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DEVELOPMENT OF GLASS CERAMIC COATINGS CONTAINING HYDROXYAPATITE

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Glass ceramic composites — to be used for coatings on titanium implants — based on leucite glass with elevated flux content and added hydroxyapatite or a mixture of hydroxyapatite and fluorite are examined. It is established that pastes containing no more than 30% hydroxyapatite in leucite glass are the best materials for denture coatings. Pastes with a higher content of hydroxyapatite $Ca_{10}(PO_4)_6(OH)_2$ (> 30%) are recommended for coatings on intramaxillary titanium implants.

Selecting materials for implant manufacture plays an important role in medical practice. The optimal variant with respect to mechanical and esthetic characteristics is a cermet.

A cermet is a combination of elements of a metal crown and a ceramic facing. Cobalt, chromium, and nickel alloys are widely used as bases for fabricating the framework. However, because of difficulties arising in the use of such materials, stomatological practice worldwide has given preference in recent years to titanium alloys, together with alloys of precious metals (gold, platinum, and palladium), over steels [1, 2].

Titanium is a light, readily producible, and corrosion-resistant metal. A thin, strong, absolutely biologically inert oxide layer, which limits the emission of free metal ions into the surrounding tissue, thereby preventing allergic and inflammatory responses of the body to the implant, can form on its surface. However, the following property of titanium must be taken into account when fabricating prostheses based on this metal: at 882.5°C α-Ti (hexagonal) transforms into β-Ti (cubic), increasing in volume by 17%. For this reason glass ceramic coatings with deposition temperature below 880°C should be used [3]. The leucite casting ceramic used traditionally has a standard deposition temperature 920 – 980°C and therefore it is unsuitable for facing a titanium framework. This is why the development of matched glass ceramic coatings on titanium alloys is an urgent problem.

It should also be noted that the microhardness of traditional oxide-silicate ceramic is more than 25% higher than that of natural teeth, which could result in premature wear of the patient's own teeth. For this reason, appropriate additives which decrease the microhardness of the finished coatings must be added to the main compositions of glass ceramics. We have proposed that natural hydroxyapatite $Ca_{10}(PO_4)_6(OH)_2$ combined with fluorite CaF_2 be used as such an additive.

It is known that the mineral component of human and mammalian bone tissue consists primarily of hydroxyapatite and that artificial materials based on it do not, ordinarily, produce negative reactions in the body [4, 5]. For this reason, articles and coatings made of hydroxyapatite have been used for quite a long time for implantation inside the human body [6, 7]. However, hydroxyapatite has not been adequately studied as a material for fabricating glass ceramic coatings for denture prostheses. Fluorite has been introduced into the composition for several reasons: it too is a component of natural bone tissue, exhibits fluorescence (this is an inherent property of natural teeth), and substantially lowers the melting temperature.

To obtain a glass ceramic composition a ready easy-melting leucite glass with a high flux content (RF Patent No. 2233650) [8] was added to hydroxyapatite or a hydroxyapatite – fluorite mixture. The compositions for fabricating stomatological porcelain are presented in Table 1. The hydroxyapatite mixture used makes it possible to melt frit in air at 1230°C.

It was found that pastes containing no more than 30%[2] hydroxyapatite in leucite glass are most suitable as glass ceramic coatings for dental prostheses, since the porosity of the coatings obtained is too high when the content hydroxyapatite is increased above this amount; in addition, additions of hydroxyapatite greatly increase the melting temperature. Pastes with more than 30% $Ca_{10}(PO_4)_6(OH)_2$ can be recommended for coatings on intramaxillary titanium implants.

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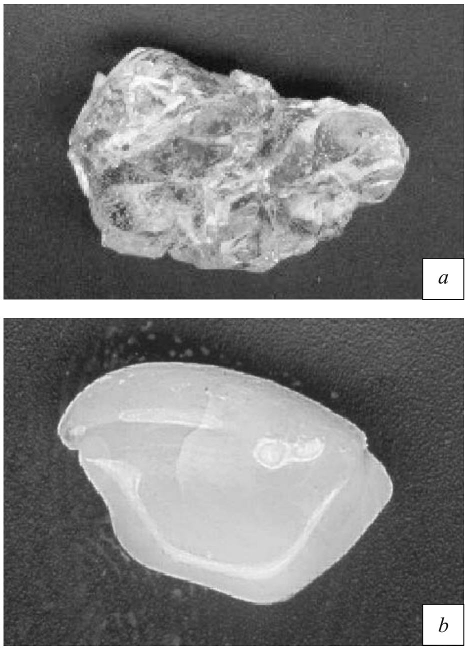

Fig. 2. Sample of transparent glass based on potassium feldspar (*a*) and the same glass with a mixture of hydroxyapatite and fluorite added (*b*).

