Fatigue properties of carbon- and porous-coated Ti–6Al–4V alloy

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A porous metal coating applied to a solid substrate implant has been shown, in vivo, to offer advantages over current polymethylmethacrylate cement fixation in orthopedic devices. These advantages may be lost, however, in devices requiring a sintering heat treatment to apply the coating since these treatments may have a detrimental effect on the substrate material mechanical properties. In addition, more biocompatible interface coating materials have come of interest with recent literature reports of metal ion release. These coatings may be of particular use in porous-coated systems since the surface area of implant in contact with the surrounding tissues is greatly increased. This study investigated the effects that both a porous Ti–6Al–4V alloy coating and a ULTI carbon coating have on the fatigue properties of a Ti–6Al–4V alloy substrate system. The fatigue properties of un-
coated as-received, uncoated sinter heat treated and notched Ti–6Al–4V material were also investigated. The results of this study revealed endurance limits for Ti–6Al–4V alloy tested with a rotating beam system of 617 MN/m² (uncoated as-received), 624 MN/m² (ULTI carbon-coated), 377 MN/m² (sinter heat treated), 220 MN/m² (notched) and 138 MN/m² (porous-coated). No effects on fatigue properties were observed when testing the material in saline compared with air. The slight increase in fatigue strength for the carbon-coated material is thought to be due to the increase in surface hardness resulting from the formation of titanium carbides on the surface. The low-endurance limit of the porous-coated material is due to both the transition from the as-received equiaxed microstructure to a lamellar microstructure upon sintering and to the notch effect created by the porous coating.

INTRODUCTION

Recently there has been increased concern about the use of polymethylmethacrylate (PMMA) cement fixation for orthopedic devices. Owing to problems associated with this system, primarily implant loosening and adverse bone remodeling, research over the past two decades has concentrated on the development of alternative methods of implant fixation. One such system is that of a porous-coated device.¹⁻³ However, these systems greatly increase the surface area of implant material in contact with the surrounding tissue and consequently can be expected to result in increased ion transfer. Thus more biocompatible interface materials between implant and tissue may be desirable for these systems, as well as nonporous systems. One such coating system, ultra low temperature isotropic (ULTI) carbon, has in fact been shown to enhance implant fixation.⁴

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A porous metal coating applied to a solid substrate implant has been shown, *in vivo*, to offer several advantages over current methods of fixation. These include a higher interface shear strength between implant and bone and a more uniform distribution of stresses throughout the implant and surrounding tissue.\(^5\) However, these advantages may be lost in devices requiring a sintering heat treatment to apply the porous coating since these treatments may have a detrimental effect on the substrate material mechanical properties.

In order to fabricate porous-coated devices suitable for bone ingrowth, it has been shown that Ti-6Al-4V alloy systems must be heat treated above the materials beta transus (992°C).\(^7\) Such a treatment results in a transformation to the lamellar alpha–beta microstructure, from the equiaxed condition suggested for surgical implants. The lamellar alpha–beta structure has been shown to exhibit the worst fatigue properties of the most common structures attainable in Ti-6Al-4V alloy.\(^8\) Yue, Pillar, and Weatherly\(^10\) have attempted to convert this structure into one in which the fatigue properties are less affected. Yue heat treats the lamellar structure by slow cooling from above the beta transus into the alpha–beta range, followed by an oil quench. The resulting structure contains coarse alpha plates in a fine martensitic matrix. Yue speculated that this structure could have better fatigue properties than the lamellar structure, but did not investigate these properties.

Research to date has typically concentrated either on the fatigue properties of the substrate material, or a porous material compact alone, ignoring any possible effects that the porous coating might impose upon the substrate.\(^7,10\) It is possible that other mechanisms could be responsible for fatigue crack initiation in such a system, compared with the uncoated substrate material.

