rupture strain (σ_{50}). Apparent specific density, apparent porosity and water absorption measurements were taken by means of an analytical scale test, according to the ASTM C20/87 standard. The mean roughness, *Ra* parameter, was then measured using a MITUTOYO-SURFTEST 301 roughness measuring instrument.

The microstructure of the two samples was analyzed by SEM (scanning electron microscopy) under a LEO 435 VPI microscope using secondary electrons and a 15 kV voltage.

The hydrophilic or hydrophobic characteristics of the alumina and titanium dioxide samples were evaluated through contact angle (θ) and surface free energy measurements. This material's wettability is directly associated with its superficial tension and with the behavior of the solid-liquid interface, assuming that the material in question is solid¹¹. The contact angle is measured by the tangent between a drop of the liquid and the solid surface, as shown in Fig. 1.

Considering a drop at rest, i.e., with the variation of the surface free energy per unit area tending to zero, one has:

$$\gamma_{SL} = \gamma_{SV} - \gamma_{LV} \cos\theta \quad (1),$$

where γ_{LV} , γ_{SV} and γ_{SL} are, respectively, the interfacial tensions between liquid and steam, solid and steam, and solid

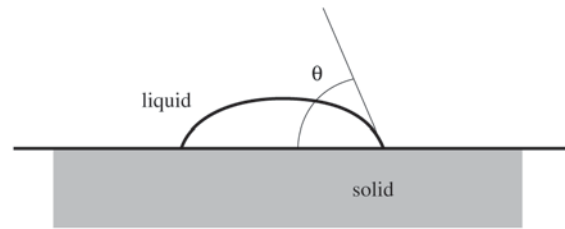


Figure 1. Contact angle measurement.

and liquid. This expression is called Young's equation.

When the angle is greater than 90°, the absorption is practically zero and the liquid tends to move slowly over the solid without penetrating into it. On the other hand, the liquid tends to flow over the solid when the contact angle tends to zero. Therefore, a dispersal coefficient *S* must be defined, since there are differences between the tensions and the energies at the solid-steam interface and only in the solid, owing to the types of attractive forces, such as the van der Waals forces, that act at the intermolecular level¹². Thus, one can write:

$$S = \gamma_S - \gamma_{SL} - \gamma_{LV} - \Pi_S \quad (2),$$

in which

$$\Pi_S = RT \int_0^{p_0} \Gamma d(\ln p) \quad (3),$$

here γ_{LV} and γ_{SL} are, respectively, the interfacial liquid-steam and solid-liquid tensions, *R* is the universal constant of the ideal gases, *T* is the absolute ambient temperature, Γ represents the superficial concentration of absorbed steam, *p*₀ is the steam's equilibrium pressure and *p* is the local pressure of the steam.

A liquid will spread spontaneously on a solid surface when $S \geq 0$, i.e., when the surface free energy of the solid is greater than the other energies existing at the aforementioned interfaces. It is worth noting that the solid's wettability will depend on other factors such as the viscosity of the liquid used and the surface roughness of the solid in question.

Contact angle and surface energy measurements of the ceramics were taken as a function of time before and after the plasma treatment, using a RAMÉ-HART model 100 goniometer in a 20 °C controlled temperature environment. Deionized water and di-iodemethane were used specifically as test liquids for these measurements. The TiO₂ and Al₂O₃ samples were plasma treated for 3 min in a stainless steel reactor excited by radio frequency (13,56 MHz, 50 W), using plasma derived from nitrogen kept under a pressure of 13 Pa.

3. Results and discussion

Figures 2a and 2b show typical SEM images of TiO₂ and Al₂O₃ samples, revealing, through the better definition of the grain outlines, that the Al₂O₃ ceramic (alumina) grains have a more regular shape than those of the TiO₂ ceramics. This finding may be evidence that, comparatively, the alumina took on a greater density, an assumption that is confirmed by the values listed in Table 1.

Table 1 shows the mechanical properties of the alumina and titanium dioxide samples.

