

Srebro - paladijeve ili paladij - srebrne slitine?

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Sažetak

Slitine na osnovi srebra i na osnovi paladija različito su dugo u uporabi za fiksno protetske radove. Kako bi se dokazalo da se zaista radi o dvjema različitim slitinama, provedene su mikrografske, SEM i EDX raščlambe kao i izmjerene su vrijednosti mikrotvrdoće odljeva (HV 0,2). Rezultati potvrđuju da se radi o dvjema slitinama koje se razlikuju po sastavu, strukturi odljeva, raspodjeli elemenata i vrijednostima mikrotvrdoće, te da ih se zato u praksi neopravdano terminološki poistovjećuje.

Ključne riječi: *slitina, mikrostruktura, mikrotvrdoća*

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Uvod

U terapijskim postupcima rekonstruktivne stomatologije kao građivni materijal upotrebljavaju se kovine. U fiksnoj protetici to su razne slitine, bilo kao samostalan konstrukcijski element bilo u kombinaciji s estetskim materijalima, polimerom i keramikom.

Uporaba čiste kovine, kao što je to npr. bilo zlato, pripada prošlosti. Međoća zlata, nedostatna antikorozivnost srebra, previsoko talište platine, nika-ko ne zadovoljavaju visoke statičke i estetske zahtjeve današnje rekonstruktivne stomatologije. No, kombinacijom dviju ili više kovina, tj. slitiniranjem, iskorištavaju se pozitivna i ujedno umanjuju loša svojstva pojedinog elementa te dobivaju slitine sa sasvim novim, traženim svojstvima (1,2,3).

Slitine su smjese kovine i kovine, ili kovine i nekovine, pri čemu prevladava kovinski karakter. Sva-

ku slitinu čini osnovna sastavnica koja je zastupljena u najvećem težinskom ili postotnom udjelu, i na temelju nje imenuje se pojedina slitina. Zbog potrebitih mehaničkih i inih svojstava doslitinirani su i drugi elementi, ali u manjim udjelima. Dugo su vremena slitine na bazi zlata bile slitine izbora, izraz bogatstva, odraz ljepote. Drugi je svjetski rat stvorio ekonomsku krizu koja je i u dentalnoj industriji potakla da se nađu zamjene, u prvome redu jeftinija rješenja. Pedesetih godina XX. stoljeća smanjuje se udio zlata a povećava srebra, paladija, platine.

Godine 1958. na tržištu se pojavila nova slitina koja se je sadržajem razlikovala od konvencionalnih zlatnih slitina. Bila je to slitina s oko 65% srebra i 25% paladija.

Slitine na bazi srebra sivo-bijele su boje, mehanički zadovoljavaju, lako se obrađuju, biološki su podnošljive. Srebro je kovina bijela sjaja, sivkaste boje, dobar je vodič topline i elektriciteta. Postojano

je na zraku, jer oksidira stvarajući pasivizirajući površinski sloj, što govori da plemenitost nije nužan ni dovoljan uvjet antikorozičnosti (2,5,6). To je razlogom što se srebro danas ne smatra plemenitom kovinom (6,7). U rastaljenju stanju apsorbira kisik, skrućivanjem ga otpušta, posljedica čega može biti porozan odljev. Da se spriječi apsorpcija plinova, a time i poroznost, te poboljša ljevljivost i antikorozičnost, tim se slitinama dodaje 5 - 10% zlata. Manji interval taljenja i bolja mehanička svojstva postižu se udjelom bakra, cinka, nikla, mangana, indija, kositra i kroma u iznosu do 10%.

Upravo dodatci neplemenitih sastavnica zahtijevaju pažljivu laboratorijsku obradu te slitine, a to čini i njezin nedostatak. Paladij pridonosi boljim mehaničkim svojstvima i postojanošću boje (2,8,9, 10,11). Zadnjih godina uporaba Ag-Pd slitina sve je manja, jer dentalna industrija nudi niz novih slitina koje potpunije ispunjavaju zahtjeve suvremene fiksne protetike.

