Characterisation of a new dental alloy with high Au content

Karakterizacija nove dentalne zlitine z visoko vsebnostjo Au

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Received: November 6, 2007 **Accepted:** December 4, 2007

Abstract: The basis for developing a new dental alloy with high Au content is appropriate chemical composition and manufacturing technology. This new Au dental alloy is based on the ternary system of Au-Pt-Zn with a nominal composition of 88.5Au-8.7Pt-1.5Zn-0.5In-0.4Ir-0.3Rh. The alloy was melted and cast in a vacuum-induction melting furnace in Zlatarna Celje. Casting was followed with subsequent thermo-mechanical treatment (procedures of profile and polish milling, thermal treatment) and cutting-off strips to form a regular shape. The heat treatments of Au alloy samples were carried out in a tube furnace under different temperatures, and over different times. Testing of the new Au dental alloy included examining the initial cast, and the different heat treated conditions of the Au alloy. The optical properties of Au-dental alloy were investigated by means of spectrophotometric colourimetry. Finally the test of cytotoxicity of new Au based dental alloys using standard in vitro assays for testing the biocompatibility with establishing new, more sensitive, in vitro tests on cell lines was done.

Izvleček: Osnovo razvoja nove dentalne zlitine z visoko vsebnostjo Au predstavljata pravilna določitev kemijske sestave in tehnologije izdelave. Nova dentalna zlitina temelji na ternarnem sistemu of Au-Pt-Zn z nominalno kemijsko sestavo 88,5Au-8,7Pt-1,5Zn-0,5In-0,4Ir-0,3Rh. Izdelava dentalne zlitine je potekala s pretaljevanjem zelo čistih komponent v vakuumski indukcijski peči v Zlatarni Celje. Temu je sledilo odlivanje taline v ustrezno formo, postopek termo-mehanske obdelave odlitka in razrez zlitine v ustrezno obliko. Toplotna obdelava je bila izvedena pri različnih temperaturah in za različne čase. Testiranje dentalne zlitine je vključevalo določitev last-

Scientific paper

nosti začetnega stanja in stanja po različnih toplotnih obdelavah. Optične lastnosti dentalne zlitine so bile raziskane s spektro-fotometrično kolorimetrijo. Na novi Au dentalni zlitini so bili narejeni še testi citotoksičnosti z uporabo standarda in vitro analize za testiranje biokompatibilnosti z uvajanjem novih, bolj občutljivih in vitro testov na celični liniji.

Key words: dental alloy, characterisation, microstructure, properties
Ključne besede: dentalna zlitina, karakterizacija, mikrostruktura, lastnosti

INTRODUCTION

Gold alloys have been used in dentistry, not only because their gold colour is preferred, but also because they have extremely high chemical stability in the mouth, plus several desirable mechanical properties such as high strength, ductility and elasticity[1]. They contain five or more elements, the essential components of the alloys being gold and platinum. The main specific physical requirements for those dental alloys used for porcelain fused to metal (PFM) technique are: a) a melting range starting at no less than 1100 °C, b) a coefficient of thermal expansion closely matched to that of high-fusing-point dental porcelain (960-980 °C) developed for the PFM technique – the values for these coefficients should stay within the ranges 12.7-14.8×10^{-6} K^{-1} for the alloys, and 10.8-14.6×10^{-6} K^{-1} for porcelain, c) minimal creep or sag when firing the porcelain, d) good wetting of alloy by the porcelain, e) tensile strength about 600 N/mm^2 and yield strength about 550 N/mm^2, f) hardness about 180 HV and g) elongation about 10 %. On the other hand, gold alloy for casting would have a melting range as low as possible whilst an Au alloy for porcelain veneers would have a solidus temperature around 100 °C higher than the firing temperature of the used porcelain, in order to ensure that the cast framework does not sag during firing.

Among various types of alloys for PMF restorations, the Au-Pt-Zn-based high noble alloys have the advantage of being around for some considerable time. They are part of clinical experience and are extremely successful[2]. The bond between the ceramic and the metal, in particular, is very strong and highly reliable[3]. Accordingly for our new Au dental alloy we selected a combination of the following alloying elements: Au, Pt, Zn and traces of: Ir, In, Rh. We wanted to keep all the favourable properties of gold and to improve its inadequate strength and hardness by Pt, Zn and Ir alloying[4]. When considering the formulations of Au-Pt-Zn-based high noble alloys for porcelain bonding, high Au contents are required to ensure biocompatibility and large Pt concentrations are necessary to sufficiently raise the melting range above the porcelain firing temperature to prevent distortion during porcelain application[2],[3]. By the addition of Zn we wanted to lower the surface tension of the liquid alloy, thus enabling the material to be cast into very thin sections. The zinc also serves as a dezoxidant, together with Ir and In. This is because of their affinity to oxygen, being the first to react with it and thus,

protect other metals from oxidation. Other micro-alloying metals are added also to form a thin oxide film at the surface of the alloy during the porcelain firing cycle[5],[6]. This new alloy has no Ag which easily reacts with oxygen, gives porous castings, forms sulphur compounds, and can lead to tarnishing and ceramic discoloration (greening). This new Au alloy also has no palladium or copper. Pd reacts with hydrogen; it gives porous castings and can cause allergic reactions. Cu gives reddish colour to an alloy, it reacts with oxygen and forms copper-oxide on the alloy's surface, which can cause ceramic discoloration. These are the reasons for the selected chemical composition of the alloy: about 88.5 w.% Au, 8.7 w.% Pt, 1.5 w.% Zn, and 1.3 w.% of different micro-alloying elements (Ir, In < 0.5 w.%, Rh). Micro-alloying elements are necessary for precipitation hardening; small additions of iridium can reduce the grain size of the alloy, while the presence of rhodium enhance both strength and colour[4].

