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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Scientific and Industrial Complex “Supermetal” (SIC “Supermetal”) is the largest Russian company, which successfully develops and produces the noble metal based alloys for dentistry.

High functionality, durability and biological inertness of noble metal based alloys can improve the healing effect on the principal dental diseases [1]. In combination with ceramic materials, the noble metal based alloys make it possible to have a better aesthetic result.

The PLAGODENT (Super-KM) alloy has been the most popular alloy in Russia for the recent ten years. The basis of this alloy is gold. The alloying elements are platinum, palladium, copper and tin (the total amount of noble metals is 98% (wt.)). The PLAGODENT alloy was developed for the production of unit-cast crowns and bridge-like dentures with the preference ceramic coating. However, its properties made it possible to use it in other dental structures, such as individual abutments for the prosthetics on implants or various inserts, which substitute the defect of a tooth part, or support the bridge-like denture.

In the connection with broadening of the application range of the PLAGODENT alloy in various dental structures and increasing its consumption volume in orthopedic prosthetics, it was a practical interest to investigate the properties of the PLAGODENT alloy in the course of manufacturing of alloy`s dental products, i.e. to estimate the properties of finished dentures.

The studies of the alloy properties in the condition of delivery were made before its development. This is necessary for SIC “Supermetal”, when the manufacturing of new dental products.

The alloy hardness and the ceramic coating adhesion were the operating characteristics of the greatest interest for investigation.

Due to an optimum thermal expansion coefficient, the PLAGODENT alloy is adapted for a wide range of ceramic coatings, used in dental laboratories for the production of metal and ceramic dentures. Earlier, at the development stage, the adhesive properties of the alloy were studied with the Duzeram ceramic mixture. In this research work, the IPS d.SIGN ceramics (one of the most widespread ceramics in the dental market) was used for the determination of adhesive properties of the PLAGODENT alloy.

The samples were fabricated by the investment casting method with the usage of a DeguDent induction foundry installation. The wax models were prepared using the Omnident base-plate wax (Germany). The Gilvest HS molding material was used for a package. With mixing the molding material, there were used 65 ml of liquid and 3 ml of water for 240 g of powder. The casting box annealing was carried out in a Bego resistance-heating muffle furnace. The packing mix was removed from the cast piece by means of a sandblaster (the diameter of the sand grains is 50 μm).

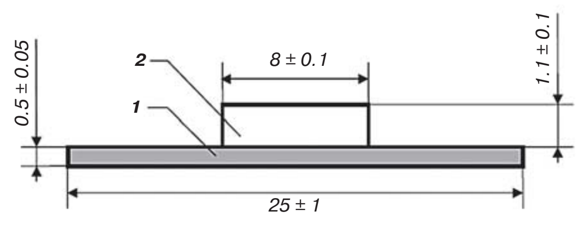

Fig. 1. Diagram of a ceramic coating sample for the testing of cohesion strength between the ceramics and metal [3]: metal plate (1), ceramic coating (2)

The adhesive properties of the alloy (the adhesive strength of metal with ceramic coating) were studied in accordance with ISO 9693:1999 (E) [2] at the department of National University of Science and Technology “MISiS” A ceramic coating, which consists of an opaque layer, dentin layers, enamel and glaze, was applied on a prepared surface of samples (Fig. 1), according to the instruction for the ceramic mass IPSd.SIGN, including the intermediate and final annealing between the application of layers. Before the application of ceramics, the samples were short-term annealed in vacuum, and sandblasted (the particle size is 110 μm; the pressure is $1.5 \cdot 10^5$ — $2 \cdot 10^5$ Pa).

The prepared samples were placed down with the ceramic coating in the loading device of a FP 10/1 “Fritz Heckert” testing machine (20 mm between the supports). The tests were carried out with 1 ± 0.5 mm/min of permanent load and loading rate, till the moment of the coat separation. The stress-strain curves were obtained during the testing. The ceramic coating scaling began at the split force F_{split}, which was also determined.

The adhesion strength τ_b was calculated by the following equation [3]:

$$\tau_b = k \cdot F_{split},$$

where k is the coefficient, depending on the thickness of the metal plate (d_m), and the Young modulus (E_m) of the alloy.

