Original Article

Corrosion resistance of Ti-6Al-4V and ASTM F75 alloys processed by electron beam melting

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The electron beam melting (EBM) is a useful technique for fabricating alloys that are difficult to machine and require expensive tools as well as the presence of inert atmosphere for further treatments. Under vacuum, EBM provides a controlled environment, reducing the drawbacks of the alloys of their processing in a conventional manner and thereby improving their microstructure, which can enhance corrosion resistance. In the present work, the corrosion resistance of the Ti-6Al-4V and ASTM F75 alloys was evaluated by using the Tafel extrapolation technique with scan rates of 0.05, 0.1 and 0.166 mV/s. The corrosion specimens were submerged in a Hank solution to simulate the corporal fluid. The specimens were characterized before and after the corrosion tests by optical microscopy and scanning electron microscopy, as well as a chemical microanalysis by EDS. The microstructural characterization before the corrosion tests revealed a dual phase (\(\alpha+\beta\)) microstructure and \(\alpha\) martensite in the Ti-6Al-4V alloy. For the ASTM F75 (Co-base) alloy, carbides were observed on the grain boundaries. Corrosion resistance increased in the Ti-6Al-4V alloy, from 0.50 to 0.14 mpy, possibly due to the formation of a TiO\(_2\) passive layer. For the case of the ASTM F75 alloy, the corrosion rate decreased from 0.21 to 0.14 milli-inches/year (mpy) due to the formation of Cr layer. The corrosion results were observed to be very similar for the EBM fabricated alloys in comparison with more commercially fabricated alloys.

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1. Introduction

One of the main problems in orthopedic implants is the loosening of the prosthesis in the bone, and the presence of residues or wear causing malfunction of the surgical implants; these problems are directly related to the wear and corrosion surface properties of the alloys, employed for this purpose. Pure metals do not have strength, elasticity, ductility, and other properties possessed by alloys; for this reason, the addition of one or more metals to the base element is necessary to modify the crystalline structure and, therefore, its mechanical properties. There are three families of alloys widely used today in biomedicine, due to their good corrosion resistance, which plays an important role in surgical implants, such as: Co-Cr-Mo alloys (ASTM F75), Ti-Al-V (Ti-6-Al-4V) and stainless steel.
AISI 316L (Fe-Cr-Ni-Mo) [1]. All materials have a specific chemical composition, but their final properties are closely related to the crystalline structure, and this is a direct result of the manufacturing methods [2]. Metallic materials can undergo a casting process, solidification, forming, and heat treatment. Each metal has its heat treatment process in order to get the best mechanical properties, while achieving high corrosion resistance properties.

Electron beam manufacturing is a variety of rapid manufacturing (RM) for the direct manufacturing of metal products from a powder precursor melted layer-by-layer with an electron beam in vacuum. The electron beam melting (EBM) machine reads in data from a digitally scanned, 3D model, sliced into individual layers, and lays down successive, 100 μm thick metal powder layers which are gradually melted through the controlled EB scanning process to build the product model. Quality products require the development of a set of optimized processing conditions or parameters which assure uniformity and control of microstructure and associated mechanical properties and performance. Especially promising directions for EBM involve the direct fabrication of custom orthopedic implants and related biomedical applications, mainly involving the production of Ti-6Al-4V components with selected structure–property features [3]. Ti-6Al-4V is of interest as a consequence of its excellent biocompatibility, light weight, outstanding balance of mechanical properties and associated corrosion resistance and human allergic response.

With the presence of a vacuum, EBM provides a controlled environment, reducing the drawbacks of the alloys of their processing in a conventional manner and thereby improving their microstructure, which strongly affects the corrosion resistance. In addition, EBM allows complex and even porous structures to be fabricated.

There are a number of Co and Ti base alloys in biomedical applications, processed in a conventional form and heat treated in order to obtain wide-ranging properties such as low elastic modulus, high tensile strength, excellent wear and corrosion resistance and good biocompatibility [4]. The corrosion variance of the EBM processing is important to know since it corrodes the same as more conventional materials. However, there are few studies reporting the corrosive behavior of these alloys obtained by EBM.

