Synthesis and properties of feldspar ceramics designated for metal–ceramics composites

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A special-purpose porcelain well suited for putting together with the Co–Cr–Mo, Ni–Cr–Mo alloys used in stomatological practice was synthesized from synthetic feldspar and spathoid with Na_2O, K_2O, CaO, MgO, BaO, CeO_2, TiO_2 and other oxides. The thermal expansion coefficient α of porcelain is in the area of $\sim 11.5 \cdot 10^{-6} - 14.5 \cdot 10^{-6}$ K^{-1} and is close to the α of the mentioned alloys. It was defined from X-ray diffraction (XRD) analysis data that the bulk crystalline phase in porcelain is potassium spathoid leucite, and the α of porcelain depends principally on its amount. The structure of a porcelain sample determined using the SEM analysis method was found to be heterogeneous and to consist of leucite crystals distributed rather uniformly in a glass matrix.

The physical-mechanical properties of porcelain were estimated: the biaxial strength $R_{l(max)}$ reaches 142 MPa, the Brinell hardness value comes to 4.67 GPa, the stroke work for individual porcelain samples varies between $13.3 \cdot 10^6$ and $16.46 \cdot 10^6$ J/m^3.

Key words: porcelain, feldspar, spathoid, leucite, alloys

INTRODUCTION

At the present time special-purpose ceramic materials are increasingly used, especially their composites with metal alloys resistant to press, bending, stretching or stroke. Such composite materials are not only resistant to mechanical impact but also are inert chemically and corrosion-proof. They are attractive aesthetically, and it is possible to impart them with a very broad spectrum of colours and tints, as well as opalescence and fluorescence characteristics.

Composites from metals and special ceramics are up-to-date and have wide applications, *e.g.*, in stomatology. Ceramic teeth look highly naturally, attractively: they have a bluishwhite or nacreous tint in the daylight and exhibit yellowish or reddish fluorescence in the artificial light.

In 1962, Weinstein with co-workers [1] patented porcelain substances and composites for dental crowns and bridges. Since then intensive production development and employment of metal-ceramic composites started. No information except their approximate composition exspressed in mass percent of Si, Al, K and other oxides is given in literature. The actual mineral composition or technological aspects of synthesis are patented. Our recent publications [2, 3] deal with porcelain of special composition.

The noble metal alloys based on Au, Au–Pt, Au–Pd, Au–Pd–Ag, Pd–Ag a. o. metals are used often for preparation of tooth crowns and bridges. Porcelain sticks together with these alloys quite good. In addition, the human organism tolerates them rather well (biological incompatibility is not observed), they do not corrode in saliva and ordinary food medium, are sufficiently mechanically strong, withstand large load when chewing food. However, the above-mentioned alloys are expensive enough, therefore there are Co–Cr, Co–Cr–Mo, Ni–Cr, Ni–Cr–Mo a.o. alloys are considerably more popular. The general requirements for these alloys are a high modulus of elasticity and the capability for strong adherence with ceramics. They should be easily fusible and their fusing temperature being higher than that of ceramics, they should be readily ground and polished, incorrodible. Their characteristic feature is a high value of the thermal expansion coefficient α ($13 \cdot 10^{-6} - 15 \cdot 10^{-6}$ K^{-1}). Many alloys of the noble metals (in the Au–Pt–Pd–Ag system) have also similar α values.

When adapting ceramics to the mentioned alloys, it was necessary to find their crystalline phases with the α close to the α of metal alloys. Since dental porcelain is characterized by rather high thermal expansion coefficients, ceramic samples of special composition with the α ranging from $12.0 \cdot 10^{-6}$ to $14.0 \cdot 10^{-6}$ K^{-1} were looked for.

