In vitro Study of the Effectiveness to Fractures of the Aesthetic Fixed Restorations Achieved from Zirconium and Alumina

LAURENTA LELIA MIHAI[1], IOANINA PARLATESCU[2], CARMEN GHEORGHE[2], CLAUDIA ANDREESCU[1], ANAMARIA BECHIR[1]* MARIANA PACURAR[3], CRISTIAN NIKY CUMPATA[1]

[1] "Titu Maiorescu" University of Bucharest,Faculty of Dentistry, Department of Dental Specialties, 67A Gheorghe Petrascu Str., 031593, Bucharest, Romania

[2] "Carol Davila" University of Medicine and Pharmacy, Faculty of Dentistry, Oral Medicine Department, 4-6 Eforie Str., floor 3, room 18, 050037, Bucharest, Romania

[3] University of Medicine and Pharmacy of Tirgu Mures, Faculty of Dentistry, 38 Gheorghe Marinescu Str., 540142, Tirgu Mures, Romania

A small percentage of the population is hypersensitive to dental alloys. For the last few decades, numerous approaches have been made to enhance the hardness of ceramics used in fixed prosthetic restorations. The aim of the research was to study, in vitro, the effectiveness to fracture tests of the aesthetic fixed restorations realized from zirconia and alumina. The experiment was conducted in a physics laboratory at the Polytechnic Institute of Bucharest for a 2 years period. For testing we used a total of 60 crowns manufactured as follows: 30 identical zirconia crowns, 30 identical alumina crowns, and for plating we used compatible ceramics. Each batch of 30 crowns was then divided in 3 groups of 10 crowns. Subsequently the crowns were cemented on resin models using zinc phosphate cement. After the setting of cement, the crowns were stored in distilled water at a temperature of 37°C. After two years, the first group of crowns was not subject to any treatment, the second group was subjected to a heat treatment in water bath at 55°C for 20 s each, and then, the 2nd and 3rd group of aesthetic crowns underwent cyclic preloading, between 30-300 N, at 1 Hz. The researches results showed that zirconia crowns were 3 times stronger and tougher than alumina crowns, and that the success rate in the zirconia crowns batch was 100%.

Keywords: Zirconia and alumina crowns, resistance to fracturing

Alumina and zirconium-based ceramics are the latest materials used for fixed partial dentures core and ceramic crowns.

Zirconium is a metal with the atomic number 40. It was first discovered in 1789 by German chemist Martin Klaproth. The material has a density of 6.49g/cm^3, a melting point of 1852°C and a boiling point of 3580°C. It has a hexagonal crystal structure and gray color. Zirconium is not found in nature in its pure state, it can be found in combination with silicon oxide under the name of zircon mineral (ZrO_2 x SiO_2) or as free oxide (zirconium, ZrO_2) named Baddeleyite. These minerals cannot be used as raw material in dentistry due to different impurities of metallic elements (that colors their mass) and natural radionuclide such as uranium and thorium (which make them radioactive).

In order to produce powders of pure zirconia complex and time-consuming procedures are necessary that result in effective separation of these elements. After purification the material can be used as ceramic biomaterial.

Zirconium is not found in nature in its pure state, thus it cannot be used as raw material in dentistry due to impurities of metallic elements uranium and thorium that make it radioactive. Complex multistage chemical transformation processes in partially stabilized zirconium, make it develop hardness and resistance to fracture. The most useful mechanical properties can be obtained when zirconium is in multiphase form, known as partially stabilized zirconias.

Pure zirconia (ZrO_2) has a high melting point (2680°C) and low thermal conductivity. In any case, its polymorphism is narrowing the scope of its use in ceramic industry. ZrO_2 is found in three crystallographic forms: monoclinic (M), tetragonal (T) and cubic (C).

The crystal structure of monoclinic, tetragonal and cubic zirconia is presented in figure 1 [1].