Testing of our new Au dental alloy included examining the solution treated and heat treated alloy. Measurements of hardness were done according to standard 6507-1:1998, and static tensile testing was performed for determination of the mechanical properties.

Dental alloys used in dentistry must also have good biocompatibility which concerns the biological acceptability and biological performance of those materials used in dentistry. Moreover, biocompatibility has been equated with the lack of a significant interaction between materials and tissues. It has been documented *in vitro* and *in vivo* that metallic dental devices release metal ions, mainly due to corrosion. These metallic components may be locally and systemically distributed and could play a role in the aetiology of oral and systemic pathological conditions. The quality and quantity of the released cations depend upon the type of alloy and various corrosion parameters. Prosthodontic restorations remain in an oral environment for many years and are exposed to the corrosive influences of saliva, temperature changes, pH changes, etc. Metals in electrolyte (saliva) release ions can lead to oxidative processes which tarnish and precipitate the metal in the surrounding tissues[7]. Until now no general correlation has been observed between alloy nobility and corrosion. Dental cast alloys very often cause local adverse tissue reactions such as gingivitis and periodontitis, due to the release of metal ions into the surrounding microenvironment. Their cytotoxic effects are well documented using different *in vitro* and *in vivo* assays. This was the reason why less cytotoxic or non-cytotoxic precisious noble-metal alloys with a high content of gold (Au) and platinum (Pt) although more expensive, are introduced in dental practice.

In this study, only the parts of *in vitro* biocompatibility tests were performed. Within this study we tested the cytotoxicity of our new Au-Pt-Zn dental alloys using standard *in vitro* assays and to establish new, more sensitive, (*in vitro*) tests on cell lines.

In addition to the extremely successful clinical experiments, the attraction of Au-Pt-Zn-based high noble alloys is with the yellow colour. Nowdays it is suggested that colour control must be taken into ac-

count as one of the criteria when manufacturing dental gold alloys for crown and bridge metal-ceramic restorations. It has been claimed that a high gold content means that the alloys impart a warm, dentin-like colour to the ceramics. Because of this feature, there is a complete elimination of gingival 'black line disease' associated with traditional metal-ceramic fixed restorations. The optical properties of our new Au-dental alloy were investigated by means of spectro-photometric colourimetry.

EXPERIMENTAL WORK

The meltings of very pure components (Au=99.99 w.%, Pt=99.99 w.%, Zn=99.99 w.%, In=99.99 w.%, Rh=99.99 w.%, Ir=99.99 w.%) were performed at Zlatarna Celje d.d. in vacuum-induction melting furnace at vacuum $p=10^{-2}$ mbar and temperature T=1400 °C. Casting of the melted alloy was performed under argon pressure above 1.03 bar in a metal cast with diameter 8 mm[8]. The alloy ingot was followed with subsequent thermo-mechanical treatment (procedures of profile and polish milling, thermal treatment) and cutting-off the strip to form a regular shape. Alloy specimens were first solution-treated at 950 °C for 30 min and quenched using water. The solution treated samples were then subjected to heat treatments which were carried-out in a tube furnace (Figure 1) at selected temperatures (400 °C, 450 °C and 500 °C) for different times (10 min, 20 min, 30 min)

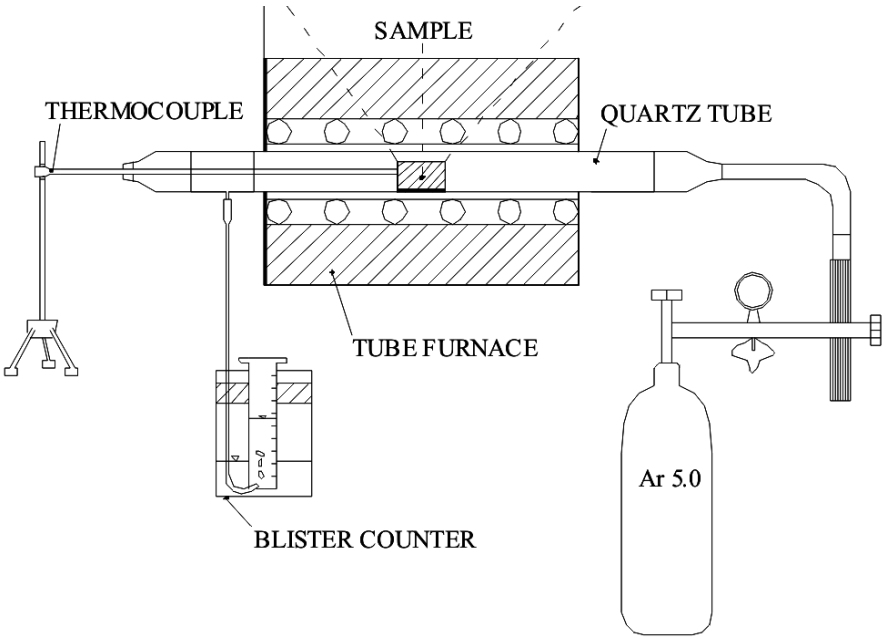

Figure 1. Schematic presentation of appliance
Slika 1. Shematska predstavitev naprave

