Morphological investigation by AFM of dental ceramics under thermal processing

E. GATIN[a, b*], C. LUCULESCU[c], S. IORDACHE[d], I. PĂTRAȘCU[b]
[a]*University of Bucharest, Faculty of Physics, Department Science Materials, P.O. Box MG 11, Bucharest-Măgurele, Romania*
[b]*University of Medicine 'Carol Davila', Faculty of Dentistry, Calea Plevnei 19, Sect.5, Bucharest, Romania*
[c] *INFLPR, National Institute for Laser, Plasma and Radiation Physics, P.O. Box MG- 36, Maăgurele – Bucharest, Romania*
[d]*University of Bucharest, Physics Department, 3Nano-SAE Research Centre, P.O.Box MG-38, Cod 077125 Măgurele, Romania*

Two of the most used dental ceramic materials are alumina (based on Al_2O_3) and zirconia (based on ZrO_2). The influence of heating treatment on dental ceramics during their manufacturing process (for applying veneer and glazer) was investigated. Alumina ceramic is more affected at the morphological level by the thermal process, predicting a grain size diameter control to a decreasing value, less or about the value $d_G \cong 1.137$ μm and almost a constant value for pore diameter size $d_P \cong 2$ μm. The affected depth inside the material of alumina core, caused by the thermal process, was estimated at the value, $d = 7.400 \pm 0.510$ μm. The smaller size for zirconia micro grains (morphologically not influenced by the heating temperature process involved in our study) predicts a possible modeling of the alumina surface with zirconia by grain infiltration. Those (zirconia grains) are acting as a grain stopper for the alumina sample cooling period.

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1. Introduction

There is no ceramic dental product that can simultaneously display, in a single material, characteristics of opacity and translucency or long lasting ageing mechanical resistance. Therefore, the manufacturers had offered ceramics for core building, opaque ceramic coverage for the construction of the dentin and translucent glazes to be used in layering techniques [1, 2].

For dental ceramic restorations, the manufacturing process presumes a high temperature sample heating treatment, over 1,100 ^{o} C, for applied aesthetic veneer and glazer. An important link was established between the heating treatment and cases of fractures and failure (delamination) of the ceramic core [3 - 5]. Even with very good optic results for aesthetic applications, the development of yttrium-stabilized tetragonal zirconia poly-crystal (Y-TZP), does not completely solve the problem of crack propagation caused by crystalline phase instability (monoclinic (M) / tetragonal (T) phase) [6 - 8]. For zirconia ceramic, the problems are at the crystalline lattice level which is metastable, heating and cooling cycles augmenting T → M phase transition. These problems are at the structural level and difficult to control [6 - 8].

The problems regarding alumina ceramic (optical properties as opacity and translucency or ageing mechanical properties) are at crystalline grain level and can be solved by controlling grain size during sintering / re-sintering process and by doping it with zirconia or/and hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$, denoted as HAp). Since the problems are located at the morphological level, the interest for crystal grain investigation and the possibility of modelling as a new design material based on alumina ceramic are motivated [8 - 10].

Reducing the grain size for the alumina ceramics improves not only the mechanical properties, such as hardness [11 - 13], strength, wear resistance and toughness, but also the transmittance of visible light [14 - 17]. Substantial researches have been done on reducing grain size below 1 μm, aiming to pursue these favourable properties [18 - 21]. Satisfying results were obtained by the called two-step sintering, designed to heat the sample to a high temperature, T_1, followed by a rapid cooling down to a lower temperature, T_2, for a long period. By this method, the grain boundary diffusion of the specimen is maintained but the grain boundary migration could be frozen under pressureless conditions [22 - 24].

A high importance is given to the evaluation of the behaviour of the grain size and voids in the alumina ceramic (already sintered). The sample surface of the final dental restoration work that is affected by the heating process of applying the aesthetic veneer and glazer. At this stage, for the proper conditions (particles size and adjusting furnace temperature), the grain growth is successfully suppressed by adding / action of zirconia ceramics (Y – TZP) with nano-sized grains and HAp on the sample surface [25, 26]. A similar method (heating and

rapid cooling down to a lower temperature) was used for our study, but adapted to the dental laboratory features and named "frozen phase" method (FPM) [8, 25].

Our contribution takes into account the surface modelling of the alumina ceramic core by inserting into it zirconia micro grains in order to improve the optical and mechanical properties of the final dental restoration work based on alumina core.

