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PROPERTIES OF DENTAL ZIRCONIUM OXIDE AND METAL-CERAMIC: A COMPARATIVE STUDY

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ABSTRACT

Zirconium oxide which is intended to be a material that is quite attractive due to its key characteristics, i.e. aesthetic appearance and mechanical resistance, compared to dental metal-ceramics, which to date it has proven to be a satisfactory solution for many of the requirements in the dental market. Understanding the characteristics and properties of these materials provides a starting point for new trends in the development or improvement of solutions for various medical conditions. The research topic of this work aims to understand the characteristics and properties of two categories of materials that are so competitive in the field of dental restoration. For this purpose, the behaviour of some dental crowns made of zirconium oxide and metal ceramic was evaluated in order to obtain experimental data regarding microhardness, corrosion and roughness, before and at different time intervals of immersion in a solution of corrosion, respectively saline solution (3.5% NaCl).

KEYWORDS: zirconium oxide, metal-ceramic, morphology, roughness, hardness, corrosion behaviour

1. Introduction

Although bioceramics are among the oldest materials used by humans in medical applications, their widespread use occurred only after 1960. A possible cause could have been the impossibility of obtaining a pure bioceramic until that date that would respect entirely the vital biocompatibility conditions, and the second cause could be related to the mechanical properties of ceramics, so controversial at the time [1]. Only after 1960, by the discovery of new properties, such as for example a high resistance to wear, a coefficient reduced friction or even the property of being inert in biological environments, allowed the use of these materials to be much more extensive in the medical field. Medical ceramics or bioceramics is a biomaterial used in various constructions of medical nature starting from the construction of prostheses, bone substitutes, stimulators and up to tooth reconstruction. The medical industry with all its cutting-edge techniques would be unthinkable without it the use of bioceramic materials, due to their valuable properties and biocompatibility [1].

Zirconium oxide (ZrO_2) (Zircona or Zirconia) is a very studied and exploited ceramic material due to its excellent mechanical properties such as tear resistance, high hardness, high density, chemical inertness [2, 3]. Pure zirconia is an oxide that presents three symmetry polymorphisms: monoclinic, temperature unstable tetragonal and cubic. So that this oxide can be used for the manufacture of various components, it is necessary to be stabilized with oxides such as yttrium oxide (Y_2O_3) [4-6]. Fabrication of pure zirconia components is not possible due to spontaneous failure. The addition of stabilizing oxides is important because it allows the tetragonal shape to be maintained at room temperature. Different oxides such as yttrium oxide (Y_2O_3), calcium oxide or magnesium oxide, may be added for stabilization, allowing the tetragonal shape zirconia to exist at room temperature after sintering.

The advantages of using dental crown made of zirconium are: it does not taste like metal and does not cause inflammation of the gums like lyserium;

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they are primarily aesthetic due to a physical principle, namely that zirconium is penetrated by light from all angles, a fact that gives the dental work a special aesthetic aspect. Zirconium dental crown have some disadvantages, such as: very expensive, not being an affordable option for many patients. Not only the material itself, but also the sophisticated equipment required to process the material leads to a high final cost. Another disadvantage is related to the fact that zirconium has an affinity for dental plaque, and poor hygiene is one of the causes of implant failure [7-11].

The present research study intends to understand the characteristics and properties of two categories of materials that are so competitive in the field of dental restoration. For this scope it was evaluate the behaviour of dental crowns made of zirconium oxide and metal ceramic in order to obtain experimental data regarding microhardness, corrosion and roughness, before and at different time intervals of immersion in a solution of corrosion, respectively saline solution (3.5% NaCl).

2. Materials and methods

The biomaterials of the case study were zirconium oxide and dental metal ceramics (SuperPorcelain EX-3 ceramic and Cr-Ni alloys), two commonly used materials for dental prostheses (Fig. 1).

Fig. 1. *Samples of zirconium oxide ceramics and metal ceramics (MC) (A3.5B-NoritakeEX-3-Cr-Ni alloy)*

Zirconium is a powder under the trade name Katana Zirconia-Noritake, type II/class 4 with coefficient of thermal expansion of 9.8 x 10^{-6}/K (25-500 °C).

