Effects of Femtosecond Laser Irradiation on the Surfaces of Alumina and Alumina-Zirconia Composites.

Aguiar, A.A.[1,a], Lima, N.B.[1,b], de Rossi,W.[1,c],Samad, R.E.[1,d],Vieira, N.D.[1,e],Braga, F.J.C.[1,f]

[1]Instituto de Pesquisas Energéticas e Nucleares –IPEN_CNEN/SP

[a]mandaabati@hotmail.com, [b] nblima@ipen.br, [c] wderossi@ipen.br, [d]resamad@ipen.br, [e]nilsondv@ipen.br , [f]fjcbraga@ipen.br .

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Abstract. Alumina and zirconia-alumina composite has been micro-structured in air using femtosecond laser. The threshold fluence of 6.2 J.cm^{-2} found in this work is close to that found published in literature [1]. In the case of Al-Zr, the threshold fluence is 2.2 J.cm^{-2}.Surface femtosecond laser treatment increase the apatite deposition by biomimetic method on alumina and alumina-zirconia composite and depends on the condition of laser treatments.

Introduction

Ceramics, in general, have some advantages in use in the biomedical field, due to some features such as: as esthetics, biocompatibility and chemical resistance [2]. When compared to metallic materials, a problematic aspect of ceramic materials is their low mechanical strength and fracture toughness [3]. Hence, some authors have suggested the use of composite alumina-zirconia as a biomaterial high density as an alternative. Alumina has an excellent biocompatibility and wears resistance, however exhibits low flexural strength and toughness [3]. Stabilized zirconia ceramic in the tetragonal phase has a good esthetical appearance after polishing and are inert in physiological environment, featuring better flexural strength and toughness, having a low modulus of elasticity when compared with pure alumina. The pure zirconia is rarely used without adding agents to stabilize the crystal structure, since the transformation of tetragonal to monoclinic phase during cooling subsequent to the sintering step causes volume expansion and consequent rupture of the ceramic. When stabilized with 3 mol% yttria, zirconia tetragonal structure can maintain its high temperatures and be metastable at room temperature. This material, called Y-TZP (yttria tetragonal zirconia polycrystals) have been an alternative to alumina as biomaterial, both for dental applications as orthopedic implants [2,3].

The adhesion of hydroxyapatite is essential for interaction with the substrate. The quality of this bond will influence their morphology and future capacity of osseointegration. The adhesion of hydroxylapatite, as well as their morphology depends on the surface properties of materials. Previous studies show that these surface characteristics depend on surface chemistry [5], surface energy [6] and surface topography [4]. Among the few published studies on surface treatment on the basis of zirconia and alumina ceramic for use as a biomaterial can highlight the work of Aguiar [7] and Uchida [8] that investigated the effect of chemical treatment on the surface of alumina-zirconia composites and Hao [9] that used a CO2 laser to modify the roughness and surface energy of magnesia stabilized zirconia

Uchida [8] determined that materials subjected to chemical attack of phosphoric acid and sodium hydroxide generates functional groups of Zr-OH on the surface of the composite. Aguiar [7] showed that these chemical attacks cause the transformation of tetragonal to monoclinic zirconia, reducing the fracture toughness of these materials, preventing its use as a biomaterial. In addition, the author found that the biomimetic deposition of apatite on the substrate of alumina-zirconia was effective in rough materials without chemical surface treatment. Hao [9] showed that the wettability, which is an important parameter for cell adhesion, was more influenced by microstructural changes and the oxygen content in the surface than by roughness. It is noteworthy that he used a CO2 laser, which causes melting of the surface when treated with a power exceeding 1.6 KW/cm^2, not allowing the control to obtain very rough surfaces.

Laser surface engineering is a method of material processing that uses high-energy density of focused light to melt, heat or modifies material on the outside or near the surface [10]. Depending on the material and process parameters microstructures changes may occur as a grain refinement, phase transformations, alloy formation and a mixture of composite materials on the surface without actually affecting the bulk of the material.

The interaction of ultra short laser pulses with matter may result in ablation almost free of heat effects. This, however, frequently is not true when high fluence or high repetition rates are employed [1], in such cases, a sequence of phenomena arise almost simultaneously producing defects and heat accumulation. To avoid buildup of heat, ablation must be produced by a pure "*Coulombian*" effect, i.e., that one where atoms in the surface layer are positively ionized and ripped off by repulsion forces from its neighbors and by attraction from the electronic cloud formed near above. This effect takes place to fluences close to the ablation threshold of the material, where the heat transmitted to the crystalline lattice is minimum and totally dissipated before the arrival of the next pulse. An increase of energy improves the ablation effect up to the point where the heat accumulated in the crystalline lattice is enough to induce other effects like fusion or even phase explosion. At this point an abrupt increase of efficiency occurs and related fluence can be determined by the onset of this effect.

