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# MODERN TECHNOLOGIES FOR THE MANUFACTURE OF GLASS-CERAMIC DENTAL PROSTHESES

The relevance of the problem of improving the quality of life and protecting human health in the context of the successful development of the modern society was presented. A literary review of well-known modern technologies for the design and manufacture of dental prostheses was carried out, as well as the leading domestic and foreign companies that were engaged in this were given. The history of the development of materials for obtaining clinical restorations (crowns, inlays, onlays, etc.) was considered and the main directions of the development of innovative ceramic materials for dental prosthetics were outlined. Based on the analysis of the properties of various types of materials for dental prosthetics, the prospects of using glass-ceramic materials in the development of dental prostheses have been substantiated. The chemical compositions of lithium silicate glasses for the synthesis of the glass matrix have been developed and the technological parameters for the production of glass-ceramic dental prostheses have been selected (Tgl. melting = 1350–1400 °C, Theat treatment = 600–650 °C). Preliminary heat treatment before the formation of products ensures the formation of the required number of the nucleus of crystalline phase and the prerequisites for creating a volume crystallized structure under conditions of shortterm heat treatment. The glass-ceramic prosthesis with a formed interpenetrating sitallized structure was obtained by the method of hot pressing with a short exposure (18-20 min). It was found that the obtained glass-ceramic material containing lithium disilicate as a crystalline phase in an amount of 40-60 vol. %, had high values of bending strength ( $\sigma = 400$  MPa) and fracture toughness. The indicated mechanical properties of the developed materials, along with the approximate values of their modulus of elasticity to natural teeth, will significantly extend the service life of products under conditions of significant alternating loads that arise during the chewing cycle. A comparative assessment of the competitiveness of the developed dental prostheses based on lithium disilicate with world analogues was carried out, in particular the products of Ivoclar Vivadent and Vita Zahnfabrik, in terms of the main operational parameters. The positive effect of the introduction of domestic developed glass-ceramic dental prostheses to reduce import dependence has been determined.

Keywords: dental prostheses, glass-ceramic materials, glass matrix, technological parameters, hot pressing, lithium disilicate.

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#### СУЧАСНІ ТЕХНОЛОГІЇ СКЛОКЕРАМІЧНИХ СТОМАТОЛОГІЧНИХ ПРОТЕЗІВ

Представлено актуальність питань поліпшення якості життя та охорони здоров'я людини в розрізі успішного розвитку сучасного суспільства. Проведено літературний огляд відомих сучасних технологій проектування та виготовлення стоматологічних протезів, а також наведено передові вітчизняні та закордонні компанії, які цим займаються. Розглянуго історію розвитку матеріалів для одержання клінічних реставрацій (коронок, вставок, накладок тощо) та означено основні напрямки розробок інноваційних керамічних матеріалів для зубопротезування. На основі проведеного аналізу властивостей різних видів матеріалів для зубопротезування обгрунтовано перспективність застосування склокерамічних матеріалів при розробці стоматологічних протезів. Розроблено хімічні склади літійсилікатних стекол для синтезу скломатриці та обрано технологічні параметри одержання склокерамічних стоматологічних протезів (Тварки = 1350–1400 °C, Ттермообробки = 600– 650 °C). Попередня термічна обробка перед формуванням виробів забезпечує утворення необхідної кількості зародків кристалічної фази та передумови для створення об'ємнозакристалізованої структури в умовах короткотривалої термічної обробки. За методом гарячого пресування з короткотривалою витримкою (18-20 хв) було одержано склокерамічний протез зі сформованою взаємопроникною ситалізованою структурою. Встановлено, що отриманий склокерамічний матеріал, який містив в якості кристалічної фази дисилікат літію у кількості 40-60 об. %, відрізнявся високими значеннями міцності на згин ( $\sigma$  = 400 МПа) та в'язкості руйнування. Вказані механічні властивості розроблених матеріалів поряд з наближеними значеннями їх модуля пружності до природних зубів дозволять суттєво подовжити термін експлуатації виробу в умовах значних знакозмінних навантажень, які виникають в процесі жувального циклу. Проведено порівняльну оцінку конкурентоздатності розроблених стоматологічних протезів на основі дисилікату літію зі світовими аналогами, зокрема продукції компаній Ivoclar Vivadent та VITA Zahnfabrik за основними експлуатаційними параметрами. Визначено позитивний ефект від впровадження вітчизняних розроблених склокерамічних стоматологічних протезів задля зниження імпортозалежності.