Prva slitina na osnovi paladija pojavila se na dentalnom tržištu godine 1973., a patentirana je sljedeće, 1974., kao slitina namijenjena za kovinokeramičke radove (4, 12). Paladij je član platinske skupine kovina, sivo bijele boje, u usporedbi s platinom manje plemenit, nižega tališta, jeftiniji i manje gustoće. Pri svjetlo crvenom žaru reagira s klorom i fluorom stvarajući slabo topive soli, a u dodiru s dušikom i sumporom netopive fosfate i sulfide. Apsorbira veću količinu vodika, što izaziva poroznost odljeva. U dentalnim slitinama povećava interval taljenja i tvrdoću slitine. Danas se u nekim zemljama javljaju kontroverzna mišljenja o biološkom učinku paladija, zbog sumnje da se njegovi ioni oslobađaju u ustima te pritom stvaraju toksični i alergijski učinak na biološki medij (13,14). Opisano je 2-18% učestalosti osjetljivosti na paladij. Važno je pri tome napomenuti da je 93-100% ljudi osjetljivih na paladijeve ione osjetljivo i na nikal. Wirz sa sur. smatra da nije samo paladij odgovoran za toksični učinak, već su to i dodatci bakra, galija i indija. Paladijeve slitine namijenjene su isključivo za kovinokeramičke konstrukcije, pri čemu ostvaruju dobru vezu s keramikom. Indij očvršćuje slitinu i odgovoran je za vezu s keramikom. Kositar i galij povećavaju tvrdoću, ali na štetu smanjene elongacije. Odnos paladija i srebra u tome tipu slitine najčešće je 50-60% Pd i 28-40% Ag (4,5,15).

Dvije opisane vrste slitina: srebro - paladij- i paladij - srebrna slitina, u praksi se vrlo često termi-

nološki zamjenjuju. Zato je svrha ovoga rada da se na temelju usporedbe sastava, strukture i svojstava, bolje upoznamo s tim tipovima slitinama te tako uklone sve nedoumice u vezi s njihovom različitošću. Budući da te slitine danomice unosimo u biološki medij, cilj je rada i potaknuti da se donese zakon o uporabi dentalnih slitina u našoj zemlji koji bi veću odgovornost izbora i primjene kovinskih terapijskih sredstava prenio na terapeute, kao što je npr. u Americi i u nekim europskim zemljama.

Materijal i postupci

Analizirani uzorci izrađeni su iz tipičnih predstavnika pojedinih slitina: uzorak Ag-Pd slitine izrađen je iz materijala tvorničkoga naziva "Auropal" (Zlatarna Celje, Slovenija), a uzorak Pd-Ag slitine iz materijala tvorničkog naziva "Pangold Keramik N₂" (Hafner, Phorzheim, Njemačka).

Uzorci su modelirani u vosku i uloženi u uložni materijal. Za lijevanje Auropala upotrebljen je uložni materijal Neoduroterm 5 (Bayern, Basel, Švicarska) a za Pangold Keramik N₂ (U.M.C. Hafner Cehacat, Phorzheim, Njemačka) i oba uzorka lijevana su centrifugalno: Auropal u lijevaču (Zlatarna, Celje, Slovenija), a Pangold Keramik N₂ u lijevaču Modular 3N (Aseg Galloni, San Colombano, Italija). Veličina kovinskih pločica bila je 20 x 7 x 1 mm. Pločice su pjeskarene 250-mikronskim česticama Al₂O₃, a daljnja obrada ovisila je o potrebi samog ispitivanja.

Na tako pripremljenim uzorcima provedena je raščlamba mikrostrukture svjetlosnim mikroskopom Olympus BHSM-L-2 (Japan), raščlamba prijelomnih površina i površinske poroznosti uzoraka pretražnim elektronskim mikroskopom Phillips 515, te EDX raščlamba na Phillipsovom analizatoru PV 990. Od mehaničkih svojstava ispitana je mikrotvrdoća uzoraka metodom Vickers s opterećenjem od 200 g - HV0.2.

Rezultati

Kemijski sastav uzoraka

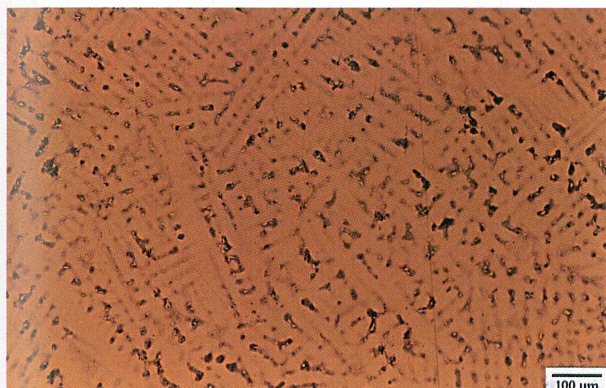
Od proizvođača analiziranih uzoraka dostupni su podatci o njihovu kemijskom sastavu. Oni su prikazani u Tablici 1.

