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Nova zlatna dentalna legura za metal-keramiku

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New gold dental alloy for metal-ceramic restorations

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ORIGINALNI RAD (OR)
ORIGINAL ARTICLE

KRATAK SADRŽAJ

Uvod: *Visoko plemenite legure za metal-keramiku (PFM legure – porcelain fused to metal alloy) su najviše korišćene legure u stomatologiji a odlikuje ih visoka biološka prihvatljivost i dobro vezivanje sa keramikom.*

Cilj: *Cilj ovog rada bio je da prikaže postupak dobijanja i tehnologiju razvoja i izrade nove dentalne legure sa visokim sadržajem zlata (Au).*

Materijal i metod: *Pretapanje komponenti dentalne legure izvedeno je u vakuumskoj peći. Tome je sledila naknadna termo-mehanička obrada odlivka (postupcima profilnog i polirnog valjanja, toplotna obrada) kao i sečenje dobijene trake u propisani oblik. Testiranje nove Au dentalne legure uključivalo je testiranje izlaznog stanja legure. Merenje tvrdoće sprovedeno je po standardu 6507-1:1998, dok je za određivanje mehaničkih karatkeristika upotrebljeno statično istezanje. Mikroskopska analiza dentalnih legura i završenog metal-keramičkog mosta uključivala je posmatranje polirane površine i izvođenje kvalitativne i kvantitativne mikro-hemijske analize.*

Rezultati: *Mehaničke karakteristike i tvrdoća nove dentalne legure sa visokim sadržajem zlata iznosi* $R_{p0.}$*=630 [N/mm*^{2}*],* R_m *=710 [N/mm*^{2}*], A= 9%, 170 HV,*

SUMMARY

Introduction: *Porcelain to metal fused alloys with Au content are most frequently used in dentistry. Their characteristic is high biocompatibility and well fusion to ceramics.*

Aim of the study: *The aim of this study was to present the procedure of production and technology of developing the new dental alloy with high gold content (Au).*

Materials and Methods**:** *The dental alloy was melted and cast in a vacuum-induction melting furnace. Casting was followed by subsequent thermo-mechanical treatments (the procedures of profile and polish milling, and thermal treatment) and the cutting strips into regular shapes. Testing of the new Au dental alloy included an examination of alloy's final condition. The measurement of hardness was carried out according to standard 6507-1:1998, and static tensile testing was performed for determination of the mechanical properties. Microscopic analysis of the dental alloy and the finished metal-ceramic bridge included an observation of the polished surface, and by performing qualitative and quantitative micro-chemical analyses.*

Results: *The mechanical properties and hardness of new dental gold alloy was:* $R_{p0.}$*=630 [N/mm*^{2}*],* R_m *=710* *a CTE (25-600°C) iznosi oko $14{,}55\times10^{-6}K^{-1}$. Makroskopski na površini metala i potom sinterovane keramike nije uočena poroznost dok je mikroskopskim pregledom ustanovljeno da je na pojedinim mestima jednog uzorka vidna poroznost metalne konstrukcije mosta kao i keramičke površine u vidu većih mehurića (tip I) i manjih sa izrazito poroznom mikrostrukturom (tip II).*

Zaključak*: Na osnovu dobijenih rezultata može se zaključiti, da nova dentalna legura Zlatarne Celje odgovara propisanim standardima u pogledu mehaničkih karakteristika i tvrdoće. Neophodno je primeniti pravilnu temperaturu oksidacije i režim hlađenja fiksne zubne nadoknade, jer u suprotnom može doći do nastanka različitih defekata.*

Ključne reči: Zlatna dentalna legura, tehnologija izrade, mehaničke karakteristike, mikrostruktura

$[N/mm^2]$, A= 9%, 170 HV and CTE (25-600°C) about $14{,}55\times10^{-6}K^{-1}$. Macro-inspection of the finished metal-ceramic bridge showed that there was no porosity. However, during scanning electron microscopic examination, one of the tested sample shows porosity in one alloy region and in the ceramic layer. Detailed examination of the ceramic layer's surface showed that there were two types of air or gas bubbles – larger with distinct bubbles (type I) and smaller with clearly porous microstructure (type II).

***Conclusions:** According to the results of this study, it can be concluded that this new dental alloy from Zlatarna Celje satisfied all the required standards regarding mechanical properties and hardness. The application of new dental alloy with high gold content depends on the adequate technology when firing ceramics. It is necessary to obtain accurate oxidation temperature and cooling rates of metal-ceramic restorations because, otherwise, different defects may appear.*

Key words: Gold dental alloy, manufacturing technology, mechanical characteristics, microstructure

Legure zlata imaju veoma dugu primenu u stomatologiji i danas se često koriste u izradi određenih fiksnih zubnih nadoknada. Najviše se koriste legure ili visoko plemenite legure za metal-keramiku (PFM legure – porcelain fused to metal alloy) koje su prema podacima iz sedamdesetih godina prošlog veka činile oko 70% svih legura za livenje u stomatologiji. Na tržištu se nalazi veliki broj različitih PFM legura, a na izbor legure utiče, pre svega, hemijski sastav, biokompatibilnost sa oralnim tkivima i organizmom, veza sa keramikom i mogućnost rada u laboratoriji.[1] Osnovu razvoja nove dentalne legure sa visokim sadržajem zlata - Au predstavljaju adekvatni hemijski sastav i sama tehnologija izrade. Zahtevi nove Au dentalne legure vezani su sa predviđenim uslovima koje ta legura mora da ispuni kako bi se koristila za izradu metal-keramičkih zubnih nadoknada. Pri određivanju hemijskog sastava dentalne legure uzeto je u obzir postizanje odgovarajućih mehaničkih karakteristika, kao što su: modul elastičnosti, zatezna čvrstoća, istezanje, tvrdoća, koeficijent termalne ekspanzije (CTE) i biokompatibilnosti. Metalni gradivni materijali moraju da budu mehanički postojani - treba da imaju odgovarajuću tvrdoću i otpornost na pritisak, savijanje i smicanje, da dobro prenose mehanička opterećenja i da su elektrohemijski postojani.