A useful relation between the fluence F and the diameter D of the produced damage [1] is given in **Erro! Fonte de referência não encontrada.**:

$$F_0 = F_{th}^N \exp\left(\frac{D^2}{2\omega_0^2}\right) \tag{1}$$

Here, ω_0 is the beam radius on the surface of the sample, F_{th} is the damage threshold and N stands for the number of superimposed pulses. The peak fluence incident on the surface F_0 is just the density of energy multiplied by 2:

$$F_0 = 2\frac{E_{pulse}}{\pi\omega_0^2} \tag{2}$$

Where E_{pulse} is the individual pulse energy.

Erro! Fonte de referência não encontrada.can be used to obtain F_{th}^N by plotting the experimental values of F_0 x D^2 in a semi-log graph. The value of ω_0 is obtained from the **Erro! Fonte de referência não encontrada.** below [1], where M^2 is the beam quality factor, λ is the wavelength of the laser, f is the focal length of the focusing lens, ϕ and ϕ_{focus} are the beam diameter behind the lens and at the focus respectively.

$$\phi_{focus.} = 4M^2 \lambda f / (\pi . \phi) \qquad (3)$$

The relation shown in **Erro! Fonte de referência não encontrada.** is hold either for single or for N overlapped laser shots, but due to "incubation" effects, the figure is somewhat different. In fact, when a laser shot hit the surface of a material it changes the local electronic structure even for fluences below the threshold for damage. So the conditions found by a laser pulse depend on the previous history in that point and the effects, of course, depend on the number and characteristics of previous shots.

In the case of machining or even texturing with overlapped pulses, these incubation effects must be taken into account if one wants to assure a pure non-thermal processing. In general, the effect of overlapping pulses is to decrease the value of damage threshold and consequently the region of low fluence.

In this paper we present a study of texturing the surface of the composite Al2O3/ZrO2 and Al2O3 using femtosecond laser in order to alter the surface without inducing deleterious phase transformations to use these materials as a implant and its behavior after soaking in SBF(simulated body fluid).

Experimental arrangement

The powder-based alumina and zirconia are prepared by the route of co-precipitation of hydroxides in an ammoniacal medium, using the following raw materials: zirconium oxychloride solution obtained by dissolution of zirconium hydroxide with purity 99.5 wt% ZrO2 + HfO2, produced in the Pilot Plant Production of Zirconium IPEN, yttrium chloride obtained by dissolving the oxide with a purity greater to 99.9% by weight of provenance Aldrich; PA grade aluminum chloride [1,11].

After drying at 80 ^{0}C for 24 hours and calcination at 800 ^{0}C for 1 hour, the powders were subjected to grinding in ethanol for 17 hours in a ball mill, and drying in roto-evaporator, in order to obtain the homogeneity of the material. The ceramic processing steps include forming pellets by uniaxial pressing and sintering in the temperature range between 1620 and 1650 ^{0}C. The samples have to finish polishing in diamond paste of 15 μ m, 6 μm and 1 μm.

The samples were irradiated by a laser beam generated in a CPA Ti:Sapphire laser system (Femtopower Compact Pro CE-Phase HP/HR from Femtolasers), which produces 100 fs (FWHM) pulses centered at 775 nm with 40 nm of bandwidth (FWHM), at a maximum repetition rate of 4 kHz. The laser beam was focused by a 38 mm focal distance lens, and the sample was moved by a 2D programmable stage. All irradiations were done in air, and the ablated areas were evaluated using an electronic microscope.

After the study of laser ablation the following conditions were chosen to texturing the surface of the samples: 2.5 F (J.cm^{-2}), N=1 and 4 F (J.cm^{-2}), N=32 for Al2O3 and 2.3 F (J.cm^{-2}), N=1 and 4.3 F (J.cm^{-2}), N=1024 for composite Al2O3/ZrO2. These materials were surface etched in squares of 4x4mm^2 by laser and soaked in SBF for 3, 6 and 15 days and the thickness of deposited apatite were measured by Rigaku x-ray fluorescence equipment.