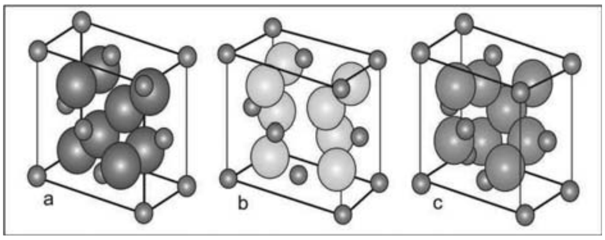

Fig. 1. Crystal structure of monoclic (a), tetragonal (b) and cubic zirconia (c)

During heating, zirconia undergoes a phase of the transformation process. The monoclinic form is stable from room temperature and up to 1170°C. Above this temperature, it transforms into a denser tetragonal phase with a 5% volume decrease and creates cracks in its structure. The tetragonal form is stable between 1170 and 2370°C. At temperatures above 2370°C, zirconium takes a cubic crystal structure. A reversible T-M transformation occurs during cooling at a temperature of about 100°C under 1070°C, with 3-4% volumetric expansion and generation of forces that cause cracks in the ZrO_2 ceramics. The forces induced during changes that take place in this phase have resulted in cracks formation.

The temperature-related phase transformation of zirconia is presented in figure 2 [2].

The addition of stabilizing oxide to zirconium, such as calcium (CaO), magnesium (MgO), cerium (CeO_2) or yttrium

---

* *email: anamaria.bechir@gmail.com*

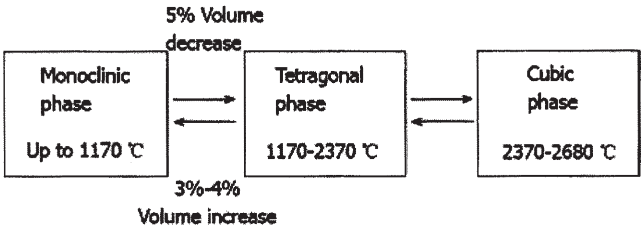

Fig. 2. Temperature - related phase transformation of zirconia

(Y_2O_3), may suppress the phases of its transformations allowing the generation of a multiphase material at room temperature, called stabilized zirconia.

Totally stabilized Zirconium is produced when more than 16mol% CaO (7.9wt%), 16mol% MgO (5.86wt%) or 8mol% Y_2O_3 (13.75wt%) is added to ZrO_2 and has a cubic form. Due to its increased hardness and high thermal shock resistance, this material is considered a valuable refractory product. The most useful mechanical properties can be obtained when zirconium is in multiphase form, known as partially stabilized zirconia (PSZ) [3].

PSZ can be obtained by adding small amounts of stabilizing oxide to pure zirconium, compared with those used for obtaining totally stabilized zirconia. At room temperature, the microstructure of PSZ consists, in general, of cubic zirconia as major phase with monoclinic or tetragonal precipitated zirconia as minor phase. These precipitates can be found at grain edges or within the granulations of the cubic matrix [4].

Diversified PSZ have been tested as ceramic biomaterials. Mg-PSZ is one of the most well-known engineering ceramics based on zirconia. The mass material residual porosity, of a rather coarse size (30-40μm) and the difficulties in obtaining precursors of Mg-PSZ without impurities decreased the interest of manufacturers to develop Mg-PSZ ceramics in biomedical applications. It has been reported that, the consolidation through solidification in the transformation phase is less pronounced in Mg-PSZ than in Y-TZP (zirconia varnished with Yttrium) [5].

It is possible to obtain PSZ ceramics at room temperature in the presence of a small amount of oxide stabilizers, only with a tetragonal phase, known as tetragonal zirconia polycrystals (TZP). Tetragonal ZrO_2 grains are dispersed within the cubic matrix, have been shown to be sufficiently small; can be maintained in a metastable state which is able to transform itself into monoclinic phase [6]. This phenomenon can be explained by the low surface energy of tetragonal ZrO_2 particles and the constraint of the rigid matrix that opposes itself to their transformation into a less dense monoclinic form. This process creates a stronger cracks inhibition mechanism and strengthening, the transformation-hardening mechanism [3].

The tetragonal ZrO_2 grains can transform themselves into monoclinic phase when the constraint exerted by the matrix is removed, for example by a crack that advances into the material. At the tip of the crack, the region of the compressor force, that is associated with a 3-5% volume expansion of the tetragonal transformed grains, acts in opposition to the thrust area which promotes crack propagation [fig. 2] [7].

The addition of approximately 2-3% Yttrium (Y_2O_3) moles as stabilizer agent at zirconia, allows sintering of fine tetragonal zirconia ceramics, made from 100% small metastable tetragonal granules, called Yttrium- Tetragonal Zirconia Polycrystals (Y-TZP). The T phase fraction retained at ambient temperature is dependent on the processing temperature, the content of yttrium, the grain size and the degree of pressure exerted on them by the matrix. The relative expansion as a function of sintering temperature for nanostructured and commercial Y-stabilized ZrO_2 measured in a dilatometer is presented in figure 3 [8].