Analysis of references [4–7] shows that feldspars and spathoids, especially tetragonal leucite with $\alpha = (20–25) \cdot 10^{-6}$ K^{-1}, are best suited for developing the desired porcelain. The judgements about its formation and crystallization of possible compositions were made from the diagram of a three-component system K$_2$O-Al$_2$O$_3$-SiO$_2$ (Fig. 1).
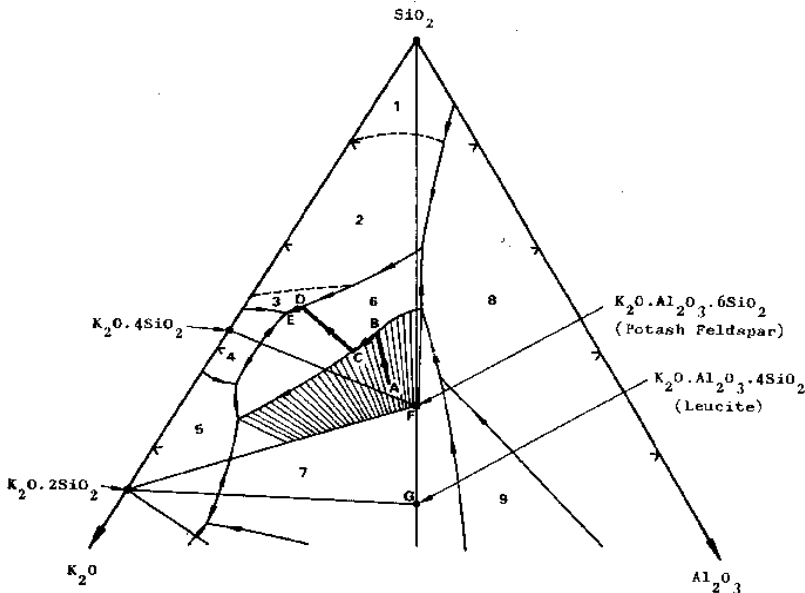

Fig. 1. Crystallization curve of composition A (15% Al$_2$O$_3$, 18% K$_2$O, 67% SiO$_2$ (by [7]). Stability fields: 1– crystobalite, 2 – tridymite, 3 – quartz, 4 – K$_2$O · 4SiO$_2$, 5–K$_2$O · 2SiO$_2$, 6 – potassium feldspar, 7 – leucite, 6 – mullite, 7 – corundum

According to heterogeneous equilibrium laws, all compositions which correspond to the shaded region of the triangular diagram (Fig. 1) will separate leucite as the first crystalline phase and potassium feldspar as the second one [8, 9]. The compositions of the feldspar porcelain are located only in this area.

Since feldspars and spathoids are characterized by a relatively high fusing temperature (orthoclase 1520 °C, leucite 1660 °C), we were looking for additives lowering the fusing temperature. For this purpose we used suitable glassy substances which were selected in such a way that they would impart a comparatively low burning temperature and at the same time lower the thermal expansion coefficient of tetragonal leucite.

Dental porcelain body synthesized on the basis of orthoclase and leucite is classified into the following groups according to functional application:

1. The porcelain body of a basic layer (dentine). At repeated fusing, a scantily clear porcelain results, which forms the greater part of metal-ceramic composite. More precisely, this porcelaine is a glass-ceramics made up of leucite crystals located in glass matrix. It must be very strong, wear-resisting and suitable for putting together with metal alloys and the porcelain of the intermediate layer.

2. The porcelain body of an intermediate layer. It is required to put together the porcelain of the basic layer and the metal alloys and to conceal the colour of metal. At repeated burning the body of the intermediate layer, a dull porcelain forms. Its structure is similar to that of dentine, just here cassiterite crystals prevail, with less leucite crystals and glass phase. The porcelain of the intermediate layer in metal–ceramic composite is required to cohere reliably with metal alloy and to cover it.

3. The body of clear solid layer (biting part). It gives wear-resistance to glass ceramics. This is the most clear porcelain which has a considerable amount of glass with plenty of dissolved feldspar and spathoid as well as Al$_2$O$_3$. The surface of metal–ceramic composite and chiefly its sharp edge (tooth edging) is covered with this porcelain layer. Dentine is scrubbed in this place and is covered with a layer of clear ceramics.

4. The glaze. In some cases a porcelain teeth can be covered additionally with a glassy substance made on the basis of quartz with the addition of sodium tetraborate and sodium carbonate. Since feldspar porcelain glazes itself spontaneously, it is not necessary to cover it additionally with a glaze.

In this work, we studied only the synthesis conditions of the basic layer body (dentine) and the properties of synthesis product.

