# Titan u stomatologiji

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Sažetak

*Uporaba titana u dentalnoj implantologiji potakla je istraživanja za njegovu primjenu i u stomatološkoj protetici. U ovome radu navedena su dobra svojstva titana, kao što su biokompatibilnost, otpornost na koroziju i niska cijena, kojima on potpuno može zamijeniti tradicionalne slitine za izradbu stomatoprotetskih radova. Titan ima i neke nedostatke, primjerice visoko talište i velika reaktivnost titanske taline s kisikom, što uzrokuje specifičan način obradbe i spajanja s estetskim materijalima (osobito keramikom). Rezultati kliničkih istraživanja potvrđuju njegova dobra svojstva, no ujedno upozoravaju i na poteškoće u njegovoj uporabi. Zbog toga treba nastaviti s kliničkim i laboratorijskim istraživanjima titana kako bi se poboljšala tehnologije izradbe i ekonomičnost primjene te bi se tako preciznije mogle odrediti indikacije za njegovu uporabu u sklopu raznih stomatoloških disciplina, posebice u stomatološkoj protetici.*

Ključne riječi: *titan, biokompatibilnost, klinička istraživanja, stomatologija*

## Uvod

U stomatologiji se kovine upotrebljavaju već nekoliko stoljeća. Najprije se je počelo rabiti zlato i njegove slitine. Zbog dentalne keramike i porasta cijene zlata, 60-ih su se godina pojavile zamjenske slitine, kao što su slitine na osnovi paladija, nikla i kobalta. No, uporabom tih zamjenskih slitina u ustima povećala se je opasnost od alergijskih i toksičnih reakcija na njih. Za neke slitine koje, primjerice, sadrže nikal i/ili berilij, utvrđena je i kancerogenost. Te su spoznaje potakle nova istraživanja, cilj im je bio pronaći nove slitine koje moraju imati visoku biokompatibilnost te poboljšana tehnološka i mehanička svojstva (1).

Budući da je biokompatibilnost titana bila već otprije poznata iz njegove uporabe u ortopedskoj kirurgiji, a dobra mehanička svojstva iz uporabe u zrakoplovnoj industriji, ranih se je 70-ih godina dogodio nagao razvoj dentalne implantologije i uporabe titana za dentalne implantate. Nakon toga titan se je počeo klinički istraživati i upotrebljavati, te je postao nezamjenjiva građa u dentalnoj implantologiji i maksilofacijalnoj kirurgiji (2).

To je pak potaklo daljnja istraživanja za širu uporabu titana u stomatologiji. Zbog njegove izvrsne biokompatibilnosti, otpornosti na koroziju, dobrih fizičkih i mehaničkih svojstava, te povoljne i cijene, posljednjih se je godina uporaba titana znatno povećala i u stomatološkoj protetici (2).

## Svojstva titana

Titan je kovina otkriven 1791. godine. Po rasprostranjenosti je četvrti strukturni element u Zemljinoj kori, iza aluminija, željeza i magnezija. Dobiva se iz rutila, koji je uz anatas i brukit najrasprostranjeniji i najstabilniji oksid titana. Danas se, međutim, najčešće dobiva metalurškim postupkom toplinskoga raspadanja titan-tetrajodida.

Titan je srebrnobijele boje. Talište mu je na 1668 °C, što je vrlo visoka temperatura koja zahtijeva posebnu tehnologiju obradbe. Gustoća mu je mala i iznosi 4,51 g/cm$^3$. Specifična toplina mu je 0,124, a koeficijent toplinskoga rastezanja je 4,49 cm/°C x $10^{-6}$. Stupanj čistoće titana koji se danas upotrebljava jest 99,5 - 99,7% (3).

Osim fizičkih svojstava titana, vrlo su važna i njegova mehanička svojstva. Vrijednost titanove tvrdoće prema Vickersu, iznosi 210. Čvrstoća mu je 530 MPa, a 0,1%-tna rastezljivost 15-24%. Vlačna je čvrstoća titana prije lijevanja 400-450 N/mm$^2$, a nakon lijevanja 750-900 N/mm$^2$ (3).

Mala gustoća i mala specifična težina, te velika rastezljivost, mala toplinska vodljivost i niska cijena ubrajaju se u dobre osobine titana. Uz to, titan ima, zajedno s tantalom, niobom i cirkonom, najbolju biokompatibilnost. Njegov neutralan okus, dobra rendgenska vidljivost i otpornost na koroziju izjednačavaju ga sa svojstvima zlata i njegovih slitina. Alergijske reakcije na titan nisu poznate (4, 5).

Titan na sobnoj temperaturi ima heksagonalnu kristalnu mrežicu ($\alpha$-faza). Zagrijavanjem titana na 882 °C $\alpha$-faza prelazi u $\beta$ kubičnu kristalnu strukturu. Ta je transformacija vrlo spora tako da se ponovnim hlađenjem kristalna struktura zadržava u $\beta$-fazi i na sobnoj temperaturi. $\beta$-faza ima nižu temperaturu taljenja, manje je reaktivna, ali ima slabija fizička i mehanička svojstva od $\alpha$-faze (4).

U krutome stanju titan nije reaktivan, no prigodom taljenja brzo reagira s kisikom. Vrijeme oksidacije je $10^{-3}$ sekunde, nakon čega mu se reaktivnost smanjuje na minimum (6). Zbog brzine reakcije oksidacija se stvara samo na površini taline, zbog čega se površinski sloj titana pretvara u titan-dioksid. Površinski sloj titan-dioksida debeo 100-200 µm poznat je pod nazivom *α-case* sloj. *α-case* sloj nije homogen i mnogo je tvrđi od čistoga titana, što dovodi do veće lomljivosti i postupnoga nastanka mikropukotina (2, 7).

Loša su svojstva titana: visoko talište, kemijska reaktivnost taline s kisikom, vodikom i dušikom, te srebrnobijela boja koja daje neestetski izgled metalno-keramičkim radovima. Oksidacija prigodom taljenja uzrokuje poroznost, a reakcija taline s fosfatnim materijalima za ulaganje uzrokom je krhosti odljeva. Titan ima mali toplinski koeficijent rastezanja, što stvara probleme pri spajanju titana s keramičkim estetskim materijalima. Reagira s fluoridima koji se upotrebljavaju u svrhu prevencije karijesa, a to je uzrokom promjene boje i korozije titanskoga rada (3, 5).