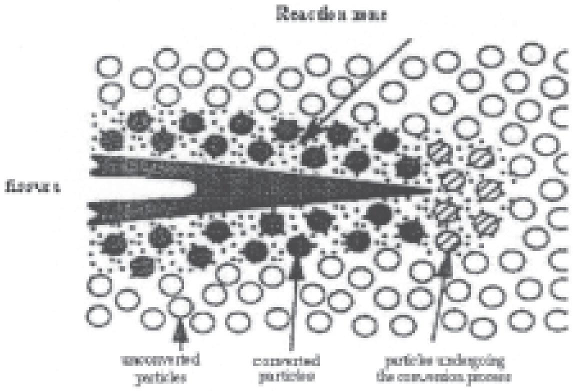

Fig. 3. The scheme of transformation - hardening mechanism at the time of force applying in TZP

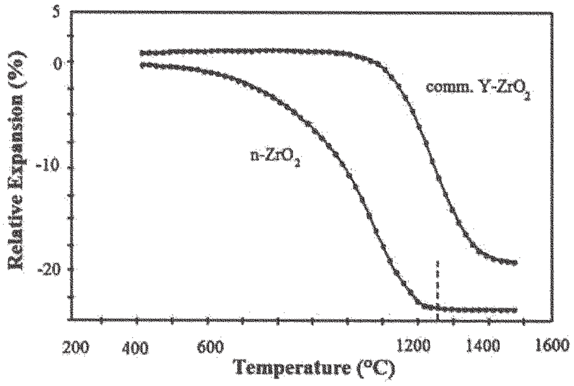

Fig. 4. Relative expansion as a function of sintering temperature for nanostructured and commercial Y-stabilized ZRO_2 measured in a dilatometer: the dashed vertical line represents 1/2 Tm

TZP ceramics mechanical properties also depend on these parameters [7].

The addition of Y_2O_3 in higher concentration produces a totally stabilized zirconia ceramics with only one cubic phase and a low level fracture resistance [9,10].

To obtain a metastable tetragonal structure at room temperature (3 mole% Y_2O_3-ZrO_2 -doped tetragonal) ceramic grain size must be less than 0.8μm [11].

There is a critical granular size, related to the concentration of yttrium, according to which any T-M grain transformation that occurs spontaneously happens even if the transformation will be inhibited in an excessively fine structure [7].

The metastable zirconia–yttria phase diagram is presented in figure 4 [12].

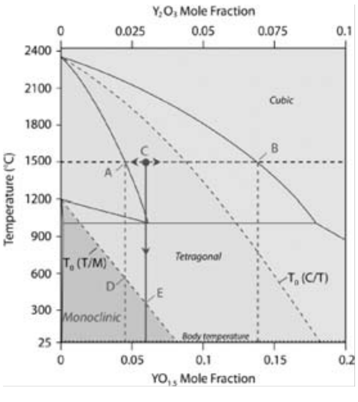

Fig. 5. Metastable zirconia-yttria phase diagram

Table 1
PHYSICAL AND CHEMICAL PROPERTIES OF Y-TZP

Properties	Y-TZP
Chemical composition	ZrO_2 +3mol% Y_2O_3
Density	>6 g/cm^{-3}
Porosity	<0.1%
Torsion	900-1200 MPa
Compressive strength	2000 MPa
Young Module	210 GPa
Resistance to fracture	7-10 MPa m^{-1}
Coefficient of thermal expansion	11x10^{-6}K^{-1}
Thermal conductivity	2 W m K^{-1}
Hardness	1200 HV

Table 2
DISTRIBUTION OF CROWNS INTO GROUPS

The used material for crowns	The applied treatment		
	1st: maintained only in distilled water	2nd: heat treatment + cyclic loading	3rd: cyclic loading
Zirconia batches	10 crowns	10 crowns	10 crowns
Alumina batches	10 crowns	10 crowns	10 crowns

Table 3
APPLIED FORCE TILL THE FRACTURE OF CROWNS (MPa)

