Development of a Co-Cr-Mo to Tantalum Transition using LENS for Orthopedic Applications

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Abstract

Biomedical implant material research using additive manufacturing is a popular field of study. Many potential material combinations exist which, if implemented properly, could have a significantly positive effect on implant life and functionality. One material combination of interest is attaching porous Ta bone ingrowth material to a CoCrMo corrosion and wear resistant bearing surface. An investigation of the ability of the LENS process to join Ta to CoCrMo was undertaken. Direct joining of CoCrMo to Ta was known to be problematic, and thus transitional layers of other biomedically-compatible materials were investigated. It was determined that a transitional layer of zirconium appeared to be the best transitional material for this application due to its excellent biocompatibility, followed by stainless steel, with a lesser biocompatibility but better adhesive properties.

Introduction

The development of multi-material and graded material structures is revolutionizing material science and engineering. This is due to the fact that a wide range of properties can be obtained, leading to more optimized properties and the development of new material systems. The material combination for the study considered here is a graded structure from porous Tantalum to Co-Cr-Mo. This material combination is desirable for biomedical implant structures where one side of the implant is a bone in-growth structure and the other side of the implant is a bearing surface. A typical problem encountered when coating porous Tantalum directly with Co-Cr-Mo is the process of crevice corrosion. Thus, a transitional material, which blends well with both Co-Cr-Mo and porous Tantalum, was sought. A number of bio-compatible materials were considered for this application, including Titanium, Zirconium, Rhenium, Niobium and Stainless Steel, as potential candidates for the interfacial layer. An investigation was undertaken to ascertain the best biocompatible transition metal between Co-Cr-Mo and Ta using an Optomec LENS 750 machine.

Background

According to Hubler[1] thin film layers can be used to protect implant materials. These layers lead to an improvement in corrosion resistance. The properties are largely dependent on the adhesive properties and the layer thickness. They also depend on the possibility of formation of intermetallics between the metals being used. The possibility of intermetallic formation when layering materials necessitates looking to phase diagrams before choosing materials as interfacial layers.

Ensinger[2] (et al.) have shown that the implanting of noble metals onto the surface of materials leads to an increase in corrosion resistance. Hence it is beneficial to choose a biocompatible material with low reactive properties to be used as the interfacial material. This would lead to retaining of the material properties of the implant substrate and also form an excellent coating for depositing the strongly corrosion resistant Co-Cr-Mo. They have shown that Tantalum suffers Hydrogen embrittlement when it corrodes in strong acids and so the use of materials like Zirconium, Rhenium and Niobium as interfacial layers is encouraged.

Matsuno[3] (et al.) have shown that Titanium, Zirconium, Rhenium and Niobium metals are biocompatible and have excellent blending with the tissues in the body. The experiments conducted by them indicate the fact that these materials have excellent corrosion resistance and can act as excellent intermediate surfaces.

Trillo [4] (et al.) have shown that Titanium and Tantalum form excellent solid solutions having properties comparable to that of Ti-6Al-4V. Also they have reported excellent hardness values. This strengthens the belief that these metals can be used as intermediate layers for implant production.

Cui [5] (et al.) have assessed the Rhenium-Tantalum system in great detail. They have indicated that Rhenium has excellent fatigue and creep failure resistance. Also the fact that the phase diagram has no intermetallics strengthens the fact that it will act as an excellent intermediate layer.

Experimental Equipment

Laser Engineered Net Shaping (LENS) produces functional metal prototypes that have excellent material properties. LENS also has a unique ability to build parts with novel geometries and multi-material as well as functionally gradient material compositions, opening the door for production of breakthrough end-products. As an additive process, LENS allows users to modify or rework existing prototypes for design iterations, rather than fabricating an entirely new part with each change. LENS has the potential to be used to cost-competitively manufacture surgical devices and anatomically customized, as well as standard-sized, medical implants with a range of functional enhancements that improve wear characteristics and quality of life for the product.

The LENS process takes place in a controlled atmosphere processing chamber. The system provides gas recirculation to remove any Oxygen that leaks into the system. The atmosphere inside is inert Argon. The presence of Argon reduces the chances of oxidation within the chamber. The continuous wave, high power Nd:YAG Laser (500-600W) operates at 1.064μm. The laser is mounted on the top of the system and is delivered to the work surface via a beam delivery system. The energy from the laser is used in melting the powder and depositing it onto the substrate material. A 3-axis motion-controlled table provides for movement of the part being fabricated.