**Ключові слова:** стоматологічні протези, склокристалічні матеріали, скломатриця, технологічні параметри, гаряче пресування, дисилікат літію.

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# СОВРЕМЕННЫЕ ТЕХНОЛОГИИ СТЕКЛОКЕРАМИЧЕСКИХ СТОМАТОЛОГИЧЕСКИХ ПРОТЕЗОВ

Представлена актуальность вопросов улучшения качества жизни и охраны здоровья человека в разрезе успешного развития современного общества. Проведен литературный обзор известных современных технологий проектирования и изготовления стоматологических протезов, а также приведены передовые отечественные и зарубежные компании, которые этим занимаются. Рассмотрена история развития материалов для получения клинических реставраций (коронок, вставок, накладок и т.д.) и обозначены основные направления разработок инновационных керамических материалов для зубопротезирования. На основании проведеного анализа свойств различных видов материалов для зубопротезирования обоснована перспективность применения стеклокерамических материалов при разработке стоматологических протезов. Разработаны химические составы литийсиликатных стекол для синтеза стекломатрицы и выбраны технологические параметры получения стеклокерамических стоматологических протезов (Тварки = 1350–1400 °C, Ттермообработки = 600–650 °C). Предварительная термическая обработка перед формированием изделий обеспечивает образование необходимого количества зародышей кристаллической фазы и предпосылки для создания объёмнозакристаллизованной структуры в условиях кратковременной термической обработки. По методу горячего прессования с кратковременной выдержкой (18-20 мин) был получен стеклокерамический протез со сформировавшейся взаимопроникающей ситаллизированной структурой. Установлено, что полученный стеклокерамический материал, содержащий в качестве кристаллической фазы дисиликат лития в количестве 40-60 об. %, отличался высокими значениями прочности на изгиб ( $\sigma = 400 \text{ M}\Pi a$ ) и вязкости разрушения. Указанные механические свойства разработанных материалов наряду с приближенными значениями их модуля упругости к естественным зубам позволят существенно продлить срок эксплуатации изделий в условиях значительных знакопеременных нагрузок, которые возникают в процессе жевательного цикла. Проведена сравнительная оценка конкурентоспособности разработанных стоматологических протезов на основе дисиликату лития с мировыми аналогами, в частности продукцией компаний Ivoclar Vivadent и VITA Zahnfabrik, по основным эксплуатационным параметрам. Определен положительный эффект от внедрения отечественных разработанных стеклокерамических стоматологических протезов для снижения импортозависимости.

**Ключевые слова:** стоматологические протезы, стеклокристаллические материалы, стекломатрица, технологические параметры, горячее прессование, дисиликат лития.

## Introduction.

Ensuring health protection is an integral part of the successful development of the legal community. After all, the state is responsible to the existing and future generations for the level of their health and the preservation of the gene pool of the nation. The modern world is experiencing a real epidemic of chronic noncommunicable diseases associated with an unhealthy lifestyle, unbalanced nutrition, low physical activity and other factors. Important health care is to ensure effective medical treatment in the event of conflicts, wars, natural disasters and epidemics. The priority for the sustainable development of Ukraine is to improve the existing and introduction of innovative technologies and materials in the field of health and medicine. This is especially important in the COVID-19 pandemic and armed conflict in the Donbas region. The need to ensure the dental health of the community population is one of the key aspects of ensuring social protection of the population.