and, finally, slowly cooled to room temperature.

Testing of the new Au dental alloy included examining the solution treated and heat treated condition. Measurements of hardness were carried out according to standard 6507-1:1998, with the Vickers test on the Zwick 3212 microhardness measurement device. For testing the samples, we used applied load F=49 N, according to standard. For every sample, we performed 12 measurements.

The static tensile testing using tensile device Zwick/Roell ZO 10 was performed for determining the mechanical properties. Measurements of mechanical properties for the all states were performed in one series with 6 samples. The research conditions, as well as the shapes and dimensions of the tensile test tubes were according to standard SIST EN 1562:2000 (chapter 6.2). Tests were performed under constant speed of increasing deformation v=1.5 mm/min. Tensile test tubes were cast and then cut-out from the cylinder shaped casting (diameter 3 mm) - see Figure 2!

Figure 2. Tensile test tube of the dental alloy with high Au content
Slika 2. Natezne epruvete iz dentalne zlitine z visoko vsebnostjo Au

Measurements of the thermal expansion coefficient (CTE) was performed in one series which consisted of 3 samples, on the Mechanical Dilatometry device (at the Chair for Engineering Materials at Faculty of natural sciences and engineering, University of Ljubljana).

For the microscopic analysis, dental alloy plates were ground and then polished using different polish pastes. The samples were, after metallographic preparation, cleaned in an ultrasound vibration cleaning device (medium alcohol). Those specimens for optical microscopy were then etched in H_2O-H_2O_2-$FeCl_3$ solution for 2 min at room temperatures. Concurrently those polished specimens for electron microscopy were put in the chamber of the Sirion NC 400 scanning electron microscope, with vacuum of 10^{-10} mbar. Sirion FEG is a high-resolution scanning electron microscope with field emission gun (FEG) which enables the observation and analysis of nano-scale particles. Microscopic analysis includes examination of the polished surface and qualitative and quantitative micro-chemical analysis at characteristic points on the dental alloy. We observed surfaces using an electron beam voltage at 30 kV, and over different working distances (6.5 mm, 7.2 mm, etc.).

For the biocompatibility (cytotoxicity) test, disk-shaped specimens (4 mm × 4 mm and 10 mm × 10 mm) from Au dental alloys

were prepared using a conventional lost - wax technique which simulates the preparation of the cast metal alloy for clinical use. The disks were polished and rinsed in distilled water. After cleaning by sonification for 5 minutes, the samples were autoclaved. Large disks were cultivated in a medium for cell cultures (RPMI medium + 10 % fetal calf serum) for 8 days, in order to test the cytotoxic effect of metals released from alloys (alloy-media), whereas small disks were used for testing the direct cytotoxic effect. Controls consisted of inert glass samples, pre-treated as test samples. Standard cytotoxicity assays were performed on L929 fibroblast cells according to ISO standards: ISO 10993-5; 1992(E) and ISO 7405; 1997(E). These procedures included morphological examinations of cells cultivated with dental alloys for 24h, and quantification of cell death by Tripan blue dye exclusion. In addition, the succinic dehydrogenase (SDH) activity was measured using the MTT assay. Optimization of these assays included prolonged incubation of cells with test samples for 7 days or a combination of direct and indirect (alloy-media) effects. New assays included proliferation of rat spleen lymphocytes in the presence of concanavalin A (Con A), and different concentrations of alloy - media, measured by ^{3}H-thymidine incorporation, and apoptosis of thymocytes and splenocytes using morphological examinations, and staining with propidium iodide or merocyanine 540.

For spectrophotometric colourimetry, the polished samples of new Au dental alloy were mounted on a disk shaped specimen (10 mm × 10 mm × 10 mm), and spectral reflectance data under the CIE standard illuminant D65 were collected at 10 nm intervals (D65/10) in wavelengths ranging from 400 to 700 nm. These measurements were done on a Spectraflash SF 600 Plus spectrophotometer and repeated 3 times, rotating the sample by 120 degree each time. Three-dimensional colour coordinates lightness L^*, chromaticity indices a^* (red green direction) and b^* (yellow-blue direction) in the CIE $L^*a^*b^*$ system, and chroma, C^* and hue angle h in the CIE L^*C^*h system were obtain to specify the