Several parameters affecting the LENS process include Laser Power, Laser Traverse Speed and Powder Feed Rate. These parameters were investigated to determine whether the various materials under consideration were capable of being processed using LENS.

Benefits of LENS for use in development of biomedical implants include:

- Enhancing components by adding layers of wear-resistant coatings, hard-facing, and other surface treatments.
- Lower per-piece production costs for low-volume or custom production
- Improved material properties for longer part life
- Broad range of materials – metals, metal alloys, ceramics, composites
- Novel geometries, material compositions and textures, to:

    1. Reduce implant wear at key points by optimizing the placement of alloys
    2. Foster implant integration with native tissue by using multiple biocompatible materials that blend with the tissue in the body more optimally

For the sintering experiments described below, a *high temperature furnace* is employed. The parameters that can be controlled in the high temperature furnace include the temperature and the pressure in the furnace as functions of the time. Also the atmosphere inside the system is inert (argon) to minimize oxidation.

Experimental Procedure

For the experiments performed, a simple observation of the compatibility of LENS-deposited material combinations was observed by looking for evidence of delamination. For some specimens this involved cutting and polishing the specimens and then observing the interface using optical microscopy. In most cases delamination would occur prior to cutting and polishing if the materials were incompatible or the procedure did not result in proper layer adhesion.

The materials used for the experiments were Zirconium powder (-100/+250 mesh size) obtained from Zirconium Research, Co-Cr-Mo powder and Stainless Steel (316L) powder obtained from Carpenter Technologies, Porous Tantalum substrates from Zimmer, Tantalum Metal Foil (0.127mm thick) from Alfa Aesar, and Co-Cr-Mo and Ti-6Al-4V substrates obtained from Medicine Lodge, Inc. Rhenium and Niobium, although potentially optimal materials, were not investigated due to the high cost of the raw materials.

It should be noted that when using a porous Ta substrate, conduction cooling is minimized due to the relatively small conductive paths through the porous structure, as compared to a traditional, solid LENS substrate where conduction cooling occurs rapidly.

Thus, LENS parameters used for solid substrate depositions will not necessarily be optimum for those on porous substrates. In particular, the cooling rates and the resultant microstructures will vary.

Although the thickness of the deposits was not recorded precisely, each layer would typically result in a deposit of approximately 0.010”. Thus, for example, a 3 layer deposit would result in a 30 thousandths thick layer.

Experimental Results & Discussion

Co-Cr-Mo to Ta depositions

From previous research it was observed that crevice corrosion might lead to problems when directly depositing Co-Cr-Mo onto a porous Tantalum substrate. The direct deposition of Co-Cr-Mo onto Tantalum using LENS provided for excellent adhesion, but the crevice corrosion resistance of these deposits was not investigated for this project.

A major drawback of all of the LENS depositions of Co-Cr-Mo was the surface finish. The surface formed is highly uneven and this unevenness increased up as the amount of Co-Cr-Mo increased. This might be due to the surface tension characteristics of Co-Cr-Mo in the molten phase.

Ta foil to porous Ta

The next step was to observe whether we could laser-deposit Tantalum foil onto the porous substrate. If a thin layer of solid Ta could be formed at the surface of the porous Ta, then it might be possible to deposit Co-Cr-Mo on top of the solid Ta and eliminate the possibility of crevice corrosion due to the elimination of crevices present at the interface. Laser glazing of the Tantalum foil onto the porous Tantalum substrate was investigated, without full melting of the foil. It was observed that the Tantalum foil did not stick properly to the substrate due to the fact that there was very limited bonding area.

A series of experiments testing laser powers which resulted in melting of the Ta foil also occurred. During formation of a melt pool, the foil started forming bead-like structures which led to the segregation of the Tantalum foil rather than a uniform distribution over the substrate. Warping of the foil was observed due to temperature gradients within the foil, and thus, after numerous tries, the idea of laser welding a Ta foil to the porous Ta was abandoned.

Transitional Materials

For the development of transitional materials, Titanium, Zirconium and Stainless Steel were chosen. From the various phase diagrams of interest it was observed that Zirconium does not form any intermetallic compounds with Cobalt, Chromium, Tantalum or Molybdenum whereas Titanium formed a few intermetallic compounds with both Cobalt and Chromium. Nothing definitive could be predicted about the behavior of Stainless Steel because of the large number of elements within Stainless Steel.

Intermetallic compound formation often results in crack propagation due to the brittle nature of the material and the concentration of stresses at the intermetallic due to its thermal expansion and stiffness differences with respect to the matrix metal alloy. Hence it is important to avoid large-scale intermetallic formation if at all possible.

