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The influence of alloying elements on the microstructure and microhardness of welded titanium alloys for medical applications

Uticaj legirajućih elemenata na mikrostrukturu i mikrotvrdoću zavarenih legura titana za medicinsku upotrebu

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Abstract

The paper presents the effects of some alloying elements (Al, Fe and Mn) on the microstructure and microhardness of titanium alloys that can be used for medical applications. The experimental alloys were produced by melting in an argon inert atmosphere of the RAV furnace, using high purity chemical elements and the commercial alloy Ti8Al4V. Were developed, under the same conditions, other binary alloys (Ti9Al, Ti5Fe, Ti3Mn, Ti6Mn) for highlighting the effects of the singular elements Al, Fe and Mn on the characteristics of titanium alloys. Microstructural analysis revealed the changes of microstructure produced by the introducing of alpha stabilizing elements (Al) or beta stabilizers (Fe, Mn). Were then analysed the effects of each type of chemical on the metal matrix microhardness and the density of the experimental alloys

1. Introduction

Some titanium alloys are getting much attention for biomaterials because they have excellent specific strength and corrosion resistance, no allergic problems and the best biocompatibility among metallic biomaterials [1]. Titanium‘s lightness and good mechano-chemical properties are salient features for implant applications [2]. Pure titanium and Ti-6Al-4V are still the most widely used ones for biomedical applications among the titanium biomaterials. For instance, the biocompatibility of Ti6Al4V alloy has since been called into question due to reports that the gradual release of aluminium, and particularly vanadium ions, from the surface of alloy can cause local adverse tissue reaction and immunological responses [1, 3 and 4]. Therefore, the developments of titanium alloys

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Key words: titanium alloys, microstructure, microhardness

Rezime

U radu su predstavljeni uticaji nekih legirajućih elemenata (Al, Fe i Mn) na mikrostrukturu i mikrotvrdoću titanovih legura koje se mogu koristiti u medicinske svrhe. Eksperimentalne legure su proizvedene topljenjem u peći sa inertnom atmosferom argona RAV, korišćenjem hemijskih elemenata visoke čistoće i komercijalne legure Ti8Al4V. Razvijene su, pod istim uslovima, druge binarne legure (Ti9Al, Ti5Fe, Ti3Mn, Ti6Mn) za isticanje uticaja pojedinih elemenata Al, Fe i Mn na karakteristike legura titana. Mikrostrukturna analiza je otkrila promene mikrostrukture nastale uvođenjem alfa stabilizirajućih elemenata (Al) ili beta stabilizatora (Fe, Mn). Zatim su analizirani efekti svake vrste hemikalija na mikrotvrdoću metalne matrice i gustinu eksperimentalnih legura.

1. Uvod

Neke legure titana dobijaju veliku pažnju kao biomaterijali jer imaju odličnu specifičnu čvrstoću i otpornost na koroziju, ne izazivaju alergijske probleme i najbolju biokompatibilnost među metalnim biomaterijalima [1]. Titanova lakoća i dobra mehano-hemijska svojstva su istaknute karakteristike za upotrebu kao implantata [2]. Čisti titan i legura Ti-6Al-4V i dalje su najčešće korišćeni za biomedicinsku primenu među titanovim biomaterijalima. Na primer, biokompatibilnost legure Ti6Al4V do tada je dovedena u pitanje zbog izveštaja da postepeno oslobađanje aluminijuma, a posebno jona vanadijuma, sa površine može izazvati lokalnu negativnu reakciju tkiva i imunološke reakcije [1, 3 i 4]. Stoga su izraziti zahtevi za razvoj legura titana za biomedicinsku targeted for biomedical application are highly required. Recently, mechanical biocompatibility of biomaterials is regarded as important factor, and therefore the research and development of β types titanium alloys, which are advantageous from that point, are increasing [1]. The β type titanium alloys show excellent cold workability and high strength. The strength of β type titanium alloys can be increased with keeping Young's modulus low by cold working after solution treatment even the elongation and reduction area are a little lowered at low cold work ratio by around 20% [1]. A low Young's modulus equivalent to that of cortical bone is simultaneously required in order to inhibit bone absorption into the implant [5, 6 and 7].

The elements which are judged to be non-toxic and non-allergenic through the reported data of cell viability for pure metals, polarization resistance and tissue compatibility, that can be used as alloying elements are: Nb, Ta, Zr, Sn, Mo, Fe, Hf. Stabilisation of titanium alloys using different alloying elements, for the α-phase (e.g. Al, O) and for β-phase (V, Fe, Mn, Nb, Ta), is a current practice. At a content of more 5wt%aluminium the precipitation of Ti_3Al in the α_2-phase begins, as can be seen from the quasi-binary section in the ternary phase diagram of Ti6Al4V. The α_2-phase provides an extremely high hardening effect so that the aluminium content in titanium alloys must be limited to a maximum value of 8% [8]. Also, grain size of as cast titanium alloy decreases significantly with boron addition [9]. The β phase field extends to higher aluminium contents and the width of the $\alpha+\beta$ two phase region is very narrow, less than 1at% Al. During recent efforts to develop TiAl-base alloys for structural applications only little information has gained on the effect of Fe additions on the mechanical properties [10]. The solid solubility for Fe in all Al-Ti phases is very limited. The maximum content of Fe in αTi is about 1at% at an Al content of 44 at% [11]. Aluminium addition increases the β transus, raising either a eutectoid ($\beta \rightarrow \alpha + Ti_5Si_3$) or peritectoid ($\beta + Ti_5Si_3 \rightarrow \alpha$) reaction temperature in the ternary system [12]. Manganese reduces the α2-Ti3Al level, but otherwise its behaviour is similar to a standard Ti-8Al type alloy [13]. The addition of Mn in Ti has depressed the transformation temperature from α to β phase. The influence of manganese on transition temperature is significant and it is confirmed that the Mn is a β stabilizing addition element for Ti metals. The hardness increased significantly ranging from 83.3GPa (Ti2Mn) to 122GPa (Ti12Mn) and the ductility decreased ranging from 21.3% to 11.7% with

primenu. U poslednje vreme, mehanička biokompatibilnost biomaterijala smatra se važnim faktorom i zato se istraživanje i razvoj legura titana tipa β koje imaju prednost sa te tačke gledišta, povećava [1]. Titanove legure tipa β pokazuju odličnu obradivost na hladno i visoku čvrstoću. Ćvrstoća legura titana tipa β može se povećati održavanjem Jungovog modula niskim, hladnom obradom posle rastvarajućeg tretmana, čak i izduženje i suženje postaju malo smanjeni pri obradi na hladno za oko 20% [1]. Istovremeno je potreban nizak Jungov modul ekvivalentan kortikalnoj kosti da bi se inhibirala apsorpcija kostiju u implantat [5, 6 i 7].