Kod dentalnih legura za izradu metal-keramičkih zubnih nadoknada, koeficijent termalne ekspanzije - CTE legure (važan za ostvarivanje međuspoja metala i keramike), mora da bude nešto viši od CTE keramike ($CTE_{leg} > CTE_{keram}$). Time se tokom hlađenja keramike, zbog većeg termalnog širenja legure, formiraju sile kompresije u keramičkom sloju i izbegnuta je pojava unutrašnjih napona

Gold (Au) alloys have a long history of being used in dentistry and today they are used frequently for producing fixed dentures. Porcelain to metal fused alloys (PMF) with gold (Au) content are most frequently. Data from 1970-ties shows that 70% of all dental PMF alloys were alloys with gold content. On the market today, there are many dental alloys but PMF dental alloys of the highest quality should have biocompatibility with orofacial system, good fusion to ceramic layer and easy handling in dental laboratory.[1] The basis for developing new dental alloy with high Au content is the adequate chemical composition and manufacturing technology. The demands required when developing this new dental alloy are linked to fulfilling the requirements necessary to make the alloy suitable for use in metal-ceramic restorations. Due to the stress generated by masticatory forces, alloys for dental restorations must have corresponding mechanical properties, such as yield strength, tensile strength, and elongation, hardness, the coefficient of thermal expansion (CTE), and biocompatibility. Metal materials have to be mechanically stable - they have to possess suitable hardness, wear resistance, yield, and shear strength in order to withstand mechanical stresses. In addition, they have to be electrochemically stable (high corrosion resistance).

An important property of alloys for metal-ceramic restorations is the coefficient of thermal expansion (CTE), which must be compatible to that of ceramics - it is desirable that thermal expansion of the alloy should be slightly above that of ceramics (important for strong interfacial bonding of metal and ceramics - $CTE_{alloy} > CTE_{ceram}$). Metal contracts slightly more and ceramics bonded to metal would be compressed. Compressive stresses are u keramici koji mogu dovesti do odvajanja keramike od metala i do pucanja keramike.

Biokompatibilnost se odnosi na sposobnost materijala da u kontaktu sa živim tkivima ne uzrokuje toksične, imunološke i bilo kakve druge štetne reakcije. Zubne nadoknade su u ustima pacijenta izložene korozivnim uticajima pljuvačke i različitih supstanci koje su rastvorene u njoj, promenama temperature, pH sredine, itd. Metali u elektrolitu (pljuvačka) otpuštaju jone, koji mogu izazvati različite vrste oksidacionih procesa sa prebojavanjem (tarnish) i taloženjem metala u okolnim tkivima.[2] Pravilno odabranom legurom sa odgovarajućim hemijskim sastavom se uglavnom može izbeći većina opisanih štetnih pojava. Jedna od mogućnosti je izbor dentalne legure sa visokim sadržajem Au zbog njegove izuzetne biološke kompatibilnosti, visoke elektrohemijske postojanosti, funkcije i dugotrajnosti. Zlato je kompatibilno i sa gingivalnim tkivima, nije podložno oksidaciji i akumulaciji dentalnog plaka.[1] Kako je čisto zlato veoma mekano (HV 25), a pored toga ima nizak napon tečenja (30 MPa) i veliko raztezanje (45%), mora se za predviđene indikacije u stomatološkoj protetici legirati.

Cilj ovog rada bio je da prikaže postupak dobijanja i tehnologiju razvoja i izrade nove dentalne legure sa visokim sadržajem zlata (Au).

Materijal i metod

Za novu leguru odabrana je kombinacija sledećih legirnih elemenata: Au, Pt, Zn i u tragovima Ir, In, Rh, Nb, itd. Želja je bila da se zadrže sve dobre osobine zlata, a da se nedovoljna čvrstoća i tvrdoća poboljšaju legiranjem sa platinom.[3] Cink je dodat kako bi se snizila temperatura topljenja i površinski napon istopljene legure, a zajedno sa Ir, In, Rh, Nb, on služi kao dezoksidant (oni zbog svog afiniteta prema kiseoniku prvi reaguju sa njim i time štite osnovne metale od oksidacije). Nova legura ne sadrži Ag - koje u istopljenom stanju lako vezuje kiseonik koji pri očvršćavanju legure daje porozne odlivke, a takođe reaguje sa jedinjenjima sumpora i može dovesti do tamnjenja legure i prebojavanja keramike. U leguri nisu zastupljeni ni paladijum ni bakar (Pd zato što u istopljenom stanju vezuje vodonik i može uticati na poroznost odlivka, a može dovesti i do pojave alergijskih reakcija; Cu legurama zlata daje crvenkastu boju, zagrevanjem u prisustvu vazduha reaguje sa kiseonikom i na površini legure stvara bakar-oksid koji, takođe, može prebojiti keramiku). Zbog svega navedenog, odabrana je legura sledećeg hemijskog sastava: oko 87% Au, 11% Pt, 1% Zn, kao i 1,5 m.% različitih

better tolerated by ceramics than tensile stresses. Internal residual stresses which can lead to debonding of the ceramic's veneer, and cracks in ceramics, are thus avoided. Thermal expansion of ceramics, in contrast to that of alloy, depends on the cooling rate. Slow cooling rates after firing lead to higher thermal expansion of ceramics, so higher CTE of the alloy can be compensated by slower cooling.

Biocompatibility refers to the ability of any material to be in contact with living tissues and not cause toxic or injurious effects. Prosthodontic restorations remain in the oral environment for many years and they are exposed to corrosive influences of saliva, temperature changes, pH changes etc. Metals in electrolyte (saliva) release ions that can lead to oxidative processes which tarnish and precipitate the metal in the surrounding tissues.[1]

Two main reactions on the surface of dental metallic materials are sulphide tarnishing and chloride corrosion. These reactions are electrochemical in nature. Chloride corrosion causes deterioration of less noble metals; this attack is usually in the form of pitting and sometimes penetrates deep into the microstructures. This effect can range from changes in appearance to loss of mechanical strength.

