Combination of Laser-Assisted Development of Novel Ti-Ta Alloys for Biomedical Applications
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Martim Teixeira\textsuperscript{1,2}, Carole Loable\textsuperscript{1,2}, Amelia Almeida\textsuperscript{1,2}, Odila Florêncio\textsuperscript{3}, J.C.S. Fernandes\textsuperscript{1,2}, Rui Vilar\textsuperscript{1,2}

\textsuperscript{1}Instituto Superior Técnico, Dep. Chemical Engineering, Universidade Técnica de Lisboa
\textsuperscript{2}ICEMS - Instituto de Ciência e Engenharia de Materiais e Superfícies
Av. Rovisco Pais, 1049-001 Lisbon, Portugal
\textsuperscript{3}Department of Physics, Universidade Federal de São Carlos, Brazil

Abstract

Ti and its alloys are commonly used for biomedical implants. These alloys, developed for aeronautical applications, are not optimized for medical use. Major limitations of current alloys are the presence of elements that are toxic or associated to neurological disorders, and excessive stiffness, that leads to stress shielding and may result in bone resorption and implant failure. A need remains to design new alloys for biomedical applications that fulfill requirements such as biocompatibility, wear and corrosion resistance, and adequate stiffness, strength, toughness and fatigue resistance. Alloying Ti with \(\beta\)-phase stabilizers allows obtaining alloys with biomechanical behavior closer to that of bone than current ones. However, new materials development using conventional alloying techniques can be time- and resources-consuming, since it requires the production, characterization and testing of a significant number of discrete composition samples. In this study, the combinatorial method based on variable composition laser deposition is used to produce new Ti-based alloys with composition varying continuously along a single clad track. The alloys are then characterized and tested using microscale techniques, allowing a rapid screening of their structure and properties over a wide range of compositions. A summary of the results obtained for the Ti-Ta alloy system will be presented and discussed in terms of alloy constitution, microstructure and resulting properties, demonstrating the potential application of the laser-assisted combinatorial method to discover Ti alloys with most promising properties for biomedical load-bearing applications.

Introduction

Titanium and its alloys are commonly used for hard tissue replacements such as artificial hip joints, bone plates and screws for fracture fixation because of its high biocompatibility, strength and corrosion resistance [1-3]. However, pure Ti and the commonly used implant alloy, Ti-6Al-4V ELI, were originally designed for use as general structural materials, particularly in aerospace applications [4]. Their mechanical properties, in particular the elastic modulus, are higher than that of bone [5]. Thus, implants of these materials support most of the stress rather than transferring part to the surrounding bone, thereby causing bone resorption around the implant and preventing it from regenerating [6,7]. In addition, Al and V are toxic elements and are associated with long-term health problems such as Alzheimer’s and neuropathy [7,8]. Thus, there is a need to find Ti alloys with non-toxic alloying elements and mechanical properties closer to that of bone than current alloys.

It has been known that \(\beta\)-Ti alloys show low modulus and high strength [9]. Among the Ti\(\beta\)-stabilizing elements, Nb, Ta, Mo are those that do not cause inflammations and harmful effects to the body [5,10,11]. The development of new Ti alloys with these elements has been a subject of significant research in the last decade and has lead to solutions with interesting properties and behavior. \(\beta\) type alloys with moduli between 55 to 85 GPa have been developed [5]. However, further developments are necessary to find solutions with improved balance between biomechanical, corrosion and biological behavior.

Ta has been considered a biocompatible metal with great potential as biomaterial. It shows excellent corrosion resistance, and good mechanical properties, the major drawback being its high density and high melting temperature. Previous research based on first principles calculations suggested that Ta has the potential to enhance the strength and reduce the Young's modulus of Ti [12]. Several authors have studied discrete composition Ti-Ta alloys and some
alloys with promising properties and behavior have been found.

Finding the optimal composition of the combination of these elements with Ti using conventional alloying techniques can be time consuming and costly as it requires the preparation, analysis and testing of a significant number of discrete composition samples. Exploring the mechanical properties, fatigue and biocompatibility of alloys with various compositions of alloying elements require a large amount of time and resources.