2. Materials and methods

Materials: The investigated material was alumina-based ceramic VITA In – Ceram blank from VITA Zahnfabrik - Germany. Sample box was ALUMINA CA – 40, LOT 12130. For modelling alumina sample surface, Y – TZP from Schultz Dental Group (Tizian Zirconia Dioxide blank) was used. Both used sample materials were sintered ceramics.

General Procedures: The test sample specimens were prepared in a rectangular shape as the blank ceramic with thickness d = 3 mm. All samples were metallographic polished and cleaned before the treatment procedure. For the heating treatment, a programmable porcelain furnace, Model Gemini 2 (manufacturer, ShenPaz Ltd) was used. The samples of alumina ceramic were processed in the furnace chamber, at heating temperature, t = 1,150 ^{0}C in two different conditions: vacuum and air. The heating protocol was in accordance with the soft equipment employed by our study: total cycle, 15 min, gradient temperature, 115 ^{0}C/min, 3 minutes heating treatment, and sample release time of 2 minutes. For the "frozen phase" method (FPM), it was no release time. Samples were rapidly cooled down to a lower temperature, being transferred in a chamber at t = 0 ^{0}C.

EDX and Scanning Microscopy (SEM) Data Collection: The equipment employed was a SEM microscope FEI Inspect S, equipped with a secondary electron detector in low vacuum and a solid state BSE detector, plus an auxiliary micro analytic EDS - SiLi radiation detector (EDAX Sapphire, UTW, 128 eV resolution).

Atomic Force Microscopy (AFM) Data Collection: For AFM topography micrographs, it was employed an Integrated Platform SPM-N Tegra, model Prima (NT-MDT trade mark) working in semi touch mode. The scanning sample area was 5×5 μm^2.

AFM Image Analyzing: The soft used for our investigation, was NT – MDT (from Nova Tech. Company), part of a platform of integrated solutions for nanotechnology. Soft for image analysis mode can perform roughness, histogram and grain / pore size investigation [26].

3. Results and discussion

Composition of Alumina Ceramic. EDX Investigation

The first step was an energy-dispersive X-ray spectroscopy (EDX) investigation, performed in order to have a complete list of chemical elements contained in the samples. The list was not available or was supplied by the manufacturer in an incomplete form. The average values were obtained, for the main specimens (carbon may be neglected) from ten areas on the surface of the samples. Regarding EDX results, we noticed that the sample material was homogeneous in respect to each specimen element distribution for the sample screening area. There were small differences between the EDX results obtained, but with error less than 0.80 wt % variations over large areas. No differences in composition were noticed (as expected) between unprocessed and processed ceramic samples. The results are depicted in Table 1.

Table 1. Composition of alumina ceramic samples. EDX results (average values for ten points).

Elements	Alumina ceramic (Vita in Ceram blank) (wt %, average values)
Al	42.81
O	41.33
C	15.86

Macro Grains Characterization on Surface and Fracture. SEM Results

In the case of the heated samples of alumina ceramic, it was noticed a growth trend for the grains, based on the conditions of the gradient cooling rate. The grain growth process is not influenced by the furnace chamber conditions, but a less porous aspect was noticed for the vacuum heated samples (Fig. 1 b, c). For the heated and quenching samples (FPM method), a decreasing grain size was obtained (Table II). While analysing SEM micrographs areas with large grains (named macro grains) and small grains (micro grains) were noticed. For SEM result evaluation, only the sectors with macro grains were taken into consideration.