Results and discussions

Surfaces of pure and zirconia alumina samples were irradiated by single laser pulses at various positions and different energies, and for every one of the different energies six replicas were ablated. The diameter of each damaged area was measured and the average D value for each fluence was used in **Erro! Fonte de referência não encontrada.** to plot the graphs seen in Figure1 - Diameter squared as function of pulse fluence for pure alumina (open square) and zirconia alumina (black circles). Peak threshold fluence found was 6.2 $J.cm^{-2}$ for pure alumina and 2.2 $J.cm^{-2}$ for AlZr.

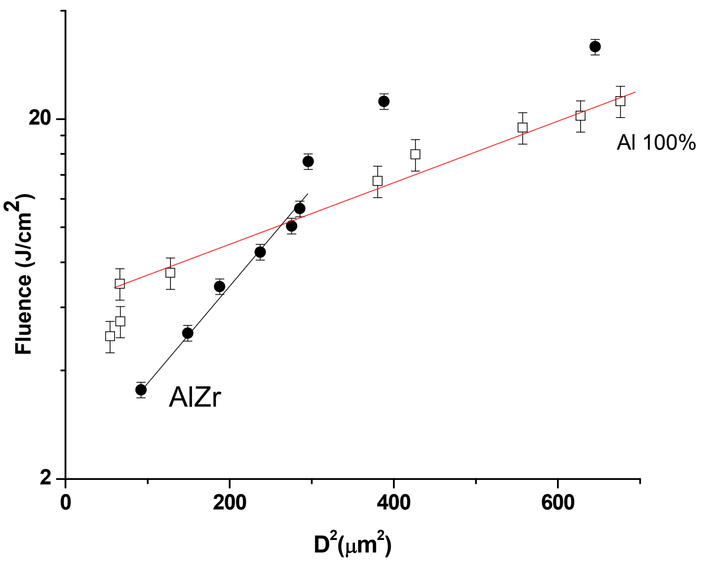

Figure1 - Diameter squared as function of pulse fluence for pure alumina (open square) and zirconia alumina (black circles). Peak threshold fluence found was 6.2 $J.cm^{-2}$ for pure alumina and 2.2 $J.cm^{-2}$ for AlZr.

In these graphs, the extrapolation of fluence for D^2 approaching to zero gives the value of damage threshold F_{th}. The value of F_{th} = 6.2 $J.cm^{-2}$ found for pure alumina is close to that of 5.6 $J.cm^{-2}$ found by other work [1] . To Zirconia alumina, the obtained value (F_{th} = 2.2 $J.cm^{2}$) was considerably smaller and as far as we know is the first reported in the literature.

It is clear from the AlZr case figure 1 an abrupt increase of efficiency for fluences exceeding 5$J.cm^{2}$. This means that thermal effects takes place beyond this point and below it an almost non-thermal ablation occurs. These two parts of the graph are said to be the "high fluence" and "low fluence" regions of ablation respectively. The same behavior is not seen in the pure alumina case, indicating that the onset of thermal phenomena must occur in fluences higher than that ones used here.

In order to found the low fluence regime for texturing, a series of experiments is being done with different energies and pulse superpositions. Prior the calculations and analysis for these data, some tracks were etched in both, alumina and zirconia alumina composite, with many different energies and scanning speeds corresponding to 2, 4, 16, 32, 128, 512, and 1024 overlapped pulses. A judicious analysis in the etched topography, as seen in electronic microscopy, showed roughly two different morphologies: one with no evidence of thermal effects and other, rougher and where fusion has apparently occurred. Figure below shows such structures; it is clearly seen a harsh ablation in Figure a), with evidence of fusion and grains much smaller than the ones found in the original structure. On the contrary, Figure 2 b) depicts a perfect and clean withdraw of grains with no signs of thermal effects.