	1st Batch (zirconia)	2nd Batch (alumina)
average	116	81
±	15	13

Table 4
OBTAINED RESULTS IN THE THREE STUDIED GROUPS

Material	1st Group (any treatment)		2nd Group (heat treatment)		3rd Group (heat treatment + cyclic preloading)	
	Resistance to Fraction (N)	Rapport of fraction manner	Resistance to Fraction (N)	Rapport of fraction manner	Resistance to Fraction (N)	Rapport of fraction manner
Alumina	905	8:2	917	9:1	904	9:1
Zirconia	975	2:8	910	3:7	1108	6:4
	p=0,38	*p=0,01*	*p>0,05*	*p<0,01*	*p<0,07*	*p>0,05*

Table 5
THE COMPARED RESULTS

	Batch 1	Batch 2	Batch 3
Study Type	In vitro	In vitro	In vitro
Material	Zirconia	Alumina	Alumina /zirconium
Control after 2 years	100%	95%	95%

Y-TZP exhibit exceptional mechanical properties, with high initial hardness and resistance to fracture. The physical and chemical properties of Y-TZP are presented in table 1 [7]. A small percentage of the population is hypersensitive to dental alloys containing noble and base metals such as palladium and nickel [13].

In vitro and *in vivo* studies have confirmed the high biocompatibility of Y-TZP when high purity zirconia powders are used [2].

These powders are purified of their radioactive content. As a result, no local (cell) or systemic adverse reactions have been reported in this material [6,7,14,15].

Experimental part

Materials and methods

To demonstrate the effectiveness to fractures of the aesthetic fixed restorations achieved from zirconia and alumina, we conducted an *in vitro* study to test the resistance to fracture of the ceramic crowns. The experiment was conducted in a physics laboratory at the Polytechnic Institute of Bucharest for a 2 years period.

For testing we used a total of 60 crowns manufactured as follows: 30 identical zirconia crowns, 30 identical alumina crowns, and for plating we used compatible ceramics. Each batch of 30 crowns was then divided in 3 groups of 10 aesthetic crowns. Subsequently the crowns were cemented on resin models using zinc phosphate cement. After the setting of cement, the crowns were stored in distilled water at a temperature of 37°C. After two years, the first group of crowns was not subject to any treatment, the second group was subject to a heat treatment in water bath at 55°C for 20 s each, and then, the 2nd and 3rd group of aesthetic crowns (each containing 10 crowns), underwent cyclic preloading, between 30-300 N, at 1 Hz.

The distribution of aesthetic crowns into the batches and groups is presented in table 2.

After treatment, all 60 crowns were subject to fracture load by applying a 2.5 mm diameter steel ball on the occlusal surface of the crown, with a crosshead speed of 0.255 mm min^{-1}.

Results and discussions

The results of these experimental researches shows that:

- in the first part of the study, the resistance to fracture of crowns showed that the exposure to saliva of a ceramic crown before glazing reduces its strength (table 3);
- all occurred fractures were in the alumina group and compared to the zirconia group, the difference were statistic significant ($p<0.001$);
- table 4, presented our results in the all three studied groups: exposed only to distilled water (the first group), exposed to heat treatment (the second group) and to heat treatment+cyclic loading (the thirds group);
- at the final of studies, we gathered the data, compared them for a clearer visualization, and the obtained results are shown in table 5.

Clinical data determined both manufacturers and dentists to place greater emphasis on data regarding the resistance of a material to define clinical indications.

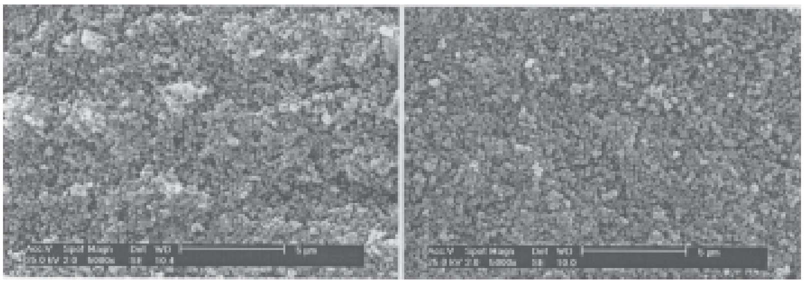

Fig.6. Micrographs of different zirconia 3Y-TZP ceramic blocks

Probability analyses assume that the maximum bite forces on previous crowns rarely exceed 900 N and maximum strength on posterior crowns rarely exceeds 2200 N, as long as most patients typically generate bite forces between 400 N and 800 N. In order to resist such loads, it is important not only to select the right materials, but also to build the prosthesis in order to reduce stress in the prosthesis center. It has been shown that resistance to fracture is related to cervical preparation that should make a "threshold" to withstand load. [3,16].

