THE ANNALS OF “DUNAREA DE JOS” UNIVERSITY OF GALATI.
FASCICLE IX. METALLURGY AND MATERIALS SCIENCE
N^0. 4 – 2010, ISSN 1453 – 083X

PHYSICO-MECHANICAL AND PHYSICO-CHEMICAL PROPERTIES OF BIO-INERT COMPOSITE CERAMICS

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ABSTRACT

Bio-inert ceramics are non-toxic, non-allergenic and non-carcinogenic materials which explain why these are frequently used as orthopedic and dental implants. Unfortunately, these are chemically inert and do not naturally form a direct link with the bone. The research carried studies micro/nanostructure properties and the porosity of the TiO_2-Nb_2O_5 ceramics, used as biocompatible polymer matrix, prepared by different technological regimes. The morphology of the composite samples of TiO_2-Nb_2O_5 was studied using scanning microscopy. The phase identification of the composites was carried by metallographic microscopy. Results obtained show the chemical composition, the technological parameters and the porosity determined, favors formation of sufficiently strong bond between the studied materials and vitreous carbon layers.

KEYWORDS: bio-inert ceramics, physico-mechanical, physico-chemical properties

1. Introduction

The class of ceramics used for repair and replacement of diseased and damaged parts of musculoskeletal systems are termed bioceramics.

Bioceramics have become a diverse class of biomaterials presently including three basic types: bioinert high strength ceramics, bioactive ceramics which form direct chemical bonds with bone or even with soft tissue of a living organism; various bioresorbable ceramics that actively participate in the metabolic processes of an organism with the predictable results (1). Alumina (Al_2O_3), Zirconia (ZrO_2) and carbon are termed bioinert. Bioglass and glass ceramics are bioactive [1-4].

The aim of the present paper is to examine the change of structure and phase composition of the inert bioceramic material based on TiO_2 with small additions of Nb_2O_5 with nanosized vitreous carbon layers for orthopedic implants.

2. Samples preparation

The studied ceramic substrate specimens, were prepared by mixing TiO_2 and Nb_2O_5 powders in proportions ensuring concentration of 8 wt.%. Nb_2O_5 in the final product. The choice of Rutile as base powder of the mixture is due to its structure. The preparation of the samples is described in details in [Teodosiev and all Artcast Galati] [5].

3. Apparatuses used for measurements of surface morphology – micro/nanostructure

For the investigation of ceramic microstructures and the identification of flaws and defects, the use of light optical microscopy Neophot 32 and digital camera ProgRes C14 JENOPTIK was used.

The nanostructure has been studied by a NanoScan Microscope NanoScan (Figure 3) is presents a scanning microscope that works in a regime of rigid contact and does not require vacuum.

The NanoScan unit has been delivered and made by TISNCM [6, 7]. The main characteristic feature of NanoScan is the use of piezoresonance probe having high bending stiffness of the cantilever. The tests have been performed at the regime of resonance oscillations measuring the contact between the probe tip and the surface, analyzing two parameters: change of amplitude A and frequency F of the probe tip oscillations.

NanoScan Measurement System allows measuring both the topography and mechanical properties. Moreover, NanoScan allows loading and scratching the surface by the probe tip and measuring the hardness. For this purpose, scanning and scratching followed by new scanning have been made to evaluate the sample hardness in comparison with a standard.

For elasticity determination dynamic measurements during loading-unloading process with oscillated probe tip have been performed.

***Fig. 1**. Scanning Probe Microscope NanoScan.*

4. Results and discussion

Fig.2 shows the ceramic's microstructure with different morphology of grains, and large pores. Fig.3 shows the hardness measurements carried on conventional microhardness machines with Knoop or Vickers diamond indenters.

These machines make impressions whose diagonal size is measured with an attached optical microscope. The procedure for testing is very similar to that of the standard Vickers hardness tests, except that it is done on a microscopic scale with high precision instruments.

The surface tested generally requires a metallographic finish; depending on the load used; the smaller the load, the higher the surface finish required. Knoop tests are good for very hard brittle materials and very thin sections.

For the ceramic material tested here, it was determined that the Knoop hardness is between 1000kg/mm^2 and 1050 kg/mm^2.

