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# Ageing of advanced biomaterials

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ABSTRACT

The paper presents the ageing processes of advanced biomaterials. The medical profession considers ageing as a syndrome of universal, progressive, irreversible processes that take place at the molecular level (DNA, proteins, lipids) and at the organ level. Ageing is treated quite differently by the engineering profession, which considers it as wear, degradation, corrosion and deformation. In the tissue over time, changes in temperature, changes in pH value and the effect of large forces lead to changes in biomaterials, which are known in the literature as biomaterial ageing processes.

*Keywords:* biomaterials, ageing, mechanisms.

## 1. Introduction

The major parts of biomaterials and medical devices are composed of synthetic materials, which are divided into three main classes: metals, biopolymers or biocomposites, and bioceramics (Géraldine, 2014). The other classes are composites and biologically derived materials. The most commonly used metals are titanium-based alloys, stainless steels, and cobalt–chromium alloys. Other metals and alloys include commercially pure titanium (Ti-Cp), nitinol (shape-memory alloys (SMAs) based on nickel and titanium), and dental alloys (Raghavendra et al., 2015). Biopolymer materials represent one of the basic groups of those used in dental technology, known as acrylates (primarily methyl methacrylate). Polyethylenes, polyethers, and polysulfides are used for dental indications. The main biocomposites in dental technology are Bis-GMA (bisphenol A-glycidyl methacrylate) or UDMA (urethane dimethacrylate) and their various molecular modifications. Bioceramics are composed of sintered alkaline aluminosilicate powders with additives (melting agents and metal oxides) for the production of porcelain inlays, crowns and bridges, as well as ceramic implants.

Due to the annual growth of the global biomaterial market, research and development at the material scale are still challenging for the production of new medical devices. The ageing of biomaterials in in vitro and in vivo conditions (in tissue) is the essence of the problem. However, understanding the ageing of biomaterials requires knowledge of ageing theory (Eliades et al., 2003). Practically, doctors ask engineers for explanations for the phenomena that take place in the biomaterial itself. Biomaterials dissolve, release ions, or otherwise act on the surrounding tissue – the host, causing or not causing reactions in the surrounding tissue, which are dealt with by doctors. However, laboratory procedures for the formation of biomaterials, as well as the surrounding tissue, act on the biomaterial causing certain changes.

## 2. Types of biomaterials and their ageing

### 2.1. *Metallic biomaterials*

In the theory of the ageing of metallic biomaterials, ageing belongs to the processes of strengthening and is often called precipitation strengthening (*Ruowei et al., 2016*). This is reflected in a change in the microstructure so that the precipitation of β phase from α phase solid solution occurs. One of the phase diagrams, in which precipitation strengthening is possible, is a eutectic system with partial solubility in a solid state (Figure 1).

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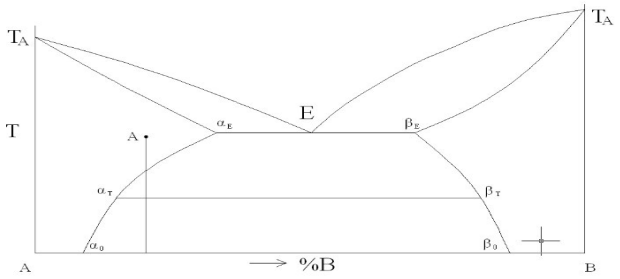



**Fig. 1.** Binary phase diagram A-B where precipitation strengthening is possible

The strengthening process consists of the formation process (nucleation of precipitates) and the growth process. Precipitates originate homogeneously or heterogeneously and grow until all component B in excess is precipitated (to be eliminated) from the α phase. Then the process of dissolution of smaller and larger precipitates begins (Ostwald ripening) - the process continues until all precipitates reach a similar size. During this process, the density of the precipitate decreases. Part of the precipitates, their density and arrangement, are primarily dependent on the ageing temperature and the composition of the alloy (Winn et al., 1999). At the ageing temperature, atoms jump over gaps in the crystal lattice and thus change their position. In most cases, diffusion is a "statistical" process, that's why it often happens that in some areas of the α phase, the concentration of B atoms is much higher than the average composition of the alloy. Strengthening in metallic biomaterials is the result of interactions between precipitates and dislocations, which depend on the type of precipitate/matrix interface and on the size and density of the precipitates (Artz et al., 1996).

