Characteristics and Properties of Ti-8Mo-6Cr Alloys with Added NbC Powders through the Vacuum Sintering Process at Various Temperatures

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In this study, three different powders are mixed and used to produce Ti-8Mo-6Cr-xNbC alloys of three different proportions: Ti-8Mo-6Cr-1NbC, Ti-8Mo-6Cr-3NbC and Ti-8Mo-6Cr-5NbC. The Ti-8Mo-6Cr-xNbC alloys simultaneously undergo a vacuum sintering process at temperatures of 1250, 1275 and 1300°C, respectively. The experimental results show that the lowest apparent porosity (0.1%) and highest hardness (66 HRA) of the Ti-8Mo-6Cr-xNbC alloys are acquired after sintering at 1300°C for 1 h. However, the transverse rupture strength (TRS) values of the Ti-8Mo-6Cr-xNbC alloys sintered at 1300°C display an obvious decrease as a result of the grain-coarsening phenomenon. Due to the TiC precipitates, grain refinement and a lower porosity appear in the 1250°C-sintered Ti-8Mo-6Cr-xNbC alloys, with the TRS showing an obvious increase (as compared with Ti-8Mo-6Cr, the TRS value increases from 1333 to 1532 MPa). These alloys also have the lowest corrosion current (Icorr was 1.47 × 10⁻⁵ A·cm⁻²) and highest polarization resistance (RP was 3.61 × 10³ Ω·cm²) in 1M H₂SO₄ solutions. These results confirm that the Ti-8Mo-6Cr-1NbC alloys sintered at 1250°C possess the suitable mechanical properties and optimal corrosion resistance. [doi:10.2320/matertrans.M2017128]

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1. Introduction

Titanium is a very light metal with unique mechanical properties and can be used over a wide range of temperatures. Despite of their great potential, the high production costs of titanium-based parts have limited their use to some specific applications in aerospace and chemical industries. Titanium alloy are expected to be much more widely used for implant materials in the medical and dental fields bearing in mind their superior biocompatibility, corrosion resistance and specific strength compared with other metallic implant materials. Among titanium-based materials, pure titanium and Ti-6%Al-4%V alloy are the most used implant materials.

In the last few years, new manufacturing techniques made this metal more competitive. Researchers have pointed out that titanium shares the hcp structure of a phase under room temperature but when sintering at 882°C the phase is transmitted into β phase BCC structure. However, a high-temperature BCC structure can be stabilized at room temperature by addition of alloy elements such as Fe, Mo, Cr, and Nb. The compound ratio must be adjusted properly to achieve the optimal mechanical properties. Previous study indicated that porous Ti-8Mo exhibits the highest mechanical properties among the porous Ti-(4-10)Mo alloys. Besides, our previous study also try to add a β stabilizer to develop a β-Ti alloy that can serve as a stable biomaterial. For example, we added the different amounts of Cr to form a trinary alloy (Ti-Mo-Cr) and then compare the mechanical properties and microstructures of the results. It has been showed that Ti-8Mo-6Cr alloy possesses the low porosity (0.10%) and the highest hardness (66 HRA) among the porous Ti-8Mo-(4-8)Cr alloys.

P/M techniques offer the advantage of manufacturing near net shape products with a considerable increase in the material utilization factor in the case of titanium alloys. One of the advantages of P/M compared to other methods is having better control on the microstructure, where better distribution of the reinforcements is possible in P/M compacts. Besides, the P/M blended elemental (BE) approach is potentially the low cost titanium P/M process available. Unfortunately, parts are limited in size and complexity, as well as less than 100% of theoretical density, which would adversely affect mechanical properties. Recent developments, such as using liquid-phase sintering (LPS) process, have enabled the fabrication of BE parts to over 99% of full density, resulting in significantly improved properties. Further studies and developments show that this approach may be well suited to reduce the cost of production of metallic implant parts, making titanium more cost competitive with other materials commonly used.

In addition, for metal cutting operations, there is a need for a tool steel that has high hot hardness, high toughness and good wear resistance. Additions of carbides such as TiC, NbC, VC, ZrC, or TaC to the powder mixtures are often done in order to increase the wear resistance for high-speed machining operations of steel. These carbides are known to inhibit grain growth in high temperature of P/M process. Among them, niobium carbide (NbC) possesses a high melting point (3600°C) and hardness (2800 HV). Moreover, the wettability with binder of NbC is much better than the others. In recent years, attention of many researchers was taken on NbC for its attractive properties. Previous literature indicated that the addition of NbC to a steel is considered to have three primary effects. The strongest contribution to strength is refinement of the final microstructure which advantages to mechanical properties.

In this research, we utilized Ti, Mo and Cr alloy powders, based on the optimal Ti-8Mo-6Cr alloys, and added different amounts of NbC powders as a strengthening element. At the
same time, the effects of the microstructural evolution on the mechanical properties and corrosion resistance of the Ti-8Mo-6Cr-xNbC alloys through the vacuum sintering process at various temperatures were determined.