Tablica 1. *Kemijski sastav uzoraka*Table 1. *Chemical composition of the samples*

Slitina Alloy	Ag, %	Pd, %	Au, %	Pt, %	Cu, %	In, %	Zn, %	Sn, %	Ga, %	Re, %
Auropal	64,0	25,0	2,0		6,0		<1			
Pangold Keramik N ₂	20,0	52,3	15,0	0,1		6,0		5,5	1,0	0,1

Raščlamba mikrostrukture, SEM i EDX raščlamba

Za raščlambu mikrostrukture uzorci su pripremljeni standardnim postupcima za tu vrstu materijala: brušeni na papiru do finoće zrna 600, polirani na DP-mol podlozi (Struers) s dijamantnim zrcima finoće 1/4 μm . Nagriženi su dvostupanjski: najprije u otopini NH₄ persulfata i H₂O, a zatim u otopini KCN i H₂O. Uzorci su potom oprani alkoholom i osušeni strujom topla zraka. Struktura je analizirana na svjetlosnom mikroskopu Olympus BHSM-L-2 i prikazana na Slikama 1 i 2.

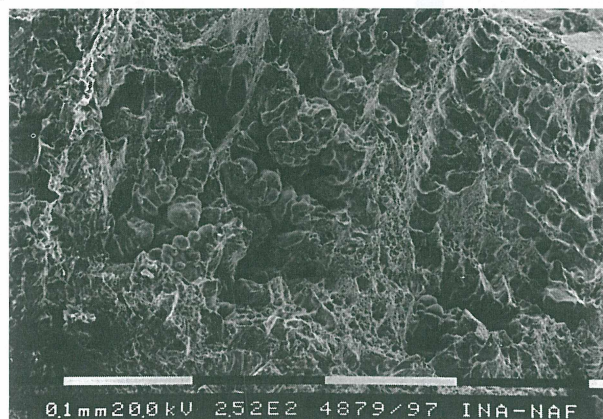


Slika 1. Mikrostruktura uzorka "Auropal"
Figure 1. Microstructure of the "Auropal" sample

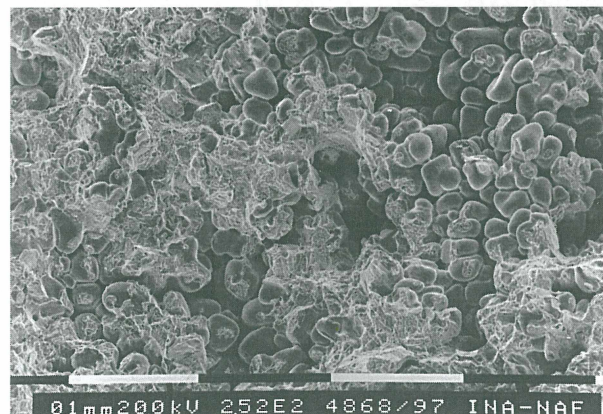


Slika 2. Mikrostruktura uzorka "Pangold Keramik N₂"
Figure 2. Microstructure of the "Pangold Keramik N₂" sample

Raščlamba mikrostrukture pokazuje bitno različitu strukturu Auropala i Pangold Keramik N₂, unatoč istim uvjetima nagrižanja. Dok Auropal pokazuje grubu dendritičnu strukturu (Slika 1), Pangold Keramik N₂ ima relativno homogenu strukturu s poligonalnim zrnima (Slika 2). Na granicama zrna obih slitina vidljive su nakupine, najvjerojatnije netopivih oksida i nižetaljivih udjela. Sličan rezultat pokazuju i SEM snimke (Slike 3 i 4).



Slika 3. SEM raščlamba uzorka "Auropal"
Figure 3. SEM analysis of the "Auropal" sample

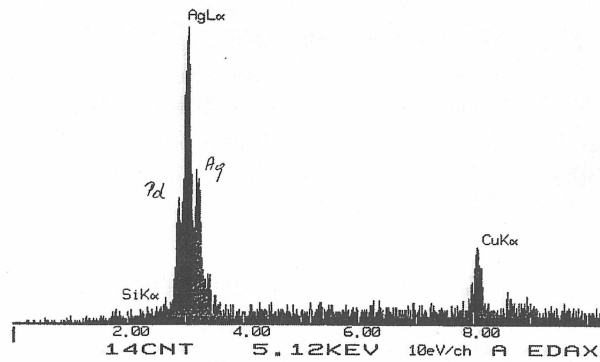


Slika 4. SEM raščlamba uzorka "Pangold Keramik N₂"
Figure 4. SEM analysis of the "Pangold Keramik N₂" sample

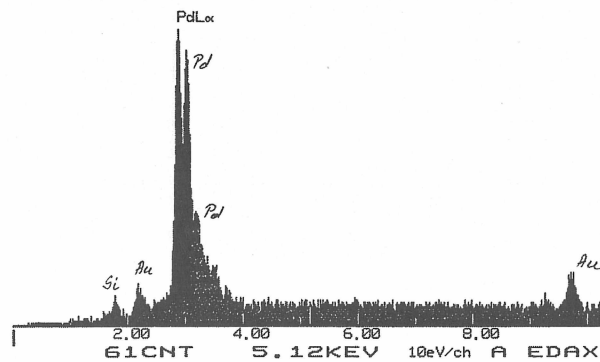
EDX raščlambom Auropala dokazano je puno bakra, srebra i silicija u lakunarnim ulošcima uzorka prikazanog na trećoj slici (Slika 5).