Titan se može upotrebljavati kao čista kovina i u slitini s drugim kovinama, a najčešće se miješa u slitinu sa srebrom, kobaltom, kromom, bakrom, željezom, manganom, paladijem i silicijem. Udio tih elemenata iznosi od 0-30 težinskih postotaka. Slitiniranjem se poboljšavaju mehanička svojstva titana, kao što su tvrdoća, rastezljivost i elastičnost. Fizička i mehanička svojstva titanskih slitina ovise i o udjelu elemenata u tragovima, kao što su kisik, željezo, dušik, vodik i ugljik (3). Istraživanja korozije titana i njegovih slitina pokazala su da postoji visoka otpornost na koroziju slitina titana koje sadrže plemenite metale (8, 9). Tomu u prilog ide činjenica da osobađanje atoma titana u usnoj šupljini iznosi $10^{-12}$ mola, što znači da bi trebalo oko 100.000 godina za dezintegraciju i gubitak funkcije protetskih radova na bazi titana koji su u ustima pacijenata (2).

U stomatološkoj protetici titan se upotrebljava za krunice, za konvencionalne i adhezivne mostove, kombinirane fiksno-mobilne radove, te za retencijske elemente suprastruktura implantata. Najčešće se rabi slitina titana s 20% Cr i 0,2% Si, te slitina titana s 25% Pd i 5% Cr. Te slitine imaju veliku čvrstoću, tvrdoću i rastezljivost.

U implantologiji se najčešće rabi čist titan i slitina titana s aluminijem i vanadijem, Ti-6Al-4V. Ona ima manju gustoću i čvrstoću od elementarnog titana, a tvrdoća, elastičnost, talište i specifična toplina su joj veći (7).

Glavni cilj implantiranja jest postići oseointegraciju implantata, što znači odgovarajuću kemijsku i mehaničku vezu između implantata i okolnoga koštanog tkiva (10). Površina implantata mora se obraditi tako da se poveća prijanjanje između implantata i kosti, što kvalitativno ubrzava proces oseointegracije. Jedna od najnovijih tehnika obradbe površine implantata jest obradba titanskom plazmom (5).

U ortodonciji se titan upotrebljava za izradbu bravica i raznih vrsta žica. Bravice se izrađuju iz titanskih slitina s različitim udjelom paladija, kroma i vanadija, a za izradbu žica rabi se titanska slitina s niklom poznata kao *memory* slitina. Slitine za izradbu bravica imaju veliku tvrdoću i čvrstoću, a memory slitine imaju veliku čvrstoću i elastičnost (11).

## Obradba titana

### *Lijevanje titana*

Glavni problemi u vezi s lijevanjem titana jesu visoko talište i reakcija titanove taline s kisikom. Titan se lijeva klasičnom metodom izgaranja voštanoga modela u materijalu za ulaganje.

Postoje tri sustava za lijevanje titana: tlačno-vakuumski sustav za lijevanje s odvojenim komorama za taljenje i lijevanje *(Castmatic)*, tlačno-vakuumski sustav za lijevanje s jednom komorom za taljenje i lijevanje *(Cyclarc)*, i centrifugalni sustav za lijevanje *(Tycast)* (12). Zbog brze oksidacije taline lijevati se mora uz nazočnost argona, koji je nereaktivan plin. U takvu je okružju lijevanje titana moguće s minimalnom oksidacijom (13).

Za lijevanje titana važan je i tlak argona. Herö i Waarli (14) ustanovili su da je poroznost rada znatno veća kod lijevanja pri tlaku argona od 50 mm Hg nego pri tlaku od 400 mm Hg.

Provedeno je i usporedno istraživanje svih triju sustava za lijevanje titana. Bessing i Bergman (12) ocijenili su centrifugalni sustav za lijevanje najboljim. Takahashi i sur. (15) također su došli do istih rezultata, no ujedno ističu, kao i Wirz (5), da je svaki sustav za lijevanje dobar u optimalnim uvjetima.

Sljedeći problem u tehnologiji lijevanja titana jest neodgovarajuće širenje materijala za ulaganje i njegova reakcija s titanskom talinom. Zbog neodgovarajućeg širenja materijala za ulaganje može se pogrešno odrediti obujam rada iz titana. Prigodom reakcije uložnoga materijala s titanom nastaje do oksidacija, pri čemu kisik prodire u površinski sloj taline, a to povećava površinsku mikrotvrdoću titana (15).

Herö i sur. (16) pokazali su da se fosfatni materijal za ulaganje dobro širi, s neznatnom pojavom površinskih oksida. Međutim, Takahashi i sur. (15) ustanovili su da fosfatni materijal za ulaganje s 20% kvarca omogućuje najbolju ljevljivost titana s najmanjim otvrdnjavanjem površine titana.

### *Proces hladne izradbe titanskih radova*

Zbog poteškoća u lijevanju titana Andersson i sur. (17) ponudili su drukčiji način izradbe titanskih radova. To je sustav *Procera* (Nobelpharma, Švedska), koji se sastoji iz dva postupka: strojnoga struganja i električnoga jetkanja.

Strojnim struganjem dobiva se vanjski izgled krunice, a električnim se jetkanjem ugljenom elektrodom oblikuje njezina unutrašnjost. Ta vrsta izradbe uključuje i dva posebna aparata. Jedan je glodalica, drugi je aparat za električno jetkanje.

Postupak strojnoga struganja i električnoga jetkanja traje 8-10 minuta. Pošto je rad gotov, provjerava mu se točnost na gipsanom odljevu, i ako je sve u redu, prelazi se na poliranje, te na nanošenje estetskog materijala.

### *Spajanje titanskih elemenata*

Provedena su mnoga istraživanja o spajanju titana i titanskih slitina. Spajanje titanskih radova obavlja se laserskim i plazma zavarivanjem. Objema je tehnikama moguće postići spojeve koji će izdržati djelovanje sila u žvačnoj funkciji (18).

Elementi za spajanje trebaju se učvrstiti posebnim instrumentom ili s pomoću materijala za ulaganje. Ne smiju se lijepiti cijanoakriličnim ljepilom, jer tako kisik i ugljik ulaze u strukturu spoja zbog čega on puca (18).