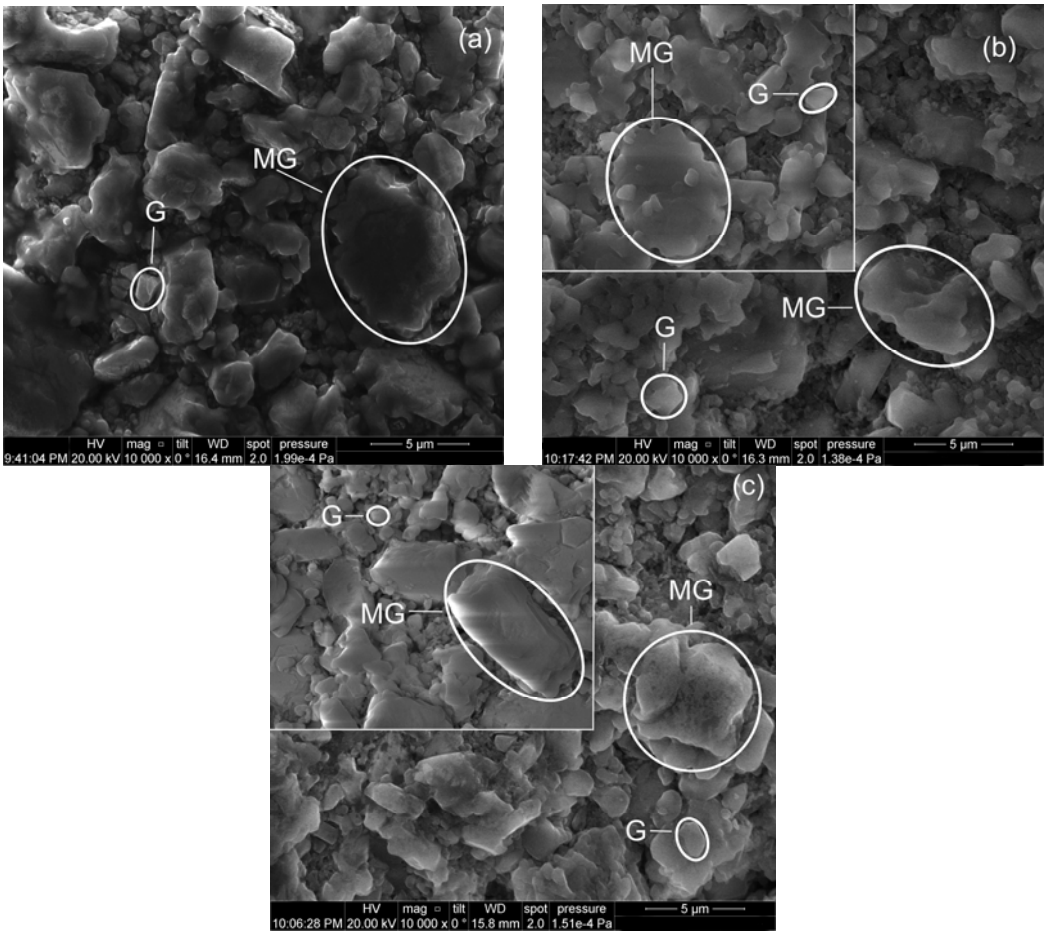

Fig. 1. Surface SEM results of alumina ceramic: (a) blank alumina, (b) heated + cooling rate in air, inset for vacuum, (c) heated + quenching in air, inset for vacuum. Details regarding the modifications made on alumina surface sample: MG (macro grains), G (grains). Magnification: ×10,000.

Table 2. Macro grains size of alumina ceramic determined by SEM

Sample	Macro grain size	
	Length (µm)* L ± SD	Wide (µm)* l ± SD
Blank alumina ceramic	7.33 ± 2.12	5.11 ± 1.57
Heated alumina ceramic (air + cooling rate)	6.62 ± 1.93	5.06 ± 1.48
Heated alumina ceramic (vacuum + cooling rate)	6.66 ± 1.82	5.32 ± 1.51
Heated alumina ceramic (air + quenching)	3.32 ± 1.09	3.00 ± 1.11
Heated alumina ceramic (vacuum + quenching)	4.66 ± 1.48	2.66 ± 1.05

*Average values (mean ± SD) for ten macro grain sectors.

The results regarding macro grain size investigation are summarized as length (L± SD) and wide (l ± SD) and depicted in Table 2.

SEM investigation of sample fracture reveals an important feature: if a surface heating treatment occurs, an evaluation of depth in the ceramic core for affected volume, as a result of the re-sintering process caused by the heating treatment, is appropriate. Evaluation indicates a value, d = 7.40 ± 0.51µm (mean ± SD) for the depth of affected volume (Fig. 2). Ten areas were subjected to evaluation on each alumina ceramic sample (in the same heating conditions).