Elementi za koje se zna da su netoksični i nealergenski, zbog objavljenih podataka o ćelijskoj održivosti čistih metala, polarizacijskoj otpornosti i kompatibilnosti tkiva, te se mogu koristiti kao legirajući elementi su: Nb, Ta, Zr, Sn, Mo, Fe, Hf. Stabilizacija titanovih legura korišćenjem različitih legirajućih elemenata, za α-fazu (npr. Al, O) i -β fazu (V, Fe, Mn, Nb, Ta), je trenutna praksa. Sa sadržajem više od 5 mas.% aluminijuma, počinje taloženje Ti_3Al u α_2-fazi, kao što se može videti iz kvazi-binarnog preseka u trojnom faznom dijagramu Ti6Al4V. α_2-faza daje izuzetno visok efekat otvrdnjavanja tako da sadržaj aluminijuma u titanovim legurama mora biti ograničen na maksimalnu vrednost od 8% [8]. Takođe, veličina zrna livene legure titana značajno se smanjuje dodatkom bora [9]. Fazno polje β se proširuje pri većem sadržaju aluminijuma i širina $\alpha+\beta$ dvofazne oblasti je vrlo uska, manja od 1at% Al. Tokom nedavnih napora za razvojem legura na bazi TiAl za konstrukcionuu primenu, stečeno je malo informacija o uticaju dodataka Fe na mehanička svojstva [10]. Rastvorljivost u čvrstom stanju za Fe u svim Al-Ti fazama je vrlo ograničena. Maksimalni sadržaj Fe u αTi je oko 1at%, a sadržaj Al 44 od 44%% [11]. Dodavanje aluminijuma povećava β , podižući temperature ili eutektoidne (($\beta \rightarrow \alpha + Ti_5Si_3$) ili peritektoidne ($\beta + Ti_5Si_3 \rightarrow \alpha$) reakcije u trojnom sistemu [12].

Mangan smanjuje nivo α2-Ti3Al, ali inače je njegovo ponašanje slično standardnoj leguri tipa Ti-8Al [13]. Dodavanje Mn u Ti je smanjilo temperaturu transformacije iz α u β fazu. Uticaj mangana na temperaturu prelaska je značajan i potvrđeno je da je Mn β- stabilizujući dodatni element za Ti metale. Tvrdoća se značajno povećala u rasponu od 83,3GPa (Ti2Mn) do 122GPa (Ti12Mn), a duktilnost se smanjila u rasponu od 21,3% do 11,7% sa povećanjem sadržaja mangana u Ti [14]. Intoksikacije metalnim increasing manganese content in Ti [14]. Intoxications with metallic aluminium are recognised in occupational medicine and in patients submitted to renal dialysis. Since the disease has been linked to a generic defect, aluminium is considered to play a minor role in the onset of Alzheimer's disease [15 and 16]. Iron is biologically omnipresent essential element. Iron is toxic only after extremely high levels of exposure. Iron released by oxidation process does not accumulate in tissues and is immediately metabolised [16]. By restricting grain growth, iron help in formation of fine grained microstructures in titanium alloy. Manganese has no toxic effect except after extreme occupational exposure. It is an essential element and plays a primary role in the activation of multiple enzyme systems [16, 17 and 18]. Manganese is also beneficial to the normal skeletal growth and development. In recent decades research has discovered the special role of manganese plays as a co-factor in the formation of bone cartilage and bone collagen, as well as in bone mineralization [14 and 19]. Beta Ti alloys are most versatile class of Ti alloys offering a wide range of processing and physical-chemical and mechanical properties combinations compared with any other class of Ti alloys [20]. Also, Beta -Ti alloys can be strengthened by heat treatment. The hardness and the elastic modulus increased significantly by increasing the manganese content in the Ti metallic matrix from 2wt.%Mn to 12 wt.% Mn, but the ductility decreased from 21.3wt.% (Ti2Mn) to 11.7wt.% (Ti12Mn). Concentrations of Mn below 8 wt. % in titanium reveal negligible effects on the metabolic activity and the cell proliferation of human osteoblasts [21, 22]. In conclusion, iron and manganese additions are likely to enhance the nucleation rate by providing additional driving force and/or slowing the growth rate by influencing the liquid/solid interfacial characteristics [23]. In the present study there are considering the effects of the elements Al, Fe and Mn on the microstructure and microhardness of titanium alloys for medical applications. Aluminium stabilizes the alpha phase in titanium alloy, having the lamellar appearance, for the content of below 8 wt. % Al. Iron increases the relative density of the alloy and forms three types of compounds. The chemical elements that substantially increases the microhardness of titanium alloy was Fe and Al, if these are introduced simultaneously (634 HV0.1 for Ti8Al5Fe) or singular (502 HV0.1 for Ti5Fe). Effect of Mn on the increasing of hardness is less important, yielding a slight increase of microhardness from 418HV0.1 for Ti3Mn to 427HV0.1 for Ti5.7Mn.

aluminijumom prepoznate su u medicini rada i kod pacijenata koji su podvrgnuti bubrežnoj dijalizi. Pošto je bolest povezana sa generičkim oštećenjem, smatra se da aluminijum igra manju ulogu u nastanku Alzheimerove bolesti [15 i 16]. Gvožđe je biološki sveprisutni esencijalni element. Gvožđe je toksično samo nakon izuzetno visokog nivoa izloženosti. Gvožđe oslobođeno procesom oksidacije ne akumulira se u tkivima i odmah se metabolizuje [16]. Ograničavanjem rasta zrna, gvožđe pomaže u stvaranju sitnozrnate mikrostrukture u leguri titana.