In this work the combinatorial alloy development method based on variable powder feed rate laser cladding, previously developed by the team [13] was used to design new Ti alloys for implant and prosthetic applications. The study involves the rapid and exhaustive preparation of a range of alloys with compositions variable along the clad track, the screening of interesting compositions based on characterization of the microstructure, and the evaluation of mechanical and wear properties by microscale techniques. This method has been recently applied by the authors to the development of Ti-Mo [14] and Ti-Mo-Zr alloys [15] with very promising microstructure and properties for orthopedic applications. In particular, it was shown that the microstructure and properties of alloys developed by laser deposition are similar to those obtained by casting methods proving the enormous potential of the technique in Ti alloy development. This is especially important as laser 3D manufacturing processes are becoming increasingly relevant for the production of customized prostheses. In the present paper, the method has been applied to the development of Ti-Ta alloys, with microstructure and properties optimized for use in implants and prostheses. The study involved the preparation of a range of continuously variable composition Ti-Ta alloys by variable powder feed rate laser cladding, followed by the screening of these alloys for their composition, microstructure, mechanical properties and corrosion behavior.

**Materials and Methods**

The laser cladding experiments were carried out using a 2 kW continuous wave Nd:YAG laser. A plate of commercially pure grade 2 titanium was used as substrate. Prior to deposition the substrates were sandblasted and cleaned in alcohol in an ultrasonic bath. The powders were heated at 100°C for 24 h. Due to the high reactivity of titanium with oxygen and nitrogen at high temperature that often lead to embrittlement, the deposition process was carried out in a chamber, under controlled argon atmosphere, to avoid contamination. Powder feeding was carried out using a lateral nozzle kept at a 45° angle to the horizontal. The laser was incident at an angle of 80° to the substrate to prevent damage to the optical fiber and the laser cavity by the reflected beam. The alloys were deposited using a two-hopper powder feeder: one hopper containing pure Ti powder and the other pure Ta powder. By computer controlling the mass flow rate of each powder it is possible to deposit variable composition clad tracks. 80 mm long tracks have been produced in two ranges of nominal compositions: one ranging from pure Ti to Ti-30%Ta and the other ranging from Ti-30%Ta to Ti-90%Ta (wt%). Deposition was carried out using a laser beam power of 2 kW at a scanning speed of 5 mm/s.

The surfaces of the tracks were metallographically polished and etched in Kroll’s reagent (2 vol.% HF, 6 vol.% HNO₃, distilled water). The composition of the alloys was measured along the tracks length by EDS microanalysis. The microstructure of the tracks was characterized in detail by optical and scanning electron microscopy. The alloys constitution was evaluated by X-ray diffraction analysis. The tests were made in Bragg-Brentano configuration, using Cu Kα radiation. The microhardness and Young’s modulus of the samples were measured by depth sensing ultramicroindentation tests (Shimadzu DUH-211S). The indentation tests were carried out using a Berkovich indenter, under a loading-creep-unloading-creep cycle and a maximum load of 500 mN. The Young’s modulus was determined from the mathematical analysis of the unloading section of the load-displacement curves obtained.

Selected fixed composition alloys were produced by laser deposition and submitted to electrochemical testing in Hank’s balanced salt solution (HBSS) at 37±0.1°C. Open circuit potentials were measured for 48 hours, Anodic polarization tests were done with a scan rate of 1 mV s⁻¹ at potentials ranging from the open circuit potential to 2 V. Both tests were conducted using a Parstat 2273 potentiostat and an electrochemical test cell with a saturated calomel electrode (SCE) as reference electrode and a platinum coil as auxiliary electrode.

**Results and Discussion**

The variation in chemical composition of the alloys along the deposited tracks is presented in Fig. 1. The compositions of Ti and Ta varied almost linearly along the distance from Ti-3%Ta to T-29%Ta on one track to and from Ti-29%Ta to Ti-86%Ta on the other. Therefore, a real continuous variation in alloy compositions from 3 to 86%Ta is obtained. The
compositions of the alloys are not very different from the nominal values, confirming the usefulness of the method as a combinatorial alloy development tool. The slight differences in composition reflect the differences normally found when feeding mixtures of powders with different density, flowability and melting temperature.