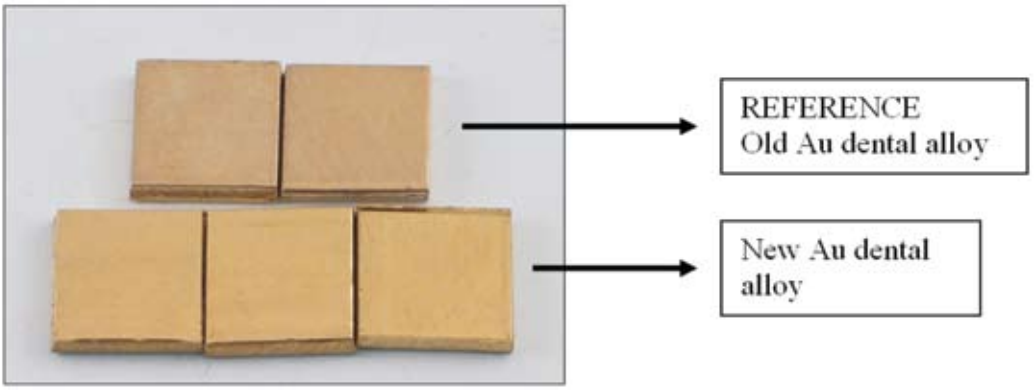

Figure 3. Old and new Au-Pt-Zn alloy specimens for testing optical properties
Slika 3. Vzorci iz stare in nove Au-Pt-Zn zlitine za testiranje optičnih lastnosti

Table 1. Results of hardness measurments [in HV5]
Tabela 1. Rezultati meritev trdot [v HV5]

Solution treated state : **125**		
Heat treated at 400 °C for 10 min: **145**	Heat treated at 400 °C for 20 min: **170**	Heat treated at 400 °C for 30 min: **175**
Heat treated at 450 °C for 10 min: **160**	Heat treated at 450 °C for 20 min: **180**	Heat treated at 450 °C for 30 min: **180**
Heat treated at 500 °C for 10 min: **160**	Heat treated at 500 °C for 20 min: **168**	Heat treated at 500 °C for 30 min: **170**

sample colour. The CIELAB colour difference parameter DE* between two samples was evaluated. For reference-sample 1 used a comparatively old Au dental alloy with nominal composition Au: 85.9 w.%, Pt: 11.7 w.%, Zn 1.1 w.% and about 1.3 w.% micro-alloying elements (In, Ir, Rh) and for sample 2 a new Au dental alloy with nominal composition was used: about 88.5 w.% Au, 8.7 w.% Pt, 1.5 w.% Zn, and 1.3 w.% of different micro-alloying elements (Ir, In, Rh) see Figure 3.

Results

The average results of the hardness measurement are presented in Table 1 for each alloy state. For the solution-treated specimen, the average hardness value was about 125 HV. It can be concluded that the alloy a solution-treated state had very low hardness. On the other hand there were different heat treated samples where hardness began to increase and reached the maximum value at isothermal holding by 450 °C for 20 min and also 30 min (the results in Table 1 are grey coloured).

The average results of the mechanical properties measurements (yield strength at 0.2 % strain, tensile strength and elongation) for all tensile test tubes are gathered in Table 2. With respect to the results for hardness, we can conclude that this optimal mechanical property also applied the samples of Au dental alloy which had been heat treated at 450 °C for 20 min (grey coloured). These samples fulfil, after heat treatment, all the necessary standards regarding mechanical properties and hardness.

Table 2. The average value of the mechanical properties measurements
Tabela 2. Povprečne vrednosti izmerjenih mehanskih lastnosti

	$R_{p0.2}$ [N/mm^2]	R_m [N/mm^2]	A [%]
Initial hom. state	340	390	15
HT 400 °C, 10 min	450	520	9
HT 400 °C, 20 min	470	530	13
HT 400 °C, 30 min	500	560	12
HT 450 °C, 10 min	520	580	10
HT 450 °C, 20 min	550	610	9
HT 450 °C, 30 min	550	610	10
HT 500 °C, 10 min	520	570	10
HT 500 °C, 20 min	540	600	10
HT 500 °C, 30 min	550	600	13

Measurements of the thermal expansion (CTE) coefficient have shown that the average value of CTE (25-600 °C) for Au-Pt-Zn alloy is about 14.45×10^{-6} K^{-1}.

The results of the chemical spectral analysis of new Au dental alloy are present in Table 3 in w.% or in at.%.

Standard cytotoxic tests showed that Au-Pt-Zn alloy has not cytotoxicity after short term (24 h) incubation of L929 cells. Prolonged incubation of cells with dental alloys showed that Au-Pt-Zn decreased the SDH activity in L929 cells by only 15.1 ± 6.2 % (the difference was not statistically significant) compared to control glass material. Similar results were obtained using the combination of alloys and alloy-media. The Au-Pt-Zn alloy did not induce apoptosis of rat thymocytes and splenocytes during a 24 h assay. However, alloy - media significantly suppressed the proliferation of rat splenocytes in the culture. Inhibition depended on the concentrations of alloy media. Au-medium was less suppressive (26.3 ± 4.6 %; $p < 0.05$ compared to glass-medium). When examining apoptosis in cultures of Con A-stimulated splenocytes, we observed apoptosis of splenocytes incubated with Au-medium at level 49.1 ± 3.0 % ($p > 0.05$; NS).

