In comparison with the platinoids, the particular alloying elements, such as silver, copper, and zinc, have a lower effect on the yellowness of two-component gold alloys (Fig.4). In more complex multicomponent alloys, with joint alloying of gold with platinum, palladium, and other elements, rhodium and tin appreciably improve the yellowness of the alloy, while silver worsens it.

The obtained data make it possible to analyze objectively the experimental data and reasonably limiting of the platinum and palladium content in the gold alloys to a level at which the alloy color is perceived as yellow.

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New gold alloys for dentistry

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The purpose of this investigation was to create a new yellow gold alloy for the casting of metal-ceramic dentures' frames. The yellow color corresponds to the consumer and aesthetic needs of some patients, because of the sign of noble and innocuous metal. At the same time, it is necessary to ensure the correspondence of the alloy properties with the properties of the ceramics, applied on the metal frame. For this purpose, the thermal expansion coefficient of the alloy (TEC) should be in the range of (13.5–14.5) · 10^{-6} K^{-1}, with the heating from 20 °C to 600 °C.

Platinum and palladium are the main alloying elements of the majority of gold alloys for metal-ceramics. These metals increase the characteristics of strength. Copper, tin, and other precious and base metals are also included in these alloys.

Alloying of gold with platinum and palladium in the two-component alloys, leads to the decrease in the TEC. However, TEC increases with introduction of copper, silver, and tin. The multidirectional influence of the alloying elements is the achievement factor in the compliance of TEC with the given values of the alloy. However, in multicomponent systems, the mutual influence of individual components on the alloy properties is unpredictable. This also applies to the color characteristics of the alloys, which vary in the direction of yellowness reduction with the increasing of platinum and palladium concentration, while other elements may have the opposite effect on the results. The yellowness index (YI), calculated according to the results of spectrophotometric studies, was chosen as an objective indicator of color. In this study, the requirement for YI was given as not less than 25. The color of such alloys can be called light yellow.

All investigated alloys contain 85% (wt.) of gold. Therefore, the higher corrosion resistance and biological inertness of finished dental products were ensured.

Two the “most yellow” alloys were selected among the alloys that met the requirements of both yellowness and TEC. The adhesive properties of these alloys met the requirements of the State Standard R 51736-2001 to the alloys for metal ceramics: bond strength with ceramics, applied on the surface of a metal sample, was above a minimum value, equal to 25 MPa (Table 2).

Key words: gold, platinum, palladium, alloying elements, alloy, yellowness, thermal expansion, metal-ceramics.

Since the late 1990s, the Scientific and Industrial Complex “Supermetal” (SIC “Supermetal”), in a creative collaboration with the Moscow State University of Medicine and Dentistry (MSUMD), has been developing and producing the dental alloys on the basis of noble metals. The ideology of the creation of new alloys, their compositions and properties, as well as the analysis of the products of other manufacturers, and the market situation, are presented in [1, 2].

The gold alloy for the metal-ceramics grade PLAGODENT (Super-KM) is the most popular alloy, produced by SIC “Supermetal”. In orthopedic dentistry, the term “alloy for metal-ceramics” means an alloy, suitable for application as a metal frame of metal-ceramic denture [3]. The metal frame

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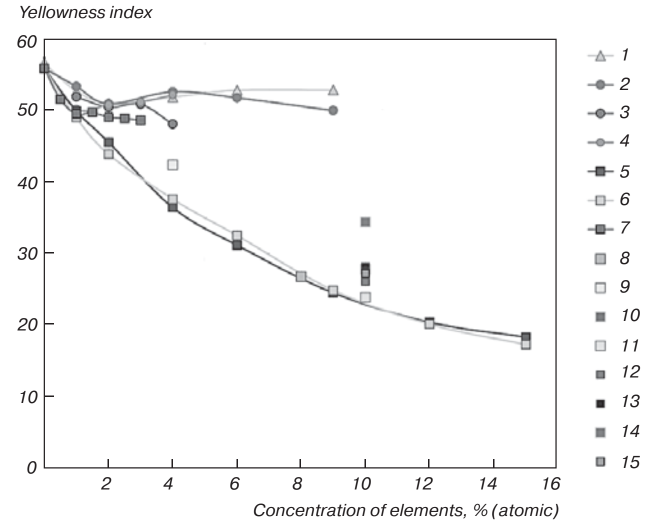