EXPERIMENTAL

Synthetical feldspars (in most cases orthoclase) and spathoids (leucite) were used as basic materials for synthesis of the porcelain body (ceramic body of the intermediate layer, dentine). Potassium spathoid leucite was syntesized from orthoclase by fusion or from zeolite (substituting K$^+$ for Na$^+$ by the ionic exchange method), using a hydrothermic technique. In addition to feldspars and spathoids, carbonates K$_2$CO$_3$, Na$_2$CO$_3$, CaCO$_3$, MgCO$_3$, oxides CaO, MgO, Al$_2$O$_3$, SiO$_2$, TiO$_2$, ZnO, BaO, B$_2$O$_3$ and sometimes Na$_2$B$_4$O$_7$ were added into the mixtures prepared for synthesis. The reagents used were of analytical and chemically pure grade (Reachim, Russia).

Synthesis of porcelain was carried out in two ways: by a one-step and a two-step process. A high-

temperature furnace (up to 1300 °C) was used for burning the raw materials. The temperature was measured with a Pt-PtRh thermocouple. The burning regime in the furnace was operated by a programmed OMRON E5CK-T temperature controller. The product obtained was ground into a powder passed through a sieve N 0056. The porcelain powder was used for dilatometric, X-ray diffraction (XRD), infrared (IR) spectroscopy investigations and for preparation of metal–ceramic composites. The phase composition of porcelain was determined by means of a DRON-2 diffractometer, using a Co anode and a Fe filter. The α value of porcelain samples was determined with DKB 5A vertical quartz dilatometer which was driven by an OMRON E5CK-T temperature controller connected to a computer. IR spectra were recorded with a Nicolet Impact 420 spectroscope at the Erlangen-Nürnberg University (Germany). The microstructure was studied using a Cambridge Stereoscan MK3scanning electron microscope (SEM). The following physical-mechanical properties of porcelain samples and metal–ceramic composites were also determined: the Brinell hardnes (GPa); the bending strength of porcelain by double-axle method calculating the biaxial strength (or the maximum limit of bending strength) $R_{1(max)}$ (MPa); adhesion of porcelain layers with metal alloy by the procedure used for paints and lacquers, with the aid of a special sledge-hammer; the stroke work for individual samples was counted up (J/m^3).

RESULTS AND DISCUSSION

1. Selection and investigation of porcelain composition of a basic layer.

When synthesizing the porcelain of a basic layer, it was very important to match the thermal expansion coefficients of the substances of various compositions with the α of metal alloys and of the porcelain of the intermediate layer. Since as the main raw material mixture of orthoclase and low-temperature leucite $[\alpha = (20\text{–}25) \cdot 10^{-6} \text{ K}^{-1}]$ was used,

additives producing glassy substances with a considerably lower α $[(6\text{–}8) \cdot 10^{-6} \text{ K}^{-1}]$ were added. It was expected that the combined composition will have a proper thermal expansion coefficient and will match the metal alloy. In addition, the raw-material compositions were selected in such a way that the resulting glasses would impart to the porcelain not only the low fussing temperature, but also chemical stability, wear-resistance and hardness. The judgements about the composition of the glass phase formed during fusing and about the course of crystallization on cooling were made on the basis of phase equilibrium diagrams of multicomponent systems [9]. CaO, MgO and a small amount of TiO_2, ZnO, BaO were added to the synthesis mixture of raw materials. These oxides are very important for glass quality; furthermore, the influence of some of these oxides on the solubility of the crystalline phase and on porcelain adhesion with the intermediate layer and the metal alloy is known [8].

The composition of the crystalline phases formed in the porcelain was determined using the XRD method. The chemical composition of some of the synthesized quality porcelain of the basic layer is presented in Table 1 and its phase constitution is shown in Fig. 2.

The XRD patterns in Fig. 2 show that the main crystalline phase in all samples is leucite (XRD peaks: 0.538; 0.343; 0.327; 0.284; 0.237 nm, etc.) [10]. However, the intensities of these peaks are different.

A comparison of the chemical composition of the porcelain samples D_1 and D_2 demonstrates that they are almost identical, but the sample D_1 contains ZnO which stimulates dissolution of leucite, therefore the intensity of XRD peaks for sample D_1 (Fig. 2, curve 1) is less in comparison with sample D_2 (Fig. 2, curve 2). However, the α of both samples are very close. The initial quantity of spar and spathoid in these samples equals to 57%. The burning temperature is 1080 °C.