Another key material property is the coefficient of thermal expansion. A transitional material should theoretically have a CTE between the materials of interest in order to minimize CTE mismatches.

Ti to Co-Cr-Mo

Initial experiments were performed using Titanium as the interfacial layer. It was observed the Titanium stuck very well to porous Tantalum. But when deposition of Co-Cr-Mo were added to the deposited Titanium, they started to delaminate. This could be either due to the build-up of residual stresses as a result of differences in CTE and the large temperature changes during the process or it might be due to intermetallic formation between the Ti and Co-Cr-Mo, or combinations of the two.

An investigation of the influence of parameter changes on depositions of Co-Cr-Mo onto Ti-6Al-4V substrates was performed to determine inherent compatibility problems. For the depositions, the following were changed:

1. Laser Power was varied from 33W – 272W
2. Powder feed rate in the range of 0.48-0.60 cc/min and
3. Laser Traverse speed from 10-30 inches/min.

In addition, laser scanning pattern was varied. There is a possibility that if the laser scanning pattern is rastered along a single direction from layer-to-layer, the development of residual stresses in that particular direction will lead to delamination. To investigate this possibility, depositions were done such that successive layers were at an angle of 120° with respect to each other. Also, some samples were allowed to cool down after each layer was deposited, which reduced the severity of delamination.

It was observed that in almost all cases there was some delamination immediately when the third layer of Co-Cr-Mo was being deposited. In the single case where delamination did not occur in the machine, the layers peeled off when the deposit was sand blasted. This showed that there was inherently poor bonding between Co-Cr-Mo and Ti-6Al-4V. Hence the search for optimized LENS parameters was abandoned for this material combination.

Ti to Zr

Since Titanium stuck well to Tantalum, it was proposed to study the characteristics of the deposition of Zirconium onto Titanium. The possibility of a graded implant with both

Titanium and Zirconium as interfacial materials was thusly investigated. An experiment was conducted to ascertain the deposition characteristics of Zirconium on Ti-6Al-4V. The deposits appeared to give excellent adhesion. A set of optimum parameters were:

1. Laser Power ~ 153 W
2. Laser Traverse speed = 30inches/min.
3. Powder feed rate ~ 1.13cc/min.

Zr to Ta

Next Zirconium was deposited onto the porous Tantalum substrate. From preliminary experiments it was quite clear that Zirconium stuck very well to Tantalum. After many iterations, excellent deposits of 0.9inch diameter were created on porous Ta specimens. Each layer of the deposit was at an angle of 60° clockwise with respect to the previous layer. The number of layers in each deposit was six. After depositing each layer the sample was allowed to cool for about 15-20 min. so that the residual stresses (if any) would be relaxed and also the chances of warping of the sample at high temperatures were reduced greatly. The LENS machine parameters worked out well and the deposits came out in excellent fashion. Once the depositions were completed onto the porous Tantalum pieces the layers were machined to obtain a flat layer of Zirconium on the substrate. The LENS parameters for the deposition process were as follows:

1. Laser Power ~ 153W
2. Powder feed rate ~ 1.45cc/min.
3. Laser Traverse speed = 30 in/min.

Zr to Co-Cr-Mo

The deposition of Co-Cr-Mo onto Zirconium was also studied. For initial studies, Zirconium powder was deposited onto a Mild Steel plate (so as not to deplete the supply of porous Ta specimens) followed by depositions of Co-Cr-Mo onto the deposited Zirconium. The deposits were of rectangular profile. During these deposits it was observed that Co-Cr-Mo delaminated slightly during deposition of 6 layers, even after significant optimization of LENS parameters. However, the bonding was significantly better than that of Ti and Co-Cr-Mo. One of the important similarities in all the delaminations is that the deposits started delaminating from the edge. This strengthens the belief that the delaminations were a result of CTE mismatch at the material interface.