Roggensack i sur. (19) ispitivali su kakvoću i izdržljivost spojeva dobivenih laserskim i plazma zavarivanjem. Rezultati nisu pokazali znatnije razlike u kakvoći. No Wirz (18) ističe kakvoću laserskoga spajanja zbog užega područja djelovanja topline lasera.

Yamagishi i sur. (20) istraživali su ovisnost kakvoće spoja o okružju u kojemu se izvodi spajanje i o njegovu intenzitetu. Rezultati su pokazali da se titanski radovi moraju spajati u okružju argona, te da intenzitet spajanja ovisi o kakvoći lasera.

Berg i sur. (21) utvrdili su da nema bitne razlike u spoju zavarenih lijevanih titanskih radova, odnosno onih izrađenih tzv. *Procera* sustavom.

Svojstva spoja dobivenog laserom u okružju argona uz odgovarajuću snagu i intenzitet lasera mogu se usporediti sa svojstvima ostalog dijela metalnoga rada (18).

*Poliranje*

Prije nego što je otkriveno postojanje $\alpha$-case sloja klinička ispitivanja titanskih radova nisu davala zadovoljavajuće rezultate. No ti su radovi bili dobra podloga za stvaranje plaka (22). Kada je potvrđeno postojanje površinskog sloja titan-dioksida, tehnologije su lijevanja poboljšane kako bi se smanjile oksidacijske reakcije. Time se sloj titan-dioksida znatno smanjio, no njegovo se stvaranje ne može potpuno izbjeći. Nakon lijevanja ostaje još tanki $\alpha$-*case* sloj, koji se mora ukloniti kako bi se smanjilo stvaranje plaka na površini nadomjestka (23).

Poliranje se obavlja pomoću raznim sredstvima za poliranje. Broj okretaja rotirajućih sredstava uglavnom je manji nego za poliranje zlatnih slitina. Broj okretaja za početno poliranje je između 5.000 i 15.000 okretaja/min (za zlatne legure 30.000), za fino poliranje je također između 5.000 i 15.000 okretaja/min (za zlatne legure 30.000), a za poliranje do visokoga sjaja iznosi maksimalno 30.000 okretaja (za zlatne legure 30.000) (24).

Poliranje okluzijskih površina titanskih nadomjestaka teško je provesti, no njihova se morfologija može bolje sačuvati zbog manjeg gubitka materijala. Najbolji se rezultati postižu kompletom sredstava za poliranje *Dentaurum* (Njemačka) (24).

## Spajanje titana s estetskim materijalima

Prigodom izradbe djelomičnih proteza, kombiniranih fiksno-mobilnih radova, te osobito krunica i mostova, čvrstoća veze između kovine i estetskih materijala bila je u početku određen problem. Svrha daljnjeg istraživanja bila je poboljšati vezu između titana i estetskih materijala (akrilati, kompoziti, keramika) (2, 5).

Na čvrstoću veze estetskoga materijala i titana utječe nekoliko čimbenika; spoj metala i estetskoga materijala mora izdržati trajno djelovanje okluzalnih sila, neprekidni tijek sline, te promjene temperature (25).

Mudford i sur. (25) ispitivali su čvrstoću veze između akrilatne estetske obloge i površine titanskoga rada. Površinu titana obradili su na dva načina. Prvim su pjeskarili aluminij-oksidom veličine čestica 250 $\mu$m, a drugim su, uz pjeskarenje, nanosili silanski sloj, kao međusloj između estetskog materijala i površine titana. Rezultati su pokazali da je veza sa silanskim međuslojem mnogo bolja.

May i sur. (26) također su došli do istih rezultata usporedbom *silicoater* postupka i pjeskarenja aluminij-oksidom veličine čestica 110 $\mu$m.

Svrha istraživanja koje su proveli Caeg i sur. (27) bila je ispitati čvrstoću veze akrilata s titanom uspoređujući obradbu površine titana električnim jetkanjem i obradbu nanošenjem silanskog sloja na površinu titana. Ustanovili su da *silicoater* postupak daje bolje rezultate.

Wirz i sur. (4, 28) ističu da se *silicoater* postupak ne smije kombinirati ni s jednom vrstom uobičajenih mehaničkih retencijskih sredstava (perlice), jer on slabe snagu veze estetskog materijala s titanom.

Daljnja istraživanja imala su svrhu ispitati mogućnost spajanja dentalne keramike kao estetskog materijala s titanom. Postoji znatna razlika u koeficijentu toplinskoga širenja titana i estetskih materijala (Ti = 9,6 x $10^{-6}$/K; keramika = 13,7 x $10^{-6}$/K; akrilati = 81 x $10^{-6}$/K). Kao važan čimbenik jakosti veze titana s keramikom mora se uzeti u obzir i temperatura pečenja keramike. Najveći problem čini sloj oksida koji se stvara na površini titana pri pečenju keramike na cca 1000 °C, što oslabljuje vezu keramike i titana, a promjena kristalne rešetke titana u $\beta$-fazu slabi mehanička svojstva titana (4, 25). Zato je trebalo pronaći keramički materijal kojega temperatura pečenja pri nanošenju na titansku konstrukciju neće prelaziti 800 °C, kao što ističu Kirmura i sur. (29).

Adachi i sur. (30) ispitivali su pečenje dentalne keramike na temperaturama od 750-1000 °C i ustanovili da niža temperatura smanjuje stvaranje oksida i poboljšava vezu dentalne keramike s titanom.

Veza estetskih materijala (akrilata i keramike) s titanom ne ovisi o načinu izradbe titanskog rada. Prema Pangu i sur. (31), kakvoća veze jednaka je za radove dobivene lijevanjem titana i radove dobivene hladnom strojnom obradbom titana.

S obzirom na temperature pečenja keramike i ograničenja koeficijenta toplinskoga širenja, razvijaju se novi estetski materijali koji bi omogućili kliničku uporabu estetskih titanskih radova.