The sample D_3 was produced by a two-step process from 46% of frit S_2 (consisting of 68.8% SiO_2, 6.68% K_2O, 16.5% Na_2O, 4.9% CaO, 3.44% MgO)

Table 1. Chemical composition and thermal expansion coefficient α (at a temperature range 20–500 °C) of ceramics of the basic layer

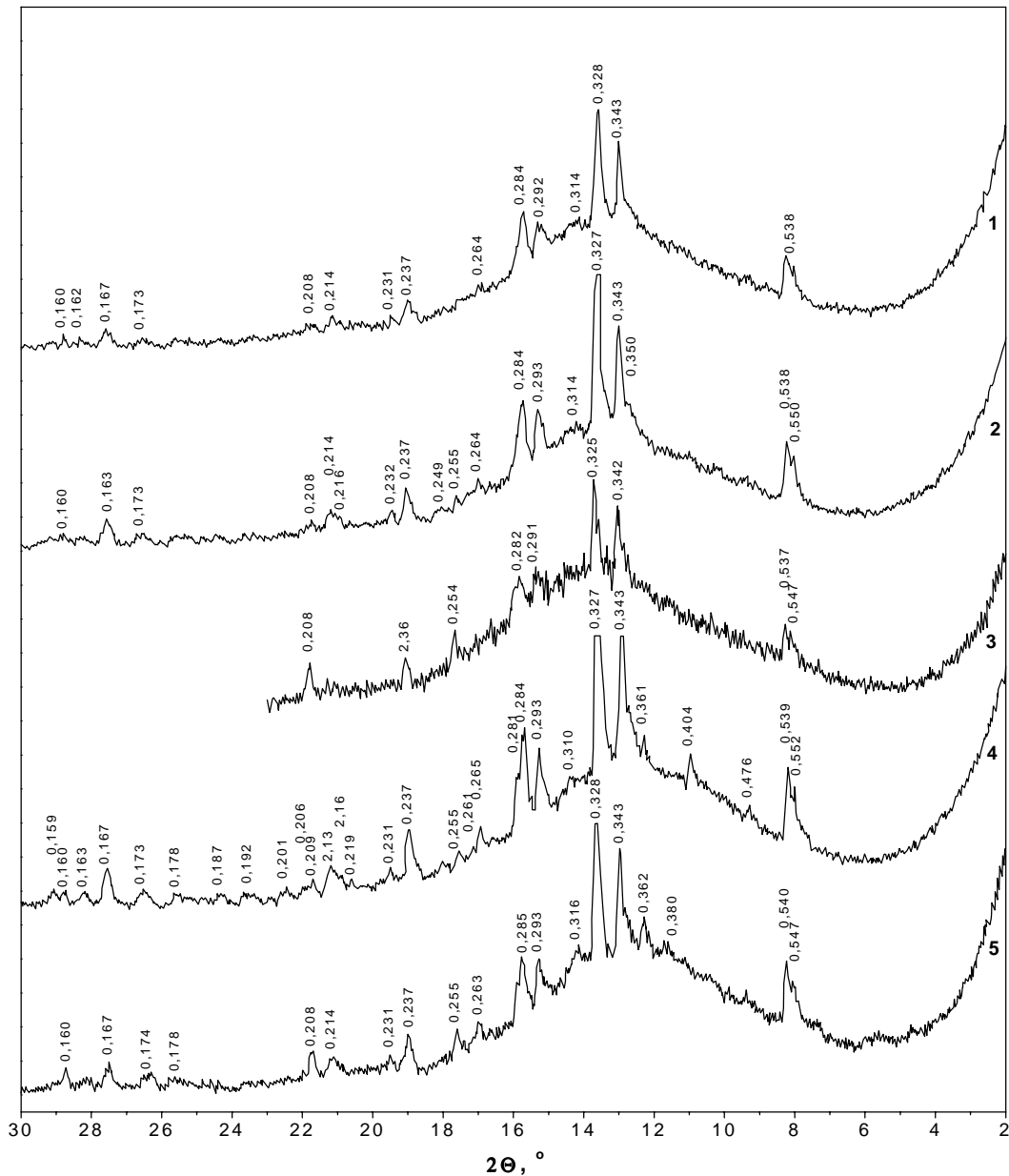| Dentine sample	Chemical composition, wt.%										α (K^{-1})
	K_2O	Al_2O_3	SiO_2	Na_2O	MgO	CaO	B_2O_3	TiO_2	ZnO	BaO	
D_1	14.9	12.4	59.3	4.4	0.9	3.2	2.0	–	1.6	1.1	$14.6 \cdot 10^{-6}$
D_2	14.9	12.4	59.3	4.4	0.9	3.2	2.0	1.6	–	1.1	$14.7 \cdot 10^{-6}$
D_3	14.8	12.8	61.2	7.3	1.6	2.2	–	–	–	–	$11.5 \cdot 10^{-6}$
D_4	21.8	18.9	55.8	2.4	–	–	1.0	–	–	–	$18.3 \cdot 10^{-6}$
D_5	18.0	17.5	58.4	4.0	0.9	1.2	–	–	–	–	$12.5 \cdot 10^{-6}$