Ti-6Al-4V alloy is the typical two-phase titanium alloy with the most extensive and mature application. For its low density, high specific modulus and strength, excellent corrosion resistance and creep resistance [5–7], Ti-6Al-4V alloy has got the wide applications in the biomechanical field where special structural components are immediately needed. These special structure components are not only complex in structures and shapes, but also strict in requirements for microstructure and mechanical property. However, Ti-6Al-4V alloy is prone to generate porosity because of its high chemical reactivity and poor flowability at high temperature. In order to significantly increase the filling and feeding ability of liquid metal during the solidification, decrease shrinkage cavity, shrinkage porosity, and porosity to obtain sound castings with high density, enhance freezing rate to make castings obtain excellent microstructure and mechanical properties which cannot be obtained in the gravity field,

This paper describes applied research involving the manufacturing of Ti6Al-4V and ASTM F75 alloys by electron beam melting (EBM). This research concerns a comparison of the alloys corrosion resistance in corporal fluid conditions. The results are supported by a microstructural characterization before and after the electrochemical tests by using Hank's solution to simulate the biological environment to observe the corrosive attack.

2. Experimental procedure

2.1. Selection of base material (powder alloy)

The powder alloys used in this investigation are: Ti-6Al-4V grade 5 (Arcam) and Co-28.5Cr-6Mo ASTM F75 [8]. The particle average size varied for both alloys between 40 and 100 μm. Tables 1 and 2 show the chemical composition of these alloys.

2.2. Electron beam melting technique

The probes were fabricated by the electron beam melting technique with an EBM Arcam A2 system shown in Fig. 1.

EBM is able to fabricate complicated geometry that in other conventional method is difficult to obtain (Fig. 2). However, in this investigation, the geometry of the samples for corrosion tests is quite simple. This test only requires 1 cm² of area of exposition, so a cylindrical form was preferred, with 1.5 cm and 3.0 cm of diameter in ASTM F75 and Ti-6Al-4V samples, respectively. The process parameters are listed in Table 3.

| Table 1 – Chemical composition of Ti-6Al-4V alloy. |
|-------------------|----------|----------|----------|----------|----------|----------|----------|----------|
| Elements (% wt.)  | Al       | V        | C        | Fe       | O        | N        | H        | Ti       |
| Arcam Ti-6Al-4V   | 6        | 4        | 0.03     | 0.1      | 0.15     | 0.01     | 0.03     | Balance  |

| Table 2 – Chemical composition of ASTM F75 alloy. |
|-------------------|----------|----------|----------|----------|----------|----------|----------|
| Elements (% wt.)  | Cr       | Mo       | Ni       | Fe       | C        | Si       | Mn       | W        |
| Arcam ASTM F75    | 28.5     | 6        | 0.25     | 0.2      | 0.22     | 0.7      | 0.5      | 0.01     |
|                   |          |          |          |          |          |          |          | 0.15     |
|                   |          |          |          |          |          |          |          | 0.05     |
|                   |          |          |          |          |          |          |          | Balance  |
2.3. Sample preparation

Samples for the microstructural characterization have been obtained by cutting. Due to high hardness of these alloys, the cut is slow with a diamond disc cutter. The samples were thinned in a Buehler grinding machine.

2.4. Microstructural characterization

The microstructural characterization of the alloys was achieved through optical microscopy and scanning electron microscopy, studying the different phases that material presents in Ti-6Al-4V alloy and distribution of carbides in the ASTM-F75 alloy.

<table>
<thead>
<tr>
<th>Variable</th>
<th>Ti-6Al-4V</th>
<th>ASTM F75</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electron beam potential (kV)</td>
<td>60</td>
<td>60</td>
</tr>
<tr>
<td>Produced energy density (kW/cm²)</td>
<td>102</td>
<td>102</td>
</tr>
<tr>
<td>Initial scan rate of beam (mm/s)</td>
<td>15,000</td>
<td>2000</td>
</tr>
<tr>
<td>Beam current (mA)</td>
<td>30</td>
<td>10</td>
</tr>
<tr>
<td>Preheating layer (°C)</td>
<td>640</td>
<td>830</td>
</tr>
<tr>
<td>Thickness layer (μm)</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>Reduction scan rate of beam (mA)</td>
<td>6</td>
<td>10</td>
</tr>
<tr>
<td>Vacuum in He (Torr)</td>
<td>–</td>
<td>104</td>
</tr>
<tr>
<td>Reduction of vacuum (Torr)</td>
<td>–</td>
<td>102</td>
</tr>
</tbody>
</table>