As can be seen, the alumina samples became more densified though less homogeneous than the titanium dioxide samples, as illustrated in the diagrams of Fig. 3 and in Table 2.

The roughness analysis revealed that the superficial finish of the Al₂O₃ samples was slightly superior, which may

have influenced the rupture strain values, increasing them in comparison to those of the TiO₂ samples.

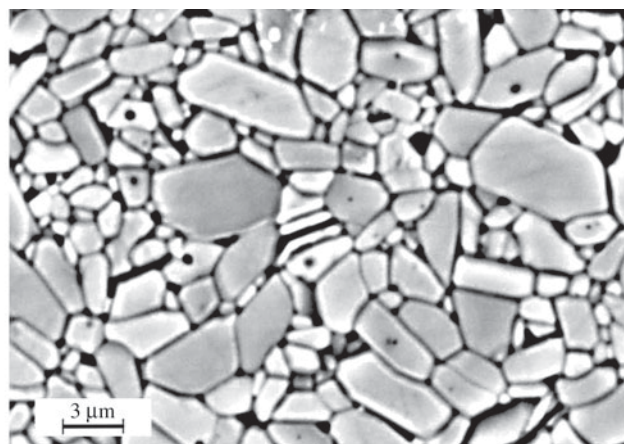
Figures 4 and 5 show the correlation between the contact angle and the surface energy as a function of time. The graphs initially show a decrease in the contact angle and an increase in the surface energy, prior to and immediately following the plasma treatment. After some time had elapsed,

Table 1. Mechanical properties of TiO₂ and Al₂O₃ samples.

| Property | TiO ₂ | Al ₂ O ₃ |
|--|------------------|--------------------------------|
| Densification (%) | 94.35 | 98.19 |
| Apparent porosity (%) | 0.26 | 0.32 |
| Water absorption (%) | 0.04 | 0.08 |
| Apparent specific density (g/cm ³) | 4.01 | 3.91 |
| Roughness Ra (μm) | 1.67 | 1.19 |

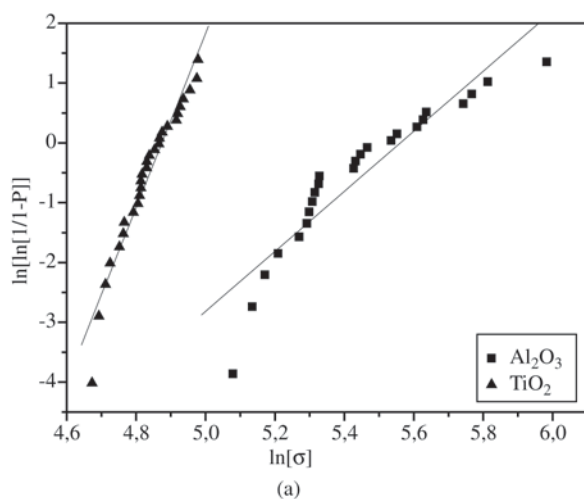


(a)

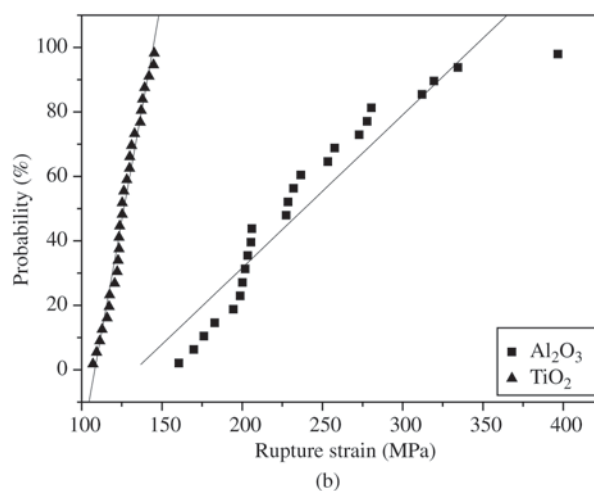


(b)

Figure 2. Images obtained by scanning electron microscopy (SEM), using a LEO 435 VPI microscope, with secondary electrons, at 15 kV voltage, for (a) TiO₂; (b) Al₂O₃ samples formed by uniaxial pressure and sintered, respectively, at 1450 °C and 1650 °C.