Fig. 2. XRD patterns of the ceramic samples of the basic layer: $D_1(1)$, $D_2(2)$, $D_3(3)$, $D_4(4)$ and $D_5(5)$

and 54% of spar with spathoid. The temperature of the second fusing was 1120 °C. In this case, the raw-material mixture contained a great quantity of glassy substances, and only an insignifficant amount of leucite remained after the second fusing (Fig. 2, curve 3). The α of such porcelain is the lowest one – 11.5 · 10^{-6} K^{-1}.

The sample D_4 was obtained by the one-step process of sintering the raw-material mixture for one hour at 1200 °C. The initial quantity of spar and spathoid was great (78.2%) and of glassy substances small. In this case the amount of leucite remained large, what is confirmed by abundant and intense XRD peaks (d = 0.552; 0.539; 0.404; 0.343; 0.327; 0.293; 0.284; 0.237 nm) for the sample D_4 (Fig. 2, curve 4). Large amount of leucite gave strength to

the porcelain (Table 2), but its α was rather high – 18.3 · 10^{-6} K^{-1}. Such porcelain is not fit for putting together with the selected metal alloys. However, it was used to compose ceramic mixtures characterized by different α values when producing a porcelain body possesing the necessary α.

The sample D_5 was obtained by a two-step process from 25% of frit S_2 and 75% of feldspar and spathoid by fusing at 1200 °C when exposing for a more extended time at the maximum temperature. Then an appropriate part of leucite dissolves in the raw-material mixture owning a sufficient amount of glassy substances. The α of such porcelain (12.5 · · 10^{-6} K^{-1}) is very suitable for arrangement with the intermediate layer ceramics and with metal alloy, and leucite contained in porcelain strengthens it.

In all these D_1–D_5 samples, a sufficient quantity of feldspar glass is formed. It dissolves a certain part of leucite (except sample D_4, for which the raw-material mixture contained the largest quantity of spar and spathoid, therefore the amount of glass produced was too little). The ratio of the quantities of crystalline and glass phase influences the α value. Thus, the ratio of the quantities of low-temperature leucite crystals and glass phase defines essentially the average value of the thermal expansion coefficient of the porcelain containing only one crystalline phase. The crystalline and glass phase ratio is dependent on burning temperature and sample exposure to the maximum temperature.

At repeated fusing of the D_1–D_5 samples followed by slow cooling, the main crystalline phase of porcelain was tetragonal leucite. Its amount was insignificantly less than in the unburnt porcelain samples. Cubical leucite was not found by the XRD method in cooled samples, and the α of porcelain did not vary. However, the transformation of tetragonal leucite to cubic one may be very important. Since this transformation is reversible, it apparently always proceeds in the dental porcelain containing leucite while burning repeatedly. The transformation ends below 600 °C (although some authors disagree on this matter), which is lower than the glass transformation temperature in porcelain. The volume change or a great difference between α values of leucite and glass generates stresses which are not reduced by glass viscosity. Therefore cracks can appear. Stresses may be also slowly diminished during the relaxation process (if it is significant). Values of transformations and α changes as well as stresses depend on the thickness of the dentine layer [11–13].

The microstructure of the fused and slowly cooled porcelains was established by the SEM method. Results are presented in Fig. 3 and 4.

The microstructure of all porcelain samples was heterogeneous, it consisted of the leucite crystalline phase arranged in a continuous glassy matrix.

Most of tetragonalic leucite crystalls were spherical or more branched out (free-form). Rather numerous leucite crystalls were lens-form. The cooled samples had microcracks, mainly in glass surrounding leucite crystals.