Mangan nema toksično dejstvo osim nakon ekstremnog profesionalnog izlaganja. To je suštinski element i igra primarnu ulogu u aktiviranju više enzimskih sistema [16, 17 i 18]. Mangan je takođe koristan za normalan rast i razvoj skeleta. U poslednjim decenijama istraživanje je otkrilo posebnu ulogu mangana koji je ko-faktor u stvaranju koštane hrskavice i koštanog kolagena, kao i u mineralizaciji kostiju [14 i 19]. Beta Ti legure su najsvestranija klasa Ti legura koje nude širok spektar kombinacija prerade i fizičko-hemijskih i mehaničkih svojstava u poređenju sa bilo kojom drugom klasom Ti legura [20]. Takođe, Beta-Ti legura mogu se ojačati termičkom obradom. Tvrdoća i modul elastičnosti značajno su porasli povećavanjem sadržaja mangana u Ti metalnoj matrici sa 2 tež.% Mn na 12 tež.% Mn, ali duktilnost se smanjila sa 21.3 tež.% (Ti2Mn) na 11.7 tež.%. Koncentracije Mn ispod 8 tež. % u titanu otkriva zanemarljive efekte na metaboličku aktivnost i ćelijsku proliferaciju ljudskih osteoblasta [21, 22].

Zaključno, dodaci gvožđa i mangana verovatno će povećati brzinu nukleacije pružajući dodatnu pokretačku silu i / ili usporavajući brzinu rasta uticajem na tečne / čvrste interfacijalne karakteristike [23]. U ovom istraživanju razmatraju se uticaji elemenata Al, Fe i Mn na mikrostrukturu i mikrotvrdoću titanovih legura za medicinske primene. Aluminijum stabilizuje alfa fazu u leguri titana, koji ima lamelarni izgled, za sadržaj ispod 8 tež. % Al. Gvožđe povećava relativnu gustinu legure i formira tri vrste jedinjenja. Hemijski elementi koji značajno povećavaju mikrotvrdoću legure titana bili su Fe i Al, ako se uvode istovremeno (634 HV0.1 za Ti8Al5Fe) ili pojedinačno (502 HV0.1 za Ti5Fe). Uticaj Mn na povećanje tvrdoće je manje važan, što dovodi do blagog porasta mikrotvrdoće sa 418HV0.1 za Ti3Mn na 427HV0.1 za Ti5.7Mn.

2. Experimental details

2.1 Obtaining of new titanium alloys

The experimental alloys were produced by melting in an argon inert atmosphere of the RAV installation, using high purity metallic materials and the commercial alloy Ti8Al4V. Under the same conditions, other binary alloys (Ti9Al, Ti5Fe, Ti3Mn and Ti6Mn) has been obtained for highlighting the effects of the singular elements Al, Fe and Mn on the characteristics of titanium alloys. The alloys composition was conducted from a trade mark alloys (Ti8Al4V), and subsequently 6 experimental titanium alloys were obtained, by changing the content of chemical elements like Fe, Mn and Al. These alloys were developed as a basis of comparison for the study of the singular effects of alloying elements Al, Fe and Mn. Chemical composition of the alloys obtained in this study, determined by spectrophotometry, is presented in Table 1.

2. Detalji eksperimenta

2.1 Dobijanje novih legura titana

Eksperimentalne legure su proizvedene topljenjem u inertnoj atmosferi argona RAV instalacije, korišćenjem metalnih materijala visoke čistoće i komercijalne legure Ti8Al4V. Pod istim uslovima, druge binarne legure (Ti9Al, Ti5Fe, Ti3Mn i Ti6Mn) su dobijene za isticanje uticaja pojedinih elemenata Al, Fe i Mn na karakteristike titanovih legura. Sastav legura je izveden iz legura trgovačke marke (Ti8Al4V), a zatim je dobijeno 6 eksperimentalnih legura titanijuma, promenom sadržaja hemijskih elemenata poput Fe, Mn i Al. Ove legure su razvijene kao osnova za upoređivanje za proučavanje pojedinačnih efekata legirajućih elemenata Al, Fe i Mn. Hemijski sastav legura dobijenih u ovom istraživanju, određen spektrofotometrijom, prikazan je u Tabeli 1.

Sample Uzorak	Chemical elements (wt.%) Hemijski elementi (tež.%)					
	Mn	Fe	Al	V	Sn	Ti
Ti8Al4V trade mark	0.03	0.03	8.26	2.44	0.82	Ba l.
Ti8Al	0.16	0.11	8.4	0.04	0.8	
Ti8Al2.8Fe	0.16	2.85	8.35	0.04	0.82	
Ti9Al5Fe	0.07	5.1	9.35	0.04	0.78	
Ti5Fe	0.07	4.9	0.06	0.04	0.78	
Ti5.7Mn	5.77	0.11	0.06	0.04	0.94	
Ti3Mn	3.07	0.10	0.06	0.04	0.72	

Table 1. *Chemical composition of new titanium alloys*
Tabela 1. *Hemijski sastav novih legura titana*

2.2 Welding of new titanium alloys

The mechanical properties of the welded titanium alloys depend on the structural characteristics of each welding zone, which in turn depends on the thermal cycles during welding and heat treatments. The fusion zone for titanium alloys is characterized by the presence of β-phase, which forms columnar grains during solidification at welding. The size and morphology of these grains depending on the heat flow loss during welding solidification. Although the welding procedures and equipment used for austenitic stainless steel and aluminium alloys can be applied in order to join commercially pure titanium and most of titanium alloys, their increased reactivity with atmospheric elements at high temperatures necessitates additional precautions to shield the molten weld pool. The titanium interacts actively with atmospheric gases, such as oxygen,

2.2 Zavarivanje legura titana

Mehanička svojstva zavarenih legura titana zavise od strukturnih karakteristika svake zone zavarivanja, što zavisi od toplotnih ciklusa tokom zavarivanja i termičke obrade. Zonu stapanja za legure titana karakteriše prisustvo β -faze koja formira stubičasta zrna tokom očvršćavanja pri zavarivanju. Veličina i morfologija ovih zrna zavisi od gubitka toplotnog protoka tokom očvršćavanja. Iako se postupci zavarivanja i oprema koja se koristi za austenitni nerđajući čelik i legure aluminijuma mogu primeniti kod komercijalno čistog titana i većine titanovih legura, njihova povećana reaktivnost sa atmosferskim elementima na visokim temperaturama zahteva dodatne mere predostrožnosti kako bi se zaštitila zavarivačka kupka. Titan aktivno stupa u interakciju sa atmosferskim gasovima, kao što su kiseonik, vodonik, azot tokom zagrevanja iznad 350 ^{o}C, što hydrogen, nitrogen during the heating more than 350 °C, conducting to decrease of the weld mechanical properties. Titanium alloys are sensitive to thermal cycle due to a heavy increase of grains during heating and cooling in the area of β phase. Therefore, during welding a minimum heat input value must be chosen. The main welding processes that can be used for joining titanium alloys are: TIG and MIG welding, friction welding, electron beam welding and laser welding [25 and 26].