Practical examples of ageing are well known in the group of dental alloys. The characteristic of all dental alloys is that they must have high corrosion resistance. Dental alloys are divided into two groups: base and noble, depending on the chemical composition. In the case of base dental alloys with nickel, cobalt, and iron, chromium content is required which provides resistance to corrosion by forming a thin, passivating layer of oxide on the surface and thus prevents the penetration of other corrosive elements into the volume of the dental alloy. A typical microstructure of the CoCrNi dental alloy imaged with an scanning electron microscope is shown in Fig. 2a. On the other hand, noble dental alloys with gold, palladium, or silver are known to have excellent in vivo corrosion resistance as a result of their content. These alloys contain small amounts of certain deoxidizers (Zn, Ir, and Sn) that form strong chemical bonds with ceramics during the ceramic firing (sintering) process. A typical microstructure of the AuPt dental alloy imaged with an optical microscope is shown in Fig. 2b.

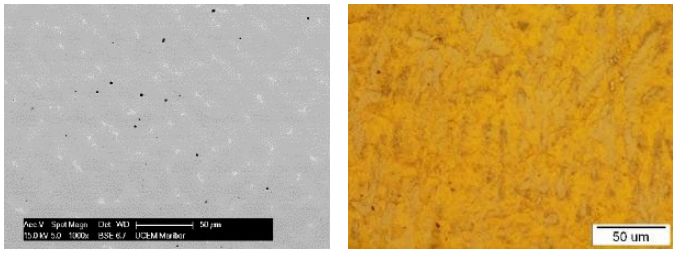
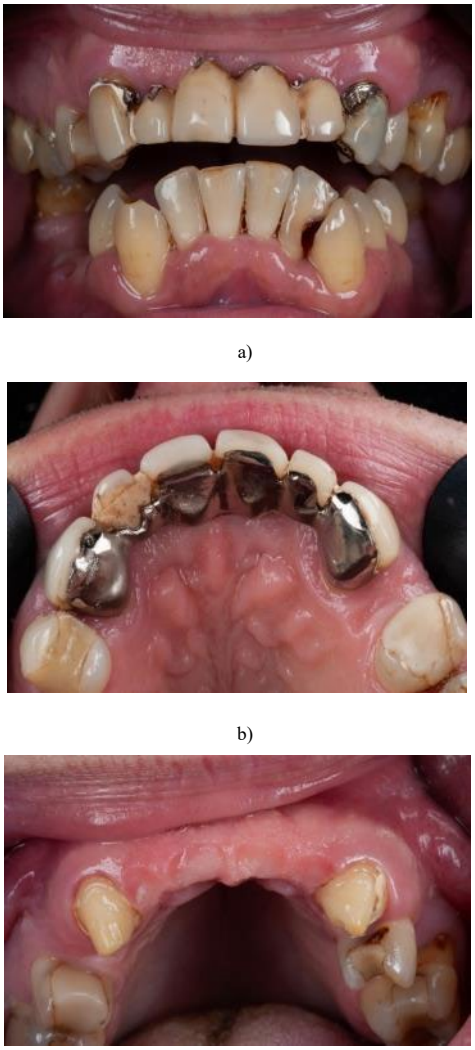



**Fig. 2.** a) CoCrNi dental alloy and b) AuPt dental alloy

Many published works describe the microstructure and properties of base and noble dental alloys in the as-cast state and after heat treatment, and often include the simulation of relevant ceramic firing cycles. However, there are only a few published studies that directly examine the ageing of dental alloys (noble metals only) at intraoral or room temperature (Rudolf et al., 2010).

The changes that occur *in vivo* during the ageing of dental alloys, despite the enormous progress of science, have not been fully explained. How to explain the fact that, for example, removing a gold alloy bridge after 20 or more years of wear does not show signs of material fatigue (ageing), while, on the other hand, a modern metal-ceramic bridge still shows serious signs of material fatigue within the "warranty" period. The lines that follow, therefore, describe some important principles of ageing of building dental alloys in in vivo conditions. Clinical tests show the exceptional durability of nolbe dental alloys in the mouth. With proper oral hygiene, the tissue under the denture is healthy and without discoloration, and the ground teeth under fixed dentures remain suitable for making new dentures without additional treatment in case of replacement. The durability of silver-palladium dental alloy produced by Zlatarne Celje d.o.o. Slovenia, after 30 years of use and the condition of the fork after removing the prosthetic structure are shown in Figure 3. Due to 30 years of use, and therefore wear, the faceted composite on the bridge was very thin, as a result of which the supporting metal structure was visible in the mouth, which represents great aesthetic discomfort for the patient. A microchemical analysis with energy dispersive spectroscopy (EDS) in an electron microscope was performed on the removed dental prosthetic construction.



a)

b)

c)

**Fig. 3.** Clinical view of the silver-palladium dental prosthetic construction after 30 years of use and the condition of the jaw after its removal: a) view of the fixed dental prosthesis in the mouth, upper jaw frontally, b) view of the fixed dental prosthesis in the mouth from the bottom up, and c) view of the upper jaw after removal of the fixed prosthesis.

