A NEW AuPdAgTi–type HIGH NOBLE CLASS ALLOY - OBTAINING AND INITIAL CHARACTERIZATION

Doina RADUCANU[1], Dana IORDACHESCU[2], Vasile-Danuț COJOCARU[3], Valentina MITRAN[4], Steliana IVANESCU[5], Ion CINCA[6]

Această lucrare de cercetare a avut în vedere obtinerea şi caracterizarea generala a unui nou aliaj biocompatibil pe baza de metale nobile pentru aplicații în stomatologie. S-au stabilit caracteristicile pe care trebuie să le indeplinească aliajul pentru aplicații de tip metalo - ceramic, compoziția chimică şi procedura de elaborare. In final este realizată o caracterizare generală preliminară referitoare la structura - biocompatibilitate.

The point in view of this research work was obtaining and general characterization of a new biocompatible noble metals based alloy for applications in stomatology. Characteristics needed for metal-ceramic applications, noble alloy composition and obtaining procedure were established. In the end a general preliminary characterization referring to structure and biocompatibility was done.

Keywords: new biocompatible alloy, noble metals, characterization, structure, biocompatibility

1. Introduction

Alloy for metal-ceramic applications in stomatology must reach high mechanical properties.

Alloy hardness must be close to dental hardness, stress and strain resistance higher compared to those needed for metal - polymer applications realized in stomatology, all accompanied by a smaller elongation [1, 2]. To reach such

[1] Prof., Dept. of Deformable Media Engineering, University "Politehnica" of Bucharest, ROMANIA; doina.raducanu@mdef.pub.ro
[2] Prof., Faculty of Biology, University of Bucharest, ROMANIA
[3] Lecturer, Dept. of Deformable Media Engineering, University "Politehnica" of Bucharest, ROMANIA
[4] Assist., Faculty of Biology, University of Bucharest, ROMANIA
[5] Eng., SC R&D Consulting and Services, Bucharest, ROMANIA
[6] Lecturer, Dept. of Deformable Media Engineering, University "Politehnica" of Bucharest, ROMANIA

properties, composition range must contain large amounts of hardening elements (palladium, titanium). Bonding properties at the interface metal- ceramic is another important feature needed to this alloy category [3, 4]. From this point of view, the alloy must contain oxidant elements to increase metal - ceramic bonding.

The obtaining of some new type of gold alloy with a small addition of titanium to pure gold was reported [1, 2, 3]. Till now it has been proved that Au-1.6 wt%Ti alloy is good both in biocompatibility, mechanical resistance and metal–ceramic bond strength [1, 2]. But the fit of metal ceramic crowns cast in Au-1.6 wt%Ti alloy which influences periodontal health, secondary caries and also the crown's retention, is not clear. Regarding multicomponent alloys, the titanium addition can replace other conventional alloying elements found usually in high noble class alloys, such as Se, Sn, etc, which prove poor biocompatibility features.

The novelty regarding the new alloy proposed composition refers to noble elements (Au, Ag, Pa) content and, more important, to Ti content. Titanium is known like the highest biocompatible metal, being used for medical implants in stomatology, orthopaedics, skeleton surgery, etc. This element can replace non-noble/noble metals in commercial alloys, excluding or diminishing any appearance of toxic corrosion products located in the contact area between alloy and human tissue.

2. Experimental data

2.1. Noble alloy composition for metal - ceramic applications in stomatology

The new alloy composition was established taking care to not decrease it's biocompatibility. New alloy established composition for metal - ceramic applications is shown in Table 1.

Table 1

New alloy composition for metal - ceramic prosthesis applications (alloy 1)

Metal	at. %	Alloy for metal - ceramic prosthesis applications (alloy 1)
Au	%	65±0,5
Ag	%	10±0,5
Pa	%	20± 0,5
Ti	%	5± 0,5

According with the New Specification of American Dental Association (ADA), the proposed alloy composition is a high noble class with up to 60% noble metal content (weight percent) and up to 40% Au content (weight percent).