Most of the described harmful processes can be avoided by appropriate selection of dental alloys. One of the possibilities is the usage of dental alloy with high Au content, because of the exceptional biological compatibility of gold, and its very high electrochemical resistance, functionality and longevity. Gold is compatible with gingival tissues and is not susceptible to oxidation and the accumulation of dental plaque.[1] Pure gold is very soft (HV 25) and has very low 0.2% proof stress (30 MPa) and large elongation (45%). Therefore, it must be alloyed with base metals for applications in fixed prosthodontics.

The aim of this study was to present the procedure of production and technology of developing the new dental alloy with high gold content (Au).

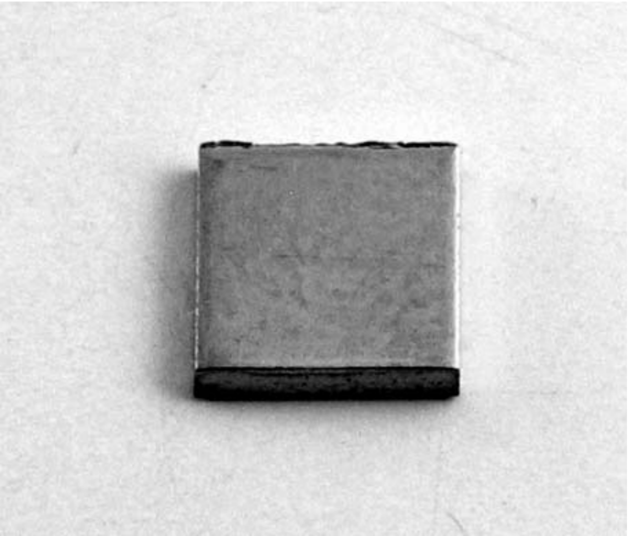
Materials and methods

For the new alloy, a combination of following alloying elements was selected: Au, Pt, Zn and traces of: Ir, In, Rh, Nb etc. We wanted to keep all the favourable properties of gold and to improve its inadequate strength and hardness by alloying it with platinum (Pt).[3] The addition of zinc was done in order to lower melting temperature and surface tension of the melted alloy. Zinc served as dezoxidant together with Ir, In, Nb. This is because of their affinity to oxygen, being the first to react with it and thus, protecting other metals from oxidation. The new alloy does not contain Ag, which easily reacts with oxygen, gives porous castings, and also reacts with sulphur compounds and can lead to tarnishing and ceramic discoloration (greening). The alloy, also, contains no palladium or copper. Pd reacts with hydrogen; it gives porous castings and can cause allergic reactions. Cu gives reddish color to an alloy, it reacts with oxygen and forms copper-oxide on the surface, which can mikro-legirnih elemenata (Ir, In, Rh, Nb, i dr.). Takvom kombinacijom elemenata želelo se postići što bolji efekat ojačanja, što znači da bi nova legura imala dobru mikrostrukturnu stabilnost i dobre mehaničke karakteristike, posebno pri visokim temperaturama pečenja (sinterovanja) keramike. Stvaranje finih, ravnomerno raspoređenih, nekoherentnih čestica različitih jedinjenja, koje su visokotemperaturno veoma stabilne, i u temperaturnom području upotrebe materijala ne reaguju sa osnovnom maticom, predstavlja tzv. disperzijsko ojačanje.[4,5] Ono omogućava da materijalu poboljšamo mehaničke karakteristike i da ih zadržimo pri visokim temperaturama.

Pretapanje veoma čistih komponenti (Au= 99,99 m.%, Pt= 99,99 m.%, Ir= 99,99 m.%, In= 99,99 m.%, Rh= 99,99 m.%, Nb= 99,99m.%) izvedeno je u Zlatarni Celje d.d. u vakuumskoj peći pri vakuumu p = 10^{-2} mbar i pri T = 1300°C, dok je izlivanje istopljene legure teklo pri pritisku argona iznad 1,03 bar u metalni kalup promera 8 mm.[6] Tome je sledila termo-mehanička obrada odlivka (postupci profilnog i polirnog valjanja, toplotna obrada) i sečenje dobijene trake, čime je dentalna legura oblikovana u propisani oblik – slika 1 (pločica debljine 2 mm). Toplotna obrada pri temperaturi 840°C bila je usmerena na smanjenje unutrašnjih napona legure, povećanje duktilnosti sa rekristalizacijom, promenu mikrostrukture, odnosno, poboljšanje mikrostrukturne homogenosti same dentalne legure.

cause ceramic discoloration. These were the reasons for the following chemical composition of the new alloy: about 87% Au, 11% Pt, 1% Zn, and 1,5 w% of different micro-alloying elements (Ir, In, Rh, Nb, etc.). They are necessary for precipitation hardening, as well as for the ability to bond ceramics to the metal`s surface. Oxides of base metals are formed at the surface of the alloy during the firing cycle. The required bond strength can be obtained by forming a very thin oxide layer - less than 1 μm on the surface of the alloy. The formation of finely dispersed, incoherent, non-shearable dispersoids in gold matrix is an efficient way of improving the mechanical properties of an alloy. In such dispersion-strengthened gold alloys the strengthening effect is obtained by dispersoids - dislocation interaction, whereby the dispersoids impede the dislocation motion.[4,5] They are fine-grained, have sufficient strength for crown and bridgework, but have to be melted and cast under protective gas atmosphere.[4]

Melting of very pure components (Au= 99,99 w%, Pt= 99,99 w%, Ir= 99,99 w%, In= 99,99 w%, Rh= 99,99 w%, Nb= 99,99 w%) was performed at Zlatarna Celje d.d. in vacuum induction melting furnace at vacuum p = 10^{-2} mbar and temperature T = 1300°C. Casting of melted alloy was performed at argon pressure above 1.03 bar in a metal cast with a diameter of 8 mm.[6] Casting was followed by subsequent thermo-mechanical treatment (the procedures of profile and polish milling, thermal treatment) and cutting of strips to regular shapes - figure 1 (plate thickness 2 mm). The goal of thermal treatment at 840°C was to reduce the internal stress of the alloy, to increase ductility with recrystalization, and to improve the homogenous microstructure of the dental alloy.