Bijela faza bogata je srebrom, paladijem i bakrom, ima nešto i cinka, dok u tamnoj fazi ima puno bakra i cinka (Slika 7).

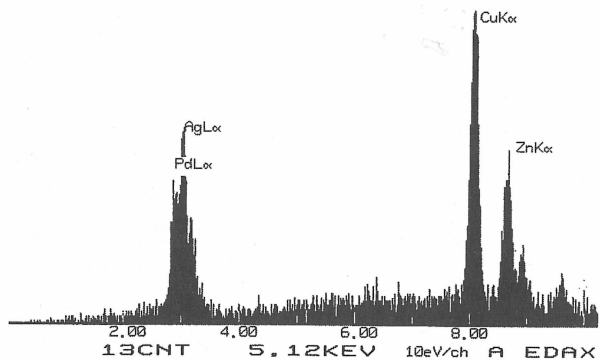
EDX analiza Pangold Keramik N₂ slitine na SEM snimci (Slika 4) pokazuje da u bijeloj fazi ima više silicija i paladija, a u tamnoj fazi ima više paladija, srebra i zlata (Slika 6).



Slika 5. EDX raščlamba uzorka "Auropal"
Figure 5. EDX analysis of the "Auropal" sample



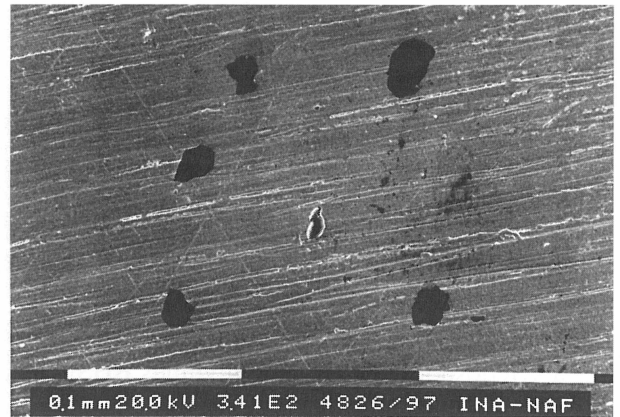
Slika 6. EDX raščlamba uzorka "Pangold Keramik N₂"
Figure 6. EDX analysis of the "Pangold Keramik N₂" sample



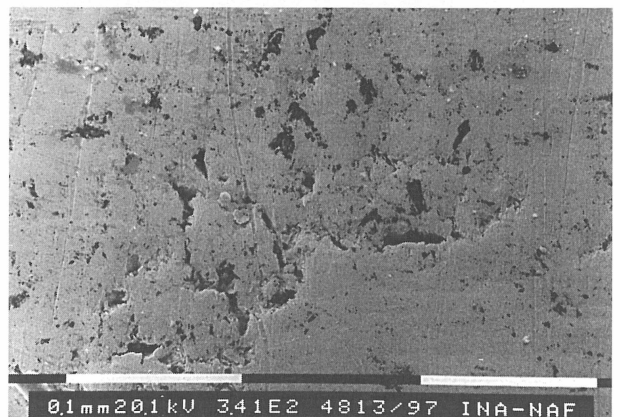
Slika 7. EDX raščlamba uzorka "Auropal"
Figure 7. EDX analysis of the "Auropal" sample

Auropal je pokazao malu površinsku poroznost. Pore su veličine 10 μm (Slika 8).

No, vidljive su i velike šupljine i mrlje, koje su sastavom iste kao i ostali dio strukture. Glede poroznosti, Pangold Keramik N₂ ima dosta šupljina, nejednoliko raspoređenih i različite veličine, od 10 do 38 μm (Slika 9).



Slika 8. Poroznost na uzorku "Auropal"
Figure 8. Porosity on the "Auropal" sample



Slika 9. Poroznost na uzorku "Pangold Keramik N₂"
Figure 9. Porosity on the "Pangold Keramik N₂" sample

Raščlamba svojstava uzoraka

Za usporedbu raščlanjenih uzoraka vrlo su važna i njihova mehanička i fizikalna svojstva. Neka su dostupna od samih proizvođača i prikazana su u Tablici 2.