The paper presents the effects of some alloying elements (Al, Fe and Mn) on the microstructure and microhardness of titanium alloys that was welded using GTAW process. The Ti-based experimental alloys were welded by TIG welding by simultaneously melting the ends of the overlapping samples without filler material, given the relatively small dimensions of the parts. The Ti6Al4V alloy 1.6 mm-thick samples were welded using the TIG process and Ti6Al4V filler material 1.6mm-thick, using a welding device that provided the inert shielding gas to the welded root. The values of welding parameters were: welding current, Is = 20A; arc voltage, Ua = 10V; Welding Gas flow = 12l/min; Root Gas flow = 5 l/min. After welding, the samples were cut and the cross sections were prepared for microstructural analyses (fig. 1).

dovodi do smanjenja mehaničkih svojstava spoja. Legure titana su osetljive na toplotni ciklus zbog velikog povećanja zrna tokom zagrevanja i hlađenja u oblasti β faze. Zbog toga se tokom zavarivanja mora odabrati minimalna vrednost unosa toplote. Glavni postupci zavarivanja koji se mogu koristiti za spajanje legura od titana su: TIG i MIG zavarivanje, zavarivanje trenjem , zavarivanje elektronskim snopom i laserom [25 i 26].

U radu su prikazani uticaji nekih legirajućih elemenata (Al, Fe i Mn) na mikrostrukturu i mikrotvrdoću titanovih legura koji su zavareni postupkom TIG. Eksperimentalne legure na bazi Ti su zavarene TIG zavarivanjem istovremeno topljenjem krajeva uzoraka koji se preklapaju bez dodatnog materijala s obzirom na relativno male dimenzije delova. Uzorci od legure Ti6Al4V su 1,6 mm debljine, zavareni TIG postupkom i Ti6Al4V dodatni materijal debljine 1,6 mm, koristeći uređaj koji je obezbedio zaštitu inertnim gasom zavarenog korena. Vrednosti parametara zavarivanja bile su: struja zavarivanja, Is = 20A; napon, Ua = 10V; protok zavarivačkog gasa = 12l / min; protok gasa za zaštitu korena = 5 l / min. Nakon zavarivanja, uzorci su isečeni i poprečni preseci pripremljeni su za mikrostrukturne analize (slika 1).

a) b)

Figure 1. *Cross sections through welded samples: a)Ti5Fe alloy; b) Ti3Mn alloy*

Slika 1. *Poprečni preseci zavarenih uzoraka a)Ti5Fe legura; b) Ti3Mn a)Ti5Fe alloy; b) Ti3Mn alloy*

3. Results

3.1 Microstructure

For metallographic analysis the samples were precision cutting and then were subsequently embedded in resin and polished using metallographic paper with different grain sizes (600 to 2500 grit paper) and abrasive paste (grain size between 0.6 to 0.1 µm). Metallographic etching reagent was used with the following composition: 10% HF + 30% HNO3 + 50ml deionized water. The samples were examined by optical microscopy (Olympus GX51 optical microscope).

In the case of the commercial Ti8Al4V alloy processed by rolling we can observe very fine grain and orientated in strings (figure 2). After remelting, the microstructure is dendritic, with clear differentiation of the aluminium-rich phase, α phase

3. Rezultati

3.1 Mikrostruktura

Za metalografske analize, uzorci su precizno sečeni, a zatim su ugrađeni u smolu i polirani etalografskim papirom različitih veličina zrna (papir od 600 do 2500 grit) i brusne paste (veličina zrna između 0,6 do 0,1 µm). Upotrebljen je metalografski reagens za nagrizanje sledećeg sastava: 10% HF + 30% HNO3 + 50 ml dejonizovane vode. Uzorci su ispitani optičkom mikroskopom (Olimpus GKS51 optički mikroskop). U slučaju komercijalne legure Ti8Al4V dobijene valjanjem možemo primetiti vrlo fino zrno i orijentisano u nizovima (slika 2). Posle pretapanja, mikrostruktura je dendritna, sa jasnom diferencijacijom faze bogate aluminijumom, α faze i Ti3Al faze. Sistem Ti-Al uključuje sledeća jedinjenja: TiAl (kongruentan, tačka topljenja 1733 and Ti3Al phase. The system Ti-Al includes the following compounds: TiAl (congruent, melting point 1733 K), $TiAl_3$ (congruent, melting point 1613 K), Ti_3Al, $TiAl_2$ and Ti_2Al_5 (incongruent). The compounds TiAl and $TiAl_3$ are the most stable [17, 18].

K), TiAl3 (kongruentan, tačka topljenja 1613 K), Ti3Al, TiAl2 i Ti2Al5 (inkoguentno). Jedinjenja TiAl i TiAl3 su najstabilnija [17, 18].

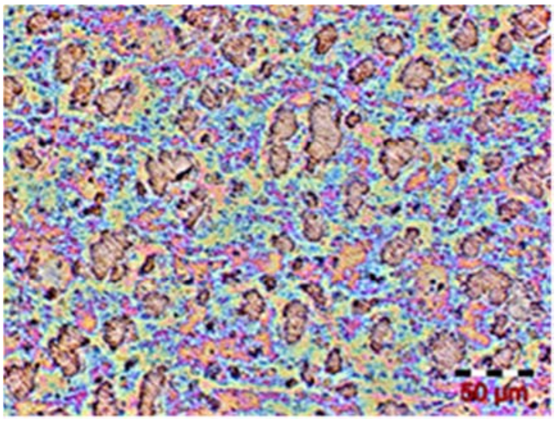

Figure 2. *Microstructure of commercial Ti8Al4V alloy*
Slika 2. *Mikrostruktura komercijalne Ti8Al4V legure*

The addition of 6 wt% aluminium to the CP titanium did not change the as-cast microstructure, and this is in correlation to the fact that aluminium has a very high solid solubility in titanium [24].

For 9 wt% Al addition or more, in conformity with the Ti-Al phase diagram, some intermetallic second phase can form (Ti_3Al) (figure 3). TiAl based materials are pursued mainly because of their high thrust-to-weight ratio of high –performance aircraft engines.