ULTI carbon-coated porous-coated Ti-6Al-4V devices have been reported in animal studies to yield both a higher interfacial shear strength between bone and implant and greater bone ingrowth compared with uncoated porous Ti-6Al-4V devices.\(^4\) However, little information exists on the effect that the carbon coating may have on the fatigue properties of an implant substrate material. It has been reported that the application of ULTI (ultra low temperature isotropic) carbon onto a Ti-6Al-4V alloy substrate, results in an approximately 40% increase in surface hardness over an uncoated substrate.\(^11\) Since fatigue properties are related to surface hardness, the application of the carbon coating may be expected to improve the fatigue strength of the composite system. However, it should be noted that the ULTI carbon coating is only approximately 0.5 μm thick.

The objective of this study was to investigate the effects that both a porous Ti-6Al-4V alloy coating and a ULTI carbon coating have on the fatigue properties of a Ti-6Al-4V alloy substrate system. Fatigue properties of uncoated as-received Ti-6Al-4V alloy material, uncoated material heat treated to the same temperature as that required to sinter the porous coating, and the notched behavior of Ti-6Al-4V alloy were also investigated.
MATERIALS AND METHODS

Uncoated wrought Ti-6Al-4V alloy test material was received machined as standard R&R Moore fatigue testing specimens. The surface of the specimens was polished to a 600 grit finish. The narrowed region of the specimen was 5.08 mm in diameter. Notched specimens were also machined with a notch root radius of 0.254 mm, resulting in a stress concentration factor of 2.9.12

All material was received in the annealed condition, which specifies a 2-h heat treatment at 700°C after the final hot working treatment. Mechanical properties were measured both by the company who supplied the original 12.7-mm diameter specimens (Elbee Metals, Inc., Hollywood, CA) and by the company who machined the specimens (Carbomedics, Inc., Austin, TX). These properties are shown in Table I.

Chemical analysis showed that the material met the ASTM specification F-136-79 for Ti-6Al-4V E.L.I. surgical implant material, with the exception of the oxygen content which was found to be 0.18 wt % (Table II). The chemical composition of the as-received Ti-6Al-4V powder is shown in Table II and is also slightly out of specification for oxygen content.

Uncoated and notched Ti-6Al-4V fatigue specimens were tested in the as received condition. The uncoated samples were tested both in an isotonic saline solution and in air. Eight of twenty-two uncoated samples were tested in saline. Eighteen notched specimens were tested in air only. The as-received material was used as a control in order to determine the relative effects of the introduction of a notch, the sinter heat treatment (without the coating), the porous coating, and the ULTI carbon coating. The application of the porous Ti-6Al-4V coating was achieved by first applying a one layer thick coating of spherical Ti-6Al-4V alloy powder (355-400 μm in diameter) using a methylcellulose binder and placing the samples in a 100°C oven for 4 h in order to remove all water from the system. Fifteen samples were then sintered in an argon atmosphere at 1250°C for 2 h and allowed to furnace cool. Post sintering chemical analysis revealed essentially no change in composition and only a small amount of additional oxygen pickup, approximately 200-300 ppm. The diameter of the porous-coated samples was mea-

<table>
<thead>
<tr>
<th>Property/Source</th>
<th>Elbee Metals, Inc.</th>
<th>Carbomedics, Inc.</th>
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</thead>
<tbody>
<tr>
<td>Tensile strength (MN/m²)</td>
<td>1017</td>
<td>1090</td>
</tr>
<tr>
<td>Yield strength (MN/m²)</td>
<td>996</td>
<td>1025</td>
</tr>
<tr>
<td>Elongation (%)</td>
<td>16</td>
<td>15</td>
</tr>
<tr>
<td>Reduction of area (%)</td>
<td>48.2</td>
<td>49.7</td>
</tr>
<tr>
<td>Hardness (Rockwell C) as-received</td>
<td>34</td>
<td>34.9</td>
</tr>
</tbody>
</table>
TABLE II
Chemical Composition of the As-Received Material and ASTM Specification F-136-79