Mikrotvrdoća uzoraka mjerena je metodom Vickers s opterećenjem od 200 g - HV0.2 i prikazana u Tablici 3.

Tablica 2. Mehaničke i fizikalne karakteristike uzorka

Table 2. Mechanical and physical characteristics of the samples

Svojstvo - Characteristic	Auropal	Pangold Keramik N ₂
Interval taljenja, °C - Melting interval, °C	960-1060	1150-1250
Gustoća, g/cm ³ - Density, g/cm ³	10,7	12,1
Konvencionalna granica razvlačenja, N/mm ₂ - Conventional border of elongation, N/mm ₂	520	545/685

Tablica 3. Mikrotvrdoća uzoraka

Table 3. Microhardness of the samples

Uzorak - Sample	HV0.2									Σx/9
	1	2	3	4	5	6	7	8	9	
Auropal	123	124	116	108	111	123	124	130	116	119,4
Pangold Keramik N ₂	203	225	218	215	218	206	215	215	222	215,2

Rasprava

Zna se da srebro i paladij stvaraju kontinuirani niz kristala mješanaca. No, metalografske snimke pokazuju nehomogenost odljeva Auropal slitine i razmjernu homogenost Pangold Keramik N₂ slitine u istim uvjetima hlađenja. Da Ag-Pd slitine kristaliziraju dendritično potvrđuju i navodi mnogih autora (2,10,16). Nehomogenost odljeva te slitine posljedica je razmjerno brzoga hlađenja (na zraku), postojanja sastavnica s velikim razlikama u točkama taljenja, te sklonosti dendritičnoj segregaciji. Međutim, Böningh i Walter (17) pišu o nehomogenoj, dendritičnoj strukturi i odljeva Pangold Keramik N₂ slitine, obrazlažući to time da u toj slitini nema sastavnica koje usitnjuju zrno, te je i struktura grubozrnata. Mnogi su autori jedinstveni u mišljenju da veliku pozornost treba obratiti i uvjetima lijevanja. Izvor topline i vrsta uložnoga materijala, uz uvjete hlađenja, također mogu utjecati na kakvoću odljeva (2,3,5,7,9,15,17,18,19,20). Tako Cohen sa sur. smatra da je Pd-slitinu bolje taliti mješavinom propana i kisika nego prirodnoga plina i kisika (15). No, razlike u ljevljivosti prije su odraz razlika u promjenama sastava slitine ili sastava uložnoga materijala negoli izvora topline. Dugo su se uložni materijali s ugljikom smatrali uzrokom krhkosti i poroznosti odljeva (21).

Srebro-paladijeve slitine mogu se gotovo potpuno homogenizirati dodatnom termičkom obradom, dok su podatci o homogenizaciji slitina na bazi pa-

ladija različiti. Tako Böningh i Walter (17) smatraju da se Pd-slitina ne može potpuno homogenizirati, a Payan sa sur. piše o potpunoj homogenizaciji nakon dva sata žarenja pri 1000 °C (21).

Izmjerene vrijednosti mikrotvrdoće slitina također govore o različitosti. Dok Auropal ima HV0.2 = 119, dotle je Pd-slitina gotovo dvostruko tvrđa (HV0.2 = 215). Auropal spada u tip III, a Pd-slitine se klasificiraju se u tip III ili tip IV.

Dentalne slitine sklone su umjetnom starenju ili precipitaciji. Živko (2) je dokazala maksimalne vrijednosti mikrotvrdoće Auropala nakon homogenizacije pri 800 °C tijekom 20 minuta i precipitacijskoga žarenja pri 350 °C tijekom 15 min (HV0.1 = 330). Syverud i Hero pišu o 900 °C /15 min kao uvjetima homogenizacije i 350 °C kao temperaturi precipitacije jedne Ag-Pd-Cu-Au slitine (16). Bessing sa suradnicima smatra da su optimalni uvjeti termičke obrade Ag-Pd slitine; temperatura homogenizacije 750 °C/15 min i precipitacije 400 °C/15 min (17), a Lenz piše o 850 °C/2 sata kao uvjetima termičke obrade ali bez potpune homogenizacije i o 425 °C kao temperaturi precipitacije, kada vrijednosti mikrotvrdoće odljeva porastu za 66% (10).

Rizik uporabe paladija u dentalnim slitinama čini se minimalnim, zbog vrlo malog otapanja paladija iz slitine što su pokazale *in vivo* i *in vitro* studije (13, 23). Fenomen pojave zelene boje dugo se dovodio u vezu s Pd-slitinama zbog otapanja srebrnog oksida u keramici. Bilo je to doba kada se na-

stojalo srebro potpuno izbaciti iz paladijevih slitina. I danas se paladijeve slitine dijele na one sa srebrom i one bez srebra.