The microstructure of these alloys can be controlled by heat treatment. The optimum desirable properties in this class of alloys could be achieved only with (α_2+γ) microstructure, which corresponds to the composition Ti48Al [2].

Dodavanje 6 tež.% aluminijuma u CP titan nije promenilo mikrostrukturu livenog materijala, a to je u korelaciji sa činjenicom da aluminijum ima veoma visoku rastvorljivost u čvrstom stanju titana [24].

Za dodavanje 9 tež% Al ili više, u skladu sa faznim dijagramom Ti-Al, može se formirati neka intermetalna druga faza (Ti3Al) (slika 3). TiAl materijali traženi su uglavnom zbog visokog odnosa snage i težine kod motora aviona visokih performansi.

Mikrostruktura ovih legura može se kontrolisati termičkom obradom. Optimalna poželjna svojstva u ovoj klasi legura mogu se postići samo (α_2+γ) mikrostrukturom, što odgovara sastavu Ti48Al [2].

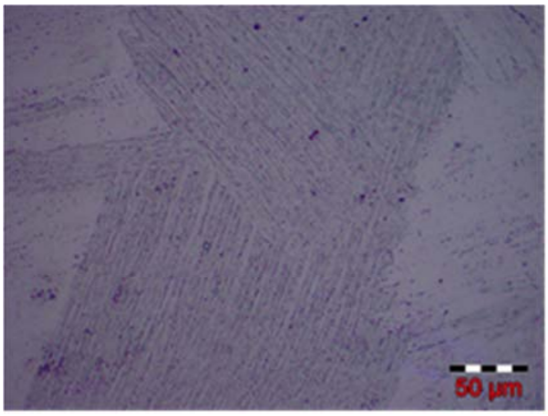

Figure 3. *Microstructure of experimental Ti8Al alloy*
Slika 3. *Mikrostruktura eksperimentalne legure Ti8Al*

The addition of 2.8% Fe in the alloy Ti8Al promotes the change of β phase proportion, although alpha phase is still predominant (figure 4). The specific aspect of metallic matrix is lamellar, with dispersed particles of intermetallic compounds (Ti3Al), both in base material and weld (figure 5).

Dodavanje 2,8% Fe u leguri Ti8Al pospešuje promenu udela β faze, iako alfa faza i dalje preovlađuje (slika 4). Specifični aspekt metalne matrice je lamelarni, sa raspršenim česticama intermetalnih jedinjenja (Ti3Al), kako u osnovnom materijalu, tako i u šavu (slika 5).

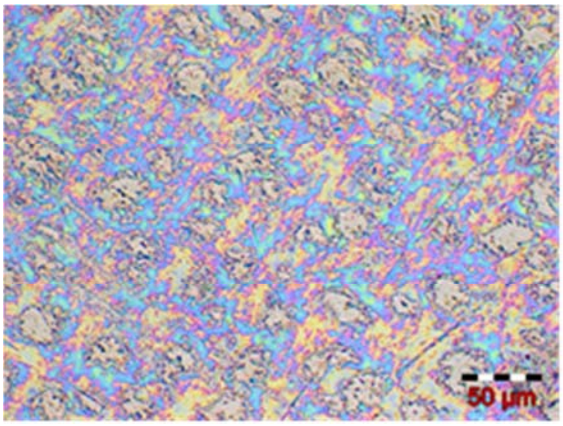

Figure 4. *Microstructure of experimental Ti8Al2*
***Slika 4**. Mikrostruktura eksperimentalne legure Ti8Al2*

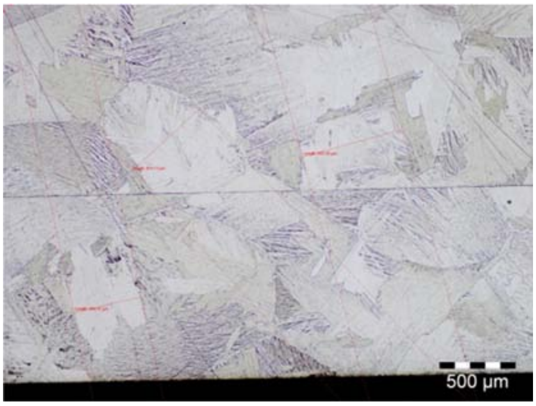

Figure 5. *Microstructure of weld for T8Al2 alloy*
Slika 5. *Mikrostruktura šava kod legure Ti8Al2*

Analysing Ti-Fe system, we can conclude that this alloy includes the following compounds: TiFe2 (congruent, melting point at 1700 K), TiFe (incongruent, melting point at 1650 K), Ti2Fe (incongruent, melting point at 1358 K). The most stable compound is TiFe2 [17, 19]. Increasing of Fe content up to 5 wt% in the alloy metal matrix Ti8Al no reveal any substantial change of the microstructure in terms of the types of existing phases (figure 6).

It notes, however, a spheroidization tendency and grain finishing compound TiFe2, with average diameter value of 25 μm in the case of the alloy with 2.5%wt Fe, to about 15 μm in the case of alloy having 5%wt Fe.

Analizirajući sistem Ti-Fe, možemo zaključiti da ova legura uključuje sledeća jedinjenja: TiFe2 (kongruentna, tačka topljenja na 1700 K), TiFe (inkongruentna, tačka topljenja 1650 K), Ti2Fe (inkoguentna, tačka topljenja na 1358 K). Najstabilnije jedinjenje je TiFe2 [17, 19]. Povećanje sadržaja Fe do 5 mas.% u matrici legiranog metala Ti8Al ne otkriva značajne promene mikrostrukture u smislu vrsta postojećih faza (slika 6).

Međutim, primećuje se tendencija sferoidizacije i završavanja zrna jedinjenja TiFe2, prosečne vrednosti prečnika od 25 μm u slučaju legure sa 2,5 mas.% Fe, do oko 15 μm u slučaju legure sa 5 mas.% Fe.

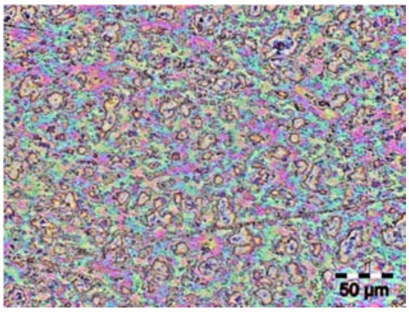

Figure 6. *Microstructure of experimental Ti9Al5Fe alloy*
Slika 6. *Mikrostruktura eksperimentalne legure Ti9Al5Fe*

The intermetallic compounds TiFe2 are relatively uniform dispersed into metallic matrix of Ti5Fe alloy (figure 7).