## Ocjena kliničke primjene titana u stomatologiji

U stomatologiji se je titan najprije počeo upotrebljavati u dentalnoj implantologiji. Proučavanjem njegovih bioloških svojstava i razvojem novih kirurških tehnika postao je nezamjenjiva građa za ugradnju endoosealnih implantata. Nakon dugogodišnjih istraživanja svojstava titana u okviru implantologije, rezultati su pokazali da bi se titan mogao upotrebljavali i u ostalim granama stomatologije, osobito u stomatološkoj protetici.

Pri izradbi suprastruktura implantata velik je problem predstavlja korozija. Njome se oslobađaju metalni ioni iz slitina, a oni, koji mogu negativno utjecati na organizam. Da bi se to izbjeglo, javila se potreba uporabe titana kao slitine za izradbu suprastruktura titanskih implantata, pa su se istraživanja usmjerila na proučavanje biomehaničkih odnosa titanskih implantata i titanskih suprastruktura te na razvoj titanskih estetskih radova (32).

Kod istraživanja fiksno protetskih radova iz titana svrha je bila ispitati točnost rubnoga prianjanja krunica, njihov anatomski oblik, površinu i boju, te usporediti lijevane i strojno izrađene titanske krunice.

Ida i sur. (33) ustanovili su da titanski nadomjesci imaju bolju točnost rubnog prianjanja od Ni-Cr slitina, a slabiju od Pd-Ag slitina.

Prema Blackmanu i sur. (34), prosječna odstupanja ruba titanske krunice od granice preparacije iznose 50 μm. Odstupanja su veća kod preparacija sa stubom od 90°, nego kod preparacija sa stubom od 45°.

Baez i sur. (35) došli su do istih rezultata. Prema njihovu istraživanju odstupanje rubova krunica kod preparacija sa stubom od 45° iznosi 7-100 μm, a kod preparacija sa stubom od 90° iznosi 8-196 μm. Ti se rezultati drže klinički dobrim.

Rubovi radova izrađenih strojnim postupkom *Procera* imaju prosječnu rubnu pukotinu veličine 270-750 μm kod preparacija sa stubom (36).

Harris i Wickens (37) ispitivali su točnost rubnoga prianjanja krunica dobivenih strojnom obradbom titana i lijevanih titanskih krunica. Rezultati su pokazali da nema znatne razlike.

Napravljene su mnoge kliničke studije titanskih radova. Andersson i sur. (17) su godinu dana nakon cementiranja estetskih protetskih radova iz titana ponovno pregledali pacijente i ustanovili da je 99,5% radova izvrsno prianjalo, 98,9% bilo je nepromijenjena anatomskog oblika, a 96,8% radova imalo je nepromijenjenu površinu i boju.

Kaus i sur. (38) proveli su 30-mjesečno istraživanje kliničkoga ponašanja lijevanih titanskih estetskih radova. Došli su do sljedećih rezultata: kod 85% krunica i 59% mostova nije bilo promjena površine i boje, a rub krunica bio je klinički prihvatljiv, dok 25,9% radova nije bilo klinički prihvatljivo. Titanske krunice pokazale su se dugotrajnijima od titanskih mostova.

Nilson i sur. (39) napravili su dvogodišnju studiju s estetskim tzv. *Procera* krunicama. Ispitivali su nastanak loma keramike, promjenu boje, anatomske oblike i rubove krunica. Dobiveni rezultati nisu se razlikovali od rezultata istraživanja na estetskim lijevanim titanskim krunicama.

Bergman i sur. (40) proveli su dvogodišnje istraživanje s tzv. *Procera* krunicama na koje je nanesen kompozit kao estetski materijal. 5,2% krunica imalo je lom kompozita, 70% krunica imalo je zadovoljavajući anatomski oblik, 83% imalo je zadovoljavajuće rubno prianjanje, a 96,8% krunica boja i površina nisu se promijenile.

Važnost male tvrdoće i modula elastičnosti titana očituje se nakon završnoga cementiranja titanskih radova, jer omogućuju laku i brzu okluzalnu prilagodbu. Tvrdoća i elastičnost titana olakšavaju i skidanje starih cementiranih krunica (40).

Osim u fiksnoj protetici, titan se počeo upotrebljavati i za fiksno-mobilne protetske radove te za izradbu retencijskih sredstava. Višečlani fiksni protetski radovi poduprti nekolicinom implantata danas često zamjenjuju mobilne djelomične i potpune proteze. Dostupnost takvih dodatnih potpornih sredstava znatno je proširila mogućnosti izradbe fiksnih protetskih radova (32, 36).

Wirz i sur. (41) rabe fiksno-mobilne radove iz titana kao suprastrukture titanskih implantata. Ovisno o broju i rasporedu implantata izrađuju se lijevane titanske suprastrukture. Kao retencijsko sredstvo upotrebljavaju se lijevane prečke koje služe za retenciju proteze. Prema Wirzu i sur., svi dijelovi fiksno-mobilnih titanskih suprastruktura, to jest baza, spojke i upirači, lijevaju se iz titana, a kvačice se lijevaju iz Co-Cr slitina. Lijevane kvačice ne izrađuju se iz titana jer on ima nizak modul elastičnosti.

Usporedno istraživanje mehaničkih svojstava kvačica lijevanih iz čistoga titana, iz Ni-Cr slitina i Co-Cr slitina, koje su proveli Hummel i sur. (42), pokazalo je da je elastičnost titanskih kvačica manja od elastičnosti kvačica iz Co-Cr slitina, a veća od elastičnosti kvačica iz Ni-Cr slitina. Retencijska sila lijevanih titanskih kvačica veća je od retencijske sile kvačica iz ostalih dviju slitina. Pri usporedbi retencijske sile kvačica lijevanih iz titanske slitine Ti-6Al-4V i kvačica lijevanih iz Co-Cr slitina sila je najprije mjerena pri prvom stavljanju proteze, a zatim nakon 500 skidanja proteze. Kvačice lijevane iz titanske slitine imaju jaču retencijsku silu od kvačica iz Co-Cr slitina.

Za lijevanje djelomičnih proteza i baza potpunih proteza iz titana debljina kovina mora biti 0,70 mm. Lijevati baze proteza iz titana teže je nego iz Co-Cr slitina, jer se mora rabiti deblji vosak kako odljev ne bi bio porozan (43).

Wakabayashi i Minoru (44) upotrebljavaju 0,75 mm debeli vosak za lijevanje titanskih baza djelomičnih proteza tvrdeći da je samo uz tu debljinu voska moguće dobiti neporozan odljev.