2.5. Optical microscopy and scanning electron microscopy

Optical microscopy allows the variety of microstructures of Ti-6Al-4V alloy and the different precipitates in the ASTM F75 alloy to be observed. The Ti-6Al-4V alloy samples were etching with a Kroll solution during 5 min, with a nominal composition of 80 ml distilled H₂O, 10 ml HNO₃ and 6 ml HF. The ASTM F75 alloy samples were electrolyte etching with a solution of HCl 1:9 in water, applied a constant potential of 3 V during 20 s. The corrosive attack of the samples was documented by scanning electronic microscopy and by analysis with energy dispersive X-ray spectroscope (EDS).

2.6. Corrosion test

A Tafel extrapolation with a Potenciostat/Galvanostat Model 273A EG&G Princeton Applied Search was used for corrosion testing. The electrochemical cell consisted of working electrode (sample), platinum counter electrode and sutured calomel electrode as a reference electrode. Three scan rates were used for both alloys: 0.166, 0.100 and 0.05 mV/s in order to evaluate the values of corrosion rates. The working temperature of the solution was 37 ± 0.1 °C. For an electrochemical reaction under activation control, polarization curves exhibit linear behavior in the E vs log (i) plots called Tafel behavior. Extrapolation of cathodic and anodic Tafel slopes back to the
corrosion potential ($E_{corr}$) was obtained. Intersection point corresponds to corrosion current density ($i_{corr}$) or corrosion rate (mpy) where $i_a = i_c = i_{corr}$ (mixed potential theory) At least one decade of linearity in Tafel extrapolation is desirable to ensure good accuracy.

2.7. Hank’s Solution (HBSS)

The electrochemical tests were performed with the samples submerged in a HBSS (Hank’s Balanced Salt Solution) solution. This solution is a saline, simulator of the composition in human physiological environment ions, emphasize Na+, K+, Mg2+, Ca2+, Cl−, HCO3−, HPO42− ions.

3. Results and discussion

3.1. Optical microscopy

According to previous studies on the Ti-6Al-4V alloy, it can acquire a variety of microstructures, depending on thermomechanical treatment [1,3]. The microstructure can be classified in different categories, such as the equiaxed, martensitic, plates and bimodal. In Fig. 3 the Ti-6Al-4V microstructure illustrates plates of α, some α’ martensite and β continuous (dark) phase.

The α’ martensite plates arise from rapid cooling which is characteristic of small sample fabrication in EBM [9].

On the other hand, the ASTM F75 alloy is formed by a matrix containing dispersed carbides that reinforces and increases its hardness, reducing the ductility and the corrosion resistance. The type, shape, size, and distribution of carbides are strongly influenced by the type of processing of the alloy and, therefore, the final properties obtained are highly dependent on the manufacturing route and heat treatments [8].

Fig. 4 shows a wide distribution of carbides in ASTM F75 alloy. Carbides of laminar type, which is generally located in the grain boundary, is observed during solidification. This originates, as mentioned above, hardness increasing that affects the alloy fatigue life and that may also lead to corrosion fatigue [9].

3.2. Scanning electron microscopy

Phases of α and β were identified by SEM in the Ti-6Al-4V alloy. Fig. 5 shows α phase rich matrix, as well the surface grains, while β phase is observed in the single small grains.

Fig. 6 shows the position of carbides in the ASTM F75 alloy cross section, mainly associated with grain boundaries.

3.3. Tafel extrapolation results

3.3.1. Ti-6Al-4V alloy

The corrosion curves in Fig. 7 correspond to the Ti-6Al-4V alloy, showing typical anodic and cathodic behavior in order to obtain a good estimate of corrosion rate (mpy) by Tafel extrapolation. While Tables 4 and 5 show the representative values of Ti-6Al-4V and ASTM F75 alloys, respectively, used in this study so a better comparison can be done.

According to Table 4 and Fig. 7, as the scan rate increases the corrosion rate increases.
3.3.2. ASTM F75 alloy

In Fig. 8, the Tafel extrapolation curves for ASTM F75 alloy are shown. As for the Ti alloy, ASTM.F75 presented a good corrosion rate. In Table 5, the corresponding corrosion parameters are reported and can be compared with Table 4.