Podatci proizvođača potvrđuju da srebro-paladijeve slitine u pravilu sadrže do 70% srebra, a Pd-slitine imaju 50-60% paladija. Unatoč svim poznatim pa i prikazanim različitostima u svojstvima često se dogode terminološke zamjene tih dviju slitina, na što upozorava i Goodacre (4). Tako, primjerice, Jochen sa sur opisuje Pd-slitinu namijenjenu pečenju keramike a naziva ju Ag-Pd slitinom, iako sadrži 54,5% Pd i 37,5% Ag (24). Isto čine i Hugget i Civjan (7).

Zaključak

Na osnovi raščlambe dobivenih rezultata može se zaključiti da se slitina na bazi srebra i slitina na bazi paladija razlikuju po sastavu, strukturi, mehaničkim (mikrotvrdoća) i fizikalnim svojstvima te po namjeni.

Auopal kristalizira dendritično, manje je tvrdoće i namijenjen je isključivo polimernom fasetiranju. Pangold Keramik N₂ ima homogeniji odljev, dvostruko veću tvrdoću i namijenjen je na pečenju keramike. Terapeut treba poznavati sastav svake slitine pa čak i uvjete njezine laboratorijske obrade da ne bi nastala terminološka zamjena koja može biti razlogom neadekvatne obrade i namjene pojedine slitine u protetskoj terapiji, ali može se dogoditi i nesnalaženje u slučaju neželjenih posljedica na organizam, inkorporacijom slitine čiji sastav se ne poznaje.

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Silver-Palladium or Palladium-Silver Alloys?

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Summary

Dental alloys based on silver and palladium have not been used equally long in fixed prosthodontics therapy. In order to prove that they really are two different alloys, micrographic, SEM and EDX analyses have conducted, and the values of the microhardness (HV 0.2) of casts been measured. Results show that they are two alloys which differ with regard to composition, microstructure, distribution of elements and values of microhardness, and that these terms are unjustifiably identified in practice.

Key words: *alloy, microstructure, microhardness*

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Introduction

In therapeutic procedures of reconstructive stomatology, metals are constantly used as construction materials. In fixed prosthodontics these materials are various alloys, either as separate construction elements or in combinations with aesthetic materials, polymers and ceramics.

The usage of pure metals such as gold is history. The softness of gold, the inadequate anticorrosion of silver and high melting point of platinum do not satisfy the high static and aesthetic requirements of modern reconstructive stomatology. However, combinations of two or more metals known as alloyage use the positive properties of these metals and simultaneously decrease the negative characteristics of some elements, resulting in alloys with completely new and desired required properties (1, 2, 3).

Alloys are mixtures of metal and metal or metal and non-metal, with greater metal characteristics. Each alloy is characterised by a main component, represented by the largest weight or percentage proportion, based on which it gets its name. Due to the needs of mechanical, physical and other properties, other elements are included in the alloy but in smaller proportions. Alloys based on gold have long been a matter of choice, a symbol of wealth and beauty. The second world war created an economic crisis which was reflected in the dental industry, and initiated research for alternative and mainly cheaper solutions. In the fifties of this century the proportion of gold was reduced and replaced by silver, palladium and platinum.

In 1958 a new alloy appeared on the market and was significantly different from conventional gold alloys. It was an alloy containing 65% of silver and 25% of palladium.

Alloys based on silver are mechanically satisfying, easy to process, and biologically tolerant. Silver is a white metal, a good conductor of temperature and electricity. It is stable on air due to its oxidation, creating a passive outer layer, which shows that the preciousness of a metal is not a necessary nor sufficient condition for anticorrosion (2, 5, 6). This is why today silver is not considered to be a precious metal (6, 7). In a melted form it absorbs oxygen, releasing it by cooling, which may result in a porous cast. In order to prevent the absorption of gases as well as porosity and to improve its castability and anticorrosion, 5 - 10% of gold is added to these alloys. A lower melting interval and better mechanical properties are obtained by a proportion of copper, zinc, nickel, manganese, indium, tin and chromium amounting to 10%. Specifically, the addition of base components necessitates careful laboratory treatment of this alloy, which is its main disadvantage. Palladium achieves better mechanical characteristics and stability of colour (2, 8, 9, 11). In recent years the usage of Ag-Pd alloys is less and less frequent, since the dental industry offers a range of new alloys which better fulfil the demands of modern fixed prosthodontics.