It was determined that deposits three layers thick stuck quite well. These layers did not peel off even after sand blasting. This is apparently due to a lesser build-up of residual stresses after 3 layers than after 6 layers. The deposits of Co-Cr-Mo onto Zirconium that bonded well had process parameters as follows:

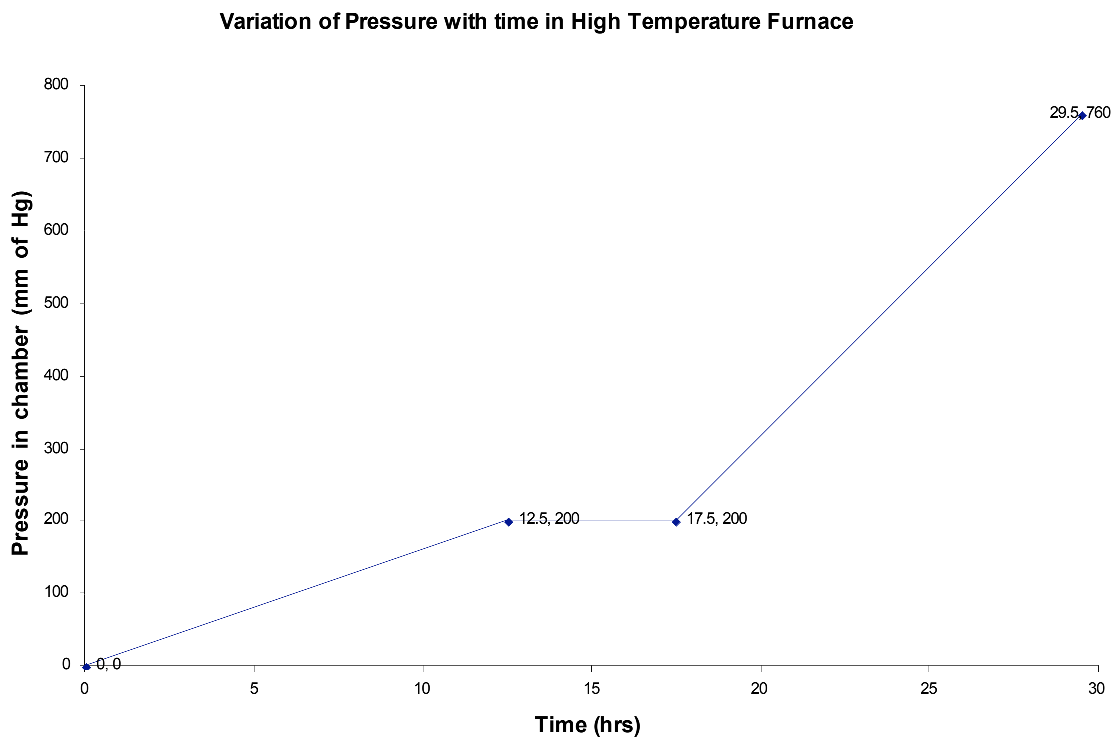
1. Laser Power ~ 93W
2. Powder Feed Rate ~ 0.81cc/min.
3. Laser Traverse Speed = 30 in/min.

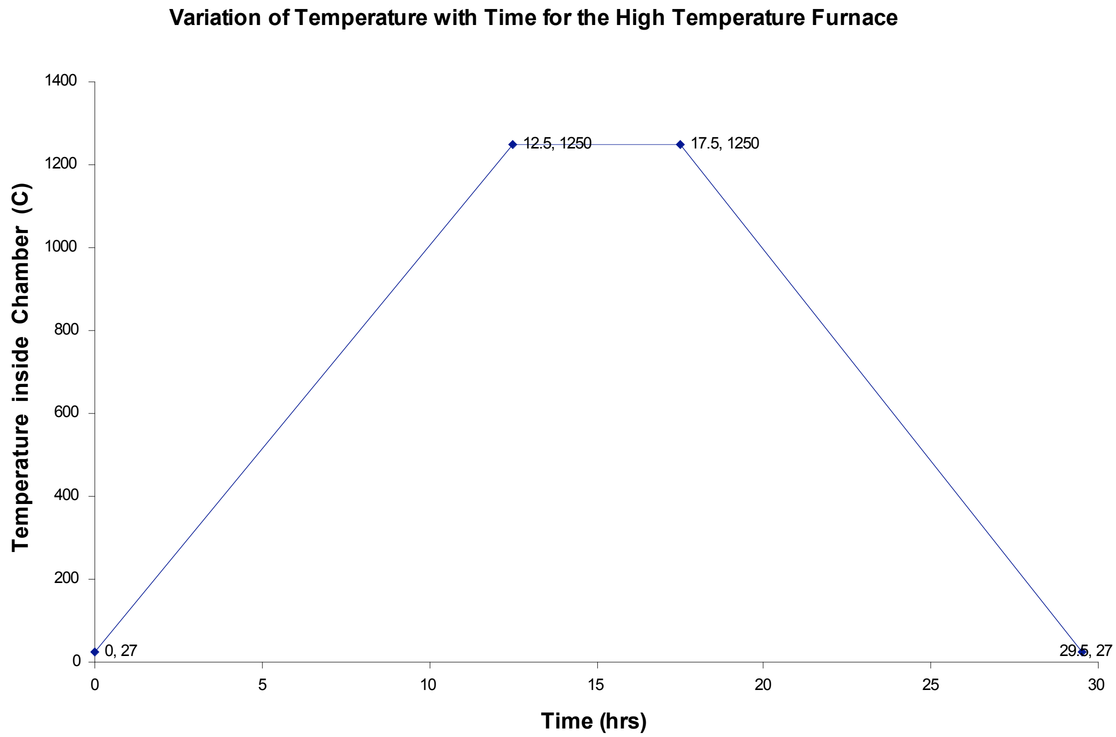
One rectangular deposit of Zirconium onto solid Co-Cr-Mo was carried out. This was to see whether delamination occurred in this case. As expected, due to CTE mismatch, the layers delaminated after only two layers of deposition. The parameters for the study were:

1. Laser Power ~ 93W
2. Powder feed rate ~ 1.13cc/min.
3. Laser Traverse Speed = 30 in/min.

Solid State Sintering

After these depositions were carried out an attempt was made to utilize solid-state sintering to join a Co-Cr-Mo piece to the LENS-deposited Zirconium layer on the porous Tantalum. A temperature of 1250°C was used for this experiment. The process was carried out in an inert atmosphere of Argon so that any chances of oxidation due to the presence of atmospheric Oxygen would be minimized. The process was controlled with the temperatures and pressures varying with time as shown in the graphs.





The result of the sintering experiment showed mixed success. The apparatus we used did not enable applying pressure to aid the bonding process, and only gravitation force was applied. Even so, limited adhesion did occur. It appears that adequate solid state sintering may be possible under more carefully controlled conditions at higher pressures.

Stainless Steel to Co-Cr-Mo, Zr and Ta

A few experiments were also conducted using Stainless Steel as an intermediate material. First, the Stainless Steel(316L) was deposited onto a Mild Steel plate and then Co-Cr-Mo onto the Stainless Steel. We observed that there was excellent sticking and no signs of delamination were visible. The parameters for these deposits are:

1. Laser Power ~ 93W
2. Laser Traverse Speed = 30in/min.
3. Powder Feed Rate in the range of 0.81-1.67cc/min (all work fine)

It was also noted that Stainless Steel stuck very well to both Zirconium as well as Tantalum. For these deposits:

1. Laser Power ~110W
2. Laser Traverse Speed = 30in/min.
3. Powder Feed Rate in the range of 1.02-1.24cc/min.

Summary

A set of experiments was performed to determine the possibility of using LENS to produce a Co-Cr-Mo to Ta transition for biomedical implant applications. A summary of the results of the adhesive characteristics observed when LENS-depositing Co-Cr-Mo, Ta, Zr, Stainless Steel and combinations thereof is summarized below.

No	Deposited Material	Substrate	Conclusions
1	Co-Cr-Mo	Ti-6Al-4V	Delamination occurs easily due to mismatch in coefficients of thermal expansion
2	Titanium	Tantalum	Excellent adhesion
3	Zirconium	Ti-6Al-4V	Excellent adhesion
4	Zirconium	Tantalum	Excellent adhesion
5	Zirconium	Co-Cr-Mo	Residual stress build-up causes delamination.
6	Co-Cr-Mo	Zirconium	Adhesion at 3 layers and below, but delamination otherwise.
7	Co-Cr-Mo	Stainless Steel	Excellent adhesion
8	Stainless Steel	Tantalum/ Zirconium	Excellent adhesion

Conclusions

It was determined that there are several possible methods for creating a Co-Cr-Mo to Ta transition using LENS. Although Stainless Steel is not considered an ideal material for long-term implant use, it has fair biocompatibility and good adhesion as a transitional material. Zirconium appears to be the best biocompatible transitional material. LENS of Zr to porous Ta proceeds smoothly, and additional LENS deposits of Co-Cr-Mo can be utilized if only a thin coating (less than 3 layers to minimize residual stresses) is required. An additional manufacturing plan might utilize LENS to deposit Zr and then solid state sintering under pressure to join the Zr to a thicker Co-Cr-Mo layer. Although Rhenium and Niobium were not studied, due to financial constraints, these materials would likely work well for this applications, as their material characteristics match well the needs of a good transition material between Ta and Co-Cr-Mo.

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