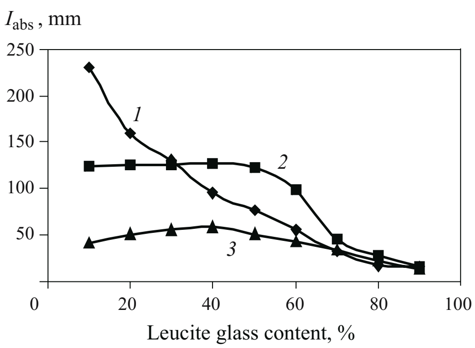

Fig. 1. Variation of the intensity of x-ray reflections from hydroxyapatite, $d = 0.281$ nm (*1*), fluoroapatite, $d = 0.279$ nm (*2*), and leucite, $d = 0.325$ nm (*3*) as a function of the content of leucite glass in the batch.

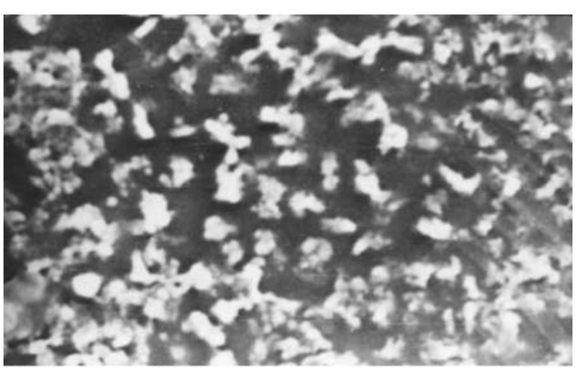

Fig. 3. Photomicrograph of a sample of frit based on leucite glass with a mixture of hydroxyapatite and fluorite added (× 10000).

TABLE 1.

Composition	Content, wt.%		Post-melting external appearance of frit samples
	HA* + CaF_2	leucite glass	
1	90	10	White porous
2	80	20	Same
3	70	30	″
4	60	40	″
5	50	50	″
6	40	60	Pale-blue opaque
7	30	70	Same
8	10	90	Pale-blue, semitransparent, opalescent
9	20	80	Pale-blue opaque, weak opalescence

* Hydroxyapatite.

X-ray phase analysis of the phase composition of the ready frit showed that as the amount of leucite glass in the batch mixture increases from 10 to 40% the intensity of the x-ray reflections of leucite increases only negligibly (Fig. 1). However, as the glass content in the batch increases further, the intensity of the leucite reflections decreases just as for fluoroapatite and hydroxyapatite, indicating that they gradually dissolve in the melt of the glass phase. For more than 70% glass content in the batch, the systems after melting are essentially x-ray amorphous with small peaks due to the principal crystalline phases: leucite and hydroxyapatite.

Pastes containing up to 20% hydroxyapatite exhibit a opal effect (Fig. 2). A large quantity of uniformly distributed aggregated nuclei of a crystalline phase — presumably hydroxyapatite — is observed in a photomicrograph (scanning electron microscope) of a frit sample containing hydroxyapatite in feldspar glass (Fig. 3). Comparing the XPA and electron-microscopy data it can be concluded that the accumulations of the hydroxyapatite phase separating from the melt of the glass phase are essentially amorphous. The small sizes (up to 1 μm) of the crystals formed and their uniform distribution in the glass phase impart to the finished material an opal effect, which is characteristic of natural teeth.

An investigation of the mechanical properties of the compositions obtained (Table 2) established that the linear shrinkage during calcinations of the samples containing hydroxyapatite does not exceed 7%. It can be concluded from the low values of the water absorption that the material is completely sintered and has a minimal porosity. Using an apatite component to modify the compositions for dentures makes the microhardness of the coatings, false teeth, and crowns close to the hardness of natural tooth enamel (3240 – 3430 MPa). Apatite crystals, which create a good masking effect, make it unnecessary to add tin, zirconium, and other oxides, which are traditionally used, to the batch. The coat-

[2] Mass content, here and below.

TABLE 2.

Composition	CLTE, 10^{-6} K^{-1}	Calcination shrinkage, %	Water absorption, %	Microhardness, MPa	Compression strength, MPa
Leucite glass	11.5 – 12.8	7 – 9	0.30 – 0.50	4322 – 6860	380 – 620
Pastes developed	9.2 – 10.0	3 – 6	0.05 – 0.50	2913 – 3610	250 – 400
Natural tooth enamel	–	–	–	3240 – 3430	400
Dentine in natural teeth	–	–	–	680	297

ing deposits very uniformly and has a finely dispersed crystalline, low-porosity, structure with a uniform distribution of the crystalline and amorphous phases. A positive property of this composition is that a wide range of values of the CLTE of the materials can be obtained by varying the composition of the batch.

In summary, two problems are solved when hydroxyapatite is combined with leucite glass: to decrease the sintering temperature of the glass ceramic enough to make the material suitable for fabricating enamel coatings for titanium alloys (to 850 – 870°C) and to decrease the microhardness of the finished coatings to values which are as close as possible to the microhardness of natural tooth enamel.

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