In the case of D_3 sample (Fig. 3), leucite crystalls were distributed quite irregularly in the glass matrix, crystalls had no cracks, but the microfissure was observed in glass phase. The strength of this porcelain was 75 MPa (Table 2).

In the case of sample D_5 (Fig. 4), porcelain was of good quality, leucite crystals were distributed most uniformly and cracks were not observed. Its strength was the highest – 142 MPa.
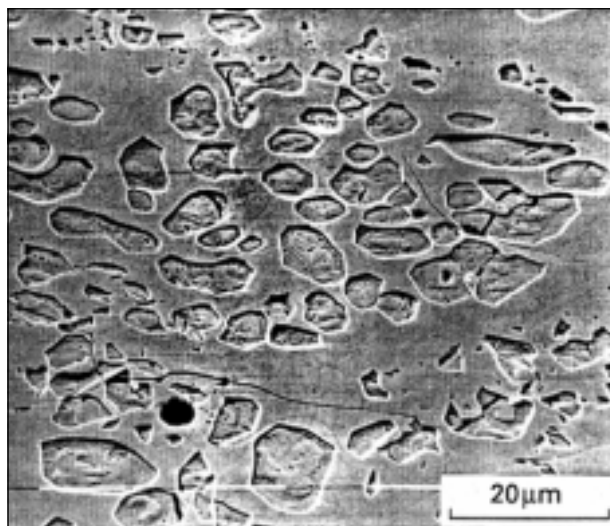

Fig. 3. Microstructure of porcelain sample D_2

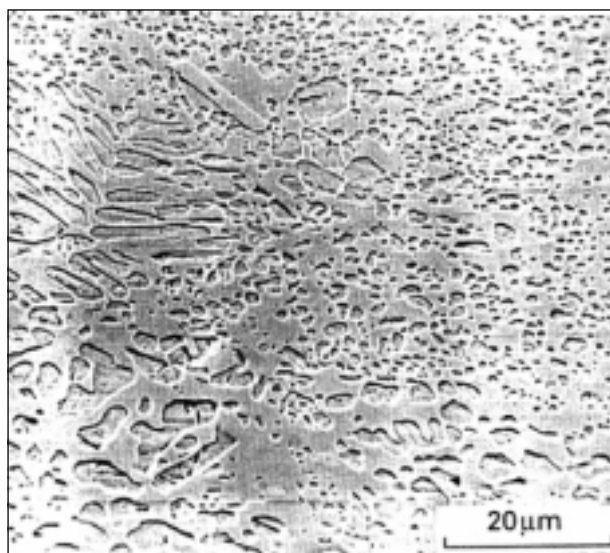| Table 2. **The strength of the basic layer porcelain**			
Sample of a basic layer porcelain	$R_{1(max)}$ MPa	σ (±)	V (%)
D_1	60	8	10.2
D_2	75	7	9.3
D_3	54	6	9.1
D_4	123	17	12.7
D_5	142	17	9.0
$R_{1(max)}$ – biaxial strengt, σ – standard deviation, V – coefficient of variation			

Fig. 4. Microstructure of porcelain sample D_5

2. Estimation of bond types of glass in porcelain

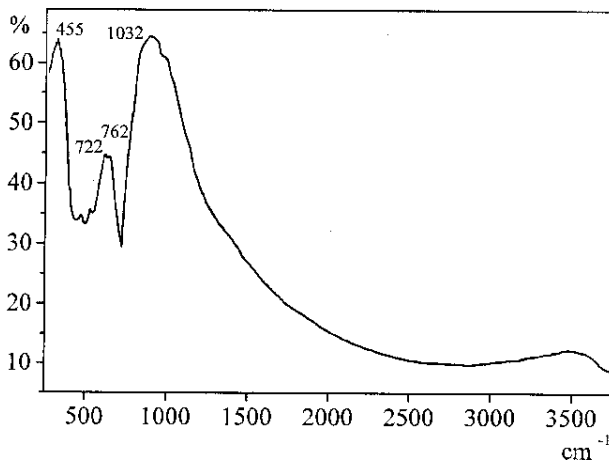The IR absorption spectrogram of the basic layer sample D_1 is shown in Fig. 5.