The microstructure of the samples was determined by the mechanical grinding with the subsequent electropolishing. As an electrolyte, there was taken a solution, containing 25 g/l of thiourea, 3 ml of the concentrated sulfuric acid, and 10 ml of acetic acid. 1/10 of the distilled water was added to the process solution. The cathode was made of graphite, the voltage was 20 V. Depending on the size of a sample, the exposure time was 10 – 30 seconds. The microstructure studies were performed by means of a Neophot-30 light microscope, equipped with a device, based on the Olympus digital camera.

The quantitative analysis was made by method of random secants. The results were processed by the mathematical statistics methods. The confidence interval was estimated with the probability $P = 0.95$.

The alloys hardness HV was determined at the room temperature in molten and annealed[1] states, because the alloy state after annealing is the working state for dentures with ceramic coatings.

The phases composition was determined by micro X-ray spectral analysis, using the EVO-50 XV5 energy and dispersion attachment to a Carl Zeiss electronic microscope. The microscope was equipped with EDX system of energy and dispersion analysis INCA Energy 450, manufactured by the Oxford Instruments. Shooting was carried out in vacuum with a residual pressure of 10^{-7} Pa with an accelerating voltage of 20 kV.

[1] Annealing mode in accordance with instruction for the ceramic mass IPS d.SIGN

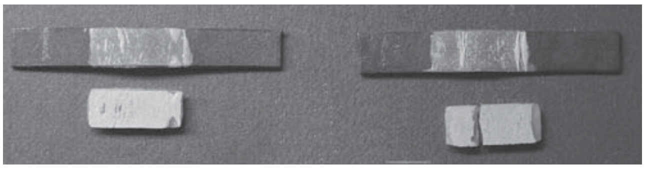

Fig. 2. Few samples after the testing of adhesion strength between the ceramic mass and PLAGODENT alloy

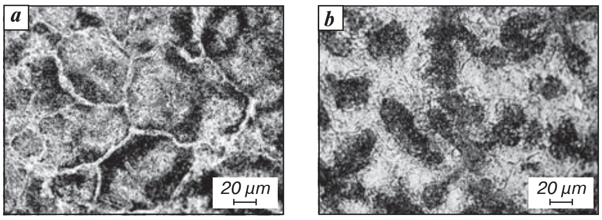

Fig. 3. Microstructure of molten (a) and annealed (b) samples

Acccording to the results of the studies, the cohesion strength of the PLAGODENT alloy with the IPS d.SIGN ceramics was 57.7 ± 3.1 MPa.

According to ISO 9693:1999 (E) [2], the adhesive strength should be not less than 25 MPa. Therefore, was made a conclusion that the investigated alloy has the required adhesive properties and can be used as the dentures with ceramic coatings.

In the considered research, the high level of adhesive properties is reached by the optimum modes of sandblasting, before the application of ceramic mass, which results in an increased roughness. The optimum relationship of the size of sand grains and pressure plays a big role for a better adhesion. The usage of fine-dispersed particles (less than 110 μm) and a high pressure leads to the introduction of the particles in the surface layer of the alloys. At the same time, the usage of large-disperse particles or a high pressure leads to the peening of the surface layer and to the loss of metal; while the fine-dispersed particles or insufficient pressure do not lead to required roughness of the surface [4, 5]. After the sandblasting, the annealing parameters also have an effect of the adhesive properties level of the PLAGODENT alloy. Considering this research, it was carried out in vacuum, because in such conditions, the content of tin oxides increases on the surface, in comparison with the copper oxides, which have a loose and chemically inactive structure [5]. Together with the thickness and structure of the oxide layer, a highly developed alloy surface promotes the formation of strong chemical and mechanical bonds between the ceramic coating and alloy [5].

This is also proved by the fact that the split of ceramic mass on all samples goes along the boundary line of opaque and dentine (Fig. 2), which is the evidence of a good adhesion of ceramic mass with the PLAGODENT alloy.

For the study of annealing influence on the mechanical characteristics of alloys, the hardness was investigated as the most convenient method of control (express method) in the molten and, subsequently, annealed states.

The hardness of the PLAGODENT alloy is 129 ± 7.4 HV in molten state and 91.3 ± 3.2 HV in annealed state. The annealing process leads to the decrease of mechanical characteristics, but it is inevitable with the ceramics application. However, the ten years' practical experience in the usage of PLAGODENT alloy in various designs of dentures showed that such level of the alloy hardness is quite sufficient to withstand the tension influence on the dentures.