<table>
<thead>
<tr>
<th>Element</th>
<th>As-received specimens</th>
<th>As-received powder</th>
<th>ASTM specifications</th>
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</thead>
<tbody>
<tr>
<td>Nitrogen, max.</td>
<td>0.009</td>
<td>0.013</td>
<td>0.05 ± 0.02</td>
</tr>
<tr>
<td>Carbon, max.</td>
<td>0.024</td>
<td>0.032</td>
<td>0.08 ± 0.02</td>
</tr>
<tr>
<td>Hydrogen, max.</td>
<td>0.0063</td>
<td>0.0058</td>
<td>0.0125 ± 0.002</td>
</tr>
<tr>
<td>Iron, max.</td>
<td>0.22</td>
<td>0.28</td>
<td>0.25 ± 0.15</td>
</tr>
<tr>
<td>Oxygen, max.</td>
<td>0.18</td>
<td>0.19</td>
<td>0.13 ± 0.02</td>
</tr>
<tr>
<td>Aluminum</td>
<td>6.28</td>
<td>6.05</td>
<td>5.5–6.5 ± 0.4</td>
</tr>
<tr>
<td>Vanadium</td>
<td>4.32</td>
<td>4.05</td>
<td>3.5–4.5 ± 0.4</td>
</tr>
<tr>
<td>Titanium</td>
<td>Balance</td>
<td>Balance</td>
<td>Balance</td>
</tr>
</tbody>
</table>

sured at approximately 5.98 mm. Twelve uncoated samples underwent similar heat treatment in order to analyze the effects of the porous coating. The porous-coated and uncoated sinter heat treated samples were tested in air only.

The ULTI carbon coated (Biolite*) samples were fabricated by the chemical vapor deposition of ULTI carbon onto a Ti–6Al–4V alloy substrate at low temperature and ambient pressure with the aid of a catalyst. The excellent bond strength of the coating to substrate (70 MPa) is attributed to the formation of titanium carbides on the substrate surface. The coating thickness is less than 0.5 μm thick and thus does not alter the surface topography. The carbon coated samples were tested in air and a 0.9% physiologic saline solution. Six of twenty-four specimens were tested in saline. An uncoated

* Biolite is a registered trademark of CarboMedics, Inc., Austin, TX.
as-received, a carbon-coated, a notched, a sinter heat treated, and a porous-
coated specimen are shown in Figure 1.

All specimens were tested on a standard R&R Moore High Speed Fatigue
Testing Machine which rotates at approximately 10,000 revolutions per
minute, while applying a uniform bending moment across the surface of
the specimen. Alternating cycles of tension and compression of equal mag-
nitude result in a mean stress equal to zero, and an $R$ ratio equal to negative
one. The results were recorded on standard strength versus log number of
cycles to failure plots ($S/N$).

Statistical analysis was performed in order to estimate the fatigue strength
at $5 \times 10^7$ cycles (approximately 30 years for a hip device). For the porous-
coated specimens, this strength was estimated using the original substrate
diameter. The porous coating was assumed to add no strength to the sam-
ples based upon the reported results of Weinstein, Klawitter, and
Koeneman$^7$ which showed a modulus of rupture of only $34 \text{ MN/m}^2$ for
porous compacts sintered at 1250°C. Thus the results for fatigue strength
of the porous coated samples must be considered maximum values since
incorporating an increased specimen diameter would increase the cross sec-
tional area and lower the stress calculated. Statistical analysis was per-
formed using the Probit method$^{14}$ by obtaining sets of tests at the same
stress level performed both at stresses above and below an approximated
endurance limit. The percentage of specimens which survived $5 \times 10^7$
cycles was plotted on probability paper versus the stress at which the sam-
ples were tested. A regression line was then drawn through these points,
and the stress at which the probability to failure was 50%, obtained from
this line. This value is defined as the endurance limit.