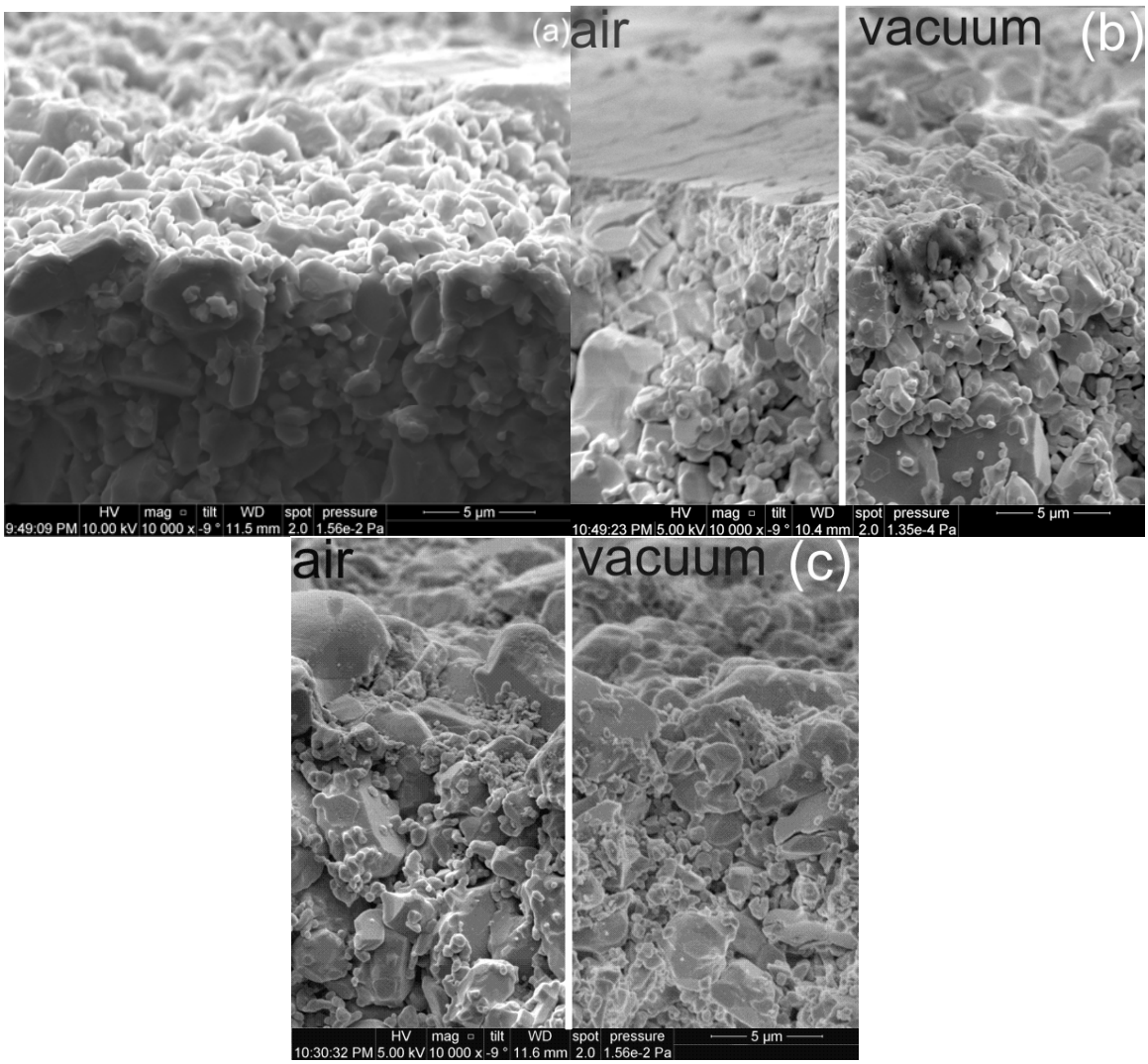

Fig. 2. Fracture SEM results on alumina ceramic,: (a) blank alumina, (b) heated + cooling rate in air / vacuum; (c) heated + quenching in air / vacuum. As details, there may be observed the depth inside the ceramic core affected by the heating process. Magnification: ×10,000.

Micro Grains Characterization. AFM Results

AFM investigation confirms the results obtained by SEM method. For the heated and quenching alumina ceramic samples (FPM method), a decreasing grain size was obtained (Table 3). Regarding pore size distribution (for the scanning area, defective sectors were included in the statistics causing larger errors), it was observed a trend of soft size increasing value or almost remaining constant. The micro grain area is the most affected by the heating process, due to the involved high temperature (even temperature value is lower than the one for the sintering process). This conducts to a 'pseudo mobility' of the micro grains in the alumina sample structure.

Table 3. Micro grains and pores size of alumina ceramic determined by AFM

Sample	Micro grain diameter (µm)* $d_G \pm SD$	Pore diameter (µm)* $d_P \pm SD$
Blank alumina ceramic	1.353 ± 1.028	1.539 ± 0.829
Heated alumina ceramic (air + cooling rate)	1.383 ± 1.142	2.003 ± 0.621
Heated alumina ceramic (vacuum + cooling rate)	1.420 ± 0.690	1.588 ± 1.010
Heated alumina ceramic (air + quenching)	1.333 ± 1.320	2.824 ± 0.283
Heated alumina ceramic (vacuum + quenching)	1.137 ± 1.018	1.388 ± 1.171

*Average values (mean ± SD) according to the soft employed to our study, on three different sectors each sample.