(a)



(b)

Figure 3. Weibull diagrams for TiO₂ e Al₂O₃ samples formed by uniaxial pressure and sintered at 1450 °C and 1650 °C, respectively.

there was an increase in the contact angle, accompanied by a reduction in the surface energy. The most significant difference for the two types of ceramic occurred between 336 and 504 h. It was also found that the Al_2O_3 ceramic displayed stronger hydrophilicity than the TiO_2 ceramic. This difference was also associated with other mechanical char-

acteristics of these materials, such as superficial roughness, which was greater in the TiO_2 ceramic.

In the case of the TiO_2 samples, the production of ultraviolet irradiation during the plasma application led to a reduction of the Ti^{+4} to Ti^{+3} ions and the appearance of surface oxygen vacancies¹³. Subsequently, the adsorption of ambient water steam led to the formation of hydroxyl groups on the surface, improving the samples' hydrophilicity. The reoxidation of the Ti^{+3} ions promoted a progressive removal of the hydroxyl groups, causing the samples to revert to a state of greater hydrophilicity.

According to Tari¹⁵, the adsorptive behavior of hydroxyl groups by alumina (Al_2O_3) may occur because the aluminum atoms can share electrons with other atoms or compounds, even after bonding with the oxygen, as is the case of the

Table 2. Results of three-point flexural test using Weibull's statistical method.

| Property | TiO_2 | Al_2O_3 |
|---------------------|----------------|-------------------------|
| σ_0 (MPa) | 130.0 | 260.0 |
| σ_{50} (MPa) | 125.0 | 239.0 |
| Weibull module | 14.6 | 5.0 |

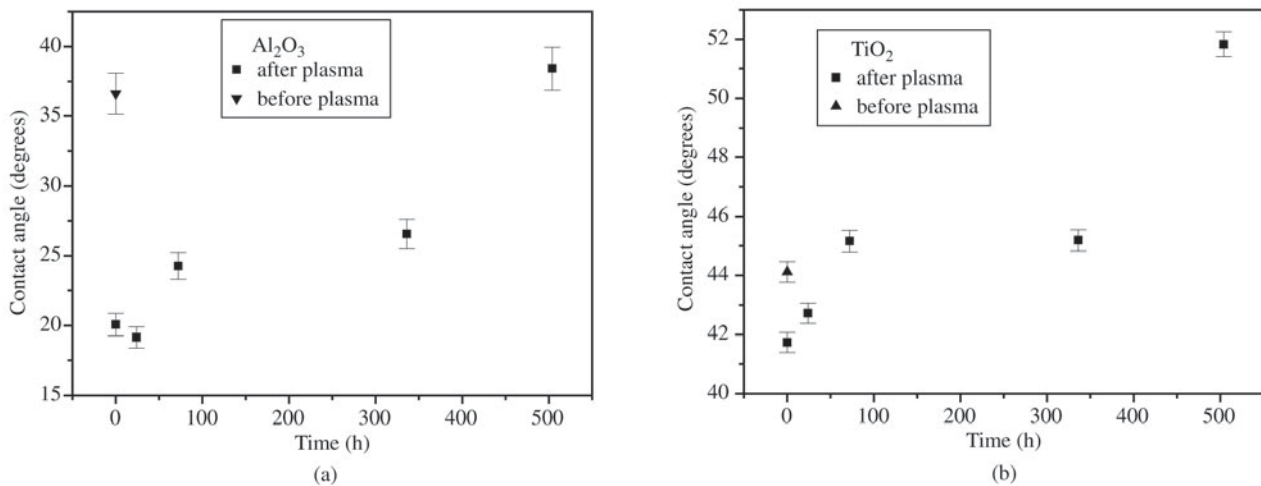


Figure 4. Contact angle (degrees) vs. time (h) plots for (a) Al_2O_3 ; (b) TiO_2 samples produced by uniaxial pressure and sintered, respectively, at 1650 and 1450 °C.