It has been found that small amounts of transition metal oxides are effective to densify Y-TZP and Y-TZP-Al_2O_3 composites at relatively low temperatures. As typical examples, MnO_x-doped Y-TZP and MnO_x-doped Y-TZP-Al_2O_3 composites have been investigated. All MnO_x-doped systems showed low-temperature sinterability, and the obtained high-density sintered bodies having small grains showed excellent mechanical properties. Although MnO_x-doping enhanced the densification for all the systems studied, it can be inferred that the densification mechanism of the doped-Y-TZP is different from of the doped-Al_2O_3. The densification behaviour for the doped-Y-TZP-Al_2O_3 composites can be explained by the combined mechanism of the doped-Y-TZP and of the doped-Al_2O_3 [17].

The T-M transition of TZP materials depends not only of the Y_2O_3 content but also of its distribution. The stabilizing oxide is introduced into ZrO_2 during the early manufacturing process stages of the ceramic powder. Y_2O_3 can also be co-precipitated with ZrO_2 salts or varnished on the ZrO_2 grains to produce the ceramic powders. The micrographs of different zirconia 3y-tzp ceramic blocks are presented in figure 5 [8].

After the researches of Habibe and al [18] (which evaluated the influence of additions on sintering bioglass and the mechanical properties of yttria-stabilized zirconia), the increasing of bioglass amount leads to the decreasing of relative density, due to tetragonal-monoclinic transformation during cooling of the sintered samples. They concluded that Y-TZP samples sintered at 1300°C, containing 5 wt.% of bioglass, presented the best results, with high relative density, hardness and fracture toughness of 11.3 GPa and 6.1 MPa m1/2, respectively. Furthermore, a preliminary biological evaluation, *in vitro* cytotoxicity tests by Neutral Red Uptake method (using mouse connective tissue cells, NCTC clone L929 from ATCC bank) were realized to determine the cytotoxicity level of ZrO_2-bioglass ceramics, and the authors observed the un-cytotoxic behaviour in all sintering conditions and bioglass amounts used in their researches.

The studies of Philipp and al [19], performed *in vivo* for comparing Ce-TZP/A nanocomposite, demonstrated that after 12months of clinical service, this material is a promising and reliable framework for posterior fixed prosthetic dentures, but a longer observation periods, studies with more patients, and randomized clinical long-term trials are needed to validate the clinical performance of their case series.

After the studies of Christensen and Ploeger [20] dentists can use metal or zirconia frameworks successfully if they are designed properly, but to avoid veneer ceramic surface crumbling and minimize chipping, use of leucite-containing pressed ceramics is indicated.

Recent studies have shown that the bacteria are less accumulated around the Y-TZP than around titanium [6,21].

Conclusions

Zirconia crowns were 3 times stronger and tougher than alumina crowns.

Alumina fracture resistance was about 400 MPa and the fracture toughness was 3 MPa. Thus, the values corresponding to zirconia were of 1200 MPa and 9 MPa, which were much higher than in alumina.

The researches results, after a two years period, showed that the success rate in the zirconia batch was 100%.

Short-term exposure to saliva, before the last firing, may have a negative effect on the strength of dental ceramics.

Ceramic crowns with zirconium core presented a higher resistance than those with alumina core.

References

1.HANNINK R.H.J., KELLY P.M.; MUDDLE B.C.: Transformation toughening in zirconia – containing ceramics. J Am Ceram Soc, Vol. 83, No 3, Mar, 2000, p. 461-487

2.SARIDAG S., TAK O., ALNIACIK G.: Basic properties and types of zirconia: An overview, World J Stomatol. 2013 August 20; 2(3): 40-47

3.GUAZZATO M., ALBAKRY M., RINGER S.P., SWAIN M.V.: Strength, fracture toughness and microstructure of a selection of all-ceramic materials. Part II. Zirconia-based dental ceramics. Dent Mater, nr.20, pag 449-456, 2004

4.NOTHDRUFT F.P., POPSIECH P.: Zirconium Dioxide Implant Abutments for Posterior Single-Tooth Replacement: First Results, J.Periodontology, Vol. 80, No. 12, Pag.2065-2072, 2009 PICONI C, MACCAURO G. Zirconia as a ceramic biomaterial, Biomaterials, nr.20(1), pag.1-25, 1999