Slika 1. Pločica dentalne legure sa visokim sadržajem Au
Figure 1. Plate of a dental alloy with high Au content

Testiranje nove Au dentalne legure uključivalo je testiranje izlaznog stanja legure. Merenje tvrdoće legure sprovedeno je po standardu 6507-1:1998, i korišćena je metoda po Vickers-u. Merenja mikrotvrdoće izvršena su na aparatu Zwick 3212. Da bi se postigao najoptimalniji pritisak i samim tim dobili merodavni rezultati, na uzorke je

Testing of the new Au dental alloy included examining the final condition of the alloy. Measurements of hardness were carried out according to standard 6507-1:1998, using the Vickers test. Measurements were done using the Zwick 3212 microhardness measurement device. We wanted to obtain optimal impressions, ie. competent results. The primrnjena pritisnu silu F = 49 N, u skladu sa standardom. Za svaki uzorak dentalne legure urađena su 12 merenja.

Za određivanje mehaničkih karatkeristika bilo je upotrebljeno statično natezno ispitivanje, koje je izvedeno na nateznom aparatu Zwick/Roell ZO 10. Merenja mehaničkih karakteristika za pojedinačno stanje legure izvedena su u jednoj seriji koja je sadržala 12 uzoraka. Uslovi ispitivanja kao i oblik i dimenzije nateznih epruveta bili su u skladu sa propisanim standardom SIST EN 1562:2000 (poglavje 6.2). Merenja su izvedena sa konstantnom brzinom povećanja deformacije, čija je vrednost iznosila v = 1,5 mm/min. Natezne epruvete su izlivene i zatim isečene iz odlivka u obliku valjka promera 3 mm, čiji su krajevi bili rašireni u nastavak (bez navoja) za natezanje, promera 6 mm.

Merenja koeficijenta termalne ekspanzije CTE izvedena su u jednoj seriji koja je sadržala 3 uzorka na aparaturi Mechanical Dilatometry (na Katedri za inženjerske materijale Prirodno tehničkog fakulteta Univerziteta u Ljubljani).

Za mikroskopske analize pločice dentalnih legura su najpre bile izbrušene i zatim fino ispolirane sa različitim dijamantnim pastama. Uzorci su posle završne metalografske preparacije očišćeni u ultrazvučnom vibracijskom aparatu za čišćenje (medijum alkohol). Očišćeni uzorci su pričvršćeni na poseban nosač (po dve pločice odjednom) i postavljeni u komoru elektronskog mikroskopa Sirion NC 400 (na Fakultetu za mašinstvo, Maribor). U komori je ostvaren vakuum 10^{-10} mbar. Sirion FEG je scanning elektronski mikroskop visoke rezolucije sa emisijom elektrona u polju, koji omogućava zapažanje i analizu čestica i u nano-metarskom području. Mikroskopska analiza dentalnih legura je uključivala posmatranje polirane površine i izvođenje kvalitativne i kvantitativne mikro-hemijske analize u karakterističnim tačkama, odnosno, fazama pojedine dentalne legure i završenog metal-keramičkog mosta. Površine su posmatrane pri naponu elektronskog mlaza 15 kV i pri različitim radnim rastojanjima (6.5 mm, 7.2 mm, ipd.).

U drugom stadijumu je, od izrađenih pločica nove Au dentalne legure, centrifugalno izlivena metalna konstrukcija mosta od četiri člana (slika 2). Dentalnu leguru smo istopili u grafitnom tiglu u visokofrekventnom indukcijskom aparatu za livenje pri T = 1290°C i centrifugalno je izlili u pripremljenu kivetu od mineralne fosfatne vatrostalne mase za ulaganje._

Nakon čišćenja odlivka, izvršena je njegova mehanička obrada, peskiranje i čišćenje parnim čistačem. Zatim je sprovedeno degasiranje i oksidacijsko žarenje legure (bez vakuuma) na 930°C/10 min. Na taj način formiran je fini oksidni film na površini legure koji ima važnu ulogu u stvaranju hemijskog međuspoja sa keramikom. Nakon oksidacije odlivak je ispran u kiselini Neacid i ponovo očišćen parnim čistačem. Prvi sloj keramike – opaker, nanošen je u dva sloja koji su odvojeno pečeni u vakuumskoj keramičkoj peći VITA Vacumat 40. Temperatura pečenja opakera bila je na 900°C. Nakon obrade i poliranja metal-keramičkog mosta, u završnoj fazi most je glaziran kako bi se obezbedile glatke površine i prirodan izgled u ustima pacijenta.

applied load was 49 N, according to the standard. Twelve measurements for every sample were carried out.

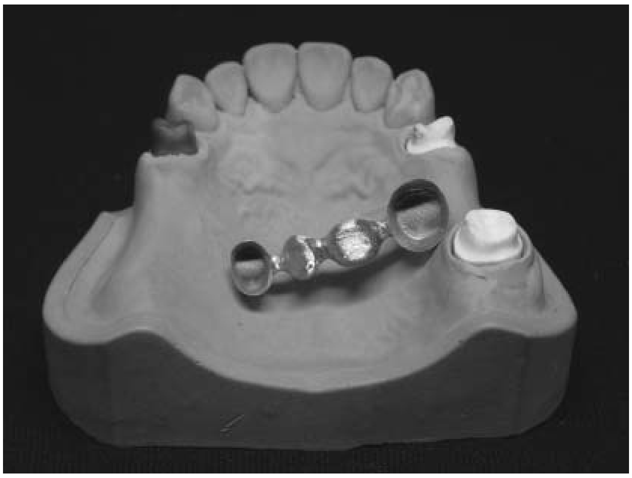
Determination of mechanical properties was performed by static tensile testing using the Zwick/Roell ZO 10 tensile device. Measurements of mechanical properties for a single alloy state were performed in one series, using 12 samples. Research conditions, as well as the shape and dimensions of the tensile test tubes were according to standard SIST EN 1562:2000 (chapter 6.2). Measurements were performed at constant speed of increasing deformation, v = 1.5 mm/min. Tensile test tubes were casted and then cut off from the cylinder shaped casting with diameters of 3 mm and extended for tensing (without coil), to 6 mm in diameter.