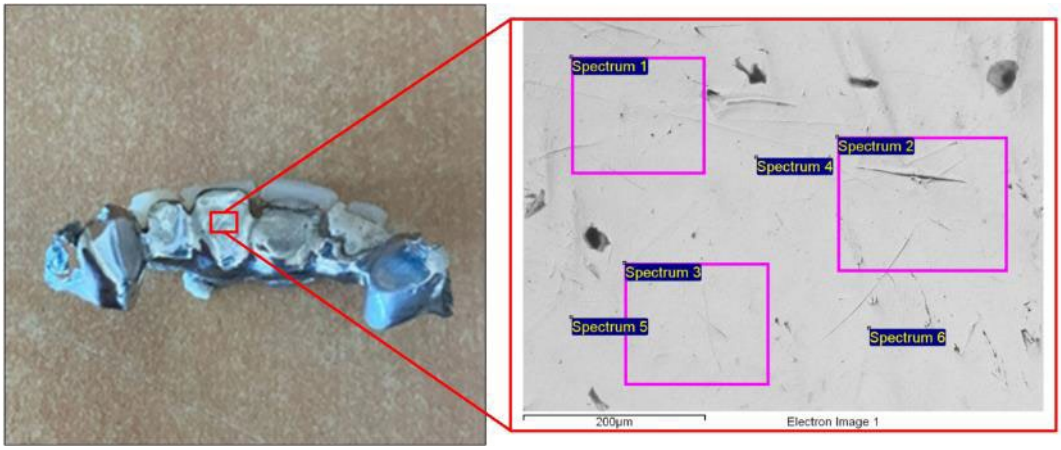



**Fig. 4.** Silver-palladium dental alloy dental bridge, removed after 30 years of use, with marked location of microchemical analysis

Microchemical analysis showed that the metal composition of the bridge is identical to the declared composition of the new silver-palladium dental alloy (Figure 4), which indicates negligible deterioration of the silver-palladium dental alloy due to years of use. The minimum deviations in the attached comparative table 1 are within the limits of the measurement error of the analysis and within the limits of the permitted deviations for the new dental alloy.

**Table 1.** Comparison of the declared metal composition of the new alloy and the chemical analysis of the dental bridge from silver-palladium dental alloy

| | Analysis of chemical elements (in mass %) |
|---|---|
| Declared values | Cu: 8 Zn: <1 Pd: 25 Ag: 64 Au: 2 |
| Values in the removed dental prosthetic structure after 30 years of use | Cu: 7.57 Zn: 0.93 Pd: 25.38 Ag: 63.81 Au: 2.30 |

All conventional base and noble dental alloys contain multicomponent elements. According to Gibbs phase rule (Brick et al., 1977), these alloys contain multiple phases at intraoral and room temperature under equilibrium conditions. Even if complex multicomponent phase diagrams are available for dental alloys, they do not provide complete information. Due to insufficient time for the diffusion of elements, which would maintain the equilibrium phase composition in the conditions of rapid hardening in the dental laboratory, the microstructure of cast dental alloys inevitably contains microsegregations of elements, as well as non-equilibrium phases. These phenomena are visible when the microstructures of gold-based alloys and alloys with a high content of palladium are compared in the cast state and after heat treatment that simulates ceramic firing cycles, where micro-structural homogenization is observed (Vermilyea et al., 1980).