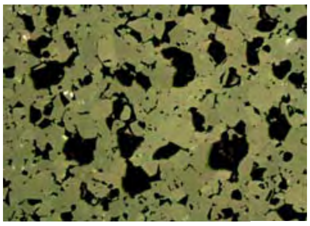


***Fig. 2**. Microstructure of the TiO_2 - Nb_2O_5 ceramics.*

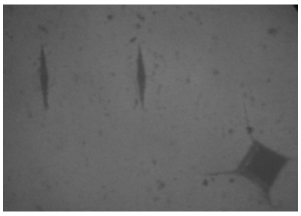
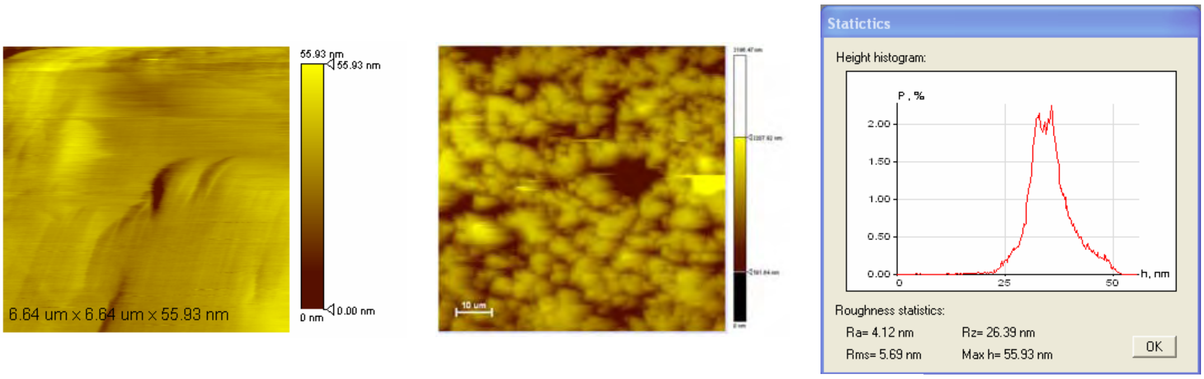


***Fig. 3**. Knoop and Vickers marks.*

The sample surface roughness, the elastic module and hardness before and after coating were scaned and measured (see Fig. 4). The coating improves the surface roughness, and improves the mechanical properties of the samples. Statistics TiO_2 - Nb_2O_5 ceramics shows that the average particle size is **Rms** = 5,67nm.

Roughness (for surface 6.64 X6, 64 um) is **Ra** = 4,12 nm. Measured values are: Elastic module: 185-230 GPa, Hardness **H**=4,1- 6,7 GPa.



Roughness statistics:
Ra= 4.12 nm Rz= 26.39 nm
Rms= 5.69 nm Max h= 55.93 nm

***Fig. 4**. Nanostructure of sample TiO_2 - Nb_2O_5 ceramics*

At the same time we studied the system Al_2O_3 - ZrO_2, where the obtained ceramic material possesses better mechanical properties. The coating with VC of this ceramic composite and the evaluation of its coefficient of friction will be a subject of another study.

The Al_2O_3 - ZrO_2 system to long time has been attracting the investigators attention as far as the two oxides do not interact with each other up to 1700^{0}C and they are in a state of mechanical mixture. Because of that they mutually hinder their grain growth during sintering. As a result a ceramic composite with very fine structure corresponding to very high strengths is obtained [8-10]. This based on alumina and zirconia composite is characterized with high compressive and bending strength, high hardness and wear resistance.

We investigated the mechanical properties of the composite material in the Al_2O_3 - ZrO_2 system with different content of the two oxides and the influence of the temperature treatment. Preliminary synthesis is made aiming at partial stabilization of the ZrO_2 with Y_2O_3.

The sintering of the composite material is carried out at temperature up to 1680^{0}C. The obtained composite ceramic possesses high hardness – 90 HRA, compressive strength - 1650 MPa and bending strength - 260 MPa.

The zirconia is preliminary partially stabilized with 3.0 wt. % Y_2O_3 at temperature 1350^{0}C for one hour. The raw materials are mixed and homogenized in planetary mill during six hours in isopropyl alcohol environment.

The received finely dispersed powders are dried and granulated with plasticizers as carboxymethyl cellulose, polyvinyl alcohol, etc. Cylindrical samples with dimensions 15x15 mm and prisms 5x5x45 mm are pressed with pressure 250 MPa from the obtained semidry mass.

The samples are sintered in two stages: to 1400^{0}C with holding time of 1 ½ hours and then to 1630^{0}C or 1680^{0}C in high temperature furnace.

We studied four compositions with different content of the two basic oxides. The mechanical properties – compressive and bending strength of the above cited compositions are determined (*Table 1*).

***Table 1.** Composition and properties of the samples vs. the sintering temperature*

Composition No	**Al_2O_3** wt. %	**ZrO_2** wt. %	**Compressive strength** MPa		**Bending strength** MPa	
			1630^{0}C	1680^{0}C	1630^{0}C	1680^{0}C
1.	86	14	700	935	90	115
2.	83	17	890	1340	115	195
3.	80	20	1045	1580	118	260
4.	77	23	805	1430	97	185

The change of the compressive and bending strength depending on the content of the two oxides and the modifying additives at different sintering temperatures is displayed graphically in *Figure 5* for the compressive strength and in *Figure 6* for the bending strength.

The investigated composite material on the base of Al_2O_3 - ZrO_2, sintered at 1680^{0}C has better compressive strength indices compared to the ceramic material sintered at 1630^{0}C (*Fig.5)*. Similar trend is observed while determining the bending strength (*Fig.6*) but the corresponding values are lower.