The constitution of the alloys varies with the Ta content in the alloy, as shown by the X-ray diffraction analysis results presented in Fig. 2. Results show that for Ta contents below 29% the major constituent in the alloys is the hexagonal α' phase and only a small amount of β is observed. At 29%Ta and above it is the orthorhombic martensite (α'') that forms. These structural evolution is similar to that observed by other authors in Ti-Ta alloys produced by casting methods, wherein the α' to α'' transition occurs at a Ta content that varies between 20 and 30%, according to different authors [16-18].

The amount of β increases with the Ta content and it only becomes a visibly dominant constituent for alloys with Ta contents above 35%. Furthermore, fully β phase alloys are only obtained for Ta contents of 76% and above. This result is contradictory to the results of Zhou et al. [18] who found that the β-phase was fully stabilized at a Ta content above 60%.

These results are confirmed by the microstructural analysis of the alloys as a function of composition presented in Fig. 3. Acicular martensite (α') is the major constituent of Ti-Ta alloys with low Ta contents (Fig. 3a and b). For Ta contents of 29%Ta and above the alloys are formed of orthorhombic martensite (α'') and untransformed β (Fig. 3c and d). As the Ta content increases the amount of martensite in the alloys decreases and that of untransformed β increases, becoming the dominant constituent only for very high concentrations of Ta (Fig. 3d and 3e). Fully β phase alloys are only obtained for 76%Ta and above (Figs. 3e), in accordance with XRD results.
Fig. 3 - Evolution of alloy microstructure as a function of the Ta content.

However, in the alloys a substructure is also clearly observed inside the $\beta$ or prior $\beta$ grains (Fig. 3). This substructure resembles small cells or dendrites and seems to have no orientation relation with the $\beta$ grains as cells often cross the grain boundaries. EDS element distribution maps show that this corresponds to a segregation pattern of Ti and Ta (Fig. 4). This segregation pattern is visible even in the lower Ta content alloys and explains the martensite distribution pattern observed that follows the Ti segregation pattern. As Ta stabilizes the $\beta$ phase martensite tends to form only in the regions were Ti concentrates, while in the regions where the Ta concentration is higher the $\beta$ phase is retained.
Fig. 4 - EDS element distribution maps for Ti-50Ta alloy.

Depth sensing ultramicroindentation tests were carried out along the variable composition laser deposited tracks. A typical load-displacement curve is depicted in Fig. 5.

The tests allow evaluating the variation of microhardness and Young’s modulus as a function of alloy composition along the variable composition clad track. The results are presented in Figs. 6 and 7, respectively.

Fig. 5 – Load-displacement ultramicroindentation curve for Ti-50%Ta alloy.

There is an initial fast increase in hardness of the Ti-Ta alloys from 1.7 to 2.2 GPa, corresponding to an increase in Ta content from zero to about 30% in the α’ region, mainly due to solid solution strengthening. There is a slight decrease in hardness corresponding to the α’→α” transition. The hardness values increase to 2.3 GPa for alloys with 30-35%Ta and then decrease again for alloys between 45 and 55%Ta into the α”+β region. This decrease is probably corresponding to the increased amounts of the β phase that starts to form more significantly above 36%Ta. For Ta contents above 55% the hardness increases again up to 2.4 GPa, again due solid solution strengthening.

The variation in hardness observed in the present study is very similar to that found by Dobromyslov et al. [19] in quenched alloys in a similar composition range, though the present hardness values are slightly higher.

Fig. 6 - Variation in microhardness along the Ti-Ta variable composition tracks.
As for the indentation elastic modulus (Fig. 7), there is a significant decrease in the values of this property from 120 to about 50 GPa with the increase in Ta content in the alloys from 3 to about 30%. The Young's modulus then remains relatively constant in values of about 50-55 GPa up to 65% Ta. For higher Ta concentrations the Young's modulus increases again up to a maximum value of 90 GPa for the 86% Ta alloy.