Today in the world in the field of modern dentistry, there is a constant development and improvement of technologies and materials. However, in Ukraine, despite the high scientific potential and the raw materials base, most of the major domestic firms (Kristar-Trade LLC, Interdent, Dentalith, Antas and others), which are engaged in the manufacture of ceramic dental prostheses, use foreign technologies and materials. Such materials are very expensive and cannot be accessible to a significant

part of the country's population. In Ukraine, well-known manufacturers of dental materials are mainly their profile for the development of plastic teeth (Stoma JSC) or metal implants that do not satisfy the growing needs of the population in high-quality dental materials.

#### Literature review.

Modern technologies for designing and manufacturing dental prostheses

For the design and manufacture of dental prostheses, computer cutting and polishing methods CAD / CAM (Computer Assisted Design / Computer Aided Manufacturing) [1] and 3D printing [2, 3] are widely used due to the high accuracy of such technologies compared to traditional manual manufacture. The practical application of additive 3D technologies in dentistry allows typing individual crowns, kapps and dentures of teeth [2, 4].

Among the modern methods of making dental prostheses, CAD / CAM technology was taken important place. Most presently known CAD / CAM systems based on automated production of dentures by cutting [1, 5]. This system is known for high performance and relative ease of operation, which allows you to significantly reduce the cost of training specialists and increase productivity. The system is distinguished by reliability and stability even with daily processing of complex materials from solid materials.

The following programs in CAD / CAM technologies are widely known [6].

Exocad Dental CAD. One of the most popular programs that accelerates the process of treatment and helps to produce implant models. It has open access and compatible with many types of equipment.

Dental System 3Shape. One of the best CAD / CAM programs in dentistry is designed in Denmark. In addition to the main option, it is possible to supplement the program by the plugin, which provides additional features of 3D modeling and prototyping.

Planmeca ProMax 3D. The system supports many functions that help in 2D and 3D visualization of objects, design and processing of scanned material. Compatible with various operating systems.

An important aspect of the quality of prosthetics is to ensure high functional and aesthetic requirements for dental prostheses with prosthetic minimum time. The most promising should be considered a CEREC (Chairside Economical Restorations of Esthetic Ceramics) technique, which allows the dentures without attracting laboratory resources directly in the patient's chair for one visit, is the so-called «chair-restoration» [1]. Then, with the help of a special computer simulation program (CAD-module), the restoration is constructed [7].

The next step is to send the obtained restoration to the cutting program (CAM module). The ceramic or plastic block is fixed by the operator in the holder of the cutting machine, and the restoration (dental crowns) is smashed under water cooling. After removal, the surface of the restoration is made and fit the ceramic substrate in the oral cavity, the shape is checked, grappling to adjacent teeth and color shade for compliance with the color of adjacent teeth.

The final stage of the CAD / CAM technology includes: individualization of the restoration with the help of paints and glazing with a firing in a low-temperature furnace (if necessary), polishing the product with special sets of polys, rubber bands and pastes in accordance with the selected material, fixation of the permanent restoration on the adhesive protocol by composite cement.

## Method of sintering ceramics (Fortess, Otec-HSP).

Ceramic mass is applied directly to a refractory stamp. The mass is dried and burnt in a vacuum furnace. On the first layer of ceramics are applied several layers of ceramic mass to reproduce features of the form of natural teeth [8].

The sintering method has a disadvantage – inaccurate addition of edges of different layers of ceramics, which is associated with a high shrinkage of ceramic mass during the firing process (30-40%). For this reason, the process of casting glass ceramics is used. In the dental market, it is represented by several

manufacturing technologies fully anatomic crowns from zirconium dioxide.

The Prettau technology involves the use of original materials from Zirkonzahn with high transparency. Modeling and cutting is performed on the CAD / CAM system Zirkonzahn. All constructions are made of raw, non-dynamic zirconium dioxide, painted without oxidative dyes, and Prettau's full-oxidic designs are painted along a specially designed map of the Aquarell Prettau dyes.

Another similar method of manufacturing full anatomical crowns from zirconium dioxide represents the German company Dental Direkt. ZX-CUT BACK technology consists of two components: zirconium dioxide with increased translucency (ability to skip light) DD Cube  $X^2$  and without third-generation oxide paints – DD Bio  $Zx^2$  Monolith Zero. The latter is a water-based paint, which is not inferior to acid dyes according to its operational properties.