Measurements of the coefficient of thermal expansion (CTE) were performed in one series which consisted of 3 samples. This was done in a Mechanical Dilatometry device (at the Chair for Engineering Materials Nature-Technical Faculty, University of Ljubljana).

The dental alloy plates were ground for microscopic analysis and then polished with different polishing pastes. The samples were, after metallographic preparation, cleaned in an ultrasound vibration cleaning device (medium alcohol). Clean samples were attached to special bearers (two at the same time), put in the chamber of a Sirion NC 400 scanning electron microscope (at the Faculty of Mechanical Engineering, University of Maribor), with vacuum of 10^{-10} mbar. Sirion FEG is a high-resolution scanning electron microscope with a field-emission gun (FEG) that allows particle observation and analysis in the nanoscale region. Microscopic analysis included examination of the polished surface and qualitative and quantitative micro-chemical analysis at characteristic points, i.e. phases of dental alloy and the finished metal-ceramic bridge. We observed the surfaces using an electron beam voltage at 15 kV and different working distances (6.5 mm, 7.2 mm, etc.).

At the second stage plates of the Au dental alloy were used to cast four unit metal bridge substructures centrifugally at the Wisil M Dental laboratory, Belgrade (figure 2). The dental alloy was melted in a graphite crucible using high-frequency induction casting device at T = 1290°C, and cast centrifugally in the casting ring with mineral phosphate investment._

After cleaning the casting, mechanical treatment, sandblasting and cleaning with a steam cleaner device were performed. The next step was to form a thin oxide layer on the surface of the alloy (Sn, In, Zn), to establish chemical bond between metal and ceramics. The metal bridge substructure was degassed and oxidized (without vacuum) at 930°C/10 min, washed in Neacid acid, and then cleaned with a steam cleaner device. The ceramic coatings were applied conventionally over several layers, which were fired separately in a VITA Vacumat 40 vaccum ceramic furnance at T= 900°C. After mechanical treatment and polishing, the metal-ceramic bridge was glazed to provide smooth and shiny surface appearance similar to that of natural teeth



Slika 2. Metalna konstrukcija mosta od četiri člana izrađen od dentalne legure sa visokim sadržajem Au
Figure 2. Metal substructure of four unit bridges made of dental alloy with high Au content

Rezultati

Dobijeni rezultati prikazani su u tabeli 1 i na slikama 3,4, 5, 6 i 7. Prosečna vrednost dobijenih rezultata merenja tvrdoće iznosi 170 HV5. Prosečni rezultati merenja mehaničkih karatkeristika za svih 12 nateznih epruveta (slika 3) prikazani su skupno u tabeli 1.

Tabela 1. Prosečne vrednosti različitih fizičkih karakteristika

Table 1. Mean values of different physical properties

	Granica tečenja $R_{p0.2}$ [N/mm^2]	Zatezna tvrdoća R_m [N/mm^2]	Raztezanje do (kidanja) pucanja A [%]
Au dentalna legura	630	710	9

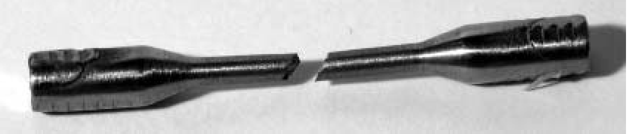
Prosečna vrednost dobijenih rezultata merenja koeficienta termalne ekspanzije CTE iznosila je oko $14,55\times10^{-6}K^{-1}$. Rezultati hemijske spektralne analize u tačkama nove dentalne legure u m.% su pokazali, na jednoj strani veći sadržaj Au (za oko 1,2 m.%), a na drugoj strani niži sadržaj Pt i Zn. Izrazito odstupanje je posebno prisutno kod Pt, pa je izmerena prosečna masa samo 10 m.%, dok je masa Zn ispod 0.5 m.%. Uzrok za takve rezultate kod Zn može da se pripiše izuzetno niskoj temperaturi isparavanja (beli dim tokom pretapanja u vakuumskoj komori). Vrednosti ostalih elemenata Ir, In, Rh, Nb i drugih su u okviru predviđene mase supstanci.

Makro-pregled odlivka pokazao je, da nema poroznosti i da odgovara dimenzijskim zahtevima, međutim mikroskopskim pregledom ustanovljeno je da je na pojedinim mestima jednog uzorka vidna poroznost metalne konstrukcije mosta (slika 4).

Na površinskom sloju keramike makro pregledom nisu ustanovljene nikakve poroznosti, dok su mikroskopskim uočene poroznosti u vidu mehurić na jednom uzorku.

Results

The results are shown in table 1 and figures 3,4,5,6 and 7. The mean value for material hardness was 170 HV5. Mean values for mechanical properties are presented in table 1.