The residual stresses of dental alloys and knowledge of their role in ageing are also very important. Residual stresses exist in all dental alloys due to the rapid solidification and limitation of alloy hardening by the refractory investment mass (*Craig et al., 2002*). The development of stresses during the solidification of dental alloys with a dendritic microstructure can lead to the formation of cracks under the effect of heat when there is not a sufficient amount of the basic metal mass that could withstand these stresses (*Guo et al., 2003*). This problem is also expected in other alloys with a high content of palladium, which in the cast state have a dendritic microstructure – Figure 5. Procedures applied in dental laboratories (such as sandblasting, mechanical processing of castings and polishing) can cause surface deformations of the alloy due to the transfer of residual stresses in the surface region. Although some residual stresses may be released during the ceramic firing cycle of metal-ceramic restorations, other residual stresses will build up in the alloy during the cooling of the metal-ceramic restoration due to the slight mismatch between the coefficients of thermal expansion of the alloy and the ceramic. These stresses provide an additional driving force for phase transformations during heat treatment at elevated temperatures, as well as during in vivo ageing, when the alloy attempts to form equilibrium phases.

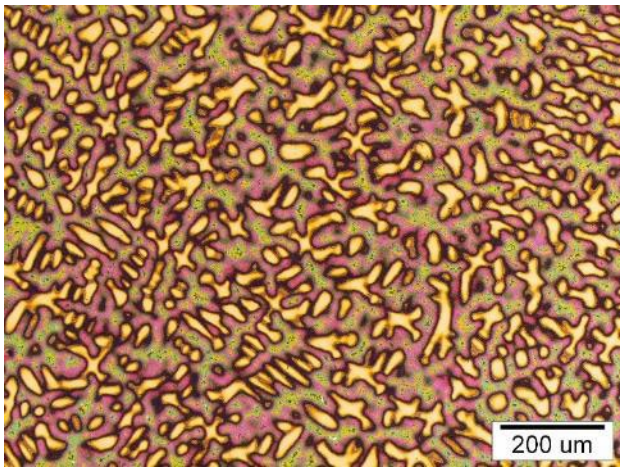



**Fig. 5.** Dendritic microstructure of dental alloys with a high content of palladium

Artificial ageing of dental alloys represents the exposure of building dental alloys to the alternating action of high and low temperatures and load is an attempt to bring the experimental conditions as close as possible to real clinical conditions. In this way, with artificial ageing, changes resulting from ageing can be observed more quickly than would be possible in clinical conditions (Szczesio-Wlodarczyk et al., 2022).

The majority of studies on artificial ageing include thermocycling (97.2%), while the number of studies that, in addition to thermocycling, also include loading is significantly lower (8.1%). Most often, alloy samples undergo thermocycling at final temperatures of 5 °C and 55 °C, and their exposure to high and low temperatures ranges from a few seconds to several hours. The number of temperature cycles to which samples are exposed during thermocycling ranges from 100 to 2,500, and most often this number is between 250 and 300 cycles (Eliasson et al., 2020). The conditions under which mechanical loading is performed are also different. Most often, the tested material is alternately exposed to thermal and mechanical loads. The number of load cycles ranges from 100 to 300,000, while the size of the forces varies between 70 and 350 N.

### 2.2. Biopolymers or biocomposites

Over time, there are undesirable changes in the properties of polymer materials and polymer components of composites, i.e., ageing. The ageing of polymers includes various physical and chemical processes: swelling, dissolution, and breaking of covalent bonds. A typical microstructure of an aged biopolymer (PMMA) is shown in Figure 6. Due to the complex structure of biopolymers, ageing mechanisms have not been fully elucidated. During application, the mechanical properties of biopolymers change, and the dynamics of these changes are highly dependent on their chemical and structural composition. The degradation of biopolymers and biocomposites refers to physical and chemical processes that have a long-term effect. The degradation of biopolymers and biocomposites can be roughly divided into physical, mechanical, and chemical degradation. Other types of biopolymer degradation also occur in nature, such as electrochemical degradation, degradation due to radiation, degradation after the formation of cracks due to stress, etc. Physical biopolymer degradation includes physical reaction processes such as sorption, dissolution and elution that biopolymers undergo when exposed to the influence of the external environment and manifest as softening, swelling or deformation of the shape. Mechanical degradation of biopolymers, wear or tear is the progressive loss of material from body surfaces (filling or replacement), due to dynamic contact with another body or fluid (antagonists or food). It is basically a physical, not a chemical process. There are four basic wear mechanisms: adhesive wear, abrasion, fatigue and corrosion (Mair et al., 1996).