Metal ceramic is a Noritake Super Porcelain EX-3, a ceramic that is superior to others dental ceramics because its coefficient of thermal expansion (CTE) remains stable over time of repeated baking. It is compatible with precious, semi-precious, non-precious silver-free alloys for metal-ceramic prostheses. Its fluorescence is ideal, and it is very resistant to greening induced by silver. This combination of characteristics makes this type of dental ceramic an ideal choice for ceramic restorations [12]. Some characteristics of Noritake Super Porcelain EX-3 ceramics are: very good tear resistance; the coefficient of expansion is 12.14 x 10^{-8}/K (50-500 °C) (the range of thermal expansion coefficients of compatible alloys with EX-3 ceramic is 13.44 x 10^{-6}/K. As a result, the alloys that fall into these ranges are compatible with EX-3 ceramic); prevention of silver-induced greening. Greening of EX-3 porcelain is minimal, even in furnaces contaminated with silver; ideal fluorescence-successfully imitates the fluorescence of natural teeth [13].

2.1. Surface morphology

The morphology of the surfaces for studied materials was evaluated with an optical microscope type Kern Optics-OLM 171, as well as with a scanning electron microscope type TESCAN VEGA coupled with energy dispersive X-Ray analysis.

2.2. Microhardness and roughness

The tests for the evaluation of microhardness were carried out with an INSIZE equipment–Digital Micro Vickers Hardness Tester and the roughness of the tested surfaces were carried out with an INSIZE-ISR C002 equipment.

2.3. Corrosion tests

The corrosion resistance (corrosion rate and penetration index) was evaluated using the gravimetric method. The determinations were made with the KERN type analytical balance (accuracy of 0.0001 g). Zirconium oxide and dental metal ceramics was tested in 3.5% NaCl solution after different times of immersion (at immersion time, after five days and 12 days).

3. Results and Discussion

3.1. Surface morphology

The morphology of the tested samples before immersion and after different times of immersion in 3.5% NaCl solution is presented in Figures 2-7. Microscopic observations from the initial stage revealed surfaces with a porous appearance, as well as some smoother surfaces, depending on the material processing technique in the laboratory. The blurriness of the images in certain samples is due to the irregularity of the samples.

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The results of microscopic observations revealed similar aspects regarding surface porosity. No representative surface changes were found.

To determine the spectrum of the chemical composition of the studied materials, observations were made using the scanning electron microscope coupled with energy dispersive X-ray spectroscopy.

SEM microscopy was used to complete information about morphology of the surfaces after corrosive tests (Figures 8-9).

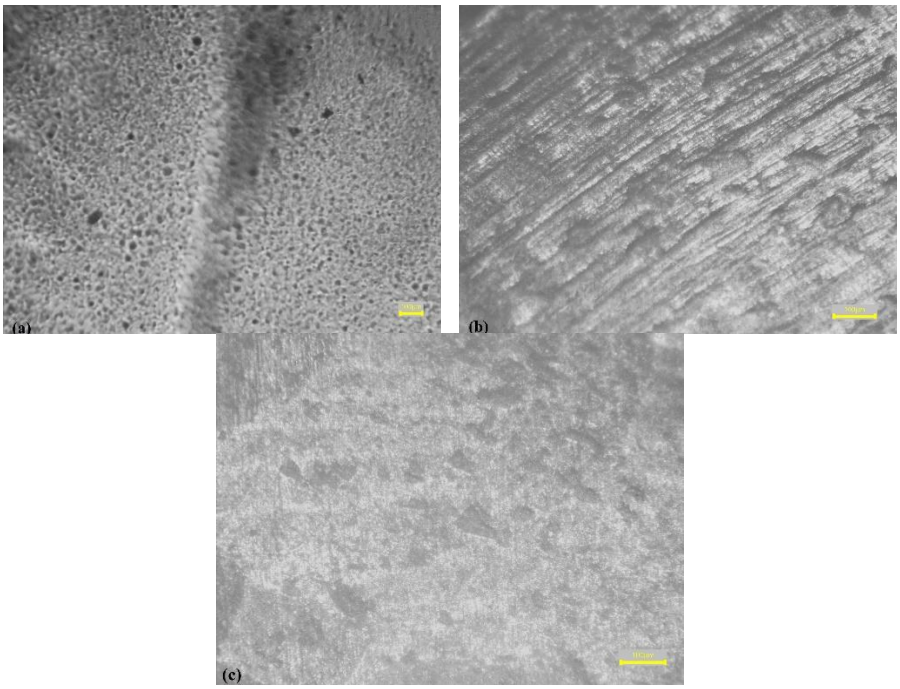

Fig. 2. *Optical microscopy of ZrO_2 samples before immersion in corrosive solution: (a) - sample 1; (b) - sample 2 and (c) - sample 3*