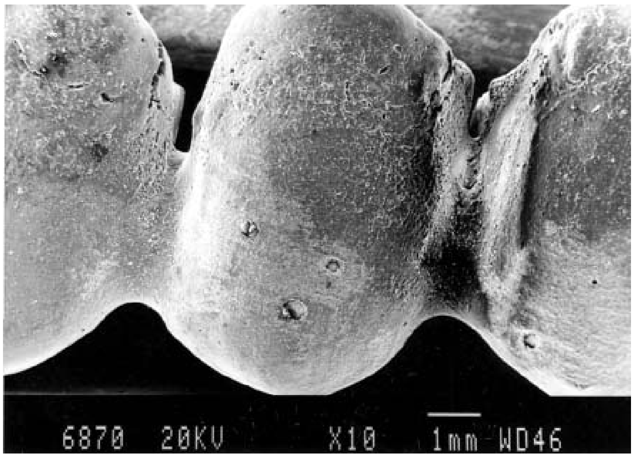


Slika 3. Natezna epruveta posle pucanja na nateznom aparatu
Figure 3. Tensile test tube after breakage of tensile device

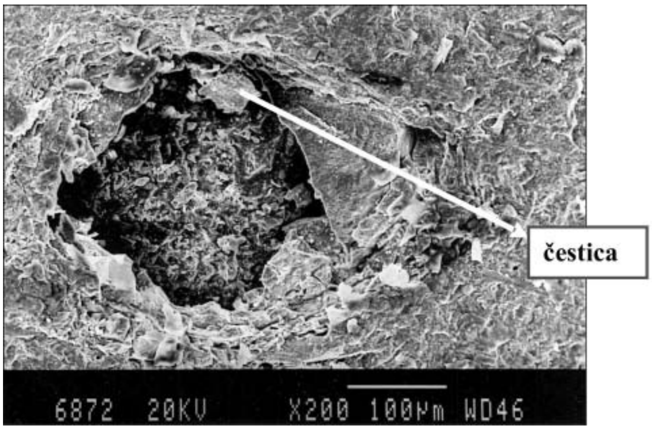
The mean value of CTE was $14.55\times10^{-6}K^{-1}$. The results of chemical spectral analysis in several points in the new dental alloy revealed higher content of Au (for about 1.2 w.%) and lower content of Pt and Zn. The mean mass values for Pt was 10 w.% and Zn below 0.5 w.%. The reason for such results was, in the case of Zn, exceptionally low evaporation temperature (white smoke during melting in a vacuum cylinder). The values for other elements Ir, In, Rh, Nb and others were within the range of anticipated limits for mass substances.

Macro-inspection of metal substructure showed no porosity and correspondence with dimensional requests. SEM examination showed visible porosity in some regions (figure 4).

Macro-inspection of the finished metal-ceramic bridge showeds no porosity, however, during SEM examination, one of the tested samples showed porosity in the ceramic layer (figure 5). Detailed examination of the ceramic layer's surface revealed two types of air or gas bubbles. The outside surface of the ceramic layer with distinct bubbles type I can be seen in figure 5.



Slika 4. Mikroskopska fotografija spoljašnje površine izlivene metalne konstrukcije mosta
Figure 4. SEM photograph of substructure surface of the metal bridge

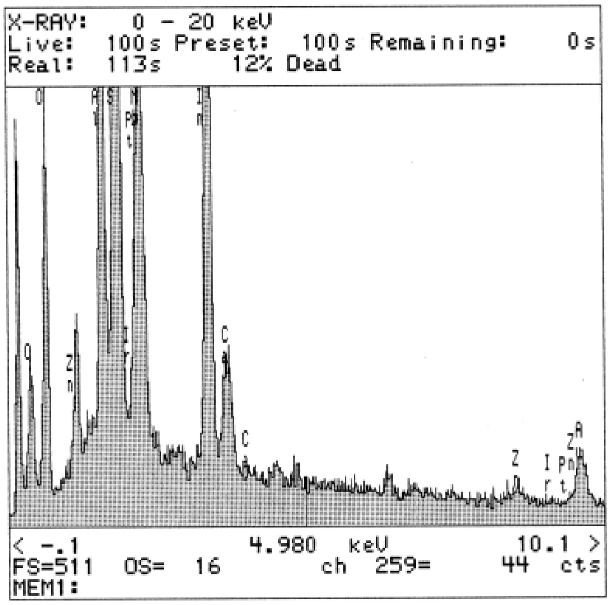


Slika 5. Mehurići na površini keramičkog sloja (tip I)
Figure 5. Bubbles on the ceramic layer surface (type I)

Na slici 5 prikazan je deo spoljašnje površine keramike, gde su prisutni izraziti mehurići I tipa (veći mehurići).

Na poroznim delovima keramike gde su uočene svetle čestice u mehurićima sprovedena je kvalitativna EDX analiza (slika 6) koja je pokazala prisustvo oksida sa mikroelementima u dentalnoj leguri.

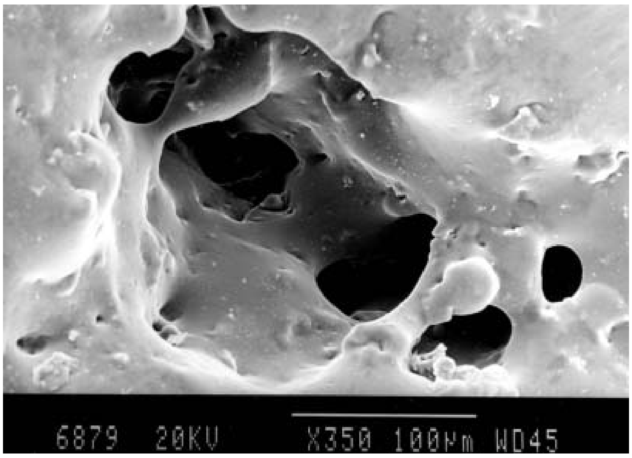
Some of the bubbles contained light particles of about 10 μm in diameter (figure 5). Most of them exhibited sharp edges and they were located at the outside margin of the bubbles. Qualitative EDX analysis (figure 6) confirmed oxides which formed microelements (components of dental alloy) in these regions.


```
X-RAY:    0 - 20 keV
Live:   100s Preset:   100s Remaining:     0s
Real:   113s      12% Dead
```
```
< -.1              4.980  keV          10.1 >
FS=511   OS=  16          ch  259=       44  cts
MEM1:
```

Slika 6. EDX – kvalitativna analiza u području unutrašnje poroznosti
Figure 6. . EDX-qualitative analysis in the area of internal porosity

Detaljnim pregledom mehurića tipa II, koji nisu vidljivi makroskoposki, ustanovljena je dendritska struktura veličine oko 100 µm. Mikroskopska analiza pokazala je da se ovaj vid poroznosti najverovatnije rasprostire kroz celu debljinu keramičkog sloja i da je područje u kome se nalaze ovi mehurići, pre svega na površini gornje bukalne strane članova mosta (slika 7).