Construction ceramic and glass materials for dentistry

The history of the development of materials that are obtained by cutting, began in 1985, when a clinical restoration was made with a clinical restoration from feldspathose ceramics on CAD / CAM technologies on the CEREC (Sirona) apparatus [7]. Feldspar «cold» ceramics did not yield their positions until the beginning of the new millennium, until in 2005 lithium disilicate was widely used for CAD / CAM technologies [8]. The blocks had a blue-lilac color due to the overwhelming presence of lithium metasilicate crystals. The presence of lithium metasilicate in the initial blocks ensured their lower hardness compared to blocks made of lithium disilicate, and, as a consequence, its better machinability and less wear of cutting elements. The crown was milled in this color, and then firing was carried out in a lowtemperature furnace, during which lithium metasilicate was converted into lithium disilicate. At the same time, the restoration acquired a color similar to the hard tissues of natural teeth and increased (in comparison with feldspar ceramics) strength [9].

All-ceramic restorations, with their undeniable advantages (biocompatibility, aesthetics, chameleon effect, etc.), had their disadvantages in certain clinical situations [10]. In some cases (for example, with insufficient polishing), increased abrasion of an intact antagonist tooth was observed as a result of microabrasion and a lack of elasticity of the ceramic restoration. In 2007 they returned to composites.

New 2013 was marked by the introduction of hybrid ceramics into clinical practice. VITA ENAMIC (VITA

Zahnfabrik) is the world's first dental hybrid ceramic with a double mesh structure. Hybrid ceramics are now a porous ceramic matrix, the pores of which are filled with a polymer material [11]. The inorganic part of the ceramics is about 86 % by weight, the organic part is about 14%. The dominant ceramic mesh structure in the material is reinforced with a polymer mesh, both mesh being interpenetrating. As a result, VITA ENAMIC, a hybrid material for clinical CAD / CAM restorations, combines the advantages of both ceramics and composition [12]. Hybrid ceramics after adhesive cementation, in addition to being load-resistant, are also characterized by exceptional elasticity. VITA ENAMIC in its properties is as close as possible to the natural tissues of teeth (hybrid ceramics has an elasticity of 30 GPa, a natural tooth - 13-30 GPa) and, due to the transitional light transmission, reproduces the natural play of colors.

One of the promising directions in the creation of modern dental prostheses, including hybrid ceramics, is the use of glass-composite materials as a mineral component, which are distinguished by extremely high fracture toughness. This is achieved due to the formation of an interpenetrating sitallized structure of glass-composite materials due to directional crystallization of nanosized crystalline phases. Along with this, the presence of an elastic glass phase in the structure of glass-composite materials will bring their elastic properties and hardness closer to the corresponding properties of natural teeth and ensure their opalescence.

**Purpose of work**. The aim of this work is evaluation of promising the technology for the production of glass-ceramic dentures.

To achieve it, the following tasks were set:

- analysis of the state of the art of social, medical and material science foundations of dental prosthetics in Ukraine;
- comparison of modern technologies for the design and manufacture of dental prostheses;
- determination of the most promising structural ceramic and glass materials for dentistry;
- the choice of technology for the production of glass-ceramic materials and the development of dental prostheses.

## The results and discussion.

For the synthesis of the glass matrix, the compositions of lithium silicate glasses with an oxide content were selected., % by weight:  $SiO_2$  50,0–71,8;  $Li_2O$  11,0–20,0;  $Al_2O_3$  0,1–5,0;  $K_2O$  0,1–2,0;  $Na_2O$  0,1–10,5; SrO 0,1–4,0; CaO 0,1–3,5; MgO 0,1–4,0; ZnO 0,1–4,0; ZnO 0,1–5,0; ZnO 0,1–2,0; ZnO 0,1–5,0; ZnO 0,1–2,0; ZnO

3,5; CaF<sub>2</sub> 0,1–2,5; P<sub>2</sub>O<sub>5</sub> 0,1–4,0; B<sub>2</sub>O<sub>3</sub> 0,1–6,0; La<sub>2</sub>O<sub>3</sub> 0,1–4,0; Sb<sub>2</sub>O<sub>3</sub> 0,1–1,5 and MnO<sub>2</sub> 0,1–4,0.