Figure 4 shows a spectral-reflectance curve and Figure 5 represents the chromaticity a^*, b^* indices of CIELAB colour space for the new Au-Pt-Zn against comparable old alloys. Table 4 shows the comparison of colour coordinates for the reference old Au-Pt-Zn alloy and the new Au-Pt-Zn alloy, and their colour difference ΔE^*.

Discussion

The present studies of heat treatment's influence on the mechanical properties of a new Au-Pt-Zn alloy show improvement in hardness and tensile strength during processing. The results indicate that the specimen which was heat treated for 20 min at 450 °C after solid solution treatment had maximum hardness and tensile strength. The reasons for these conclusions are the chemical composition of the Au-Pt-Zn alloy, microstructure formation

Table 3. The average value of the chemical spectral analysis of Au-Pt-Zn dental alloy
Tabela 3. Povprečne vrednosti spektralne kemijske analize Au-Pt-Zn dentalne zlitine

Element	Weight %	Atomic %
Zn K	1.55	4.48
Rh L	0.39	0.63
In L	0.49	0.89
Ir L	0.39	0.39
Pt L	8.67	8.42
Au L	88.51	85.19
Totals	100.00	100.00

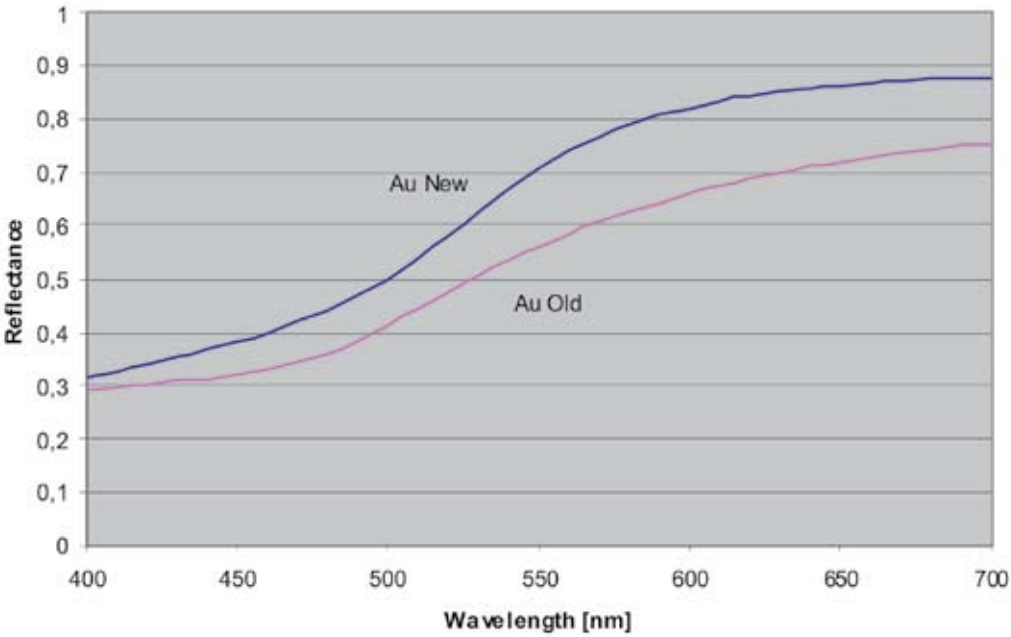

Figure 4. Spectral reflectance curves for both Au-Pt-Zn alloys
Slika 4. Refleksijska krivulja za obe Au-Pt-Zn zlitini

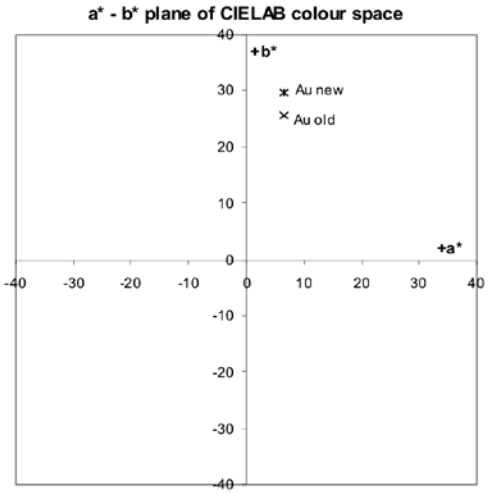

Figure 5. a* and b* plane of CIELAB colour space
Slika 5. a* and b* ploskvi CIELAB barvnega prostora

Table 4. Colour coordinates (standard illuminant D65/10)
Tabela 4. Barvne koordinate (standardna razsvetljava D65/10)

Alloy	L*	a*	b*	DE*	Batch is
Reference: old Au-Pt-Zn	78.97	6.64	25.62		
New Au-Pt-Zn	86.06	6.43	29.62	8.137	yellow

and, consequently, the strengthening effect which occurred during heat treatment.

The Au-Pt-Zn alloy is characterized by the ternary Au-Pt-Zn system, which has 5 important marginal phase diagrams: Au-Pt, Au-Zn Pt-Zn Pt-In and Au-In.