Taking into account that Au and Ag are soft and easy processing metals, to the composition with 65% Au and 10% Ag content it is necessary to add hardening

elements to increase mechanical resistance. This must be done in order to avoid prosthesis shape changes under the forces located in metal - ceramic separation area. Hardness and mechanical resistance are expected to increase by adding 20% Pd and, in this case, a high (5% at.) titanium percent.

2.2. New AuPdAgTi noble alloy obtaining

Binary equilibrium diagrams for noble metals alloying show that Au, Ag and Pa can be easily alloyed, solid solutions being located in all compositions ranges. Some problems occur when Ti is alloyed due to its high melting temperature of this and density (the lowest).

Ti alloying was carried out using an indirectly alloying method, with a starting pre-alloy Pd -Ti (48% Ti + 52% Pd) whose melting temperature is lower and density higher that for pure Ti.

An electric induction furnace type LEYBOLD HERAEUS EMA-MFAS 40, with an instaled power of 40 kW was used.

The melting was performed inside a chemical neutral ceramic graphite crucible whithout chemical interactions between crucible and melted metals. The crucible was located in the central area of the furnace inductor. Melting parameters were controlled by furnace power and frequency variations. Alloy's elaboration was made in normal atmosphere. Alloy casting was made in a cylindrical graphite die, with inner dimensions as follow Φ10 x 100 mm. The graphite die supported a previous heat treatment in order to eliminate any water traces existing in graphite die material. The applied heat treatment consists in 24 hour heating at 1000 °C. Alloy's solidification was realized inside graphite die at room temperature.

2.3. Alloy general characterization

2.3.1. Structure analysis

For structure analysis, samples were metallographically investigated from both longitudinal and transversal sections of the ingot.

The as-cast alloy structure is shown in fig. 1 and 2.

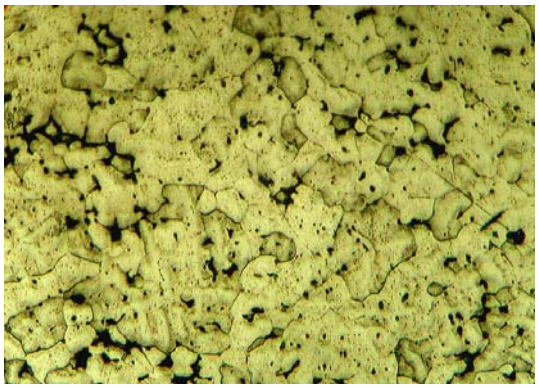


Fig. 1 As-cast alloy structure; Longitudinal section; Original magnification: x250

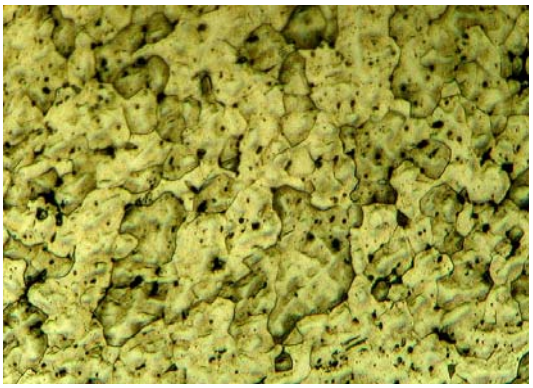


Fig. 2 As-cast alloy structure; Transversal section; Original magnification: x250

2.3.2. Biocompatibility characterisation

The knowledge regarding base mechanisms of living cell-artificial material interactions are essentials to biomaterials development.

Some of these mechanisms can be evaluated using different microscopic procedures [5].

Cell culture.

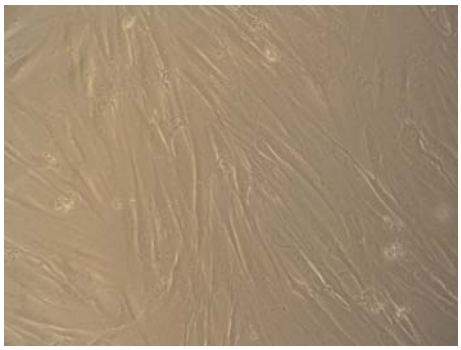
Alloy samples were sterilized in UV light six hours long, each side. One hour before seeding the samples were immersed in sterile conditions in phosphate buffered saline – PBS (pH 7.4). Studies were realized on two Petri plates, 6 mm long: sample (alloy) and control. In both Petri plates a cell suspension (1,5 x 10^4 human gingival fibroblaste/5 ml- ATCC (*American Type Culture Collection*) called HGF – human gingival fibroblasts) was introduced in such way to cover completely the alloy sample.