An extremely low value of Young's modulus (32 GPa) has been measured for the Ti-52% Ta alloy. This alloy composition is being further investigated for confirmation purposes. Nevertheless, despite the scatter in the Young's modulus values for alloys with Ta contents in the range 30-65% Ta, it is clear that several alloys presenting very low stiffness formed in this region. Though the fully β phase alloys are only obtained for Ta contents above 76%, the lowest Young's modulus values are obtained for alloys in the α" and α"+β regions, making this the most interesting range of alloys for prosthetic applications.

The values for Young's modulus attained in the present study are lower than those found by Zhou et al. [18]. The authors found the lowest values of Young's modulus, 69 and 70 GPa, for alloys with 30 and 70% Ta, respectively, that were simply attributed to variations in unit cell volume of the phases. However, though not yet fully understood, the reason for the low stiffness values in these alloys is more complex, as suggested by other authors [19,20].

Three alloys with compositions in the lowest Young's modulus region were selected for electrochemical testing. The fixed composition alloys Ti-30%Ta, Ti-52%Ta and Ti-63%Ta were produced by laser deposition and then submitted to corrosion tests in Hank's solution at 37 °C.

Fig. 8 shows the variation of open-circuit potential (E_{oc}) of these alloys in Hank's solution at 37 °C. It can be seen that the curves of all alloys are typical of passive metals and that the corrosion resistance improves during the first 24 to 48 hours of immersion, as shown by the increase in the OCP values, indicating that a thickening of the passive films formed on the surface is occurring until a steady state is attained. However, for the Ti-30%Ta alloy it was noticed that after 48 hours the E_{oc} was still not completely stabilized, continuing to increase at a rate of ca. 1 mV per hour. The Ti-52%Ta alloy achieves the highest E_{oc}, reaching values in the order of -200 mV, showing that it is the noblest of the three alloys.

Fig. 8 - Open circuit potential vs. time curves of Ti-30%Ta, Ti-52%Ta and Ti-63%Ta alloys in Hank’s solution at 37 °C.

After 48h in the open circuit, the alloys were submitted to anodic polarization tests in the same environment. The results are shown in Fig. 9. The polarization patterns show a very similar behaviour for the three alloys. They all present a well-defined passivation region. For potentials higher than 1.200 V the current density begins to increase, which is characteristic of the thickening of the passive oxide layer on the surface of the alloys, as normally found on valve metals anodizing.

For a passive metal with a polarization curve similar to those depicted in Fig. 9, the corrosion current density corresponds to the passive current density. Corrosion current densities and potentials are shown in Table 1. The values vary between 4 and 7 μAcm^{-2} the Ti-63%Ta alloy presenting the lowest current density. Thus, among the three alloys, Ti-63%Ta shows the highest resistance to corrosion. These results are comparable to those obtained by Mareci et al. [21] for Ti-Ta alloys in HBSS and may be attributed to the formation of a passivation film containing Ta oxide (Ta_{2}O_{5}) instead of the TiO_{2} film formed in low Ta concentration alloys. It has been shown that the Ta
pentoxide film is more stable than TiO₂ and that it tends to form in Ti-Ta alloys with Ta contents above 30% [22].

![Graph showing potential vs. current density for Ti-30%Ta, Ti-52%Ta, and Ti-63%Ta alloys in Hank’s solution at 37 °C.](image)

**Table 1. Corrosion current densities (i_corr) and potentials (E_corr) for the Ti-Ta alloys in Hank’s solution**

<table>
<thead>
<tr>
<th>Alloy</th>
<th>i_corr (µAcm⁻²)</th>
<th>E_corr (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti-30%Ta</td>
<td>5.697</td>
<td>-0.265</td>
</tr>
<tr>
<td>Ti-52%Ta</td>
<td>7.273</td>
<td>-0.165</td>
</tr>
<tr>
<td>Ti-63%Ta</td>
<td>4.152</td>
<td>-0.240</td>
</tr>
</tbody>
</table>

**Conclusions**

This study showed that variable composition laser cladding could be used successfully as a tool to rapidly develop Ti alloys with continuously varying compositions, allowing discovering new compositions with interesting properties for orthopedic implant applications.

The method has been applied to the development of new alloys in the Ti-Ta system in the range of compositions Ti-3Ta to Ti-86%Ta. The use of microscale characterization and testing techniques enables a rapid evaluation of the microstructure and mechanical properties evolution along the track as a function of alloy composition allowing selecting the promising composition ranges for further testing of other properties relevant for the application.