The Au-Pt binary phase diagram is characterized by the presence of three metastable phases (Au_3Pt, AuPt and $AuPt_3$)[9]. The existence of Au_3Pt superlattice in alloys is possible up to 40 at.% Pt after severe cold working, followed by annealing at 900 °C. Other diffraction studies[10] of 10 and 25 at.% Pt alloys showed that the Au_3Pt, AuPt and $AuPt_3$ phases materialize as meta-stable phases during the heating of a two-phase mixture of Au and Pt. The Au-Pt system could also contain a miscibility gap (Au) + (Pt), the critical point of which is about 61 at.% Pt and at 1260 °C. Miscibility gap could occur in the solid solution field, as well as the controversial form of the liquidus and solidus boundaries.

The Au-Zn system is characterized by more reactions: five congruent, four peritectoid, three peritectic, two eutectic, and one eutectoid and martensitic. There are four well-known intermediate phases (α_3, α_1, α'_2 and α_2) in the composition range between 10 and 30 at.% Zn, the intermetallic compound Au_5Zn_3 with unknown homogeneity[11], and many other phases. Maximum solid solubility is 33.5 at.% Zn in solid solution of Au and inversely 7.5 at.% Au in solid solution of Zn.

A complete Pt-Zn binary system is unavailable. The assessed diagram is provisional and shows the low-temperature regions[12]

with the modifications within the range of the intermediate phase Pt-Zn. The assessed Pt-Zn system is characterized by two peritectoid, two eutectoid, and two peritectic reactions.

The assessed In-Pt phase diagram is based on[13] and showed InPt as line compound, forming peritectoidally at 944 °C and stable down to at least 0 °C. InPt is one of the most conspicuous phases at low temperatures, if it exists, and has peritectoid formation. The In-Pt phase diagram is characterized by many other reactions. Pt_3In[14] which has perictectic formation is important phase for the Au-Pt-Zn system used in dental alloys. The maximum solubility of In in (Pt) is 11 at.% at 1458 °C.

There are many different phases in the binary phase diagram Au-In. The known phase diagram is based on the work of[15]. The maximum solubility of In in Au is of 12.7 at.% at 680 °C, which is only 0.2 at.% more than the solubility of In at the peritectic point. No evidence of solid solubility for Au in (In) was detected.

Detailed microstructural examination of the solution and heat treated of the Au-Pt-Zn alloy revealed the existence of two main components: the base matrix which is identified as an Au-rich α_1-phase, and an other phase, which appears to be small particles (1-8 μm) and is known as a Pt-rich α_2 -phase[6]. These phase assumptions were confirmed by nano EDX analysis (Figure 6). The gained EDX results show

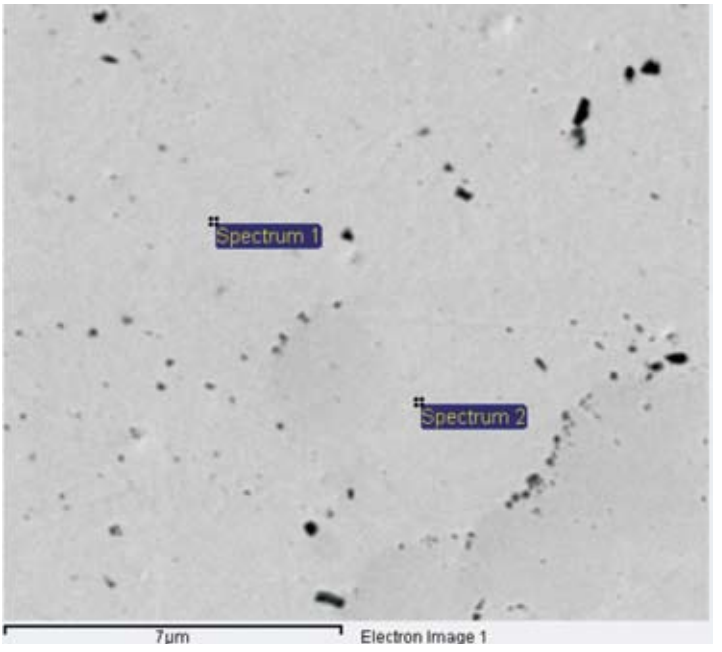

Figure 6. Electron micrograph and the typical places of EDX analysis for the Au-Pt-Zn alloy
Slika 6. Elektronska slika in tipično mesto za EDX analizo Au-Pt-Zn zlitine

that the α_1-phase has about 87-93 w.% Au, 4-8 w.% Pt and approximately 1.2 w.% Zn, 1.22 w.% Ir, In and Rh are traceable (< 1 w.%). On the other hand, the α_2 -phase contains about 60-75 w.% Pt, 20-30 w.% Au, approximately 4.12 w.% Rh, In and Zn are in traceable, while in this phase no Ir was detected.