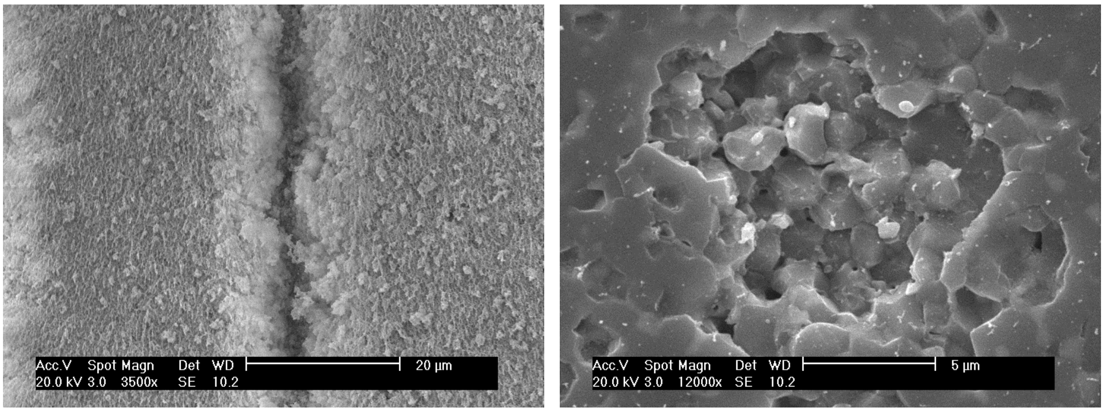

Figure 2- a) Individual track on alumina zirconia surface; F=4,3J.cm^{-2}, N=1.024. b) Single shot on alumina zirconia surface F=2,3J.cm^{-2}, N=1.

Two of such cases, i.e., with and without thermal effects were chosen for texturing pure and zirconia alumina. These conditions are shown in **Erro! Fonte de referência não encontrada.**.

Table 1- Energy, fluence and number of pulses used for surface engineering

	E (µJ)	F (J.cm^{-2})	Ra (µm)	N	condition
Pure alumina	20	2,5	*0,53*	1	No thermal effects
	32	4	*1,43*	32	thermal effects
Zirconia alumina	7	2,3	*0,33*	1	No thermal effects
	13	4,3	*1,92*	1024	thermal effects

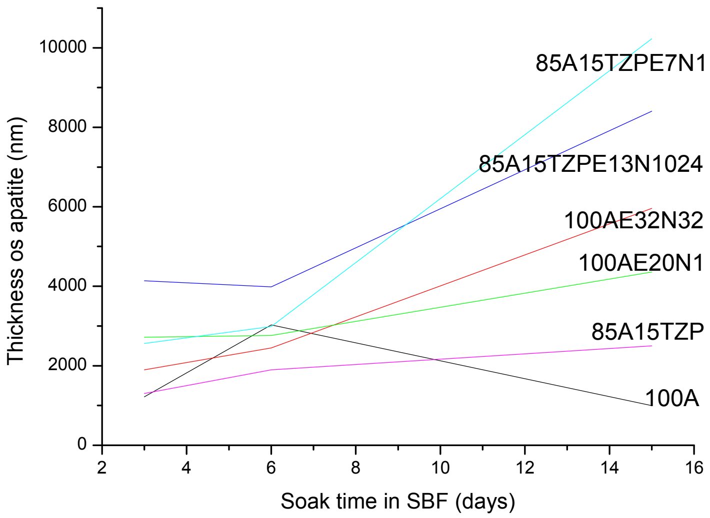

Figure 3- Thickness of apatite layer formed on the untreated samples and treated with femtosecond laser immersed in SBF for 3, 6 and 15 days

The Fig. 3 shows the apatite thickness after 3, 6 and 15 days measured by x-ray fluorescence. In both cases, for pure alumina and alumina-zirconia composite, the condition of no thermal effects shows that apatite layer is thicker compared to the samples that underwent thermal effects. In addition, samples of alumina-zirconia composite present thicker than the samples with pure alumina. All the samples that underwent laser texturing show better results than samples not treated.
The higher the laser energy and pulse number, greater is the surface roughness. This fact is important because the deposition of apatite increases with increasing roughness. So surface that underwent no thermal effects, despite of lower roughness than samples that underwent thermal effects, seems activated more functional groups than surface that underwent thermal effects. Besides, seems the Zr-OH functional group activation is more effective than Al-OH group.

Conclusion

The threshold fluence of 6.2 $J.cm^{-2}$ found in this work is close to that found by Sung Hoo Kim [1]. In the case of AlZr, the threshold fluence is considerable smaller, and the value of 2.2 $J.cm^{-2}$ found here is, as far as we know, the first reported to this material.
Surface femtosecond laser treatment increase the apatite deposition by biomimetic method on alumina and alumina-zirconia composite.
The condition of "no thermal effect" during laser texturing produce higher thickness layer of apatite when compared to the condition of "thermal effects"
The activation of the Zr-OH functional groups is more effective than Al-OH functional groups.

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