Cell morphology and proliferation

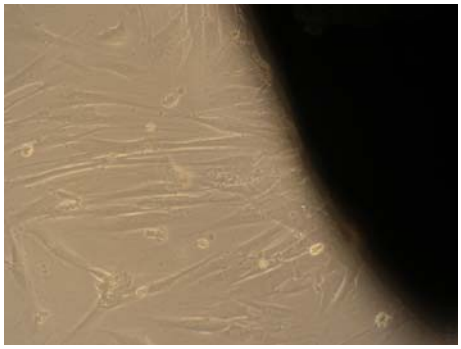
As regarding fibroblast type cells seeded on an opaque substrate, number and proliferation type tests are very restricted. For example, living cells numbering would suppose cells extraction form culture medium after adhesion which compromise observations.

A first possibility is cell culture observations on 24-48 hours after seeding on all samples.

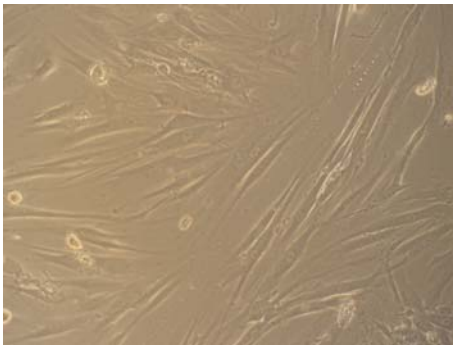
In Figs. 3 and 4 are presented micrographs of HGF culture acquired using a Nikon contrast-phase microscope.



(a) control sample after 24 h, Original magnification × 20

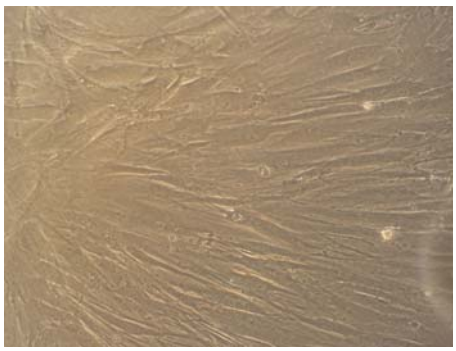


(b) alloy sample after 24 h, at interface
Original magnification × 20

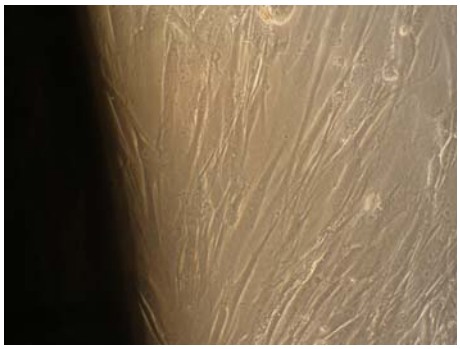


(c) alloy sample after 24 h,
Original magnification × 20

Fig. 3. HGF culture micrographs after 24 hours from seeding.



(a) control sample after 48 h,
(b) Original magnification × 20



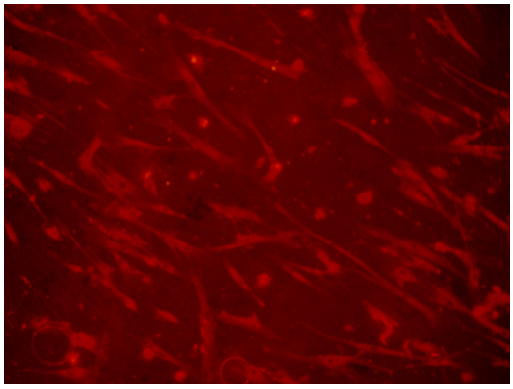
(b) alloy sample after 48 h, at interface
Original magnification × 20