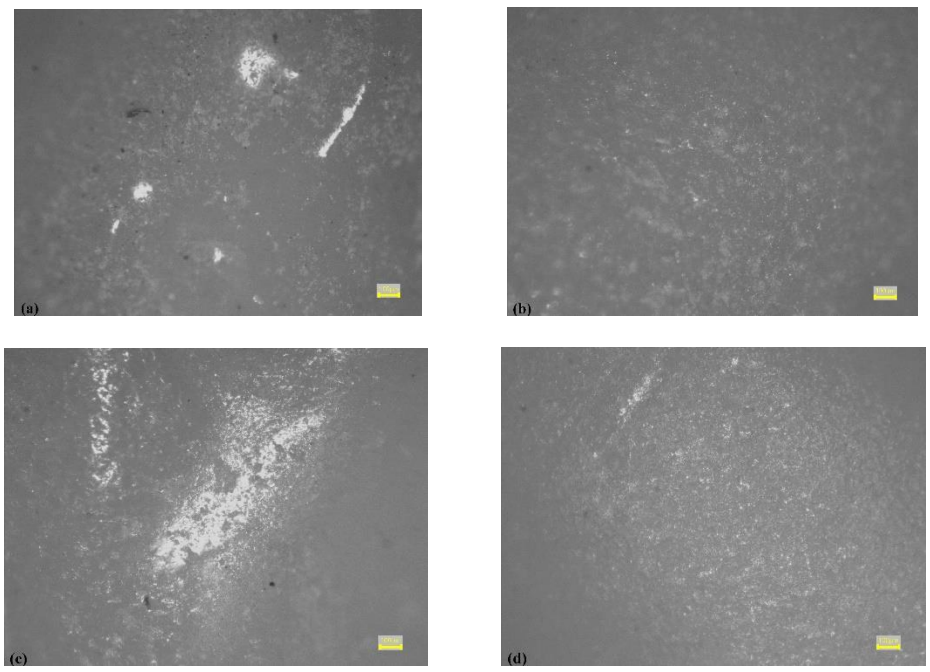

Fig. 3. *Optical microscopy of MC samples before immersion in corrosive solution: (a) - sample 1; (b) - sample 2; (c) - sample; (d) - sample 4*

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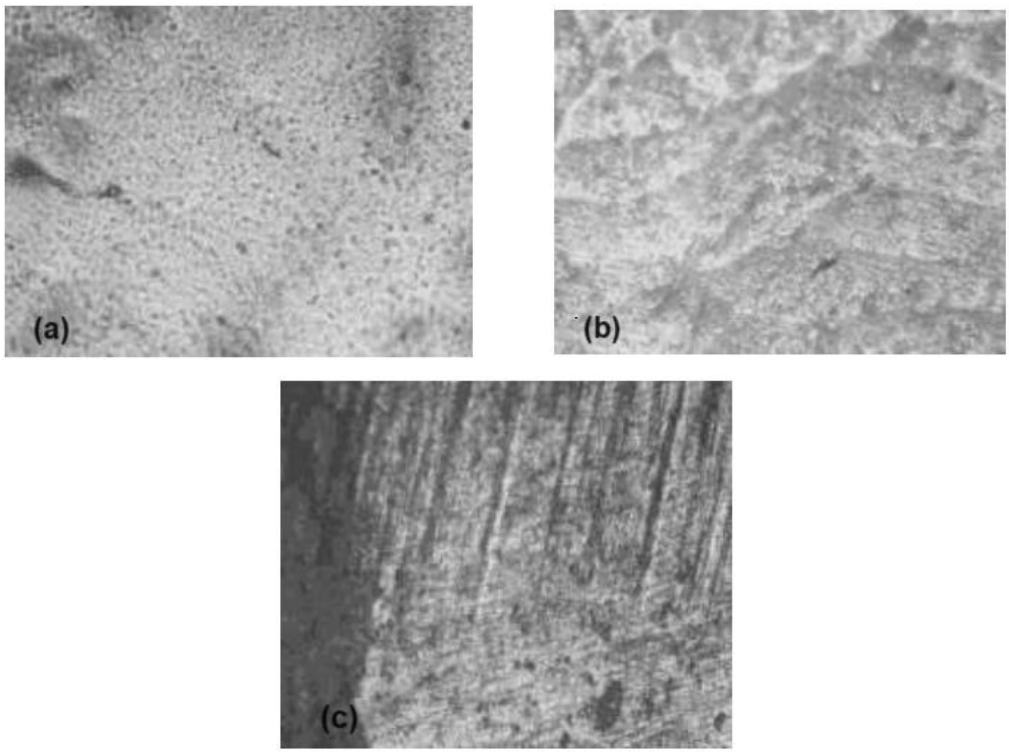