Optical microscopy shows that the α_1-phase has approximately equal sizes in the solution and heat-treated states (Figure 7). Examinations only showed that the microstructure became homogeneous with the performing of heat treatment. On the other hand, no big difference was found in grain size during the α_2-phase between the two different states. It was only discovered that the number and density of the α_2-phase increased when the performing heat treatment. α_2-phase (in the form of small particles) is located at the grain boundaries and within the grains. We envisage that optimal value was achieved by the Au-Pt-Zn sample which had the best mechanical properties and hardness and was heat treated at T=450 °C for t=20 min after solution treatment.

The immiscibility is well-known[9] for Au-Pt system in a solid state. After casting, a solid solution nucleates from the melt. During cooling the alloy enters the miscibility gap separating into Au-rich and Pt-rich phases. With heat treatment at 950 °C the alloy enters the single phase zone between the miscibility gap and the solidus line. At this temperature, a solid solution

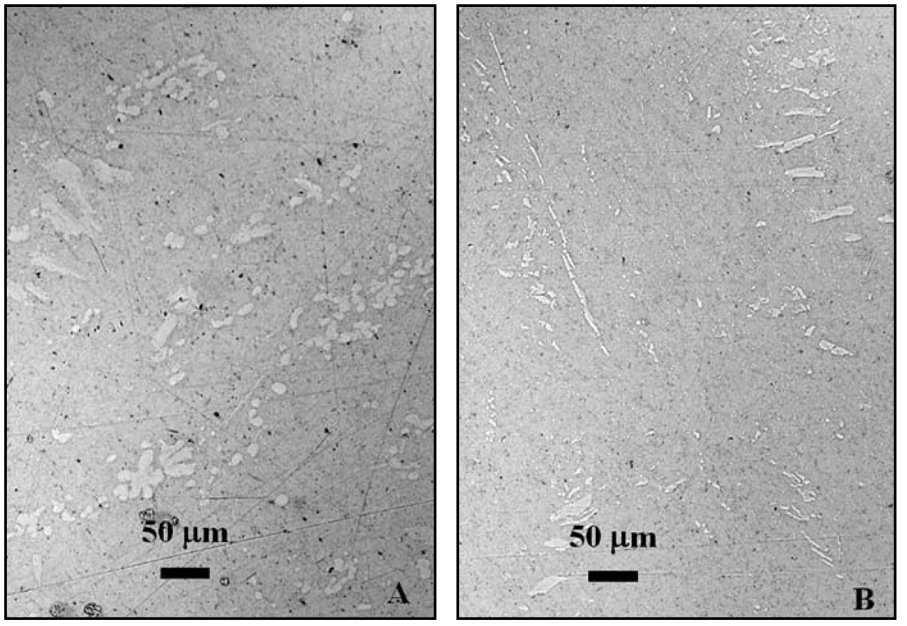

Figure 7. The optical microstructure of Au-Pt-Zn alloy after: A) solution treatment at 950 °C for 30 min and B) heat treatment at 450 °C for 20 min
Slika 7. Optična mikrostruktura Au-Pt-Zn zlitine po: A) raztopinskem žarjenju pri 950 °C za 30 min in B) toplotni obdelavi pri 450 °C za 20 min

is thermodynamically stable with random distribution of the atoms within the crystal lattice[6]. The inhomogeneous texture formed after casting therefore is thermodynamically unstable. Owing to the high energy, the atoms could diffuse in the crystal lattice and be forced to distribute randomly on the atomic sites. Subsequently, the alloy became homogeneous. Then during the cooling process, the homogenized microstructure kept in balance. But a small amount of the Pt-rich phase could still precipitate from the solid solution, depending on the cooling rate. Thus, all the specimens showed a microstructure composed of, not only α_1-phase, but some α_2-phase too. In the solution treatment process at 950 °C combined with water quenching, many crystal defects remained and supersaturated solid solution was achieved. After this treatment the alloy was thermodynamically in a metastable state. When metastable, specimens were put under different heat treatment temperature they were subjected to isothermal treatment, precipitation reactions occurred driven by diffusion. Many fine precipitates of α_2-phase appeared within the grains, this lead to hardening of the Au-Pt-Zn alloy.

The optical properties investigations show that our new Au-Pt-Zn alloy has yellow colour compared with the old alloy with less Au content. It seems that the difference of Au at value 2.6 w.% for total chemical composition of the alloy has an influence on the colour difference parameter DE^* cca 8.1. Since the DE^* value of 1.0 is said to be just discernible by the average human eye[16], the colour of the new dental alloys may be very well-distinguished from that of the referenced old alloy. With the analysis of spectral reflectance curves for both Au-Pt-Zn alloy it is shown, that the new Au-Pt-Zn alloy has a higher reflectance of about 10 % in those wavelengths ranging from 400 to 700 nm. On the other hand in the CIE $L^*a^*b^*$ system chromaticity indices a^* for both alloys is equally comparable, while the indice b^* of the new alloy has a higher value for about 4 units. This is the reason that new Au-Pt-Zn alloy is yellower than the old. The yellow colour on the surface plays an important role in developing the restoration aesthetics[17]. Although the alloy is covered with successive layers of porcelain, light travels through the porcelain and is reflected back out. If the surface of the alloy is silver (white) in colour then the entire light spectrum is reflected out. This includes the blue region which, when passing through the pink gum tissue, produces a dark unsightly outline. Au-Pt-Zn dental alloy is opaque and highly reflective, the perceived colour is determined by wavelength distribution of the radiation, which is reflected and not absorbed[16]. Material possessing a much higher reflectivity for the low-energy end of the visible spectrum (red and yellow light) than for the other parts of the spectrum will have a reddish to yellow colour[17].