Fig. 1. The yellowness of the gold-based alloys (according to the standard ASTM E 313): *1* — Ag; *2* — Cu; *3* — Sn; *4* — Zn; *5* — Pt; *6* — Pd; *7* — Rh; *8* — Au–Pt–Pd 4–4; *9* — Au–Rh–Pt 2–2; *10* — Au–Pt–Pd–Rh 4–4–2; *11* — Au–Pt–Pd–Ag 4–4–2; *12* — Au–Pt–Pd–Cu 4–4–2; *13* — Au–Pt–Pd–In 4–4–2; *14* — Au–Pt–Pd–Sn 4–4–2; *15* — Au–Pt–Pd–Zn 4–4–2

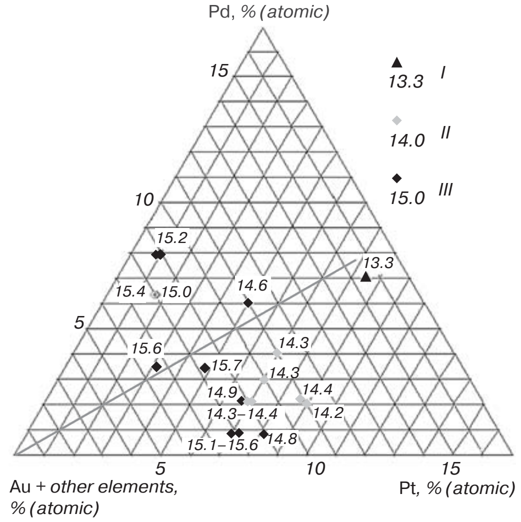

Fig. 2. The influence of gold alloy compositions on the TEC:
I — the PLAGODENT alloy and TEC value;
II — the alloy composition and TEC value, which meet the requirements;
III — the alloy composition and TEC value, which does not meet the requirements

makes a structure more stable to very high masticating loads. The ceramics is applied on a frame layer by layer, which, after annealing, makes dentures look like natural teeth. The ceramics is chemically inert and does not cause allergy [4, 5], which is also characteristical for the gold PLAGODENT alloy frame. The usage experience of the dentures with the frames, made of this alloy, confirms their high quality and clinical efficiency [6].

Although the PLAGODENT alloy has very high consumer properties, it is not ideal from aesthetic point of view, because it does not have a pronounced yellow color in spite of a very high content of gold (85% (wt.)). At the same time, a lot of consumers of dental alloys prefer yellow alloys, since some patients have been showing aesthetic preference to yellow color as an attribute of noble and innocuous metal. Dental technicians prefer yellow alloys, too, for making the ceramics imitation frames, because it helps to obtain warm and natural shades of the coating.

So, the demand for a yellower alloy has always been urgent; and the SIC "Supermetal", together with the MSUMD have developed two new yellow alloys for the orthopedic dentistry. Platinum and palladium are the major alloying elements for the PLAGODENT alloy, as well as for the majority of other gold alloys for metal-ceramics. These elements effectively strengthen gold, forming a solid solution; reduce the thermal expansion coefficient (TEC); and considerably change the color towards a decrease of the alloy yellowness. The other alloying elements (silver, copper, tin, and zinc) have an effect on the mentioned properties of gold alloys.

The two-component systems [7, 8] were mostly used to estimate the concentration dependences of the effect of various alloying elements on hardness, TEC, and color of gold alloys. It was shown that platinum and copper are the best strengtheners. Tin is also a good strengthener, but its solubility in gold is limited by several percents. The hardness continuously in-