5.SCHWARTZ M.M.: Encyclopedia of materials, parts, and finishes-2nd ed., CRC Press LLC, Boca Raton London New York Washington, D.C., 2002

6.SCARANO A., PIATTELLI M., CAPUTI S., FAVERO G.A., PIATTELLI A.: Bacterial adhesion on commercially pure titanium and zirconium oxide disks. J Periodontol, nr.75, pag.292-296, 2004

7.PICONI C, MACCAURO G. Zirconia as a ceramic biomaterial, Biomaterials, nr.20(1), pag.1-25, 1999

8.MAZIERO VOLPATO C.A., D´ALTOÉ GARBELOTTO L.G., FREDEL M.C., BONDIOLI F.: Application of Zirconia in Dentistry: Biological, Mechanical and Optical Considerations, Chapter 17, in Advances in Ceramics – Electric and Magnetic Ceramics, Bioceramics, Ceramics and Environment, Edited by Costas Sikalidis, Published by InTech, 2011, Croatia, pp. 397-420, Available from: http://www.intechopen.com/books/advances-in-ceramics-electric-and-magnetic-ceramics-bioceramics-ceramics-and-environment/application-of-zirconia-in-dentistry-biological-mechanical-and-optical-considerations

9.SCHROETER P, JURGENSEN B, ZOLLNER M. Cercon move-a navigation aid for dental CAD applications. Int J Comput Dent., no. 7(4), p.371-377, 2004

10. BLATZ MB, SADAN A, MARTIN J, LANG B. In vitro evaluation of shear bond strengths of resin to densely-sintered high-purity zirconium-oxide ceramic after long-term storage and thermal cycling. J Prosthet Dent, nr.91, p.356, 2004

11.CHRISTEL P., MEUNIER A., HELLER M., TORRE J.P., PEILLE C.N.: Mechanical properties and short term in vivo evaluation of ytrium-oxide-partialy stabilized zirconia, J.Biom.Mat.Resar, nr.23, p.45-61, 1989

12.CHEVALIER J., GREMILLARD L., VIRKAR A.V., CLARKE D.R.: The Tetragonal-Monoclinic Transformation in Zirconia: Lessons Learned and Future Trends, J. Am. Ceram. Soc., 2009, 92 [9], pp 1901-1920

13.GEURTSEN W.: Biocompatibility of Dental Casting Alloys , Crit. Rev. Oral Biol. Med., 2002, 13(1):71-84

14.COVACCI V, BRUZZESE N, MACCAURO G, ANDREASSI C, RICCI GA, PICONI C -In vitro evaluation of the mutagenic and carcinogenic power of high purity zirconia ceramic.Biomaterials, nr.20, p.371-376, 1999

15.SANDHAUS S.: Cerasand ceramic implants, Actual Dent nr.31, pag.14-18, 1991

16.FERRARIO V.F., SFORZA C., ZANOTII G., TARTAGLIA G.M.: Maximal bite force in healthy young adults as predicted by surface electromyography. J Dent 2004; 32: 451-457

17.KIMURA N., ABE S., MORISHITA J., OKAMURA H. : Low-Temperature Sintering of Y-TZP and Y-TZP-AL_2O_3 Composites with Transition Metal Oxide Additives, Springer Netherlands, Sintering '87, 1988 p. 1142-1148

18. HABIBE A.F., MAEDA L.D., SOUZA R.C., BARBOZA M.J.R., DAGUANO J.K.M.F., ROGERO S.O., SANTOS C.: Effect of bioglass additions on the sintering of Y-TZP bioceramics, Materials Science and Engineering,C29, 2009, 1959-1964

19.PHILIPP A., FISCHER J., HEMMERLE C.H.F., SAILOR I.: Novel ceria-stabilized tetragonal zirconia/alumina nano composites frame work material for posterior fixed dental prostheses: Preliminary results of a prospective case series at1year of function, Quintessence International, April 2010, vol. 4, 4:313-319

20.CHRISTENSEN R.P., PLOEGER B.J.: A clinical comparison of zirconia, metal and alumina fixed-prosthesis frameworks veneered with layered or pressed ceramic: a three-year report, J Am Dent Assoc. 2010 Nov;141(11):1317-29

21.MODGI C.M., ARAS M.A.: International Journal of Oral Implantology and Clinical Research, January-April 2012;3(1):39-42

Manuscript received: 19.12.2013