Standard metallurgical procedures were utilized on selected specimens in
order to both examine the effects of the sintering heat treatment on the
microstructure, and to determine the orientation of both primary and sec-
ondary cracks. Grain size determination of both the heat treated and as-
received materials was performed using the lineal intercept method as de-
scribed in ASTM specification E112-80. Fracture surfaces were examined
with scanning electron microscopy to determine sites of crack initiation.
Energy dispersive x-ray analysis was performed in order to detect the pres-
ence of any metallurgical discontinuities near crack initiation sites.

RESULTS

The strength versus number of cycles to failure curves ($S/N$) are shown
for the uncoated as-received and the carbon-coated specimens (Fig. 2) and
the uncoated as-received, notched, sinter heat treated, and porous-coated
specimens (Fig. 3). Endurance limits of 617 MN/m$^2$ (as received uncoated),
624 MN/m$^2$ (carbon-coated), 230 MN/m$^2$ (notched), 377 MN/m$^2$ (sinter heat
treated), and 138 MN/m$^2$ (porous-coated) were found in this study. There
was no observed effect on fatigue properties of testing the uncoated as-
received or carbon-coated material in saline compared with in air.
Figure 2. Stress versus log number of cycles to failure plot for uncoated as-received and ULTI carbon-coated Ti–6Al–4V alloy. The numbers indicated on each curve are the endurance limits. Carbon coated (--), uncoated (—).

The uncoated as-received, notched, and carbon-coated specimens were found to have an equiaxed alpha–beta microstructure, as shown by a section taken transverse to the long axis of the specimen [Fig. 4(a)]. The dark areas are the retained beta, while the light areas are composed of alpha. After the sinter heat treatment of the material with or without the porous coating, the microstructure transformed into a lamellar structure as shown in Figure 4(b). This microstructure was found to be continuous from the powder to the substrate in the porous-coated samples [Fig. 4(c)].

A typical fracture surface for the as-received and carbon-coated materials is shown in Figure 5, with the arrow indicating the initiation site. In general, the smooth surfaced as-received material exhibited an initiation region, a region consisting of gross fatigue striations (about 25% of the surface), and a smooth final failure region (about 75% of the surface). The fact that all initiation sites were found on the smooth surface indicates that the initiation of a crack was probably not related to pores or inclusions. This fact was confirmed by SEM analysis which revealed no evidence of subsurface initiation sites or foreign inclusions.

The fracture surface of the porous-coated and the sinter heat treated specimens (Fig. 6) revealed regions of a dimpled morphology indicative of a ductile type of failure. The characteristic elongated troughs, typical of the dimpling phenomenon, were found on the fracture surface of the heat treated material. A higher magnification of the initiation site of a sinter heat
Fatigue properties of Ti-6Al-4V alloy

Figure 3. Stress versus log number of cycles to failure plot for uncoated as-received, sinter heat treated, notched, and porous-coated Ti-6Al-4V alloy. The numbers indicated on each curve are the endurance limits. (—) uncoated, (---) heat treated, (— - —) notched, and (- * -) porous coated.

The treated specimen is shown in Figure 7. The orientation between the secondary crack and the smooth surface of the specimen (area to the left of the picture), is similar to the cracking found near initiation sites in the uncoated as-received samples.

Primary and secondary cracking was observed to occur in directions both perpendicular to and parallel to the alpha grains, for both the porous-coated and sinter heat treated materials. Figure 8(a) shows a section taken transverse to the fracture surface of a heat treated sample. Upon examination, this revealed that the primary and secondary cracking was associated with directions perpendicular to the alpha grains. Figure 8(b) shows a secondary crack, located 3 mm from the primary crack. In this specimen, the crack propagated in directions both parallel and perpendicular to the long axis of the alpha grains. SEM analysis confirmed that secondary cracking did occur at the alpha-beta interfaces. This fact was confirmed by measuring the average grain width in the fractographs (4.2 μm), and comparing it with that found on metallographic sections (3.9 μm).