Blackman i sur. (45) ispitivali su dimenzijske promjene prigodom lijevanja titanskih baza djelomičnih proteza. Izmjerene su promjene volumena od 2,6% vodoravno i 1,8% okomito. Zbog tih razmjerno visokih postotaka mora se nastaviti s istraživati čimbenike koji stvaraju dimenzijske promjene pri lijevanju titanskih baza djelomičnih proteza kako bi se ono moglo nadzirati.

Provedena su i klinička istraživanja na kombiniranim fiksno-mobilnim protetskim radovima iz titana. Trogodišnje kliničko ispitivanje titanskih djelomičnih proteza pokazalo je da se mehanička svojstva protetskoga rada nisu promijenila, jedino se mogla opaziti blaga promjena boje površine titanskoga rada (44).

Dvogodišnja klinička studija pratila je ponašanje laserski spojenih titanskih baza proteza. Kontrola protetskih radova u 87 pacijenata nakon dvije godine pokazala je da je jedna baza pukla. Drugih promjena na protetskim radovima nije bilo. Zanimljivo je da je više implantata izgubljeno ispod laserski spojenih proteza nego ispod lijevanih proteza (46).

Većina bravica koje se upotrebljavaju u ortodonskoj mehanoterapiji izrađuje se iz kovine zbog njezine mehaničke snage i jednostavne izradbe različitih oblika bravica. Budući da se plastične bravice izobličuju zbog apsorpcije vode i djelovanja torzijalnih sila, a keramičke bravice abradiraju antagonističke zube, rješenje problema je izraditi titanske bravice koje imaju visoku biokompatibilnost i neutralnu boju (47). Titanske se bravice mogu vrlo dobro vezati s površinom zuba pa su zato vrlo važne u kliničkoj uporabi (11).

## Zaključak

Izvrsna svojstva titana, kao što su visoka biokompatibilnost, otpornost na koroziju, niska toplinska vodljivost, tvrdoća, mala gustoća, mala težina, neutralan okus, dobra rendgenske vidljivost i prihvatljiva cijena, čine ga modernim materijalom u stomatologiji. Do danas nije opažen ni jedan slučaj sustavne ili lokalne, alergijske ili toksične reakcije na titan i njegove slitine.

Titan ima i neka loša svojstva: niski modul elastičnosti, visoko talište i ekstremnu reaktivnost taline s kisikom. To uvjetuje promjene u tehnologiji lijevanja i obradbe titana. Problemi se javljaju i pri vezanju estetskih materijala za površinu titana. Vezanje estetskih materijala s titanom pokazuje dobre rezultate ako se kao estetski materijal upotrebljavaju akrilati i kompoziti, a rezultati vezanja s keramikom su slabiji. Jedna od dodatnih poteškoća jest i visoka cijena uređaja za lijevanje, strojnu obradbu i zavarivanje titana.

Iako se titan već široko rabi u dentalnoj implantologiji i ortodonciji, u protetici se još uvijek ne rabi mnogo. Rezultati kliničkih ispitivanja pokazuju da se lijevanjem i strojnom izradbom titanskih radova može dobiti protetski rad zadovoljavajuće kakvoće, no da bi se potpuno ispitala njegova učinkovitost, a time i mogućnost da zamijeni postojeće kovine, treba nastaviti s istraživanjima.

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# Titanium in Dentistry

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Summary

*Application of titanium in dental implantology encouraged research into its use also in restorative dentistry. This paper describes the advantages of titanium, such as its biocompatibility, resistance to corrosion and low price, by which it can completely replace traditional alloys in dental restoration (production). Titanium also has certain disadvantages, like a high melting-point and extreme reactivity with oxygen in its molten state, which calls for specific technology of processing and bonding with aesthetic materials (especially ceramics). Results of clinical investigations confirm its advantageous properties, and at the same time point to difficulties in its application. This is the reason why it is necessary to continue with clinical and laboratory research on titanium, in order to improve its production technology and economical application, so that indications for its application within various branches of dentistry, especially prosthetic dentistry, can be more precisely determined.*

Key words: *titanium, biocompatibility, clinical investigations, dentistry*

## Introduction

In dentistry metals have been used for centuries. At first gold and its alloys were used. With the introduction of dental ceramics and with the rise in the price of gold, substitute alloys were developed in the 1960s, such as alloys based on palladium, nickel and cobalt. However, with the application of these substitute alloys in oral surroundings, the danger of allergic and toxic reactions to them increased. Some alloys, which contain nickel and/or beryllium, were found to be carcinogenic. This has stimulated new research, the aim of which was to find new alloys that would have high biocompatibility, as well as improved technological and mechanical properties (1).

Since titanium's biocompatibility was already known from its use in orthopaedic surgery, and its excellent mechanical properties from its use in the airation industry, the early 1970s rapid development of dental implantology occured and use of titanium for dental implants. In the following years titanium was clinically investigated and applied, and has since become an irreplaceable material in dental implantology and maxillofacial surgery (2).

This has encouraged further research aiming at a wider application of titanium in dentistry. Due to its excellent biocompatibility, resistance to corrosion, good physical and mechanical properties, as well as price, in recent years the use of titanium has also considerably increased in prosthetic dentistry (2).

## Properties of Titanium

Titanium is a metal discovered in 1791. According to its spread, it is the fourth structural element in the earth's surface, after aluminium, iron and magnesium. It is produced from ruthile, which is, together with anatas and brouxite, the most widespread and stable titanium oxide. Today, however, it is mainly produced by the metallurgical procedure of thermal decomposition of titanium-tetraiodinum.

Titanium is silver white. Its melting-point is at 1668 °C, which is a very high temperature, calling for specific processing technology. The density of titanium is low and amounts to 4.51 g/cm$^3$. Its specific heat is 0.124, and the coefficient of thermal expansion amounts to 4.49 cm/°C x $10^{-6}$. The degree of purity of the titanium used today is 99.5-99.7% (3).

Beside the physical, properties the mechanical properties of titanium are also very important. Titanium's hardness according to Vickers amounts to 210. Its strength is 530 MPa, and its 0.1%-elasticity 15-24%. The yield strength of titanium before casting is 400-450 N/mm$^2$, and after casting to 750-900 N/mm$^2$ (3).