Fig. 4. *Optical microscopy of ZrO_2 samples after five days of immersion in 3.5 % NaCl solution: (a) - sample 1; (b) - sample 2 and (c) - sample 3*

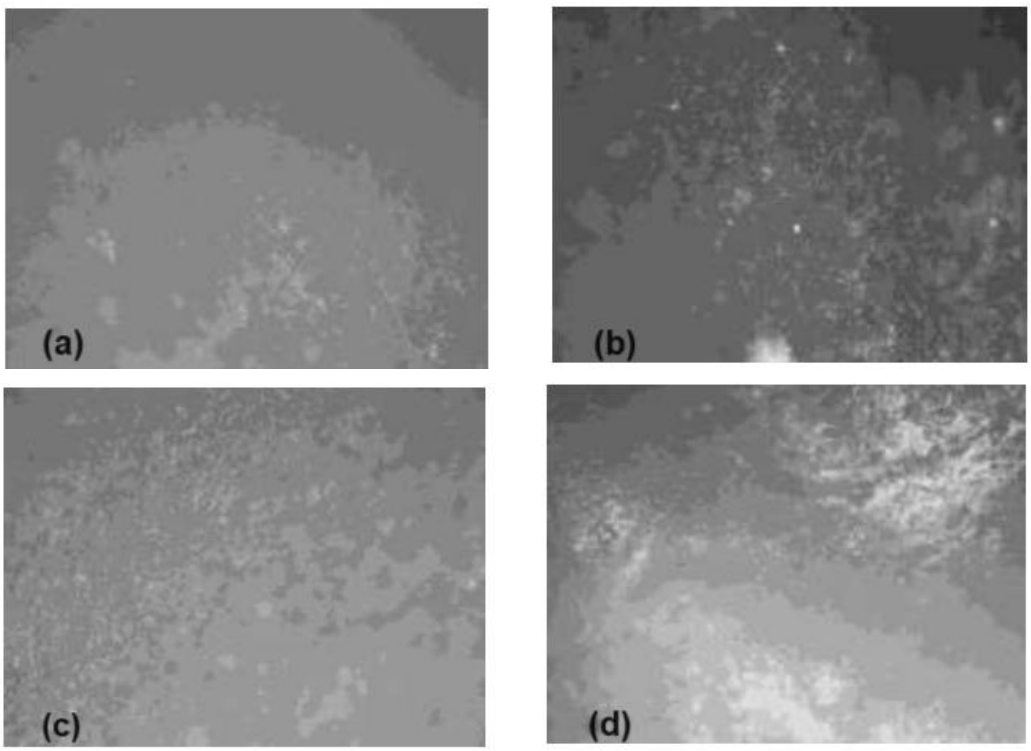

Fig. 5. *Optical microscopy of MC samples after five days of immersion in 3.5 % NaCl solution: (a) - sample 1; (b) - sample 2; (c) - sample; (d) - sample 4*