Fatigue cracks in the porous-coated material were found to initiate at one or more powder particles. SEM analysis revealed that the morphology of the porous-coated fracture surface was similar to that of the heat treated material in that the failures were generated from the surface and were evidently crystallographically oriented. The failures differed in terms of the
Figure 4. Light micrograph of sections of (a) the as-received material, revealing an equiaxed alpha-beta microstructure, (b) the heat treated material revealing a lamellar microstructure, and (c) the porous-coated material revealing the continuous microstructure from coating to substrate (original magnifications 200×). Figure 4 (c) on following page.

initiation sites. The porous-coated samples were found to fail at one or more surface initiation sites, associated with one or more powder particles. This failure was associated with the area under the powder particles. Failure in the porous-coated material is demonstrated by examining Figures 9 and 10. Two initiation sites can be identified in Figure 9, one at point A and
one at point B. Figure 9 also shows the typical secondary cracking which occurred on the smooth surface, helping to identify the initiation sites. An example of the relationship between powder particles and initiation sites is shown in Figure 10. This fractograph shows one initiation site associated with the particle at A, and one at B where the powder has broken off (note the cracking of the powder).

**DISCUSSION**

Initially, it was theorized that the application of a porous coating would introduce two important variables that might result in a change in the fatigue strength of the alloy. The first variable encompasses the effects of microstructural variations induced by the heat treatment necessary for sintering. The second variable includes the effects of a possible stress concentration created by the porous coating, which might behave like a notch. These two variables were examined both individually, and in conjunction with the porous-coated and as-received material.

The endurance limit for the uncoated as-received Ti-6Al-4V alloy material was found to be in close agreement with previous data on the equiaxed structure under rotating cantilever beam loading. Stubbington and Bowen, Bartlo, Bowen, and Sutter and Comet measured endurance limits of 590, 600, 620, 565, and 560 MN/m², respectively, which differ by less than 10% of the value found in this investigation. In order to more accurately compare the values one can examine the fatigue ratio (fatigue strength–ultimate tensile strength). Frost, Marsh, and Pook reported that the fatigue ratio for wrought titanium alloys should be between 0.4 and 0.55. Stubbington and Bowen, Bartlo, Bowen, and Sutter and Comet found fatigue ratios of 0.57, 0.58, 0.58, 0.58, and 0.56, respectively. This is of excellent agreement with the results of this investigation, which yielded a fatigue ratio of 0.58.
Figure 5. SEM fractograph of a typical initiation site in the uncoated as-received and ULTI carbon-coated specimens (original magnification 50×).

Figure 6. SEM fractograph of a heat treated specimen, showing the direction of dimpling and the initiation site of A (original magnification 36×).
The presence of the saline environment resulted in no effect on the fatigue properties of either the uncoated as-received or carbon-coated materials. Given the fact that the R&R Moore rotating beam system is a rapid test (~165 Hz) compared with in vivo cyclic loading (~1 Hz) and that Ti–6Al–4V alloy does not exhibit rapid corrosion in either a saline or air environment this result not surprising.

All fracture surfaces for the as-received material demonstrated a morphology similar to that reported by Fuchs and Stephens\textsuperscript{19} for a rotating beam in bending. The transition from the initiation site, to an area comprised of a "dimpled" structure was noted on some samples. Hall and Hammond\textsuperscript{20} found a similar morphology in testing Ti–6Al–4V alloy material. The detection of a ductile fracture is an expected result, due to the high elongation to failure (15.5%) and reduction of area (49%) measured in the tensile testing of the as-received material.

The endurance limit for the ULTI carbon-coated material (624 MN/m\textsuperscript{2}) was found to be slightly higher than that of the uncoated material (617 MN/m\textsuperscript{2}). The slight increase in fatigue strength can be theorized to be due to the carbon coating adding approximately a 40% increase in surface hardness: however, this difference is certainly in the range of expected data scatter. It is important to note that the fatigue strength was not lowered, as might be expected due to the formation of a titanium carbide phase on the surface of the specimens.
Figure 8. Light micrographs of a heat treated specimen showing (A) both primary and secondary cracking and (B) secondary cracking found 3 mm from the primary crack (original magnifications 200×).