Low density and low specific weight count are the advantages of titanium, as well as its great elasticity, low thermal conductivity and low price. In additions, titanium, together with tantalum, niobium and zirconium, has superior biocompatibility. Its neutral taste, good radiographic visibility and resistance to corrosion equals the properties of gold and its alloys. There has been no reports of allergic reactions to titanium (4, 5).

At room temperature titanium has a hexagonal crystalline structure ($\alpha$-phase). By heating titanium to 882 °C, the $\alpha$-phase is transformed into a $\beta$ cubic crystalline structure. This transformation is very slow, so that when cooled down again, the crystalline structure remains in the $\beta$-phase even at room temperature. The $\beta$-phase has a a lower melting temperature, is less reactive, but has poorer physical and mechanical properties than the $\alpha$-phase (4).

In solid state titanium is not reactive, but during melting it becomes extremely reactive with oxygen. The oxidation time is $10^{-3}$ seconds, after which its reactivity is reduced to the minimum (6). Due to the short reaction time, the oxidation reaction takes place only on the surface of the mould, so that the surface layer of titanium changes into titanium dioxide. The surface layer of titanium dioxide is 100-200 $\mu$m thick, and it is known as $\alpha$-case layer. $\alpha$-case layer is not homogeneous and is much harder than pure titanium, which results in higher fragility and leads to a gradual development of microfractures (2, 7).

Titanium's disadvantages are its high melting-point, chemical reactivity with oxygen, hydrogen and nitrogen in its molten state, as well as its silver white colour, which does not look aesthetic in metallic-ceramic restorations. Oxidation during melting causes porosity, and reactivity of molten titanium with phosphate investment materials results in a fragile cast. Titanium has got a low coefficient of thermal expansion, which causes problems in bonding with ceramic aesthetic materials. Titanium reacts with fluorides, which are used for the prevention of caries, which cause a change in colour and corrosion of titanium restorations (3, 5).

Titanium can be used as a pure metal and in combination with other metals. It is most commonly alloyed with silver, cobalt, chromium, copper, iron, manganese, palladium and silicon. The share of these elements is 0-30 weight percentages. Alloying improves themechanical properties of titanium, such as its hardness, flexibility and elasticity. Physical and mechanical properties of molten titanium depend also on the share of trace elements, like oxygen, iron, nitrogen, hydrogen and carbon (3). Studies concerned with the corrosion of titanium and its alloys have shown that there is a high resistance to corrosion of precious alloys of titanium (8, 9). This is justified by the fact that the release of titanium atoms in oral surroundings amounts to 10-12 mol, which means that it would take ca 100000 years for loss of integrity and function of a titanium based restoration in a patient (2).

In prosthetic dentistry titanium is used for crowns, conventional and adhesive bridges, combined fixed-removable restorations and for retention elements of implant superstructures. A titanium alloy with 20% of Cr and 0.2% of Si and a titanium alloy with 25% of Pd and 5% of Cr are most commonly applied. These alloys persens grreat hardness, strength and elasticity.

Pure titanium and a titanium alloy with aluminium and vanadium, Ti-6Al-4V, are mainly used in dental implantology. This alloy is less dense and strong than pure titanium, but its hardness, elasticity, melting-point and specific heat are greater (7).

The main goal of implanting is to achieve osseointegration of implants, which means an adequate chemical and mechanical bond strength between an implant and surrounding bone tissue (10). The implant surface must be processed in order to gain better implant-bone interface, which qualitatively speeds up the osseointegration process. One of the most recent processing techniques is by titanium plasma (5).

In orthodontics titanium is used for the production of brackets and various types of wires. Brackets are made of titanium alloys containing a different share of palladium, chromium and vanadium, whereas for wires production a titanium alloy with nickel is used, known as *memory* alloy. Alloys for bracket production have great hardness and strength, while *memory* alloys have great strength and elasticity (11).

## Processing of Titanium

### *Casting of titanium*

The main problems associated with casting titanium are its high melting-point and the reactivity of molten titanium with oxygen. Titanium is cast by a classic method of burning a wax model in the investment material.

There are three different systems for casting of titanium: a pressure-vacuum casting system with separate chambers for melting and casting *(Castmatic)*, a pressure-vacuum casting system with one chamber for melting and casting *(Cyclarc)* and a centrifugal casting system *(Tycast)* (12). Due to the fast oxidation of the mould, casting must be performed in a medium with argon, which is a non-reactive gas. In such atmosphere casting is possible with a miminum possibility of oxidation (13).

Argon gas pressure is also important for casting titanium. Herö and Waarli (14) established that the porosity of a restoration is considerably greater when casting is performed under argon pressure of 50 mm Hg than under pressure of 400 mm Hg.

Parallel research of all three systems for casting titanium has been conducted. Bessing and Bergman (12) assessed the centrifugal casting system as the best. Takahashi et al. (15) came to the same conclusion, at the same time pointing out, as well as Wirz (5), that any casting system is statisfactory in optimal conditions.

Another problem in casting technology is inadequate expansion of the investment material and its reaction with molten titanium. Inadequate expansion of the investment material can result in false determination of the volume of a titanium restoration. During the reaction of the investment material with titanium, oxidation reaction takes place, and oxygen penetrates into the surface layer of the mould, which results in higher surface microhardness of titanium (15).

Herö et al. (16) showed that the phosphate investment material gives adequate expansion with negligible surface oxides. However, Takahashi et al. (15) established that the phosphate investment material, with 20% of quartz, enables the best castability of titanium with minimum hardening on the surface of titanium.

### *Process of cold production of titanium restorations*

Due to problems in titanium casting, Andersson et al. (17) offered an alternative for titanium restorations production. This is the *Procera* system (Nobelpharma, Sweden), which comprises two procedures: milling and spark erosion.

The outer shape of the crown is formed by milling, and the inner surface is processed by spark erosion with a carbon electrode. This type of production includes two special tools; a milling machine and a spark erosion apparatus.

The process of milling and spark erosion lasts for 8-10 minutes. After the restoration is finished, its accuracy is proved on a plaster cast, and if it corresponds, polishing and bonding with aesthetic materials can be performed.