The microstructure analysis revealed a two-phase nature of the samples (Fig. 3), i.e. the sections of a lighter phase on the darker matrix represent a solid solution, on the basis of gold. The white particles of surplus phases are situated mainly at the grain boundaries and have a coarse prolate form. According to the X-ray phase analysis, these particles are probably of the Pt_3Sn type, because the basic component of the lighter phase is platinum (62% (wt.)).

The microstructure analysis showed that annealing did not eliminate the dendrite segregation in the alloys (Fig. 3), because the temperatures and exposures, typical for the ceramics annealing (0.8 – 0.9 of $T_{melting}$), are not sufficient. It is necessary to increase the temperature (to 0.95 of $T_{melting}$) and the annealing time, which, practically, is not possible, because such parameters do not meet the strict requirements in the instructions of ceramics application.

The bodies of grains are very inhomogeneous, which is shown in a different extent of the crystallites etchability. The size of grains in the cast state is 41.4 ± 2.4 μm. After the annealing, the particles morphology remained the same. The boundaries of the grains in the annealed state are etched more slowly than in the molten state, which is, probably, connected with the liquation of a more corrosion-resistant element towards the boundaries. Practically, the sizes of grains in the annealed state do not change (42.8 ± 3.5 μm). Therefore, the decrease of hardness is connected not with the grain growth, but with a partial redistribution of components, which leads to a more equilibrium state.

It is necessary to note that the pores in the samples on the junctions of grains are both in the molten and in annealed states, typical for the casting alloys.

The foregoing studies showed that in the course of production of dental articles of the PLAGODENT (Super-KM) alloy, there occurs an insignificant decrease in hardness. However, this fact does not have any essential influence on the functional properties of the alloy, which has been confirmed by the ten-year practice of application of the PLAGODENT alloy in orthopedic dentistry. According to ISO 9693:1999 (E), the adhesive properties of the alloy are more than twice better than the standard properties.

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Sorption of the chloride complexes of palladium and platinum by the chemically modified silica

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This article considers the study of sorption of palladium (II), platinum (II), and platinum (IV), from the hydrochloric-acid solutions by chemically modified silica. Using the methods of infra-red and electronic spectroscopy, there were established such types of complexes, which are obtained in the phase of sorbent (silica, which is modified by the groups of γ- aminopropyltriethoxysilane), depending on the solution acidity. The hydrochloric-acid solutions of thiourea were proposed as the eluent. A sorption separation diagram for Pd (II) and Pt (IV) was proposed on the basis of the study.

Key words: sorption, platinum, palladium, chloride complexes, desorption, extraction, separation.

The sorption method is one of the most efficient and progressive methods of extraction, concentration and separation of elements with similar properties. In comparison with other methods, the advantages of this method consist of the technological efficiency, selectivity and relatively high rate of balance achievement. The high temperatures and complex equipment are not required for the sorption process [1]. Besides, sorption is an environmentally appropriate method. That`s why it is quite attractive for the selective concentrates production in the technology. Recently, the chemically modified silica (CMS) has been used to concentrate nonferrous and platinum metals. The CMS is characterized by the swelling absence in aqueous solutions, high rates of sorption, and mechanical strength of particles. According to this, CMS distinguish from the organic and polymer sorbents. That`s why, the attaching capability of any functional group on the silica surface makes it possible to create sorbents for extraction of ions of various metals [2]. However, in many cases, the sorption extraction mechanisms of platinum group metals (including platinum and palladium), were insufficiently investigated. Investigation of composition and structure of the complexes, which have been formed during the interaction with functional groups of sorbents, promotes the perfection of methods of sorption separation, extraction and concentration [3].

The purpose of this study is to determine the special features of sorption extraction of chloride complexes Pd (II), Pt (II), and Pt (IV), from hydrochloric acid solutions by the CMS. The nitrogen containing functional groups are included in the composition of this silica. The hydrochloric-acid and aqueous-chloride media are the most widespread in the technology, analysis, and preparative practice. According to this, the revelation of the sorption laws of chloride complexes of platinum metals shows the greatest interest.

The experimental part

The Silokhrom C-120 grade silica, chemically modified by the groups of γ-aminopropyltriethoxysilane CMS-N, was used in this research work as a sorbent. The quantity of grafted functional groups is 163 mcmol/g. The specific surface of the researched silica is 120 m^2/g, its fraction is 0.1–0.2 mm; the diameter of average pore is 45 nm.