Fig. 5. IR absorption spectrum of the basic layer sample D_1

The absorption bands corresponding to the Si–0 tetrahedral bond ($v = 1032$ cm^{-1}) and to the Si–0 bond deformation vibrations ($v = 722$ cm^{-1} and $v = 762$ cm^{-1}) are seen. The absorption peak at $v = 455$ cm^{-1} is attributed to the bond of heavier metals with oxygen (Ba–0) [14].

3. Estimation of physico-mechanical properties of porcelain.

The data on the bending strength determined for burnt porcelain samples D_1–D_5 by the double-axle method are presented in Table 2.

The average value of stroke work determined for burnt porcelain samples D_2, D_4 and D_5 was $13.3 \cdot 10^6$, $15.9 \cdot 10^6$ and $16.46 \cdot 10^6$ J/m^3, respectively. Strength variations of these porcelain samples were essentially less than, *e.g.*, for the samples produced from lode quartz porcelain (the average value $6.8 \cdot 10^6$ J/m^3 [15]).

In addition, the strength of extra 7 porcelain samples burnt in a vacuum oven was determined. They contained from 55 to 75% synthetical feldspar and spathoid and their stroke work varied from $9.8 \cdot 10^6$ to $13.75 \cdot 10^6$ J/m^3. The stroke work value was higher in the samples that had been synthesized from mixtures containing more synthetical feldspar and spathoid or that had been better sintered.

The Brinell hardness of the porcelain produced was found to be 4.67 GPa *versus* the hardness of natural teeth 3.5–4.5 GPa.

CONCLUSIONS

The half product was synthesized by thermal treatment of synthetical feldspar and spathoid with Na$_2$O, K$_2$O, CaO, MgO, BaO, TiO$_2$, CeO$_2$ or other oxides; from it the special-purpose porcelain was produced by further burning. The α of the porcelain obtained was equal to $11.5 \cdot 10^{-6}$–$14.5 \cdot 10^{-6}$ K^{-1} and was close to the thermal expansion coefficient of non-toxic, very strong Co–Cr–Mo, Ni–Cr–Mo alloys.

It was determined by XRD analysis that potassium feldspar leucite constituted the crystalline phase of the half-product of the basic layer and of porcelain burnt from the half-product. The crystalline to glass phases ratio modified the α of porcelain: the α inceased with increasing leucite content in porcelain. The identified XRD peaks belonged to the tetragonalic leucite modification. It was established by the SEM method that leucite crystals of the basic porcelain layer were distributed more or less uniformly in the glass matrix. The IR spectra indicated undeformed and deformed Si–O bonds.

The maximum limit of the bending strength of porcelain was sufficiently high and varied from 54 up to 142 GPa. Samples of the porcelain showed a high density (tested in a vacuum oven) and stroke strength and would be suitable, together with the intermediate layer ceramics and metal alloy, for developing a stable, lasting composite material.

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METALOKERAMINIAMS KOMPOZITAMS SKIRTOS LAUKO ÐPATINËS KERAMIKOS SINTEZË IR SAVYBËS

S a n t r a u k a

Iš sintetinio lauko špato ir špatoido bei Na_2O, K_2O, CaO, MgO, BaO, CeO_2, TiO_2 ir kt. oksidø susintetintas specialiosios paskirties porcelianas, tinkamas komponavimui su stomatologijos praktikoje naudojamais Co–Cr–Mo, Ni–Cr–Mo lydiniais. Gauto porceliano α lygus ~11,5 · 10^{-6}–14,5 · 10^{-6} K^{-1} ir artimas minëtø lydiniø α. RSD analizës metodu nustatyta, kad pagrindinë kristalinë fazë porceliane yra kalio ðpatoidas leucitas ir nuo jo kiekio ið esmës priklauso porceliano α. SEM analizës metodu nustatyta porceliano bandiniø struktûra: ji heterogeniðka ir susideda ið leucito kristalø, pakankamai tolygiai pasiskirsèiusiø stiklo matricoje.

Nustatytos porceliano fizikinës ir mechaninës savybës: stiprio lenkiant didþiausia riba $R_{l(max)}$ yra 142 MPa, kietumas pagal Brinelá sudaro 4,67 GPa, dûþio darbas atskiriems porceliano bandiniams kinta nuo 13,3 · 10^6 iki 16,46 · 10^6 J/m^3.