The microstructural evolution analysis shows that Ti alloys with compositions up to 29%Ta are formed of the hexagonal α' martensite with acicular morphology, while for higher Ta contents it is the orthorhombic α'' martensite that forms. The Ti-Ta alloys contain initially a small fraction of untransformed β phase that increases with the Ta content and becomes a major constituent only for alloys above 36%Ta. A minimum of 76%Ta was necessary to fully stabilize the β phase in the present study. The evaluation of the mechanical properties as a function of composition shows that the microhardness of the alloys increases considerably with the addition of Ta in the α' alloy region. It then decreases slightly in the transition to the α'' region and increases again into the α''+β region with the increasing amounts of Ta, showing the tendency for Ti-Ta alloys to show increased strength with the amount of Ta. The elastic modulus follows a very different trend with Ta composition. With the addition of Ta up to 30% the Young's modulus of the alloys decreases to a minimum value of 50 GPa (from the α' into the α'' region) and then it stabilizes around this values up to 65%Ta (α''+β alloys). For higher Ta contents the Young's modulus increases again into the β phase region up to 90 GPa for the Ti-86%Ta alloy. The electrochemical tests performed on alloys in the α' and α''+β regions show that they have a high capacity to form stable protective oxide layers that enhance corrosion resistance in Hank’s solution. Therefore, Ti-Ta alloys in these regions show the lowest values of Young's modulus while keeping high strength and good corrosion resistance, are, thus, the most promising for orthopedic applications.

**References**


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Meet the Authors

Martim Teixeira is a researcher at Instituto Superior Tecnico. He has a Master degree in Materials Engineering from Instituto Superior Tecnico, Universidade Tecnica de Lisboa, Portugal. His research interests are laser materials processing of biomedical alloys and materials characterization.

Carole Loable is a Ph.D. student in Materials Engineering at the Department of Chemical Engineering, Instituto Superior Tecnico, Universidade Tecnica de Lisboa, Portugal, in collaboration with Grenoble INP, France, in the scope of IDS-FunMat - International Doctoral School in Functional Materials for Energy, Information Technology and Health. She has a Master degree in Chemistry from Ateneo de Manila University, Philippines. Her research interests include laser materials processing of biomedical alloys.

Amelia Almeida is Assistant Professor in the Department of Chemical Engineering of Instituto Superior Tecnico (IST), Universidade Tecnica de Lisboa, Portugal. She has a Ph.D. in Materials Engineering. Since 1992 she has worked in LaserMat - Materials Processing and Design Group of IST and has collaborated in several National and European funded research projects. Amelia has authored more than 90 publications in international journals and conferences. Her research interests include laser surface modification of biomedical alloys, laser development of alloys and composites, phase transformations,
structural, wear and mechanical characterization of materials.

Odila Florêncio is a Professor in the Physics Department, Universidade Federal de São Carlos, Brazil. Her research interests are development of Ti based alloys and study of elastic properties of materials by vibrational methods. She is currently staying at Instituto Superior Tecnico for one year on sabbatical leave.

J.C.S. Fernandes is Assistant Professor in Department of Chemical Engineering, Instituto Superior Técnico (IST), Universidade Técnica de Lisboa, Portugal. He has a Ph.D. in Chemical Engineering. His research interests are corrosion and protection of materials, interfaces and surfaces engineering, electrochemical impedance spectroscopy, materials for biomedical applications, aluminum alloys for aircrafts.

Rui Vilar is Full Professor in the Department of Chemical Engineering, Instituto Superior Técnico (IST), Universidade Técnica de Lisboa, Portugal. He has a degree in Metallurgical Engineering, Ph.D. in Physical Metallurgy at University of Paris Sud, Orsay, France. He is the head of LaserMat - Materials Processing and Design Group of IST and of the IST’s Platform in Materials and Nanotechnology. Rui has more than 30 years of experience in research and teaching and has been involved and coordinated a significant number of national and international research projects. He has been working in industrial applications of lasers and laser materials processing since 1987 and has authored more than 300 scientific publications in international journals and conference proceedings.