2. Experimental Procedure

In our previous study, three different powders (titanium, molybdenum and chromium) were mixed and used to produce Ti-8Mo-6Cr-xNbC alloys of three different proportions (4, 6 and 8 mass%). The Ti-8Mo-xCr alloys underwent a vacuum sintering process at the temperatures of 1200, 1250, 1275 and 1300°C for 1 h. Those experimental results confirmed that the Ti-8Mo-6Cr alloys possessed the optimal microstructure and mechanical properties after sintering at 1300°C for 1 h. The present study further utilized Ti-8Mo-6Cr alloy powders and added different ratios of refined NbC powders (1, 3 and 5 mass%) as a strengthening element in order to explore the effects of a series of vacuum sintering processes. Here, in Ti-8Mo-6Cr-xNbC, x is the added amount of refined NbC powders. Furthermore, the Ti-8Mo-6Cr-xNbC powder samples with various NbC powders (0, 1, 3 and 5 mass%) added, are denoted as N0, N1, N3 and N5, respectively. A Microtrac X 100 laser was used to analyze the particle size of the submicron sized Ti, Mo, Cr and NbC powders. The mean particle sizes of the submicron sized Ti, Mo, Cr and NbC powders were about 28.1 ± 0.5, 13.8 ± 0.5, 26.7 ± 0.5 and 6.6 ± 0.3 μm, respectively. Moreover, the morphology of Ti and Mo reduced powders shows an irregularly shaped surface (polygon), and Cr reduced powders shows a nearly round surface. Besides, the morphology of refined NbC revealed an irregularly shaped crystal.

To evaluate the effects of microstructure evolution on the Ti-8Mo-6Cr-xNbC alloys via vacuum sintering process, this study conducted volume shrinkage rate, apparent porosity, hardness, Transverse Rupture Strength (TRS) tests, and Optical Microscopy (OM) and Scanning Electron Microscopy (SEM) microstructure observations. Porosity test was conducted in accordance to the ASTM C373-88 standard. Hardness tests were measured by HRA with a loading of 588 N, which followed the ASTM E18-3 standard. The Hung Ta universal material test machine (HT-9501A) with a maximum load of 25 tons was used for 3-point bending (TRS) tests (ASTM B528-05). Meanwhile, the TRS was obtained by the equation $R_{bmn} = 3FLk/2bh^2$, where $R_{bmn}$ is the TRS, which is determined as the fracture stress in the surface zone, $F$ is maximum fracture load. In this work, $L$ was 30 mm, $k$ was chamfer correction factor (normally 1.00–1.02), $b$ and $h$ were 5 mm, respectively. The specimen dimensions of the TRS test were $5 \times 5 \times 40$ mm$^3$ and tests at least three pieces.

Furthermore, corrosion potential analysis uses three electrodes method and follows by ASTM G59-97: the reference electrode is a saturated of silver-silver chloride electrode, auxiliary electrode uses a platinum electrode, and the working electrode is connected to the test specimens. The contact area of the specimen was 0.78 cm$^2$. The corrosive solvent used 1M H$_2$SO$_4$ was maintained at room temperature. A scanning speed of 0.01 V.S$^{-1}$, initial potential of −2.0 V, and the final potential of 2.0 V were controlled. The polarization curve was obtained by Corr-View software to analyze and compare the corrosion potential ($E_{corr}$), corrosion current ($I_{corr}$) and polarization resistance ($R_p$) of Ti-8Mo-6Cr-xNbC sintered specimens.

3. Results and Discussion

3.1 Effect of NbC content and sintering temperature on microstructure

Table 1 lists the volume shrinkage ratio of the Ti-8Mo-6Cr-xNbC alloys under different sintering temperatures. The volume shrinkage of the Ti-8Mo-6Cr-xNbC specimens evidenced a decreasing trend as the amount of NbC added increased. Moreover, increasing the sintering temperature improved the volume shrinkage, with the N1 specimen possessing the highest volume shrinkage after being sintered at 1300°C for 1 h. As shown in Table 2, the apparent porosity of the Ti-8Mo-6Cr-xNbC specimens first decreased and then increased as the amount of NbC added increased, but dramatically decreased as the sintering temperature increased. Although the porosity level increased as the amount of NbC additive increased (>1%), the porosity in the N1 specimen evidenced a significant decrease as compared with the Ti-8Mo-6Cr specimen. It is reasonable to suggest that a small amount of refined NbC powders (1%), when added to the Ti-8Mo-6Cr-xNbC alloys, is helpful in filling the voids during the sintering process, which then leads to a decrease in the apparent porosity of the N1 specimens after high-temperature sintering.