THE ANNALS OF "DUNAREA DE JOS" UNIVERSITY OF GALATI
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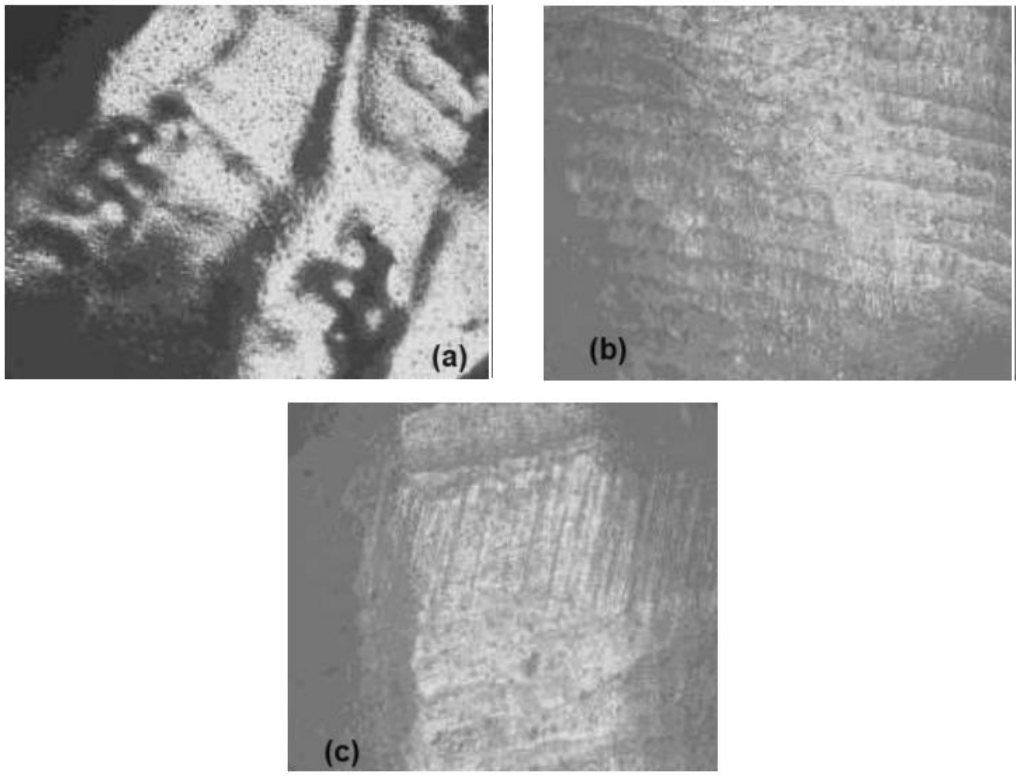

Fig. 6. *Optical microscopy of ZrO_2 samples after 12 days of immersion in 3.5 % NaCl solution: (a) - sample 1; (b) - sample 2 and (c) - sample 3*

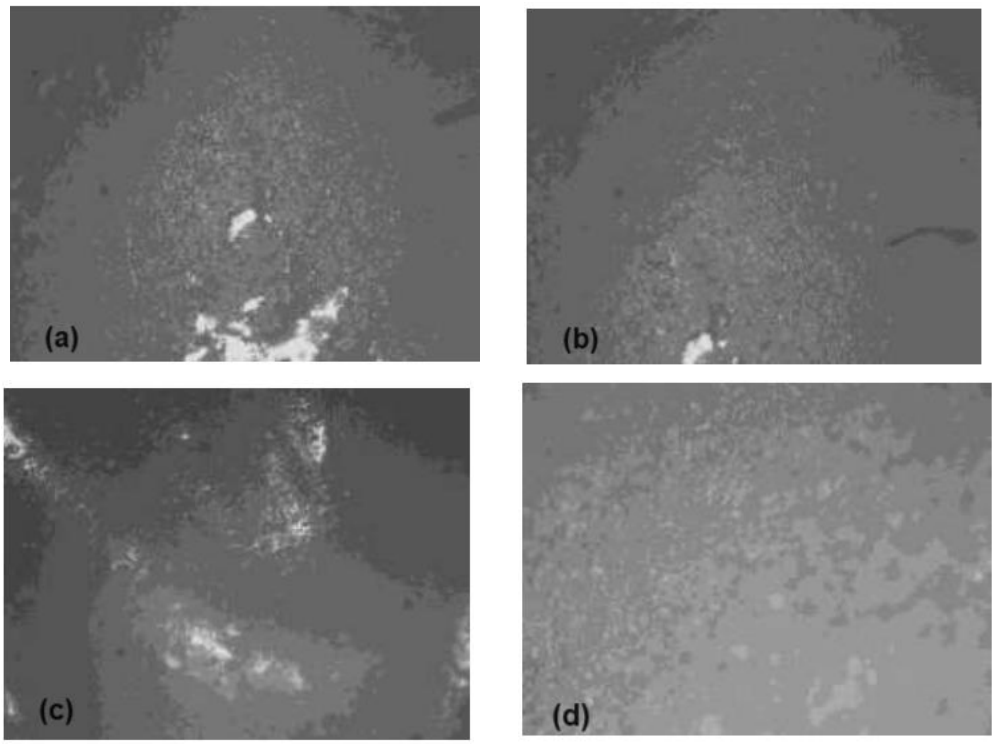

Fig. 7. *Optical microscopy of MC samples after 12 days of immersion in 3.5 % NaCl solution: (a) - sample 1; (b) - sample 2; (c) - sample; (d) - sample 4*