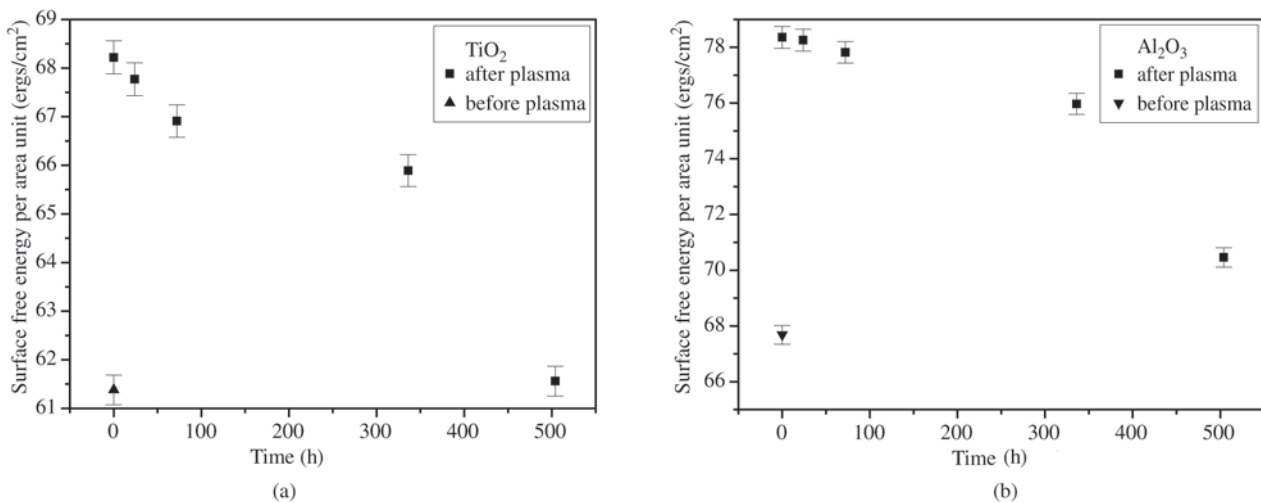


Figure 5. Surface free energy per area unit (ergs/cm²) vs. time (h) for (a) TiO_2 ; (b) Al_2O_3 samples formed by uniaxial pressure and sintered at 1450 and 1650 °C, respectively.

oxygen present in the water steam that exists in the atmosphere. The application of plasma, in this case, may have modified the action of polar forces acting on the sample's surface, thus altering the nondispersive component of the superficial tension¹⁴ and improving the material's hydrophilicity. In time, the inclusion of oxygen on the alumina surface and the rearrangement of superficial charges tend to invert the material's behavior, repelling electrons and polar liquids, as is the case of water. Therefore, the application of plasma using gases such as nitrogen can modify the surface energy and contact angle, which are a function of the power applied to the system and of the pressure inside the reactor in which the plasma is processed¹⁶.

The changes in contact angle and surface free energy that occurred over time in the TiO₂ and Al₂O₃ samples tended toward values at which the system's equilibrium was configured at levels of minimum energy.

4. Conclusions

The TiO₂ and Al₂O₃ samples displayed dissimilar mechanical characteristics, with the TiO₂ samples showing a greater degree of homogeneity than the Al₂O₃ samples, although the latter possessed greater mechanical resistance than the titanium dioxide samples. However, after being plasma treated, both samples showed the same behavior in regard to the contact angle and surface energy measurements. The variation in the hydrophilicity of the titanium dioxide samples was attributed to oxidation and reoxidation processes of the titanium ions, with adsorption and loss of hydroxyl groups on the samples' surfaces. With regard to the alumina samples, the adsorption of hydroxyl groups possibly originated from bonding of the aluminum atoms and a subsequent reversal to the energy equilibrium of both samples to their minimum values.

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