Detailed examination of bubbles type II, unseen with the naked eye, showed dendritic structure and bubbles of around 100 µm in diameter. The examination showed that they probably spread through the whole ceramic layer and that the area with bubbles was located on the upper buccal side of the metal-ceramic bridge (figure7).



Slika 7. Mikroskopska fotografija unutrašnje poroznosti keramike (tip II)
Figure 7. SEM photograph of internal porosity in ceramics (type II)

Diskusija

Postupak dobijanja i tehnologija izrade nove dentalne legure je dosta složen. Pri samom livenju metalne konstrukcije mosta nije bilo većih problema. Makro pregledom odlivka nije ustanovljena nikakva poroznost dok je mikroskopskom analizom konstatovana poroznost na nekim mestima (slika 4). Pretpostavlja se da je do poroznosti došlo zbog kontrakcije legure pri njenom hlađenju i očvršćavanju. Makro-pregled završenog metal-keramičkog mosta je pokazao da nema poroznosti i da odgovara dimenzijskim i estetskim zahtevima. Međutim, pregledom pomoću elektronskog mikroskopa jednog od probnih uzoraka keramike ustanovljena je poroznost u keramičkom sloju. Pri detaljnom pregledu spoljašnje površine keramičkog sloja mosta, registrovane su dve vrste poroznosti u vidu mehurića (vakuola) - veća sa izrazitim mehurićima (tip I) i manja sa izrazito poroznom mikrostrukturom (tip II). Mikroskopski pregled ukazuje da je poroznost nastala zbog pritiska molekula gasa koji su u vidu okruglhi mehurića sa zatvorenom spoljašnjom ljuskom i u njima se nalaze različite čestice. U okolini mehurića ne zapažaju se pukotine, ali su prisutne manje pore. Uzrok za nastanak ove poroznosti može se pripisati neusklađenim koeficijentima termalne ekspanzije (CTE) dentalne legure i upotrebljene keramike. Pukotine u keramici su najverovatnije nastale usled pojave velikih unutrašnjih napona tokom hlađenja keramike, od temperature pečenja keramike do sobne temperature, i to posebno u međuspoju legure sa keramikom i na spoljašnjoj površini keramičkog sloja. Visoka unutrašnja napetost je posebno nepovoljna u metal-keramičkom međuspoju, jer kod velikog okluzalnog pritiska, može doći do odvajanja keramike od metala ili do pucanja keramike.

Discussion

There were no serious problems during casting of the bridge metal substructure. Macro-inspection of metal substructure showed no porosity and correspondence with dimensional requests. SEM examination showed visible porosity in some regions (figure 4). We suggest that this porosity might ahve occured beacuse of alloy contraction during cooling and hardening.

Macro-inspection of the finished metal-ceramic bridge showed no porosity and correspondence with dimensional and esthetic requests. However, during SEM examination, one of the tested samples revealed porosity in the ceramic layer. Detailed examination of the ceramic layer surface showed two types of air or gas bubbles – larger with distinct bubbles (type I) and smaller with clearly porous microstructure (type II). The porosity occured because of the pressure of air/gas molecules, which could be seen as round bubbles, with a closed outer shell and with different particles inside. There were no cracks in the bubbles'surroundings, but there were smaller pores.

Some of the bubbles had light particles of about 10 µm in diameter (figure 5). Most of them had sharp edges and they were placed at the outer margin of the bubbles. In those areas we performed qualitative EDX analysis (figure 6), which showed oxides which formed microelements (components of dental alloy). Microelements diffused through the outside surface of the ceramic layer and formed oxides with O and C during the oxidation process.

Pri tome je potrebno naglasiti da CTE keramike zavisi još i od brzine hlađenja nakon pečenja keramike. Sporo hlađenje metal-keramičkog mosta po pečenju keramike daje viši CTE keramike. U skladu sa tim može se zaključiti da ukoliko hlađenje nije obavljeno po ranije opisanim principima, dolazi do nastanka poroznosti (evidentno prilikom posmatranja obrađenog mosta). Kod pojedinih mehurića zapažene su svetle čestice veličine oko 10 µm (pogledati česticu na slici 5). One nisu okruglog oblika, većina ima oštre ivice i nalaze se na spoljašnjem rubu mehurića.

Na tim delovima sprovedena je kvalitativna EDX analiza (slika 6). Ona je pokazala prisustvo oksida sa mikroelementima koji se nalaze u dentalnoj leguri. Mikroelementi su prilikom procesa oksidacije zbog koncentracijskog gradijenta difundovali kroz spoljašnju površinu keramike, gde su sa O i C stvorili jedinjenja tzv. okside. U zabeleženom EDX spektru može se primetiti povećana koncentracija sledećih elemenata: C, O, Si, Nb, In i Ca. Mikroskopskim pregledom mehurića tipa II ustanovljena je dendritska struktura veličine oko 100 µm, koja se najverovatnije rasprostire kroz celu debljinu keramičkog sloja i da je područje u kome se nalaze ovi mehurići pre svega na površini gornje bukalne strane članova mosta (slika 7). Na istoj slici uočava se tipična porozna mikrostruktura, koja je po svoj prilici nastala zbog izlaska gasova kroz kristalnu rešetku keramičkog sistema, takođe, je vidljiva trajna plastična deformacija keramike koju je prouzrokovao izlazak gasova. Na temelju činjenice da okside stvaraju pre svega mikroelementi (Zn, Ir, In, Nb), može se zaključiti, da je temperatura oksidacije bila previsoka. Zbog previsoke temperature je za vreme pečenja keramike došlo do povećane brze difuzije mikrolegirnih elemenata iz dentalne legure ka spoljašnjoj površini keramičkog sloja. Time se rezerva elemenata O i C iz keramike potrošila, ili je bila preniska da bi svi mikroelementi uspeli da se vežu u čvrste okside. Zato se višak mikroelemenata, kao npr. Zn, izdvojio u obliku gasova koji su sa jedne strane ostali zarobljeni u kristalnoj rešetki keramičnog sistema, a sa druge strane su imali mogućnost prolaska kroz još nesinterovanu spoljašnju površinu opakera. Pri prolasku su prouzrokovali trajnu plastičnu deformaciju keramičkog sistema t.j. nastanak spoljašnje otvorene porozne mikrostrukture keramičnog sistema.