Intermetalna jedinjenja TiFe2 su relativno jednoliko dispergovana u metalnoj matrici legure Ti5Fe (slika 7).

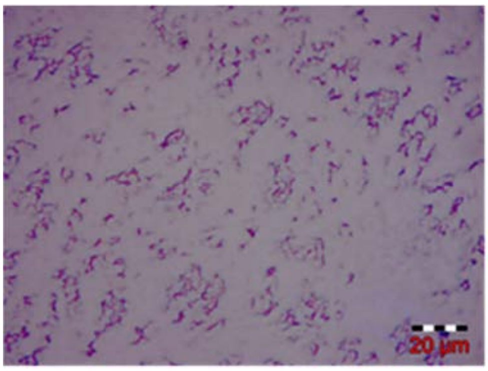

Figure 7. *Microstructure of Ti5Fe alloy*
Slika 7. *Mikrostruktura legure Ti5Fe*

Increasing the Fe content in titanium above the maximum solubility value has led to the separation of some compounds on the grain boundaries of the weld (figure 8).

Povećanje sadržaja Fe u titanu iznad maksimalne vrednosti rastvorljivosti, dovelo je do izdvajanja nekih jedinjenja na granicama zrna u šavu (slika 8).

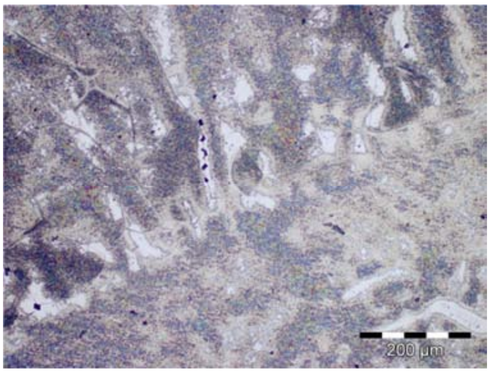

Figure 8. *Microstructure of weld and heat affected zone for Ti5Fe alloy*
Slika 8. *Mikrostruktura šava i zone uticaja toplote kod legure Ti5 Fe*

By alloying titanium with Mn, phase stabilization is achieved, with uniform equiaxed grains β (figure 9).
The Mn could be used in lower concentrations as an alloying element for biomedical titanium.
The Ti2Mn, Ti5Mn, and Ti8Mn alloys with good mechanical properties and acceptable cytocompatibility have a potential for use as bone substitutes and dental implants [23].

Legiranjem titana sa Mn postiže se fazna stabilizacija, sa ravnomerno izjednačenim β zrnima (slika 9).
Mn se može koristiti u nižim koncentracijama kao legirajući element za biomedicinski titan.
Legure Ti2Mn, Ti5Mn i Ti8Mn sa dobrim mehaničkim svojstvima i prihvatljivom cito-kompatibilnošću mogu se koristiti kao zamena za kosti i kao zubni implantat [23].

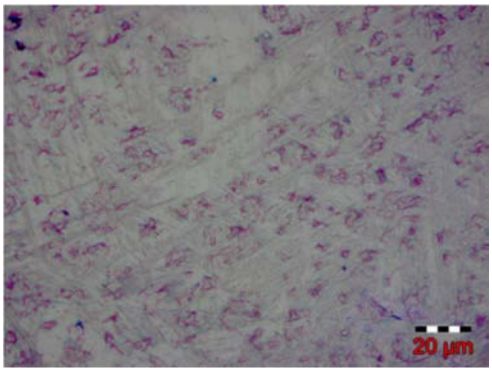

Figure 9. *Microstructure of Ti3Mn alloy*
Slika 9. *Mikrostruktura legure Ti3Mn*

Further increasing of Mn content (5.7%wt Mn) increases the proportion of intermetallic compounds that will separate into the metallic matrix having fine and lamellar aspect, even into base material (figure 10) and weld (figure 11).

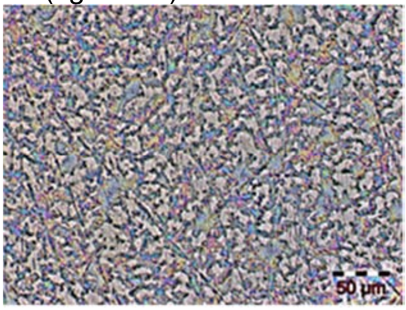

Figure 10. *Microstructure of experimental Ti5.7Mn*
Slika 10. *Mikrostruktura eksperimentalne legure Ti5,7 Fe*

3.2 Microhardness

The general trend of the increase in hardness for the TiFe and TiMn alloys can be explained by solid solution strengthening mechanism. When the titanium lattice is disorder by substitutional solid solution additions, it becomes strained or there is an increase in internal energy of the system due to lattice straining caused by an increase in amount of the doping element which results in localized straining on substitutional sites [23 and 24]. The average values of microhardness, measured using a Shimadzu HMV 2T apparatus in 10 different points of the alloys analysed in this paper, are shown in Figure 12.

Daljnjim povećanjem sadržaja Mn (5,7 mas.% Mn) povećava se udeo intermetalnih jedinjenja koja će se odvojiti u metalnu matricu koja ima fini i lamelarni oblik, čak i u osnovni materijal (slika 10) i šav (slika 11).

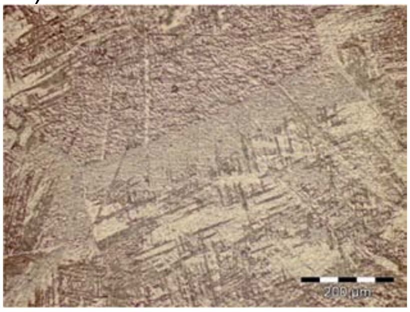

Figure 11. *Microstructure of weld for Ti5.7Mn alloy*
Slika 11. *Mikrostruktura šava kod legure Ti5.7Mn*

3.2 Mikrotvrdoća

Opšti trend povećanja tvrdoće za TiFe i TiMn legure može se objasniti mehanizmom ojačavanja rastvaranjem. Kada je rešetka titana poremećena dodavanjem supstitucionih čvrstih rastvora, ona postaje deformisana ili dolazi do povećanja unutrašnje energije sistema usled deformacije rešetke izazvane povećanjem količine "doping" elementa što dovodi do lokalizovane deformacije na mestu zamene [23 i 24]. Prosečne vrednosti mikrotvrdoće, merene uređajem Shimadzu HMV 2T u 10 različitih tačaka na analiziranim legurama u ovom radu, prikazane su na slici 12.