The first alloy containing palladium appeared on the dental market in 1973, and was patented a year later (1974) as an alloy developed for ceramics veneering (4, 12). Palladium belongs to the platinum group of metals. It is silvery-white in colour, less precious compared to platinum, of a lower melting point, cheaper and less dense. At a light red flame it reacts with chlorine and fluorine producing almost insoluble salts, and in contact with nitrogen and sulphur insoluble phosphates and sulphates. It absorbs a larger amount of hydrogen, resulting in porosity of the cast. In dental alloys it increases the melting interval and its hardness. However, controversial opinions about the biological influence of palladium have appeared in some countries, as it is suspected that this metal's ions are released in the mouth, creating a toxic and allergic effect on the biological media (13,14). Sensitivity to palladium reported amounts to a 2-18%. It is important to mention that 93 - 100% of the people sensitive to palladium ions are also sensitive to nickel. Wirz et al. believe that palladium is not the only element responsible for the toxic effect, and that additions of copper, gallium and indium are toxic as well. Palladium based al-

loys are intended for metal-ceramic constructions, since they bond well with ceramics. Indium hardens the alloy and is responsible for bonding with ceramics. Tin and gallium increase the hardness, but at the cost of a decrease in elongation. The proportion of palladium and silver in this type of alloy is usually 50 - 60% Pd and 28 - 40% Ag (4, 5, 15).

The names of the two types of alloys described: silver - palladium and palladium - silver are often identified in practice. The aim of this study was to get a better insight into these alloys, based on the comparison of their composition, structure and characteristics, and to eliminate all doubts in relation to their difference. As these alloys are constantly inserted into a biological medium, the need to establish a law on the usage of dental alloys in our country has also been a motive of this work, which would transfer most of the responsibility of the choice and usage of metal to therapeutics, as is the case in America and some European countries.

Material and Methods

The samples analysed consisted of two alloys: the Ag-Pd alloy sample consists of a material called "Auropal" (Zlatarna Celje, Slovenia), and the Pd-Ag sample of the material "Pangold Keramik N₂" (Hafner, Phorzheim, Germany).

The phosphate-bound investment material Neoduroterm 5 (Bayern, Basel, Switzerland) has been used for melting Auropal, and for Pangold Keramik N₂ (U. M. C. Hafner, Cehacat, Phorzheim, Germany). Both samples were casted by centrifuge; Auropal in the casting machine (Zlatarna Celje, Slovenia), and Pangold Keramik N₂ in casting machine Modular 3N (Aseg Galloni, San Colombano, Italy). The size of metal plates was 20 x 7 x 1 mm. These plates were sandblasted by 250-micro particles Al₂O₃, and further processing depended on the needs of the analysis itself.

The microstructure analysis of samples prepared in this way was conducted by a light optical microscope Olympus BHSM-L-2 (Japan), the analysis of fracture surfaces and surface porosity of the samples by a scanning electronic microscope (SEM) Phillips 515, and the EDX analysis on the Phillips analyser PV 990. As for the mechanical characteristics the microhardness of the samples was tested by a Vickers method with a load of 200 g - HV0.2.

Results

The chemical structure of the samples

The chemical composition of the samples, obtained from their manufacturers, are presented in Table 1.

Microstructure, SEM and EDX analyses

In order to conduct the microstructure analysis the samples were prepared according to standard procedures for this type of material: ground on with silicon carbide paper until the fineness of the granules became 600, polished on a DP-moll base (Stuers) with diamond granules of a 1/4 μm fineness. They were etched on two levels: first in the solution of NH_4 persulfate and H_2O , and later in the solution of KCN and H_2O . The samples were then washed with alcohol and dried by hot air. The microstructure was analysed on a light microscope Olympus BHSM-L-2 and shown in Figures 1 and 2.

The microstructure analysis shows the significantly different structure of Auopal and Pangold Keramik N_2 , despite the same etching conditions. While Auopal shows a rough dendritic structure (Figure 1), Pangold Keramik N_2 has a relatively homogeneous structure with polygonal grains (Figure 2). Small particles are visible along the grain boundaries, consisting probably of insoluble oxides and precipitates of a lower melting point.

A similar result was obtained by SEM images (Figures 3 and 4).

The EDX analysis of Auopal (Figure 5) shows a significant amount of copper, silver and silicon in the lacunar of the sample shown in Figure 3.

The white phase is rich in silver, palladium and copper, with traces of zinc, while the dark phase is reached in copper and zinc (Figure 7).

The EDX analysis of the Pangold Keramik N_2 alloy shows that the white phase contains more silicon and palladium, while the dark phase contains more palladium silver and gold (Figure 6).