Table 1
Composition and properties of the researched alloys

Alloy	Content of elements, % (atomic)							Amount of Pt, Pd, %		Properties	
	Au	Pt	Pd	Rh	Ag	Cu	Sn	atomic	wt.	TEC	Yellowness (YI)[1]
0[2]	80.0	8.5	7.0	—	—	2.9	1.6	15.5	13.0	13.3	21.2
1	74.7	5.0	6.0	0.8	—	12.8	0.7	11.0	9.3	14.6	23.7
2	76.6	7.0	4.0	0.9	—	10.9	0.7	11.0	10.1	14.3	23.8
3	78.2	8.8	2.2	0.9	—	9.1	0.8	11.0	10.8	**14.4**	**25.8**
4	75.6	6.9	2.1	0.8	—	13.7	0.7	9.0	9.0	14.9	25.1
5	76.8	8.2	0.8	0.9	—	12.6	0.7	9.0	9.5	14.8	26.4
6	75.4	7.1	0.8	0.8	—	15.1	0.7	8.0	8.5	15.6	25.2
7	78.8	9.0	2.1	0.9	—	7.7	1.5	11.0	10.8	**14.2**	**26.1**
8	78.2	6.9	2.1	0.9	5.6	5.6	0.8	9.0	8.7	**14.3**	**27.9**
9	75.1	7.2	0.8	—	—	16.2	0.7	8.0	8.6	15.1	25.3
10	79.9	6.9	2.1	0.9	9.2	0.3	0.8	9.0	8.5	**14.4**	**31.5**
11	76.1	7.0	3.0	0.9	—	12.3	0.7	10.0	9.6	14.4	24,6

[1] Yellowness of gold 99.99: YI = 56.7
[2] The PLAGODENT alloy

Table 2
Composition and properties of new alloys

Alloy / Alloy grade	Content of elements, % (wt.)							Properties								
	Au	Pt	Pd	Rh	Ag	Cu	Sn	$T_{solidus}$, °C	TEC, 10^{-6} K^{-1}	YI	$\sigma_{p.l.}$	$\sigma_{0.2}$	δ	*HV* cast	*HV* th. tr*	Adhesion τ, MPa
0 / PLAGODENT (for comparison)	85.0	9.0	4.0	—	—	1.0	1.0	1,115	13.3	21.2	351	246	15	165	97	57.7
8 / PLAGODENT-PLUS	85.0	7.4	1.3	0.5	3.3	2.0	0.5	1,057	14.3	27.9	347	211	11	119	87	47.3
10 / PLAGODENT-BIO	85.0	7.3	1.2	0.5	5.4	0.1	0.5	1,055	14.4	31.5	291	159	18	90	69	40.1

Symbols: $\sigma_{p.l.}$ stands for the proportionality limit; $T_{solidus}$ stands for the solidus temperature

*Thermal treatment according to the ceramics annealing mode

creases, with the gold alloying with palladium. However, palladium is considerably inferior to platinum.

Alloying of gold with platinum and palladium decreases the TEC, while the introduction of copper, silver, and especially tin, increases it. Such a different direction of the influence of gold alloying is an achievement conformity factor of the alloy`s TEC to the initial requirements for the metal-ceramics materials. However, in a real multicomponent system, the influence of individual elements on the structure and properties of the alloy can not be definitely predicted and depends on the influence of other alloying elements, both separately and in the combination with each other.

The special attention was given to the dependence of the gold alloys color from the alloying extent by the mentioned components. The yellowness index (YI), calculated according to the results of spectrophotometric studies [9, 10], was chosen as an objective indicator of color. According to the Fig. 1, there is shown, that the yellowness coefficient of two-component gold alloys decreases abruptly in the alloying process of the platinum and palladium alloy. The influence of silver, copper, and zinc on the yellowness of two-component gold alloys is not as considerable as the influence of the platinum metals. Rhodium and tin considerably improve the alloy yellowness, while silver decreases it. It happens in more complex multicomponent alloys, in case of joint alloying of gold with platinum, palladium, and other elements.

Subjectively, the alloys with a YI < 20 look like white alloys with a weakly yellow shade. For example, an alloy with 15% (atomic) of palladium looks white, however, the yellowness is recorded instrumentally (YI = 17.2).

The alloys with YI < 25 look like pale yellow. In this research paper, the requirement for the YI was specified as not lower than 25. Hence, such alloys can be called light yellow.

The complexity of the task solution about the creation of yellow alloy for metal-ceramics consisted of different influences of alloying elements for metal ceramics on the strength properties (hardness), color properties and the TEC of the alloy. Certain unpredictability of results for multicomponent systems was also the part of the complex task.