*Joining of titanium elements*

Various studies on the joining of titanium and its alloys have been undertaken. Joining of titanium restorations is performed by laser or plasma welding. With both techniques it is possible to create joints capable of enduring stresses resulting from chewing activity (18).

The elements for joining must be fixed using a special instrument or by means of the investment material. They must not be glued together with a cyanoacrylic resin, since this causes inclusion of oxygen and carbon into the structure of the joint, which can result in fractures (18).

Roggensack et al. (18) examined the quality and endurance of joints created by laser and plasma welding. The results did not show any considerable differences in quality. Wirz (18), however, strenses the quality of laser welding because of the thinner heat-affected zone.

Yamagishi et al. (20) investigated the dependence of joint quality on the atmosphere in which welding is performed, as well as on its intensity. The results showed that welding of titanium must be performed in an argon atmosphere, and that the intensity of welding depends on the laser quality.

Berg et al. (21), found no relevant difference between joints of welded titanium castings and titanium castings produced by the so-called *Procera* system.

The properties of a joint created by laser in an argon atmosphere with an adequate power and intensity of the laser, can be compared to the characteristics of other metallic parts of the restoration (18).

*Polishing*

Before the existence of the α-case layer had been determined, clinical trials of titanium restorations did not offer satisfactory results. Such restorations had large affinity to plaque deposits (22). After the existence of the superficial titanium dioxide layer had been confirmed, casting technologies were improved in order to minimize the oxidation reactions. The titanium dioxide layer was considerably reduced, but its formation cannot be completely avoided. After casting there is still a thin residual α-case layer, which must be removed in order to reduce the plaque build-up on the restoration surfaces (23).

Polishing is performed by means of various polishing kits. The revolution rates are mainly lower than those required for polishing gold alloys. The revolution rates for smoothness are between 5 000 and 15 000 rpm (for gold alloys 30 000), for fine polish they are also between 5 000 and 15 000 rpm (for gold alloys 30 000) and for high polish they amount to a maximum 30 000 revolutions (for gold alloys 30 000) (24).

Polishing of occlusal surfaces of titanium restorations is difficult, but their morphology can be better preserved because of the lower material reduction. The best results are achieved by the *Dentaurum* polishing kit (Germany) (24).

## Bonding of Titanium to Aesthetic Materials

When constructing partial dentures, combined fixed-removable restorations and especially crowns and bridges, the bond strength between the metal and aesthetic material was at first an issue of concern. Further research was oriented towards improvements in bonding titanium to aesthetic materials (PMMA, composite resins, ceramics) (2, 5).

Several factors influence the bond strength between the aesthetic material and titanium; the joint of the metal and aesthetic material must withstand continual exposure to occlusal forces, constant flow of saliva and temperature variations (25).

Mudford et al. (25) examined the bond strength between a PMMA aesthetic veneer and titanium restoration surface. The titanium surface was processed in two ways. The first was by sandblasting with 250 μm aluminium oxide, whereas the second included, beside sandblasting, application of a silica layer, as an intermediate layer between the aesthetic material and the molten titanium surface. The results showed that the bond with an intermediate silica layer is much better.

May et al. (26) reached the same conclusion by comparing the silica coating procedure to sandblasting with 110 μm aluminium oxide.

The purpose of the trial undertaken by Caeg et al. (27) was to examine the PMMA- titanium bond strength, by comparing processing of the titanium surface by spark erosion and by applying silica layer to the titanium surface. They concluded that the silica coating procedure gives better results.

Wirz et al. (4, 28) emphasized that the silica coating method must not be combined with any conventional mechanical retention elements (pearls), because they weaken the bond strength between the aesthetic material and titanium.

The aim of further research was to determine the possibility of joining dental ceramics as an aesthetic material with titanium. There is considerable difference between the coefficient of thermal expansion of titanium and aesthetic materials (titanium = $9.6 \times 10^{-6}$/K; ceramics = $13.7 \times 10^{-6}$/K; PMMA = $81 \times 10^{-6}$/K). The temperature of ceramic firing must also be taken in to consideration as an important factor in the titanium-ceramics bond strength. The greatest problem is the oxide layer which builds up on the titanium surface when firing ceramics at ca 1 000 °C, which reduces the ceramics-titanium bond strength, whereas the change of the titanium's crystalline structure to the β-phase weakens the titanium's mechanical properties (4, 25). This is the reason why a need was recognised for finding a ceramic material, the temperature of whose firing in the course of its application to the titanium construction would not exceed 800 °C, as Kirmura et al. (29) require.

Adachi et al. (30) investigated dental ceramics firing at temperatures from 750-1 000 °C and concluded that a lower temperature reduces adherence of oxides and improves the dental ceramics-titanium bond.

The bond between aesthetic materials (PMMA and ceramics) and titanium does not depend on the production technology of titanium restorations. As described by Pang et al. (31), there is no difference in the bond quality for the restorations produced by titanium casting and restorations produced by cold machine processing of titanium.

With regard to the temperature of ceramics firing and thermal expansion coefficient limitations, new aesthetic materials are being developed to enable clinical use of titanium aesthetic restorations.

## Assessment of Clinical Applications of Titanium in Dentistry

In dentistry titanium was first used in dental implantology. With the examination of its biological characteristics and the development of new surgical techniques it has become an irreplaceable material for endoosseous implants loading. The results of long-time research of titanium's properties in dental implantology indicated that titanium could also be used in other branches of dentistry, especially in prosthetics.

Corrosion is a great problem in implant superstructure production. Corrosion brings about the release of metal ions from alloys, which can have adverse effects in the body. In order to avoid this, a need was recognized for the use of titanium as an alloy for the production of titanium implant superstructures. Therefore, current research is oriented towards the examination of biomechanical relations between titanium implants and titanium superstructures, and also towards the development of titanium aesthetic restorations (32).

In the course of the study of titanium fixed prosthetic restorations, the object was to examine the marginal fit of crowns, their anatomical shape, surface and colour, and to compare cast titanium crowns with titanium crowns produced by machining.

Ida et al. (33) established that titanium implants have better marginal accuracy than Ni-Cr alloys, and worse than Pd-Ag alloys.

According to Blackman et al. (34), the average deviation of a titanium crown from the preparation boundary amounts to 50 μm. Deviations are greater with preparations with a shoulder of 90° than with preparations with a shoulder of 45°.