THE ANNALS OF "DUNAREA DE JOS" UNIVERSITY OF GALATI
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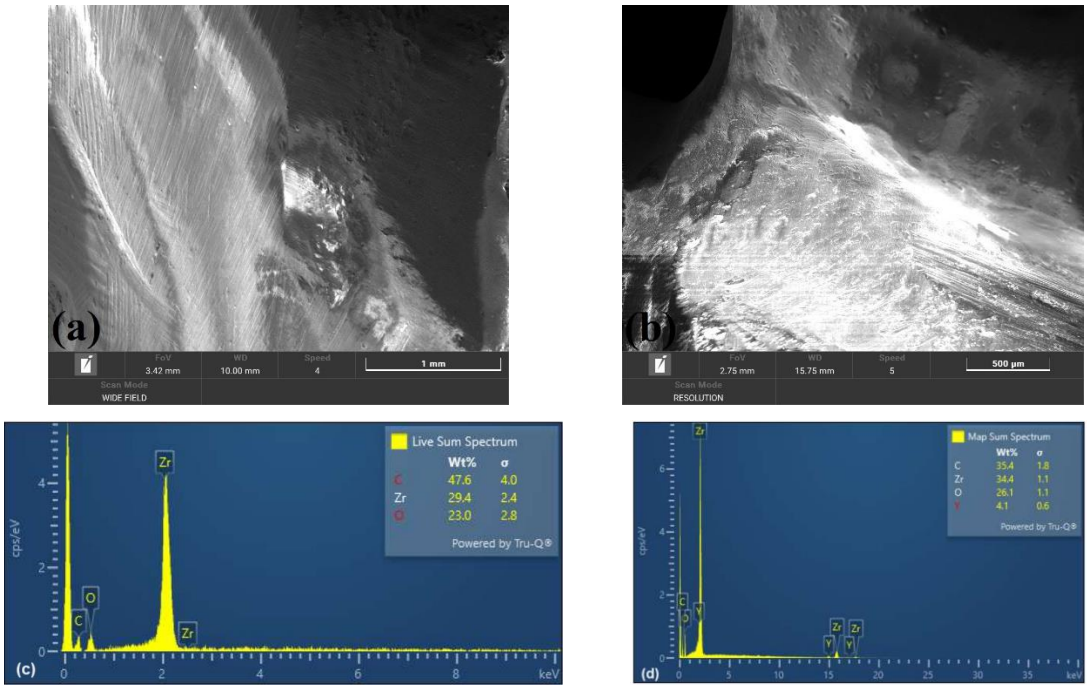

Fig. 8. *SEM -EDX of ZrO_2 samples after 5 days of immersion in 3.5 % NaCl solution: (a, c) - sample 2; (b, d) - sample 3*