Selection of compositions for experimental alloys was based on the following principles:

— the initially chosen high gold content (85% (wt.), as in the PLAGODENT alloy), due to which, the high corrosion resistance and biological inertness of the alloy are provided;

— the limitation of the maximum total content of platinum metals for the prevention of the decoloration of the gold alloy and excessive reduction of the TEC;

— the limitation of the minimum total content of platinum metals for the strengthening of gold alloy and reduction of TEC to the required values, corresponding to the properties of the applied ceramics;

— the introduction of copper, tin, and silver, in the composition for the additional strengthening and color control.

The requirements for the TEC of alloy should consist of the following: with the heating from 20 °C to 600 °C, the value of average (technical) expansion coefficient should be (13.5 – 14.5) · 10^{-6} K^{-1} for the thermal corresponding to the ceramic mass, used for coating. The research results of influence of the composition on the TEC of multicomponent gold alloys are presented in a concentration triangle. The platinum and palladium content is given on two sides of this triangle. The vertex of the angle corresponds to gold, together with other alloying elements (Fig. 2). In spite of a conditional character of such representation, the figure shows that the compositions, which meet the specified requirements, are situated in the concentration field of platinum and palladium (not lower than 9% (atomic) and not higher than 11% (atomic)). Taking into account the content of other alloying elements, chosen for this experiment (Table 1), the area of comprehensible concentrations is below the bisectrix of the gold angle, i.e. the concentration of platinum should be above the concentration of palladium. It is interesting to look at a group of three spots on the line of compositions with ~ 2% (atomic) of palladium. One of these spots is unacceptable. The alloys, corresponding to them, are almost identical (considering gold, platinum, palladium, and the amount of other elements), but essentially different from the concentration of elements (in particular, of copper and silver). Two of these alloys contain silver, and have an optimum value of the TEC and good color results.

The results of measurement of the samples color are given in the Table 1. They confirm the rightness of limitation of the total of platinoids (above 11% (atomic)). Only four of all investigated alloys have similar values of the major properties, which meet the requirements: the TEC in the set range and YI > 25 (the numerical symbols in the Table 1 are black-fonted). Two of the yellowest alloys were chosen for the medical tests, production and application (Table 2).

The mechanical characteristics of the mentioned alloys were determined using two types of non-standard (economic) samples: the cast strips (37 × 7 × 1.1 mm) and cold-rolled hexahedral rods with a 1.4 mm thickness. The yield point and specific elongation were determined using the cast samples; the proportionality limit was determined using deformed and thermally treated samples. Taking into account the fact, that the cast metal had a more non-equilibrium and defective structure, the magnitudes of $\sigma_{p.l.}$ in the experiment were found to be higher than $\sigma_{0.2}$. However, the results, obtained only with the same type samples, were compared in this research paper.

For the estimation of adhesive properties, there were tested the cast samples of the researched alloy. The surfaces of these samples were preliminarily coated with a multilayer ceramic coating IPS d.SIGN. After the coating of each layer, the thermal treatment was carried out at the temperatures up to 890 °C. When bending the sample with the downwards directed coating, there was determined the breaking load, at which began the ceramic layer separation. The calculated bonding strength of metal and ceramics (τ) for all samples was found to be higher than 25 MPa.

Thus, the hardness and plasticity of the new alloys, as well as the strength of bonding with dental ceramics are quite acceptable for the manufacturing of metal-ceramic prostheses, according to the State Standard R 51736-2001.

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Changes of the properties of PLAGODENT (Super-KM) alloy in the process of dentures production

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The prosthetics dentistry requires more noble metal based PLAGODENT (Super-KM) alloy, developed and produced by Scientific and Industrial Complex "Supermetal". This company conducted the additional studies of the material operating characteristics. The optical and electronic microscopy was carried out along with the mechanical tests. According to ISO 9693:1999 (E), there were held the tests for adhesive properties.

It was shown that, in the production process of dental articles, made of the alloy, its properties are connected with the high function level, which ensures the durability and comfort of dentures. It was confirmed by a successful 10-years practice of the PLAGODENT (Super-KM) alloy in dentistry.

Key words: gold and platinum alloy, PLAGODENT (Super-KM), adhesive properties, operating characteristics, dentistry, microstructure, dentures.

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