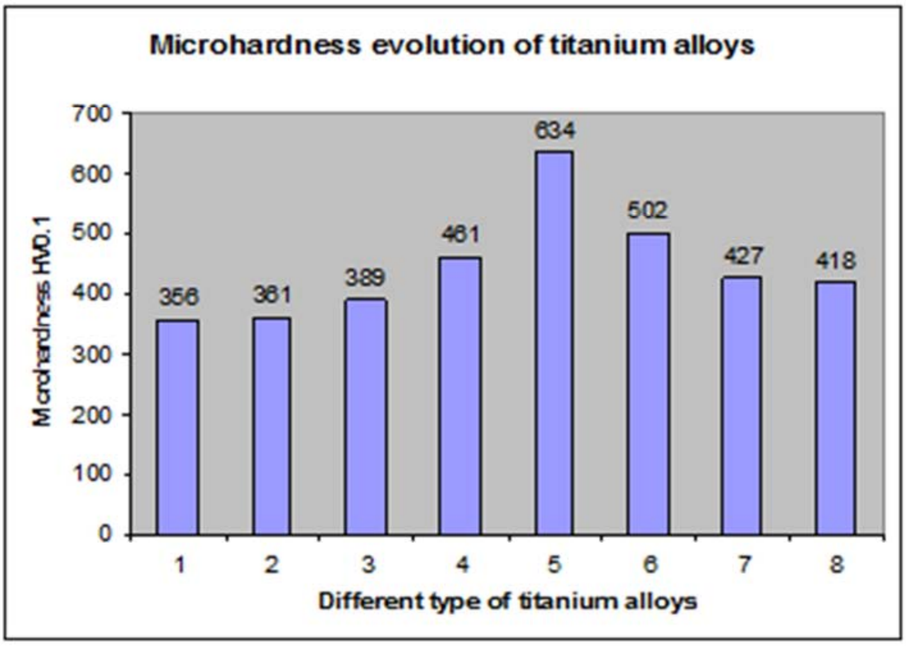

Figure 12. *The microhardness average values for different type of titanium alloys: 1 - Ti8Al4V trade mark alloy; 2 - Ti8Al4V remelted; 3- Ti8Al; 4- Ti8Al2.8Fe; 5- Ti9Al5Fe; 6- Ti5Fe; 7- Ti5.7Mn; 8- Ti3Mn*
Slika 12. *Srednje vrednosti mikrotvrdoće za različite legure titana: 1 - Ti8Al4V komercijalna oznaka legure; 2 - Ti8Al4V pretopljena; 3- Ti8Al; 4- Ti8Al2.8Fe; 5- Ti9Al5Fe; 6- Ti5Fe; 7- Ti5.7Mn; 8- Ti3Mn*

The highest value of hardness was recorded for the Ti9Al5Fe alloy (634HV0.1), benefiting from the presence of aluminium and iron, which causes the formation of hard secondary phases. Significant hardness values were also measured for Ti8Al2.8Fe (502HV0.1) and Ti5Fe (461HV0.1) alloys.

4. Conclusion

Alloying elements introduced in titanium alloy have different effects on the microstructure, the relative density and the microhardness.

Aluminium stabilizes the alpha phase in titanium alloy, having the lamellar appearance, for the content of below 8 wt% Al. Above this value, the precipitation of the compound Ti3Al appears in the form of scattered islands of irregular shape.

Iron forms three types of compounds, the most stable being TiFe2. The presence of iron increases the relative density of the alloy.

The addition of Mn in titanium reduces the alpha to beta transformation temperature and increase the relative density. Also, the presence of Mn in the titanium increases the proportion of intermetallic compound separately in the metallic matrix with finely lamellar appearance. The chemical elements that substantially increases the microhardness of titanium alloy are Fe and Al, if these are introduced simultaneously (634 HV0.1 for Ti8Al5Fe) or singular (502 HV0.1 for Ti5Fe). Effect of Mn on the increasing of hardness is less important, yielding a slight increase of microhardness from 418HV0.1 for Ti3Mn to 427HV0.1 for Ti5.7Mn. The welding behaviour of the new titanium alloys using TIG process is appropriate if the requirements for a good protection with inert gas both on the surface of the samples and at the root of the weld is respected. A more pronounced tendency of welding pore formation was recorded for Ti5Fe alloy.

By keeping low values of linear welding energy, the tendency of grain size increasing in the weld and the heat affected zone can be avoided.

Rapid cooling after welding of biocompatible titanium alloys with Mn leads to the emergence of acicular phases without the excessive increase in hardness, which is a beneficial effect in maintaining the mechanical characteristics close to those of the human bone.

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Najveća vrednost tvrdoće zabeležena je za leguru Ti9Al5Fe (634HV0.1), koja ima koristi od prisustva aluminijuma i gvožđa, što izaziva stvaranje čvrstih sekundarnih faza. Značajne vrednosti tvrdoće su takođe merene kod legure Ti8Al2.8Fe (502HV0.1) i Ti5Fe (461HV0.1).

4. Zaključak

Legirani elementi uvedeni u leguru titana imaju različite efekte na mikrostrukturu, relativnu gustinu i mikrotvrdoću.

Aluminijum stabilizuje alfa fazu u legurama titana, koji ima oblik lamele, za sadržaj ispod 8 tež.% Al. Iznad ove vrednosti talog jedinjenja Ti3Al se pojavljuje u obliku raštrkanih ostrva nepravilnog oblika.

Gvožđe formira tri vrste jedinjenja, od kojih je najstabilnija TiFe2. Prisustvo gvožđa povećava relativnu gustinu legure.

Dodavanje Mn u titanu smanjuje temperaturu transformacije alfa u beta i povećava relativnu gustinu. Takođe, prisustvo Mn u titanu povećava udeo intermetalnog jedinjenja odvojenog u metalnoj matrici sa fino lamelarnim izgledom.

Hemijski elementi koji značajno povećavaju mikrotvrdoću legura titana su Fe i Al, ako se uvode istovremeno (634 HV0.1 za Ti8Al5Fe) ili pojedinačno (502 HV0.1 za Ti5Fe). Uticaj Mn na povećanje tvrdoće je manje važan, što dovodi do neznatnog povećanja mikrotvrdoće sa 418HV0.1 za Ti3Mn na 427HV0.1 za Ti5.7Mn.