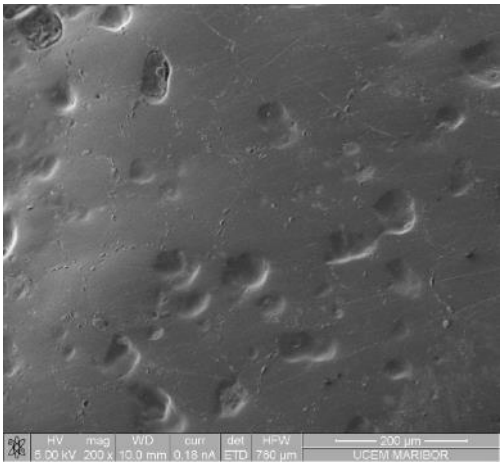



**Fig. 6.** Microstructure of aged PMMA biopolymer for dental prostheses

Adhesive wear occurs when two smooth surfaces slide over each other, and the particles of one surface separate and adhere to the other surface. This is a negligibly small form of mechanical degradation of polymers and is most often combined with abrasive wear (Mair et al., 1996). A metal matrix - a polymer matrix is found on the surface of attachments (sliders, crossbars).

Abrasive wear occurs when the rough surface of a harder material slides over the surface of a softer material. This creates furrows on the surface and particles (sawdust) of softer material. This is the most common type of mechanical degradation of biopolymers and biocomposites in dentistry. There are a large number of combinations of materials that are in contact (enamel - composite filling, acrylate teeth in mobile prostheses, ceramic crowns; composite filling/acrylate teeth - ceramic crowns, metal occlusal rests, etc.). Softer material is used, and compared to natural teeth, ceramic or metal, it is always polymer. The degree of wear depends not only on the composition of the materials that are in contact, but also on the number and length of contact between the antagonists, chewing force, the existence of parafunctions (bruxism), the smoothness of the surfaces, and the combination with other mechanisms of material degradation. The described type of abrasive wear is two-body abrasive wear. When solid particles (absorbed solid food, abrasive toothpaste) are found between the antagonists, an abrasive wear mechanism of the building material also occurs, described in the literature as three-body abrasive wear (Soderholm et al., 1998).

Fatigue wear occurs when the surfaces of two materials repeatedly slide. During the interaction of two surfaces, which slide over each other, stress zones are formed, namely pressure zones and traction zones. Under the surface of the material, cracks appear that can spread due to cyclic alternating repetitions of pressure and traction. Over time, surface or internal cracks in the material cause separation of parts of the surface (Mair et al., 1996).

Corrosion occurs when two surfaces slide in a corrosive environment, so chemical degradation of the material is added to wear. This type of corrosion is rarest in biopolymers.

Chemical degradation of biopolymers can lead to the formation of some new compounds or the release of existing ones. Oxidation reactions in some resins reinforced with composites release formaldehyde [Oysaed, 1988]. Some enzymes from saliva (esterases) can degrade the PMMA matrix from acrylate, which leads to the release of the final alcohol product [Peutzfeldt, 1997].

The change in color of the biopolymer and the polymer component of the composite, due to chemical reactions, is also included in the chemical degradation of the material. Over time, some biopolymer compounds can absorb coloured liquids from food and beverages, which leads to a change in the colour of the polymer (Uchida, 1998).

The degradation of materials in the biological environment is called biodegradation. Although degradation in the biological environment (oral cavity and maxillo-mandibular region) occurs with all dental materials, biodegradation is greatest with biopolymers and polymer components of composites. Biodegradation of polymeric materials is, in fact, the chemical decomposition of materials by living organisms, which leads to changes in the physical characteristics of the material.

There are many different ways and synergistic pathways for the biodegradation of polymers in the mouth. Thus, for example, cracks that occur due to material stress create new reactive surface sites (Leinfelder, 1987). Polymer hydrolysis can generate new chemical reactions that lead to swelling. The environment to which biopolymers and biocomposites are exposed during long-term use (the oral cavity) is described as an aqueous medium containing various anions, cations, organic substances and dissolved oxygen. Anions are $Cl^-$, $PO^{4-}_3$, and $HCl^{-3}$, while primary cations are $Na^+$, $K^+$, $Ca^{2+}$, and $Mg^{2+}$. Among the organic substances, species with low molecular weight can be found. This biological environment acts on biopolymer materials causing its degradation.

Biopolymer materials and polymer components of composites, as building materials, are generally reliable in their expected lifetime. No biopolymer is completely impermeable to chemical processes and mechanical actions in the mouth. The swelling of the organic matrix, the weakening of the bond between the matrix and the filler, and the final “falling out” of the nano and/or microfiller from the matrix are the reasons for the weakening of the physical and mechanical characteristics of biopolymer materials.