Baez et al. (35) came to the same results. According to their investigation, the deviation of crown edges with preparations with a shoulder of 45° is 7-100 μm, and with preparations with a shoulder of 90°, 8-196 μm. These results are considered clinically good.

The edges of the restorations produced by the machining procedure *Procera* have an average marginal gap of 270-750 μm in the case of preparations with a shoulder (36).

Harris and Wickens (37) examined the marginal fit of crowns produced by machine processing of titanium and of cast titanium crowns. Their results showed no significant differences.

Numerous clinical studies on titanium restorations have been conducted. Andersson et al. (17) examined their patients a year after cementing titanium aesthetic prosthetic restorations, and they determined that 99.5% of the restorations fitted very well, the anatomical shape of 98.9% remained unchanged, and with 96.8% of the restorations there were no changes in their surface and colour.

Kaus et al. (38) conducted a 30-month-study on clinical use of cast titanium aesthetic restorations. They achieved the following results: with 85% of the crowns and 59% of the bridges the surface and colour were not changed, and the crown edge was clinically acceptable, whereas 25.9% of the restorations were clinically un acceptable. Titanium crowns proved to be more durable than titanium bridges.

Nilson et al. (39) conducted a two-year-study with aesthetic, so-called *Procera* crowns. They examined the development of fractures in ceramics, the change in colour, anatomical shape and crown edges. The achieved results were not different from the results of studies on cast titanium aesthetic crowns.

Bergman et al. (40) conducted a two-year-study with *Procera* crowns, on which composite resin is applied as the aesthetic material. In 5.2% of the crowns there were fractures in the composite resin, 70% of the crowns had a satisfactory anatomical shape, 83% satisfactory marginal integrity, and with 96.8% of the crowns the colour and surface remained unchanged.

The importance of titanium's low hardness and module of elasticity is manifested after the final cementing of titanium restorations, since they enable easy and a quick occlusal adjustment. Titanium's hardness and elasticity also facilitate easy removal of old cemented crowns (40).

Apart from in fixed prosthodontics, titanium also began to be used for fixed-removable prosthetic restorations, as well as for retentive element production. Multiple-unit fixed prosthodontic restorations supported by dental implants are now often used instead of removable partial and complete dentures. The availability of these additional means of support has greatly expanded the scope of fixed prosthodontic treatment (32, 36).

Wirz et al. (41) use titanium fixed-removable restorations as superstructures of titanium implants. Cast titanium superstructures are produced, depending on the number and position of implants. Cast bars are used as retention elements, which serve to support dentures. As described by Wirz et al, all parts of titanium fixed-removable superstructures, ie frameworks, connectors and retention elements, are cast from titanium, whereas clasps are cast from Co-Cr alloys. Cast clasps are not made of titanium, since it has a low module of elasticity.

Parallel research on the mechanical properties of clasps cast from pure titanium, from Ni-Cr alloys and Co-Cr alloys, conducted by Hummel et al. (42), showed that the elasticity of titanium clasps is lower than the elasticity of the clasps made of Co-Cr alloys, and higher than the elasticity of the clasps made of Ni-Cr alloys. The retentive force of cast titanium clasps is greater than the retentive force of the clasps made of the other two alloys. When comparing the retentive force of the clasps cast from the titanium alloy Ti-6Al-4V and clasps cast from Co-Cr alloys, the force was first measured when the denture was attached for the first time, and then after it had been removed 500 times. The clasps cast from the titanium alloy possess greater retentive force than the clasps made of Co-Cr alloys.

For casting partial dentures and frameworks of complete dentures made of titanium, the metal must be 0.70 mm thick. Casting of titanium denture framework is more difficult than from Co-Cr alloys, since thicker wax must be used, to ensure that the cast is not porous (43).

Wakabayashi and Minoru (44) use 0.75 mm thick wax for casting titanium frameworks of partial dentures, claiming that only with such a thick wax is it possible to obtain a non - porous cast.

Blackman et al. (45) measured dimensional changes in casting titanium frameworks of partial dentures. There were changes in volume of 2.6% horizontally and 1.8% vertically. This rather high percentage requires further investigation of factors that cause dimensional changes in casting titanium frameworks of partial dentures, so that this can be controlled.

Combined fixed-removable prosthodontic titanium restorations were also clinically examined. A three-year-clinical study of titanium partial dentures showed that their mechanical properties were not changed, and there was only slight change in the colour on the surface of the titanium restorations (44).

The object of a two -year-clinical study by were laser-welded titanium frameworks for dentures. A check-up of the prosthetic restorations in 87 patients after two years showed that one framework was broken. There were no other changes in prosthodontic restorations. It is interesting to note that there were more lost implants under laser-welded dentures than under cast dentures (46).

Most of the brackets used in orthodontic mechanotherapy are made of metallic materials because of their mechanical strength and because they can easily be formed into various shapes. Since plastic brackets might deteriorate due to water absorption and deform from applied torque force, and with ceramic brackets the antagonistic teeth are subjected to abrasion, the production of titanium brackets which possess high biocompatibility and neutral colour offer a solution to the problem (47). Since the bonding strength of titanium brackets is very high, they are very important in clinical applications (11).

## Conclusion

Titanium's superior properties, such as its high biocompatibility, resistance to corrosion, low thermal conductivity, hardness, low density, neutral taste, good radiographic visibility and acceptable price, make it an excellent contemporary dental material. There have been no reports of systemic or local, allergic and toxic reactions to titanium and its alloys.

Titanium also possesses some less advantageous properties: a low module of elasticity, a high melting-point and extreme reactivity with oxygen in its molten state. This calls for changes in casting and processing technology of titanium. Problems also arise in bonding aesthetic materials to the titanium surface. Bonding aesthetic materials to titanium shows good results if PMMA and composite resins are used as aesthetic materials, whereas the results of bonding with ceramics are less favourable. The high price of instruments for casting, machine processing and welding of titanium are an additional problem.

Although titanium already has a wide spectrum of application in dental implantology and orthodontics, it is still not sufficiently applied in restorative dentistry. Results of clinical investigations show that by casting and machine production of titanium restorations prosthetic restoration of satisfactory quality can be constructed. However, research must be continued to fully examine titanium's effectiveness, and the possibility of it replacing existing metals.