Ponašanje pri zavarivanju novih legura titana TIG postupkom je pogodno ako se poštuju zahtevi za dobrom zaštitom inertnim gasom i na površini uzoraka i na korenu zavara.

Zabeležena je izraženija tendencija stvaranja pora pri zavarivanju legure Ti5Fe.

Zadržavanjem niskih vrednosti linearne energije zavarivanja može se izbeći tendencija povećanja veličine zrna u šavu i zoni uticaja toplote.

Brzo hlađenje nakon zavarivanja biokompatibilnih legura titana sa Mn dovodi do stvaranja acikularnih faza bez prekomernog povećanja tvrdoće, što povoljno utiče na održavanje mehaničkih karakteristika bliskih onima ljudske kosti.

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References
Reference

[1] M. Niinomi, Recent research and development in titanium alloys for biomedical applications and healthcare goods, Science and Technology of Advanced Materials 4 (2003) 445-454.

[2] C. Oldani, A. Dominguez, Titanium as a Biomaterial for Implants, Recent Advanced in Arthroplasty, (2012) 149-162.

[3] E.A. Levashov, M.I.Petrzhik, D.V. Shtansky, Ph.V. Kirykhantsev-Korneev, A.N. Sheveyko, R.Z. Valiev, D.V. Gunderov, S.D. Prokoshkin, A.V. Korotitskiy, A.yu. Smolin, Nanostructured titanium alloys and multicomponent bioactive films: Mechanical behaviour at indentation, Materials Science and Engineering A 570 (2013) 51-62.

[4] H. Michelle Grandin, S. Berner, M. Dard, A Review of Titanium Zirconium (TiZr) Alloys for Use in Endosseous Dental Implant, Materials 2012, Vol.5, 1348-1360.

[5] C.N. Elias, J.H.C. Lima, R.Valiev, M.A. Meyers, Biomedical Applications of Titanium and its alloys, Biological Materials Science, JOM (2008) 47-49.

[6] M. Niinomi, Biologically and Mechanically Biocompatible Titanium Alloys, Materials Transactions, Vol. 49, No 10 (2008) 2170-2178.

[7] H.W. Jeong, S.E. Kim, Y.T. Hyun, Y.T. Lee, J.K. Park, Microstructures and Elastic Moduli of Binary Titanium Alloys Containing Biocompatible Alloying Elements, Materials Science Forum, Vols. 475-479 (2005) 2291-2294.

[8] H.J. Breme, J.A. Helsen, *Metals as Biomaterials-Selection of Materials*, Biomaterials Science and Engineering Series, Wiley, (1998) 20-21.

[9] J. Malek, F. Hnilica, J. Vesely, Beta Titanium Alloy Ti35Nb6Ta with Boron Addition, *Metal 2012*, Brno, Czech Republic, p. 6.

[10] I. Ohnuma, Y. Fujita, H. Mitsui, K. Ishikawa, R. Kainuma, K. Ishida, Phase equilibrium in the Ti-Al binary system, Acta Mater. Vol. 48, Iss. 12 (2000) 3113-3123.

[11] Y.L.Hao, D.S. Xu, Y.Y. Cui, R. Yang, D.Li, Acta mater. 47 (1999) 1129.

[12] C.R. de Farias Azevedo, H.M. Flower, Microstructure and phase relationships in Ti-Al-Si System, Materials Science and Technology, Vol. 15 (1999) 869-877.

[13] N. Saunders, Phase Equilibria in Multi-Component γ-TiAl Based Alloys, “Gamma Titanium Aluminides” (1999), p. 183.

[14] F. Zhang, E. Burkel, Novel Titanium Manganese Alloys and Their Macroporous Foams for Biomedical Applications Prepared by Field assisted Sintering, Biomedical engineering, Trends in materials Science, (2011) 203-224.

[15] H.J. Breme, V.Biehl, J.A. Helsen, Metals and implants, Biomaterials Science and Engineering Series, Wiley (1998) 54-55.

[16] H.F. Hildebrand, J.C. Hornez, Biological response and biocompatibility, Biomaterials Science and Engineering Series, Wiley (1998) 268-270.

[17] F. Shank, Structure of binary alloys, Metallurgy (1973) p. 759.

[18] M. Hansen, K. Anderko, Structure of binary alloys, vol. 1 (1962) p. 607.

[19] Hansen, M., Anderko, K., Structure of binary alloys, vol. 2 (1962) p. 1487.

[20] M. Ikeda, M. Ueda, R. Matsunaga, M. Ogawa, M. Niinomi, Isothermal Aging Behaviour of Beta Titanium – manganese Alloys, Materials Transactions, Vol. 50, no.12 (2009) 2737 -2743.

[21] R. Baloyi, Investigation into the Effect of Solid Solution Chemistry on Lattice Parameters and Microstructural Properties of beta-Ti Alloys, dissertation Johannesburg, 2010.

[22] S. Tamirisakandala, R.B. Bhat, J.S. Tiley, D.B. Miracle, Grain refinement of cast titanium alloys via trace boron addition, Scripta Materialia, Vol. 53 (2005), 1421-1426.

[23] M.J. Bermingham, S.D. McDonald, M.S. Dargusch, D.H. StJohn, Microstructure of Cast Titanium Alloys, Materials Forum, volume 31 (2007) 84 – 89.

[24] Zhang F., Weidmann A., Nebe J.B., Beck U., Burkel E., Preparation, microstructures, mechanical properties and cytocompatibility of TiMn alloys for biomedical applications, J. Biomed Mater, Res B, App. Biomater, (2010), 94 (2) 406-13.

[25] I.Voiculescu, V.Geanta, E.M. Binchiciu, P. Vizureanu, H. Binchiciu. Welding behaviour of new biocompatible titanium alloys. VIIIth International Metallurgical Congress, Ohrid, Macedonia, 2018.

[26] I. Voiculescu, O.G. Donţu, V. Geantă, S. Ganatsios, Effect of the Laser Beam Superficial Heat Treatment on the Gas Tungsten Arc Ti-6Al-V Welded Metal Microstructure, Conference on Industrial Laser Applications (INDLAS 2007) Bran, ROMANIA , INDUSTRIAL LASER APPLICATIONS, Proceedings of SPIE, Vol. 7007, Article no.: 70070M (2007).