While analysing AFM micrographs, using the soft equipment employed to our study for some sectors, the option "Grain" is not working (just "Pore" does). The existence of macro grain sectors is confirmed. AFM details regarding alumina ceramic samples are depicted in Figure 3.

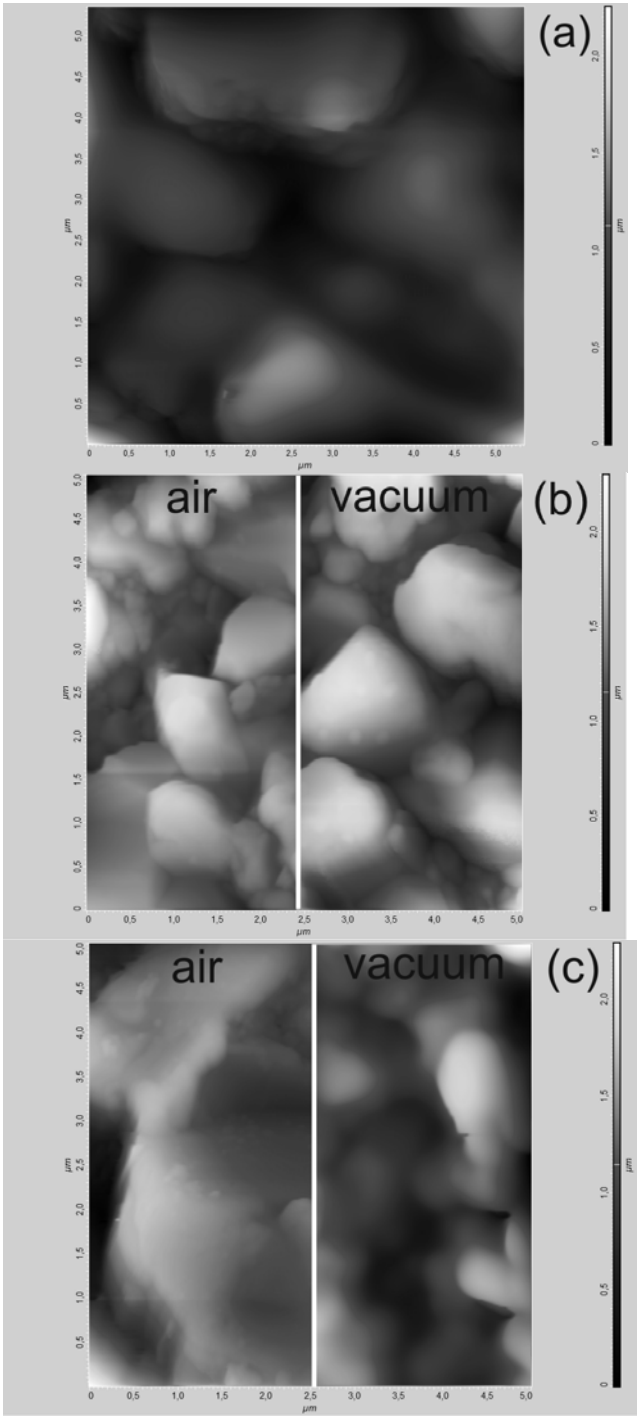

Fig. 3. AFM nanomicrography results on alumina ceramic,: (a) blank alumina; (b) heated + cooling rate in air / vacuum; (c) heated + quenching in air / vacuum. Details are regarding micro grains modifications due to the thermal treatment process.

Regarding alumina sample surface topography, the roughness analysis was performed. The results indicate an average point of height, h = 0.741 μm, with a maximum value, h_{max} = 1.421 μm, for the heated and quenching alumina ceramic samples (FPM method). These values are similar to those obtained for pore size diameter (Table III) and to the depth core affected by the heating process. It is confirmed that a surface active modelling process at the morphological level is caused by the thermal processing of alumina sample (heated and quenching).

AFM investigation of Y – TZP sample confirms the compact appearance of zirconia material. Using the soft of the equipment, only the pore size (diameter, d_P) was determined: d_P = 0.196 ± 0.059 μm. Micro grain size (diameter, d_G) was determined by measurements on AFM micrographs (fifty grains): d_G = 0.380 ± 0.057 μm. The results are presented in Fig. 4.