Table 4 – Corrosion test results by Tafel extrapolation in Ti-6Al-4V alloy.

<table>
<thead>
<tr>
<th>Scan rate (mV/s)</th>
<th>E_{corr} (mV)</th>
<th>i_{corr} (μA)</th>
<th>Corrosion rate</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>(mpy)</td>
</tr>
<tr>
<td>a</td>
<td>0.166</td>
<td>−353.743</td>
<td>1.507</td>
</tr>
<tr>
<td>b</td>
<td>0.05</td>
<td>−379.018</td>
<td>0.4335</td>
</tr>
</tbody>
</table>

Table 5 – Corrosion test results by Tafel extrapolation in ASTM F75 alloy.

<table>
<thead>
<tr>
<th>Scan rate (mV/s)</th>
<th>E_{corr} (mV)</th>
<th>i_{corr} (μA)</th>
<th>Corrosion rate</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>(mpy)</td>
</tr>
<tr>
<td>a</td>
<td>0.166</td>
<td>−148.146</td>
<td>0.5424</td>
</tr>
<tr>
<td>b</td>
<td>0.05</td>
<td>−229.472</td>
<td>0.3649</td>
</tr>
</tbody>
</table>

According to other studies of these alloys in biomedical applications, the results obtained in this study are within the average obtained in these studies. A corrosion rate of 0.0013 mm/y has been obtained with the same parameter used in the present study for Ti alloy in [9], that value is not far from the 0.003 mm/y here obtained (Table 5). Likewise, other investigations, which compare the corrosion rate [10–12] under different corrosion techniques and parameters such as scan rate and type of solution, results reached 0.0015 and 0.01 mm/y.

Other studies on ASTM F75 alloy [12] report corrosion rates of 0.0067 and 0.0008 mm/y, these data are in accord with the rate of 0.005 and 0.00104 mm/y obtained in the present study.

The HBSS solution reveals localized pit corrosion, which is associated with a micro galvanic corrosion for this type of Ti-6Al-4V alloys. Fig. 9 shows the microstructure obtained for Ti-6Al-4V alloy before and after corrosion testing.

Fig. 10 presents the corrosion phenomenon which occurred in the grain boundaries. This type of corrosion is due to precipitates that are formed inside the grain boundaries when Cr depletion has occurred. At the same time, these precipitates are present not only in the grain boundaries but intergranular pitting as well.

![Fig. 6 – SEM ASTM F75 alloy micrograph.](Image)

![Fig. 7 – Tafel extrapolation curves for Ti-6Al-4V alloy in HBSS at 37 °C: (a) 0.166 and (b) 0.05 mV/s.](Image)
Fig. 8 – Tafel extrapolation curves for ASTM F75 alloy in HBSS at 37 °C: (a) 0.166 and (b) 0.05 mV/s.

Fig. 9 – MO micrographs of Ti-6Al-4V alloy: (a) before and (b) after corrosion test.

Fig. 10 – MO micrographs of ASTM F75 alloy: (a) before and (b) after corrosion test.
4. Conclusions

- In the alloy Ti-6Al-4V, α and β phases as well as α’ martensite have been identified with optical microscopy and scanning electron microscopy. These phases are preferential sites for corrosion.
- For ASTM F75 alloy, optical microscopy and scanning electron microscopy revealed carbides on grain boundaries and intergranular arrays.
- For Ti alloy, in corrosion test the increasing of sweep time results in a point at which the passive layer is formed and maintained, reducing the corrosion rate of 0.50–0.14 mpy.
- The corrosion occurred in the Co-base alloy (ASTM F75) along intergranular arrays of carbides and in the grain boundaries because Cr depletion when forming the carbides.
- The comparison of corrosion results for EBM fabricated Ti-6Al-4V alloy and ASTM F75 Co-base alloy were similar to corrosion data.

Conflicts of interest

The authors declare no conflicts of interest.

References

[8] Hernández Rodríguez Marco Antonio Ludovic; Influencia Microestructural y Dimensional en el Desgaste de Prototipos de Prótesis de Cadera Metal-Metal Fabricados en Co-Cr-Mo-C; Tesis; Universidad Autónoma de Nuevo León FIME; Diciembre (2004).