### 2.3. Bioceramics

The ageing of bioceramics in the mouth can vary greatly, from bioceramics that are very resistant to corrosion and degradation (infiltration ceramics for dental restorations) to highly soluble, degradable bioceramics (ceramic bone substitutes – ZTA - zirconia-toughened alumina, HA- hydroxyapatite).

The decomposition of degradable bioceramics depends on their chemical composition. So, for example, tricalcium phosphate, $(Ca_3(PO_4)_2$, breaks down quite quickly, unlike hydroxyapatite, $Ca_{10}(PO_4)_6(OH)_2$, which is quite stable. The microstructure also affects the rate of decomposition, so solid forms of ceramics are more difficult to decompose than porous, canalicular forms – see Fig. 7 and Fig. 8.

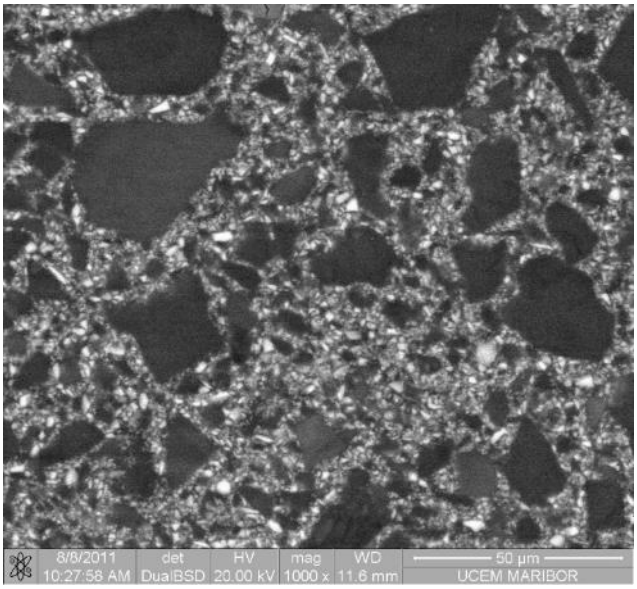



**Fig. 7.** Microstructure of aged bioceramics for dental application

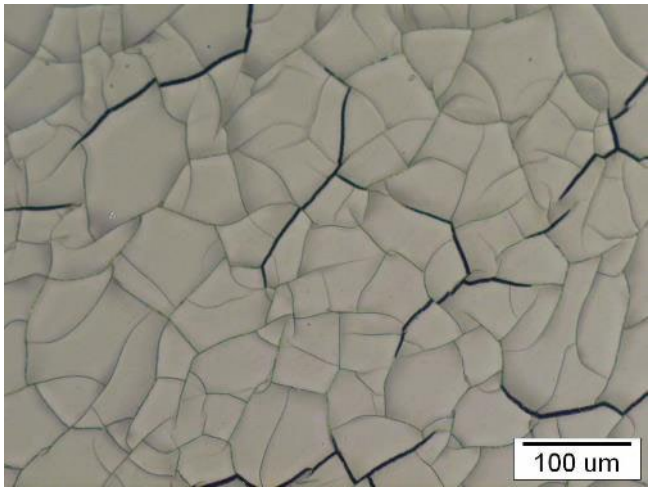



**Fig. 8.** Microstructure of aged zirconia-toughened alumina (ZTA) for dental application

On the basis of the problem with ageing, development is being done on the reformulation of the chemical composition and technological process of bioceramic systems in the direction of improving mechanical and other characteristics. The aim is to increase the precision of edge closure in ceramic restorations in dentistry, the improvement of the machinability characteristics of bioceramics and the possibility of achieving levels as an alternative to autogenetic bone grafting in the substitution of bone tissue.

## 3. Conclusions

The presented ageing processes and ageing methods for advanced biomaterials are very complex and practically cannot be carried out reproducibly in laboratory conditions, if the conditions that biomaterials have in their function are to be ensured. A realistic aggressive environment, as represented by the human body, exerts various influences on all types of biomaterials, which over time result in the ageing or degradation of some of their properties. Therefore, it is necessary to take into account the processes of their ageing in the intended use of biomaterials, so that their expected lifetime can be predicted. Also, it is well recognized that diverse experiments and events of multidimensional simultaneous phenomena occurring under laminar conditions, evident in the human body, necessitate the development of a new, simple, and accurate simulation technique (Raić, 2018).

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