Natural raw materials, technical products and fine chemicals were used in the preparation of charge for glass preparation. Glasses were melted in corundum crucibles in a laboratory electric furnace for 6 hours: lithium silicate glasses were synthesized at temperatures of 1350–1400 °C and casting into heated graphite molds, after which they were annealed in a muffle furnace. Glass cylindrical billets based on lithium silicate glass were preliminarily kept at the stage of nucleation in the temperature range 600–650 °C for 30–60 minutes to provide the required number of crystallization centers and crystal nuclei.

The formation of the prostheses was carried out by the method of hot (high temperature) pressing, which is partially based on the investment casting technique. A potential benefit of hot pressing is the improved marginal bonding of restorations when compared to sintered restorations. As with casting metal frameworks, the restoration is waxed up and then filled with refractory molding material. The wax is burned out, and in the resulting form there is room for filling with glass ceramics.

The process of forming products marked DL st.glass using high-temperature pressing technology consists of heating the billet from a temperature of 700 °C to the softening temperature of glass materials (850–900 °C), then filling a plaster mold with molten glass and followed by a short exposure (18–20 min) and slow cooling. After high-temperature pressing, the glass-ceramic prosthesis is characterized by volumetric finely dispersed crystallization with the presence of a strong crystalline phase – lithium disilicate in an amount of 40-60 vol. %.

The glass-ceramic prosthesis, which was obtained under conditions of low-temperature two-stage heat treatment, is characterized by high flexural strength ( $\sigma \geq 100$  MPa according to ISO 6872: 2015). The high fracture toughness of the developed domestic glass-ceramic prostheses, close to the approximate values of the elastic modulus for natural teeth, will ensure a significant service life of the product under conditions of contact with the teeth by antagonists of the lateral row during the chewing cycle.

Comparative characteristics of the developed DL st.glass dental prosthesis with the products of the world leaders in dental prosthetics Ivoclar Vivadent (Liechtenstein) and VITA Zahnfabrik (D-Bad Säckingen, Germany) [9] (table 1) made it possible to establish that the developed dental prostheses are distinguished by high operational properties at the level of imported analogues.

Glass-ceramic dental prosthesis	Phase composition	Bending strength, MPa	Crack resistance index	Manufacturing method	Field of application
VITA ENAMIC VITA Zahnfabrik	Feldspar glass and polymer material Lava Ultimate	150–160	1.50	Baking	Tabs, overlays, veneers, crowns for the front and side sections
IPS Empress Ivoclar Vivaden	Glass phase, leucite	120–200	_	Hot pressing	Veneers, single crowns for the frontal department
E.max Press Ivoclar Vivaden	Glass phase, lithium disilicate, lithium orthophosphate	400	2.75		Crowns for front and side sections, bridge prostheses up to 3 units
DL st.glass (O.M. Beketov National University of Urban Economy in Kharkiv)	Glass phase, lithium disilicate	400	8.00		

Table 1 - Phase composition, properties and areas of application of glass-ceramic dental prostheses

#### Conclusions.

Peculiarities of design and manufacture of dental prostheses by technologies of computer milling and grinding of CAD / CAM and 3D-printing are analyzed. The effectiveness of the use of glass-ceramic materials based on feldspar glass, leucite and lithium disilicate for the production of dental restorations has been established. The prospects of using the method of high-temperature pressing in obtaining glass-ceramic prostheses have been determined. Compositions of glass-ceramic materials based on lithium disilicate and technological parameters for obtaining prostheses by hot pressing have been developed. The introduction of the developed materials will increase the social protection of the population in the direction of dental services by reducing costs and reduce import dependence in the field of dental prosthetics.

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