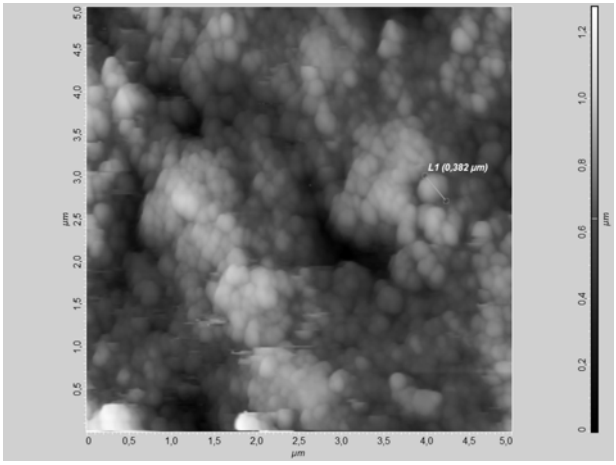

Fig. 4. AFM nanomicrography on zirconia ceramic,. Details: grain diameter evaluation.

4. Conclusions

In this work we have reported the results regarding structural investigation of two dental ceramic materials: alumina based on Al_2O_3 and zirconia based on ZrO_2 . The first sample presents a depth from surface with a value of d = 7.40 ± 0.51 μm affected by the thermal treatment where grains size may be under control. We emphasize that both materials are complementary regarding mechanical and optical properties required for a dental ceramic core: alumina ceramic for mechanical properties and zirconia for optical properties [19, 22]. For a long lasting dental alumina ceramic core with better optical properties, the use of zirconia is recommended. The insertion of zirconia micro grains into alumina surface pores is possible at appropriate temperature, pressure and time conditions. As it was noticed on micro grain characterization, the areas of alumina micro grains are subject to modification, and allow a modelling design. AFM results are confirming in the case of zirconia based on ZrO_2 a perfect match at the morphological level with the desired purpose for material alumina based on Al_2O_3 (Fig. 5). Finally, the action is conducting to a "composite,,

material just on sample surface improving optical and mechanical properties.

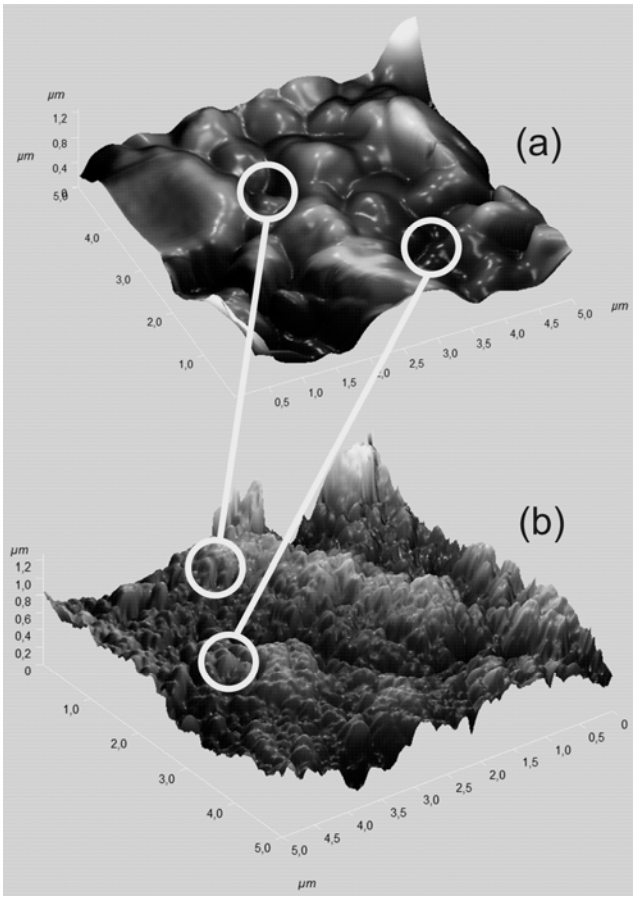

Fig. 5. AFM 3D nanomicrography modelling alumina ceramic (heated + quenching) in vacuum (a) with zirconia (b). Details: possibility of small zirconia micro grains to be inserted into alumina ceramic pores and to act as grain stoppers.

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*Corresponding author: edgatin@netscape.net
masterdent2009@yahoo.com