(c) alloy sample after 48 h,
Original magnification × 20

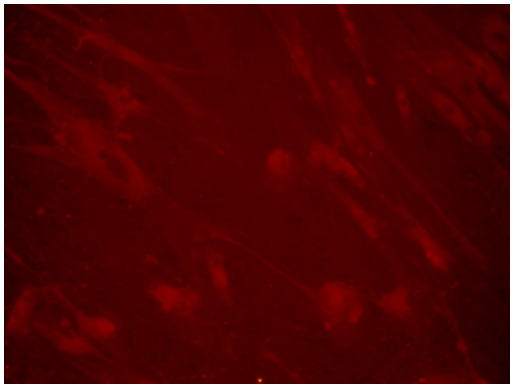
Fig. 4. HGF culture micrographs after 48 hours from seeding.

To visualize cell spread on alloy surface it was realized their fluorescent marking using hypericine which permits cell proliferation monitoring.

In Fig. 5 are presented HGF cells image spread on alloy surface after 48 hours from seeding.



(a) Original magnification × 10



(b) Original magnification × 20

Fig. 5. HGF cells image spread on alloy surface after 48.

Colorimetric MTT assay

Cell proliferation was assessed by studying the activity of mitochondrial dehydrogenases (MTT assay). Cell treatment with MTT [3-(4, 5-dimethyltiazol-2-yl)-2, 5-diphenyltetrazolium bromide)] in concentration of 1 mg/ml allows the evaluation of the oxidative metabolism and of the cell response to external factors that can have a positive or negative effect on cell survival in culture. This quantitative colorimetric

method is based on the reduction of the yellow compound MTT to a purple formazan. The MTT reduction realized by mitochondrial enzymes (especially succinate dehydrogenase) is directly proportional to the number of viable cells. The optical density is evaluated by spectrophotometry, resulting in a relationship between absorbance, colorant concentration and number of metabolicaly active cells.

3. Disscusion

An alloy system formed by biocompatible noble metals has specific features as regarding:

- structure type;
- phases distributions and phases transformations;
- eventually presence of intermetallic compounds;
- hardening by precipitations and eventually order - disorder transformations.

Preliminary investigations were focused only on structure of as-cast alloy. A dendritically two phase crystallization with large dendrite continuously developed in all sample area was observed.

Regarding alloy biocompatibility information referring to cell morphology, cell adhesion and cell proliferation were obtained.

Monitoring of HGF cells culture on alloy the surface shows a process of cell adhesion early in the first 24 hours from seeding, which goes on and accelerate in time. The cells migrate without a morphological changes in comparison with control probe. The morphological analysis in contrast-phase microscopy shows that in the alloy presence HGF cells proliferate both at interface (alloy surface) (fig. 3.b, 4.b) and at distance from the alloy (fig. 3.c, 4.c).

After marking with hypericin one can observe that HGF cells have an ovoid nucleus placed almost-central with cytoplasmatic developed bonds which indicate the cells effort to adhere to the alloy surface (fig. 5.a, 5.b).

The results of MTT test after 24 and 48 hours from seeding demonstrate the cells proliferation (see Table 2) in both cases: on control culture and on alloy samples. The proliferation index is 1,9 for control culture and ~ 2 for alloy samples.

Table 2

MTT test results.

Tested specimen	DO to 550 nm - 24 h	DO to 550 nm - 48 h
HGF control sample	1.18 ± 0.16	2.24 ± 0.22
HGF alloy sample	0.94 ± 0.10	1.87 ± 0.20

4. Conclusions

A multicomponent high noble class alloy with high titanium content, without other conventional alloying elements usually found in high noble class such as Se, Sn was realized. Comparing with commercial compositions typical for this alloy class and with compositions proposed by patents it has an original composition, also proposed to be patented.

The alloy obtaining is possible by using a starting master-alloy Pd -Ti (48% Ti + 52% Pd).

In as cast condition the alloy has a quite homogenous structure, of dendritic type.

Alloy biocompatibility was preliminary investigated to see cell morphology, cell adhesion and cell proliferation.

Data referring to mechanical behavior will be reported elsewhere.

Regarding investigated aspects, the new realized high noble class alloy shows good behavior. This indicates that this alloy has promising properties, this stage being a start point for further in-deep investigations.

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R E F E R E N C E S

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