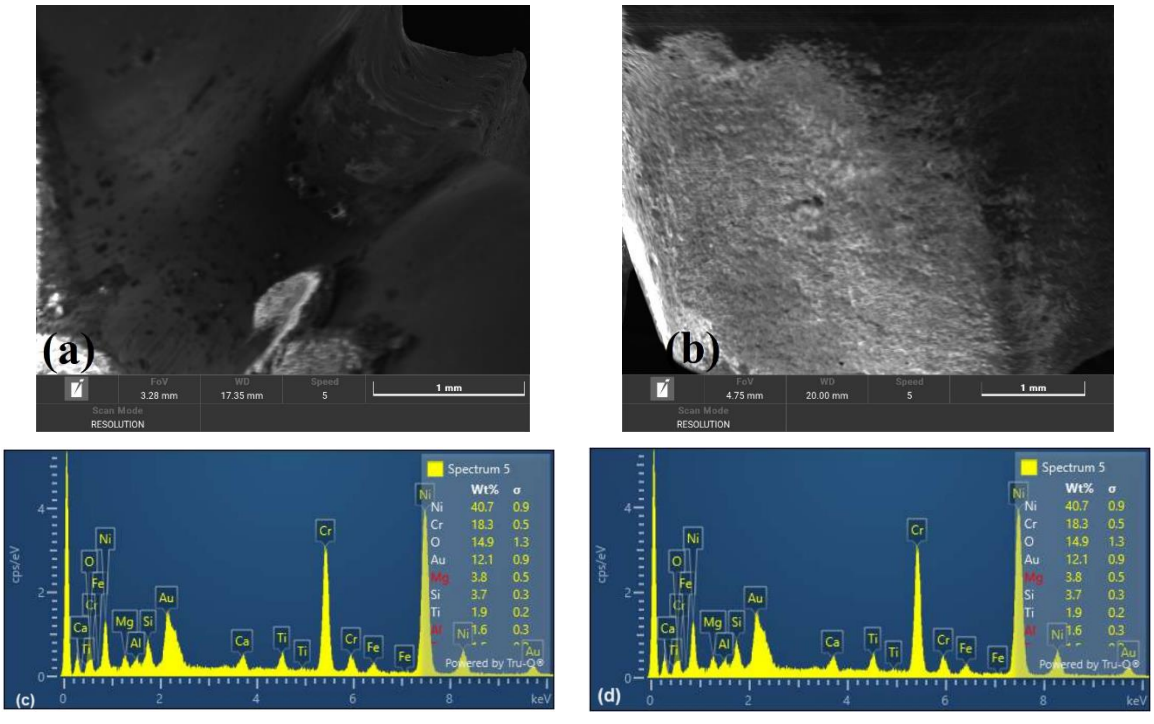

Fig. 9. *SEM -EDX of MC samples after 5 days of immersion in 3.5 % NaCl solution: (a, c) - sample 1; (b, d) - sample 2*

From the analysis of the samples, variations can be observed in the composition of the ZrO_2 ceramic that could be determined by an incorrect preparation of the product in the laboratory.

Regarding the spectral analysis for metal-ceramics, the composition of the alloy is similar for all tested samples.

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3.2. Microhardness and roughness

Microhardness testing was performed on two types of materials, zirconium oxide and metal-ceramic. During the testing it was used a load of 0.5 kgf, at an exposure time of 10 seconds. The results obtained for the evaluation of microhardness are presented in Table 1.

The results vary both depending on the quality of the tested material and depending on the technological conditions of manufacturing the respective sample.

Table 1. *Microhardness values for the tested materials*

Tested material	Microhardness, HV
ZrO_2 – sample 1	153.2
ZrO_2 – sample 2	121.8
ZrO_2 – sample 3	118.4
MC – sample 1	215.2
MC – sample 2	7.3
MC – sample 3	853.1

The roughness value can be calculated either on a profile (line) or on a surface (area, zone). The parameter for the profile roughness, Ra, is the most frequent [13]. The values of the tested samples before corrosion tests are presented in Table 2.

Table 2. *Roughness values for the tested materials*

Tested material	Roughness values, µm
ZrO_2 – sample 1	0.510
ZrO_2 – sample 3	0.780
MC – sample 1	0.250
MC – sample 2	1.961

After corrosion tests the microhardness and roughness of the samples was not evaluated because the samples surfaces were not uniform.

3.3. Corrosion tests

Corrosion testing was performed using the gravimetric method in 3.5% NaCl corrosive solution.

The gravimetric methods for corrosion evaluation have applications in the study of general corrosion (uniform and generalized) of metals, applying to solutions of electrolytes or substances non-polar organics as a corrosive environment. Using this method, the mass variation (gravimetric index), corrosion rate and average penetration depth (penetration index) of corrosion in the mass of the metal/alloy can be determined [15].

The gravimetric index (Kg) is expressed in $g/m^2 \cdot h$ or in $mg/dm^2 \cdot day$ and represents the weight variation of a metal/material sample (Δm) corroded, per unit area (S) in unit time (t), according to relation (1). The gravimetric index can express the weight loss of the material, but it can also express the increase in weight of the material if products appear on its surface adheres to the surface or forms corrosion-resistant oxide films.

$$K_g = \frac{\Delta m}{S \cdot t} \quad (1)$$

The corrosion rate can also be calculated with the relationship (2):

$$v_{corr} = \frac{K \cdot W}{A \cdot t \cdot d} \quad (2)$$

where: v_{corr} represents the corrosion rate; K is a constant depending on the unit of measurement of the corrosion rate; W is mass loss; A is the surface of the corroded material; t is the exposure time of the material to corrosion and d represents the density of the corroding material.

The penetration index (P) expresses the average depth of penetration of the corrosive medium into the metal mass or the average decrease in the thickness of the exposed sample (d) in the unit of time (t) and is expressed in mm/year (relation 3):

$$P = \frac{d}{t} \quad (3)$$

Relation (4) represent the relationship between the gravimetric index and the penetration index:

$$P = \frac{K_g}{d} \cdot 8.760 \quad (4)$$

where: d - metal/material density (g/cm^3); K_g - gravimetric index ($g/m^2 \cdot h$); 8.760 - the number of hours in a year [16].

To test the corrosion behavior, the samples were immersed for 12 days in 3.5% NaCl corrosive solution. Table 3 shows the physico-chemical parameters of the corrosion solution. After 5 days of immersion in 3.5% NaCl solution, the samples were weighed again, and the results indicate a slight weight loss of the tested samples. The same tendency was observed after 12 days of immersion. Since no significant mass loss was observed during this interval, the tests will be continued for a period of three and six months for further observations.