The endurance limit for the notched material was found to be 220 MN/m² as compared with that of the uncoated as-received material (617 MN/m²). Bartlo⁹ also has conducted rotating beam tests on notched Ti–6Al–4V alloy specimens in the equiaxed condition. Although Bartlo used a stress concentration factor of 3.5, his work revealed a reduction in endurance limit from 620 to 230 MN/m², which is in excellent agreement with the value found in this investigation which employed a stress concentration factor of 2.9. The significant decrease in fatigue strength as a result of the introduction of a stress concentration geometry indicates that Ti–6Al–4V alloy is a notch sensitive material. Notch sensitivity assumes significance in the design of orthopedic implants where areas of a bend in the device or a hole in the device could cause a stress concentration, and subsequently lower the expected fatigue life of the material.

Fatigue results revealed that the uncoated sinter heat treated samples
exhibited a lowering of endurance limit to 377 MN/m² from the as-received material value of 617 MN/m². Microstructural analysis revealed an increase in alpha grain size to 3.5 for the heat treated material from the 8.5 value measured for the as-received material. The microstructure of the heat treated material was found to be the "plate-like" or lamellar structure, consisting of plates of alpha with retained beta. Several theories exist explaining why the lamellar structure is inferior to the equiaxed structure, but there is a general agreement that it does exhibit the worst fatigue properties relative to the other Ti-6Al-4V alloy structures.

Fatigue testing of the porous-coated material revealed it to have an endurance limit of only 138 MN/m². This value is approximately one-third (36%) that of the heat treated material (377 MN/m²), and less than one-fourth (22%) that of the uncoated as-received materials value (617 MN/m²). The poor fatigue properties of the porous coated material, relative to the heat treated material, can be explained in terms of the effects of the porous coating. As was discussed previously, Ti-6Al-4V alloy is a notch sensitive material. Since the area between powder and substrate could effectively create a notch, this might result in a degradation of properties relative to the heat treated material. Another reason for the relatively poor properties of the porous-coated specimens is a result of the heat treatment which transformed the equiaxed structure to the lamellar structure. Early fatigue crack initiation can be explained by the fact that powder particles create several possible initiation sites. The more potential initiation sites, the more likely a crack will initiate early. Both metallurgical and electron microscopic anal-

Figure 9. SEM fractograph of a porous-coated specimen, showing initiation sites at A and B (original magnification 100×).
yses also revealed some powder particles to be porous. It is possible that a poor quality of powder could lead to crack initiation within the powder itself. Further, powder may break off of an implant and become lodged in the surrounding tissue.

This work has demonstrated that any improvement in the porous-coated system must treat the system as a composite, not its individual porous and substrate components. Weinstein, Klawitter, and Koeneman\textsuperscript{7} attempted to characterize the mechanical response of the sintering of powder compacts alone. Yue, Pillar, and Weatherly\textsuperscript{10} attempted to improve the characteristics of the substrate material, producing a structure consisting of coarse alpha plates in a fine martensitic matrix. Both of these studies have ignored any possible effects that the porous coating may have on the substrate material. This becomes important when considering porous-coated Ti–6Al–4V alloy as an implant material due to its notch sensitivity. Although Ti–6Al–4V alloy substrate material may exhibit a higher fatigue strength relative to cobalt chromium and stainless steel alloys, it may be inferior once a porous coating is applied due to this notch sensitivity.

**CONCLUSIONS**

Based upon the results of this investigation, it may be concluded that for a Ti–6Al–4V alloy substrate tested under rotating beam conditions:
(1) The application of a ULTI carbon coating had minimal effect on the endurance limit of Ti–6Al–4V alloy compared with the uncoated material.

(2) The low endurance limit of the porous-coated material is due to both the transition from the as-received equiaxed microstructure to the lamellar microstructure upon sintering and to the notch effect created by the porous coating.

(3) Testing in a saline environment results in no effect on the fatigue properties of either uncoated or carbon-coated Ti–6Al–4V alloy material.

References


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