Conclusions

With the results of our examinations, we can conclude that the new Au-Pt-Zn dental alloy from Zlatarna Celje fulfils all the requested standards in the sense of mechanical properties and hardness, optical properties, and biocompatibility. The ob-

tained results for this alloy are: $R_{p0.2}$=550 N/mm^2, R_m=610 N/mm^2, A=9 %, 180 HV, CTE=14.45×10-6 K^{-1}.

The analyses of different heat-treated states show that the above-mentioned mechanical properties and hardness of the Au-Pt-Zn alloy could be reached with combinations of heat treatment for 20 min at 450 °C and slowly cooling after that, if the alloy was solution treated at 950 °C for 30 min and water quenched.

The microstructure of the Au-Pt-Zn alloy consists of two phases: α_1-phase rich in Au and α_2-phase rich in Pt. It was found that the number and density of α_2-phase increased by the performing of heat treatment.

The α_2-phase, in the form of small particles, is the main factor for the strengthening mechanism in our Au-Pt-Zn alloy.

The optical property investigations show that our new Au-Pt-Zn alloy has yellower colour compared to the old alloy with less content of Au. It seems that the difference of Au at value 2.6 w.% in the total chemical composition of the alloy influences on the colour difference parameter DE* cca 8.1, which may very clearly be distinguished from that of the referenced old alloy.

The Au-Pt-Zn alloy did not show cytotoxicity when using standard short-term *in vitro* assays on L929 cell and prolonged cell incubation did not revealed any adverse effect on the L929 cells manifested by reduced SDH activity. The Au-Pt-Zn alloy did not show any pro-apoptotic effect on rat thymocytes and splenocytes in culture, and significantly decreased Con A - stimulated proliferation of these cells.

Acknowledgments

Zlatarna Celje d.d. is working on the development of a new high Au content dental alloy with the support of associates from the Institute of Materials Technology, Faculty of Mechanical Engineering, University of Maribor; School of Dentistry, University of Belgrade and Zlatarna Celje d.o.o. Belgrade.
This paper is part of a Slovenian applied project no. L2-7096, Bilateral project SLO/SR BI-CS/06-07-031 and EUREKA Programme E!3555 DEN-MAT. The authors gratefully acknowledge the Ministry of Higher Educations, Science and Technology and Slovenian Research Agency.

POVZETEK

Karakterizacija nove dentalne zlitine z visoko vsebnostjo Au

Na osnovi rezultatov naših raziskav lahko zaključimo, da nova Au-Pt-Zn dentalna zlitina Zlatarne Celje ustreza zahtevanim standardom v smislu mehanskih lastnosti in trdote, optičnih lastnosti ter biokompatibilnosti. Dobljeni rezultati za to zlitino so: $R_{p0.2}$=550 N/mm^2, R_m=610 N/mm^2, A=9 %, 180 HV, CTE=14.45×10-6 K^{-1}.

Analiza stanj po različnih vrstah toplotne obdelave Au-Pt-Zn zlitine je pokazala, da zgoraj omenjene mehanske lastnosti in trdoto dosežemo s kombinacijo toplotne obdelave pri 450 °C za 20 minut ter počasnim

ohlajanjem do sobne temperature, potem ko je zlitina raztopinsko žarjena pri 950 °C za 30 minut in gašena v vodi.

Mikrostruktura Au-Pt-Zn dentalne zlitine je sestavljena iz dveh faz: α_1-faze bogate z Au in α_2-faze bogate s Pt, pri čemer število in gostota α_2-faze naraščata s toplotno obdelavo.

Delci α_2-faze so v obliki manjših delcev in so odgovorni za mehanizem utrjanja v Au-Pt-Zn zlitini.

Raziskave optičnih lastnosti nove Au-Pt-Zn zlitine so pokazale, da ima bolj rumeno barvo v primerjavi s staro zlitino, ki vsebuje manj Au. Še več, ugotovljeno je bilo, da razlika 2,6 m.% Au v skupni kemijski sestavi bistveno vpliva na razliko v barvnem parametru DE*, ki znaša 8,1 v primerjavi glede na referenčno staro zlitino.

Au-Pt-Zn zlitina ne kaže citotoksičnosti potem, ko je bila v okviru standardnega hitrega *in vitro* testa izpostavljena L929 celicam. Tudi rezultati testov s podaljšano celično inkubacijo niso pokazali nobenega nasprotnega efekta na L929 celicah, ki bi se posledično odražali na zmanjšani SDH aktivnosti. Au-Pt-Zn zlitina tudi nima proaptotičnega efekta na timocitih in splenocitih celičnih kultur podgan in bistveno zmanjšuje Con A stimulirano profileracijo teh kultur.

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