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Tabel 4. *Physico-chemical parameters of corrosive solution*

pH	5.77
Potential, V	+73.82
Conductivity, mS	57
Salinity, g/L	41.4
Total dissolved solids, ppt	38.1

The values of corrosion rate and penetration index are presented in Table 5 (density of ZrO_2 was 6.05 g/cm^3 and density of metal-ceramic tested samples was 0.9 g/cm^3 - according to technical data give from producers).

The penetration index is correlated with a conventional scale of resistance of metals to corrosion (Table 6), which provides indicative information on the corrosion tendency of a material in a corrosive environment [17].

Tabel 5. *Corrosion rate and penetration index for tested samples*

Sample tested	Corrosion rate after five days of immersion, mm/an	Penetration index after five days of immersion	Corrosion rate after 12 days of immersion, mm/an	Penetration index after 12 days of immersion
ZrO_2 - sample 1	0.1508	0.218	0.213	0.308
ZrO_2- sample 2	0.0402	0.058	0.040	0.057
ZrO_2-sample 3	0.0006	0.0008	0.185	0.267
MC - sample 1	0.506	4.925	5.388	52.326
MC 2 - sample 2	1.216	11.835	33.835	329.32
MC 3 - sample 3	0.234	2.277	10.557	102.75
MC 4 - sample 4	2.676	26.052	91.65	892.06

Table 6. *Conventional scale of corrosion resistance of materials*

Corrosion resistance	Mass losses, g/m^2·h	Penetration index P, mm/year	The stability coefficient
Perfectly stable	< 0.007	< 0.001	1
Very stable	0.007 – 0.035	0.001 – 0.005	2
	0.035 – 0.07	0.005 – 0.01	3
Stable	0.07 – 0.35	0.01 – 0.05	4
	0.35 – 0.7	0.05 –0.1	5
Relatively stable	0.7 – 3.5	0.1 –0.5	6
	3.5 – 7.0	0.5 –1.0	7
Little stabile	7.0 - 35	1.0 – 5.0	8
	35 - 70	5.0 – 10.0	9
	> 70	>10	10

In correlation with Table 6 the zirconium samples vary from the Perfectly stable category < 0.007 with a stability coefficient of 1 in the first five days of immersion in corrosive solution and respectively the Very stable category 0.007 – 0.035/0.035 – 0.07, with a stability coefficient of 2 and 3. For MC samples, they range from the Very stable category 0.007 – 0.035/0.035 – 0.07. with a stability coefficient of 2 and Stable 0.07 – 0.35 with a stability coefficient of 3.

4. Conclusions

From practical observations the greatest advantage of zirconium crowns is their resistance. The hardness of the material makes this type of dental crown an optimal choice for both teeth and molars, being able to withstand very high forces. On the other hand, it has been found that they can last as long as metal-ceramic works.

The hardness of ceramics made of zirconium oxide ZrO_2 (zirconia) is very high, if one takes into account the correct technological process of preparing ceramics from ZrO_2, namely baking in sintering furnaces at the right temperature and the necessary time. Thus, the hardness of the material can be affected in the sense that it can vary in places, as was observed in the case of samples from this study.

Metal-ceramic crowns are very durable and are widely used in molar areas, where the mastication process is more concentrated. The hardness of metal-ceramic dental works is also increased, due to the metal support, but failure to comply with the indications for wearing, maintenance of dental works

can cause major defects such as cracking of the ceramic or even its detachment from the metal support.

The spectral analysis of the composition of the zirconium oxide ceramic identified a slight difference in composition between the studied samples, a fact that could also be related to the technological process, in the sense of faulty homogenization.

The porosity of the surfaces observed in the microscopic analysis, both optical and SEM, indicates a medium sintering biscuit firing, in the case of samples of zirconium oxide. In the case of samples with a smooth surface, the ceramic indicates a high sintering The roughness of the surfaces in the case of ceramic masses indicates that there was no proper vibration and condensation of the ceramic mass layers.

From the first investigations, a reduced mass loss was found. The samples have been shown to be resistant to corrosion and should be left for a longer interval of at least three-six months to observe a significant change.

From the results obtained in the corrosion tests, it was observed that the ZrO_2 samples had a lower mass loss. The same was found to be the corrosion rate in the five- and 12-days interval respectively, implying a lower penetration index.

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