Detaljan pregled morfologije keramičkog sloja pokazao je da je morfologija dvojna. U manjim regijama gde je ravna, bez inkluzija i drugih defekata, može se govoriti o zadovoljavajućem kvalitetu površine, međutim morfologija keramičkog sloja je u većem delu izrazito stepenasta, šupljikava, porozna, sa različitim inkluzijama i česticama.

Zaključak

Na osnovu dobijenih rezultata može se zaključiti, da nova dentalna legura izrađena u Zlatarni Celje odgovara propisanim standardima u pogledu mehaničkih karakteristika i tvrdoće: $R_{p0.}$=630 [N/mm^2], R_m=710 [N/mm^2], A= 9%, 170 HV i da CTE (25-600°C) iznosi oko 14,55×10^{-6}K^{-1}.

Istraživanje ukazuje da je upotreba nove dentalne legure sa visokim sadržajem zlata za metal-keramiku, u

In the recorded EDX spectrum we observed increased concentrations of the following elements: C, O, Si, Nb, In and Ca. Detaliled examination of the bubbles type II, , showed dendritic structure and bubbles of around 100 µm in diameter.

The examination showed that they probably spread through the whole ceramic layer and that the area with bubbles was located on the upper buccal side of the metal-ceramic bridge (figure 7). Figure 7 reveals typical porous microstructure, formed because of the diffusion of gases through the crystal structure of the ceramic system. It could also be seen that gases caused permanent plastic deformation of ceramics. These oxides were formed by microelements (Zn, Ir, In, Nb) and due to this fact, we can conclude that the oxidation temperature was too high. High temperature during ceramics firing caused increased diffusion of micro-alloyed elements from the dental alloy to the outer surface of the ceramic layer. The reserves of the O and C vanished or they were too low for all micro-alloying elements to form hard oxides. So, excess microelements (as Zn) were separated as gases and remained captured in the crystal structure of the ceramic system. On the other hand, they could pass through still unsintered outer surface of ceramics – the opaque layer. Therefore, they caused permanent plastic deformation of the ceramic system, i.e. formation of outer opened-porous microstructure of the ceramic system.

A detailed examination of the morphology of ceramic layer revealed that morphology was twofold. In the smaller areas where it was flat, with no inclusions and other defects, surface quality was satisfactory but the morphology of the ceramic layer was largely inconsistent, with voids, pores, and different inclusions and particles.

Conclusions

It can be concluded from the results of this study that new dental alloy from Zlatarna Celje satisfies all required standards, regarding both mechanical properties and hardness $R_{p0.}$=630 [N/mm^2], R_m =710 [N/mm^2], A= 9%, 170 HV, and also CTE (25-600°C) – 14.55×10^{-6}K^{-1}.

The application of this new dental alloy with high gold content depends on adequate technology when firing ceramics. It is necessary to obtain accurate oxidation temperature and cooling rates of metal-ceramic restorations because, otherwise, different defects may appear. Two kinds of bubbles could be formed - larger with distinct bubbles (type I) and smaller with clear porous microstructure (type II), which lower the quality of the prosthodontic restoration and its long term success.

zubotehničkoj laboratoriji zavisna od pravilne tehnologije pečenja keramike. Pri tome se misli na pravilnu temperaturu oksidacije i režim hlađenja fiksne zubne nadoknade, jer u suprotnom može doći do nastanka različitih defekata. Uglavnom mogu nastati dve vrste mehurića (vakuola) - veći sa izrazitim mehurićima (tip I) i manji sa izrazito poroznom mikrostrukturom (tip II), što svakako smanjuje kvalitet same zubne nadoknade, a samim tim i njen vek trajanja u funkciji.

Zahvalnica. Razvoj Au-dentalnih legura odvija se u Zlatarni Celje d.d. u okviru međunarodnog istraživačkog projekta Eureka E!3555 DEN-MAT, u kome učestvuju pored Slovenačkih partnera, Fakulteta za mašinstvo Univerziteta u Mariboru i Zlatarne Celje d.d. i partneri iz Srbije i to Stomatološki fakultet Univerziteta u Beogradu, Zlatarna Celje Beograd d.o.o. i Zubotehnička laboratorija Wisil M Beograd. Isto tako deo navedenog rada je sufinansiran od strane slovenačke agencije ARRS u okviru projekta L2-7096-0795 sa naslovom: »Razvoj nove dentalne legure sa visokim sadržajem Au«, u kome učestvuju pored Fakulteta za mašinstvo Univerziteta u Mariboru i Zlatarne Celje d.d. i Katedra za inženjerske materijale i Katedra za toplotnu tehniku Prirodno-tehničkog fakulteta Univerziteta u Ljubljani. Rad je, takođe, deo Bilateralnog projekta SLO/SRB, sa naslovom: »The development of the production technology for new Au dental alloy«, čiju su rukovodioci Prof.dr Dragoslav Stamenković i dr. Rebeka Rudolf.

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