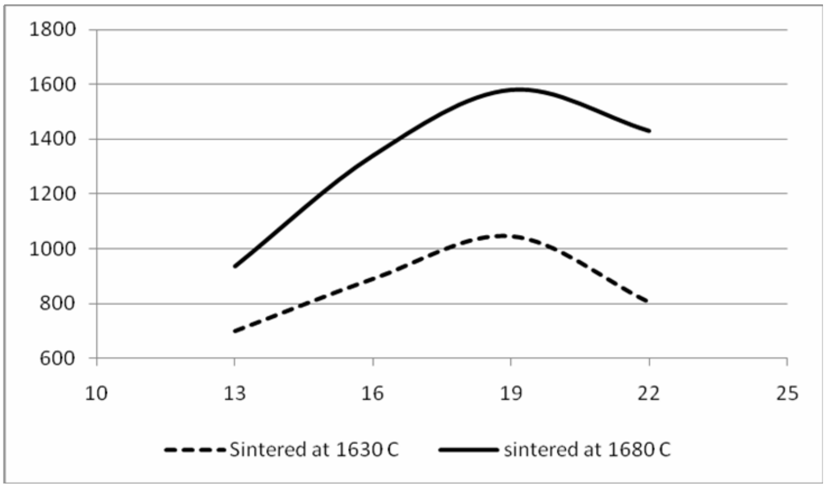


***Fig.5**. Compressive strength (MPa) of the composite material sintered at 1630^{0}C and 1680^{0}C depending on the ZrO_2 (wt. %).*

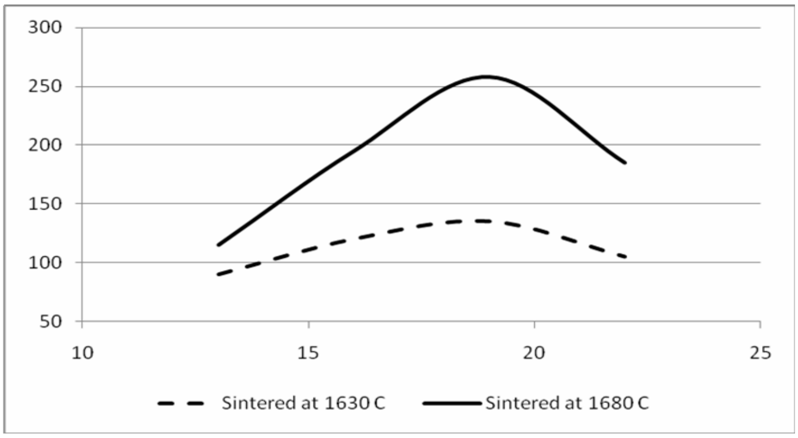


***Fig.6**. Bending strength (MPa) of the composite material sintered at 1630^{0}C depending on the ZrO_2 (wt. %).*

Along with the sintering temperature and the additives, the physical and the mechanical properties are influenced strongly also by the content of the ZrO_2 added. The ZrO_2 is found in three polymorph forms: m-monoclinic, t-tetragonal and c-cubic. Depending on the type and quantity of the additives and the sintering temperature, ZrO_2 can be partially or totally stabilized in one or several modification forms.

The most interesting is the transition from monoclinic to tetragonal structure and vice versa in the temperature range 1000^{0}C – 1200^{0}C. These phase transitions exhibit volume changes.

To avoid this shrinkage and expansion, leading to destruction of the product, partial stabilization of the ZrO_2 is made. We use additives such as Y_2O_3 CaO for this purpose and TiO_2 - to lower the sintering temperature and to compact the structure.

The high mechanical strength of the samples is a result of the tetragonal ZrO_2 located on the boundaries of the Al_2O_3 grains. It can be transformed from tetragonal into monoclinic form when external load is applied which contributes to the strength increase [11]. Based on the carried out experiments and analysis of the results obtained it is found, that the composite material of the Al_2O_3 - ZrO_2 system, containing partially stabilized ZrO_2 in the range 17 – 20 wt. % and modifying additives CaO and TiO_2, possesses the highest mechanical properties – compressive strength 1600 MPa and bending strength 260 MPa.

The Rockwell micro hardness measurements were performed on the same ceramic material sintered at temperature 1680^{0}C showing values in the range of 85 – 90 HRA, This ceramic composite is suitable for production of different construction components enduring high mechanical loads and possessing high wear resistance.

4. Conclusions

Bio-inert ceramics are different materials used in the manufacture of orthopedic and dental implants for humans. These are: stainless steel, biocompatible, pure titanium and titanium alloys, cobalt alloys, polymer materials, inert bioceramic (Al_2O_3, ZrO_2), glassy carbon.

All of them have different advantages and disadvantages, but they have one common quality - they meet the standards for the materials used for making implants in human body (ISO 5832-1).

Developed by us TiO_2 - Nb_2O_5 composite materials have good layers of vitreous carbon and an extremely strong connection to the basic ceramic material.

Acknowledgements

The authors are grateful to the National Science Fund, Ministry of Education and Science of Republic of Bulgaria (Grant DO 02-234/2008) for the financial support of the project.

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