Auopal showed slight surface porosity. The size of the pores is 10 μm (Figure 8).

However, large pores and stains are visible, in composition identical to the other parts of the struc-

ture. Regarding the porosity of Pangold Keramik N_2 , there are lots of pores of an irregular size and position from 10 to 38 μm (Figure 9).

Analysis of sample characteristics

The mechanical and physical characteristics of the samples analysed are very important for their comparison. Some of them are available from the manufacturers, and are shown in Table 2.

The microhardness of the samples was measured by the Vickers method with a load of 200 g - HV0.2, and is shown in Table 3.

Discussion

It is well known that silver and palladium form one-phased microstructures because of their complete solid solution series. However, micrographs show the unhomogeneous state of the Auopal alloy cast and relatively homogeneous state of the Pangold Keramik N_2 alloy in the same cooling conditions. Results obtained by numerous authors (2, 10, 16) confirm the dendritic crystallisation of Ag-Pd alloys. The heterogeneous state of this alloy's cast is a result of the relatively fast cooling (on air), the presence of components with significantly different melting points, as well as the tendency to dendritic segregation. However, Böningh and Walter (17) write about the unhomogeneous, dendritic structure of casted Pangold Keramik N_2 alloy, explaining that this alloy does not contain components fragmenting the grains, and the structure therefore contains large grains. Numerous authors agree that great attention should be given to the conditions of melting. The source of heat as well as the type of the investment material, in the conditions of cooling, may influence the quality of the cast (2, 3, 5, 7, 9, 15, 17, 18, 19, 20). Thus Cohen et al. consider that it is better to melt the Pd alloy with a propane/oxygen fuel source than with natural gas/oxygen (15). However, the melting differences are more a result of changes in the composition of the alloy or the composition of the investment material than the source of heat. The investment materials with carbon have long been regarded as the cause of the casts' fragility and porosity (21).

The silver-palladium alloys may almost totally become homogeneous by heat treatment, while the data on the homogeneity of alloys based on palladium is different. Thus Böningh and Walter (17) consider that the Pd alloy may not become completely homogeneous, while Payan et al. report about the total homogeneity after two hours of annealing at 1000 °C (21).

The measured values of the alloy microhardness also show differences. While Auropal has HV0.2 = 119, the Pd based alloy is almost twice as hard (HV0.2 = 215). Auropal belongs to type III, while Pd -alloy is classified as type III or type IV.

Dental alloys are likely to harden. Živko (2) has obtained maximal values of Auropal microhardness after homogenization at 800 °C for 20 minutes in normal atmosphere and after additional annealing at 350 °C for 15 minutes (HV0.1 = 330). Syverud and Hero write about 900 °C/15 minutes as conditions for homogeneity and 350 °C as the hardening temperature of one Ag-Pd-Cu-Au alloy (16). Bessig et al. consider that the optimal conditions for heat treatment of the Ag-Pd alloy are: homogenization at 750 °C / 15 minutes and annealing at 400 °C / 15 minutes (17), while Lenz reports about 850 °C / 2 hours as conditions for heat treatment without complete homogeneity and about 425 °C as the precipitation temperature, when the microhardness value of the cast increases by 66% (10).

The risk of using palladium in dental alloys seems minimal, due to the very small percentage of palladium melting from the alloy which has been shown both by *in vivo* and *in vitro* studies (13, 23). The "greening" phenomenon has long been connected to Pd alloys due to the melting of silver oxide

in the ceramics. The tendency at the time was to eliminate silver completely from palladium alloys. Still today palladium alloys are divided into those that contain silver and those that do not.

The manufacturer's data confirm that silver-palladium alloys in general contain up to 70% of silver, while Pd-alloys have 50-60% of palladium. Despite all established and reported differences, there is frequent identification of these two alloys, which has also been reported by Goodacre (4). Thus Jochen et al. describe the Pd-alloy as intended for firing ceramics, and call it an Ag-Pd alloy, although it contains 54.5% Pd and 37.5% Ag (24). Huget and Civjan do the same (7).

Conclusion

Based on analysis of the obtained results it may be concluded that an alloy based on silver and an alloy based on palladium differ in composition, structure, mechanical (microhardness) and physical properties and purpose.

Auropal crystallises dendritically, is less hard and is intended only for polymeric veneers. Pangold Keramik N₂ has a more homogeneous cast, is twice as hard and is intended for the firing of ceramics. Therefore it is absolutely necessary that therapeutics know the composition of each alloy and the conditions for its laboratory processing, in order not to identify these two terms, which may result in inadequate processing and usage of a certain alloy in prosthodontic therapy. It is also necessary to know the composition of the incorporated appliance, in the case of allergic reaction to it.