The apparent porosity tended to increase as the added amount of NbC powders increased (>1%), which can be ascribed to the diffusion defect. Previous study has indicated that with an increased sintering temperature, the dissolution of the niobium particles continues with consequent increases in the volume fraction of the two-phase structure (Ti-Nb alloy), since the Nb dissolution reaches the more distant titanium areas. The literature has also indicated that sintering at higher temperatures promotes additional particle-to-particle bonding and more complete alloying due to the higher diffusion rates and mass transport. Hence, it is reasonable to surmise that the diffusion velocity of niobium is faster in the Ti-8Mo-6Cr-xNbC alloy. The niobium can more easily per-
meante the titanium and leave the voids after the high-temperature sintering. Therefore, the increased porosity of the specimens is resulted from the diffusion defect due to the Kirkendall effect. In addition, the specimens with higher amounts of added NbC required higher temperatures to provide sufficient sintering energy for a complete liquid phase sintering (LPS). Consequently, the porosity level of the N3 and N5 specimens was less than 2% after sintering at 1275 and 1300°C, respectively, for 1 h (> 98% theoretical density). The near-full theoretical sintered density of all the Ti-8Mo-6Cr-xNbC alloys was acquired.

In this study, the adding of smaller amounts of NbC (1%) in the Ti-8Mo-6Cr-xNbC specimens was advantageous to the porosity, which resulted from an increased diffusion rate at relatively low sintering temperatures. As compared with the volume shrinkage and the porosity level, increasing the porosity of the Ti-8Mo-6Cr-xNbC specimens led to the decrease in the volume shrinkage as the amount of NbC additive increased. As Figs. 1–3 show, the SEM and OM images of the Ti-8Mo-6Cr-xNbC specimens confirmed that the pores increased as the added amount of NbC increased. The SEM and OM images of the specimens also show that the grain size tended to decrease as the added amount of NbC increased. The final values of the average grain size are listed in Table 3. Taking the specimens sintered at 1275°C for 1 h as an example, the average grain size of the N0, N1, N3 and N5 specimens of 37.1 µm (no NbC added) decreased to 36.3, 29.8 and 29.3 µm, respectively. As a result, a suitable amount of NbC additive was effective in inhibiting the grain growth. Meanwhile, acicular precipitates clearly appeared in specimens with an added 1% of NbC powders and sintered at the different temperatures, as shown in Fig. 1(a). However, the acicular precipitates disappeared when the added amount of NbC was over 1%.

Previous literature has indicated that the diffusional transformation structure (Widmanstatten structure) easily forms when α+β titanium alloys are rapidly cooled from the β region; the Widmanstatten microstructure of the Ti-8Mo alloys developed is then formed. In the present work, the microstructure of the sintered Ti-8Mo-6Cr specimens (Fig. 1(d)) rapidly cooled from 1250–1300°C in the β region to room temperature. Thus, the α phase was preferentially precipitated needle-like at the grain boundaries of the β matrix under the different sintering temperatures, where diffusional transformation was fully possible. As the cooling time was extended, the side-plate α phase formed. After that, the side plates formed into aggregates within the β matrix, thus forming the so-called Widmanstatten structure. Niobium is an

Table 3  Comparison of the average grain size of various mass% NbC added Ti-8Mo-6Cr-xNbC after the different sintering temperatures.

<table>
<thead>
<tr>
<th>Sintering Temperatures (°C)</th>
<th>Ti-8Mo-6Cr</th>
<th>N1</th>
<th>N3</th>
<th>N5</th>
</tr>
</thead>
<tbody>
<tr>
<td>1250</td>
<td>32.7 ± 1</td>
<td>31.5 ± 1</td>
<td>29.3 ± 1</td>
<td>27.3 ± 1</td>
</tr>
<tr>
<td>1275</td>
<td>37.1 ± 1</td>
<td>36.3 ± 1</td>
<td>29.8 ± 1</td>
<td>29.3 ± 1</td>
</tr>
<tr>
<td>1300</td>
<td>42.8 ± 1</td>
<td>37.1 ± 1</td>
<td>33.4 ± 1</td>
<td>32.7 ± 1</td>
</tr>
</tbody>
</table>
important β-phase stabilizer, and more niobium elements dissolved into the matrix to form a typical β stable titanium alloy as the added amount of NbC powders increased (>1%). As a result, the acicular precipitates (Widmanstatten structure) within the β matrix disappeared as the added amount of NbC increased to 3%. The results agree with the XRD finding (Fig. 3(d)).

The compositions and amounts of the elements of the Ti-8Mo-6Cr-xNbC alloys were determined. Figure 4(a) shows the high-magnification image of the N1 specimens after sintering at 1300°C with a few of the fine plate-like precipitates (black) gathered in the grain boundaries and the needle-like (black) titanium surrounding the grains. Furthermore, the Widmanstatten structure showed a significant decrease as compared with the Ti-8Mo-6Cr specimen (Fig. 4(b)). The EDS analysis of the N1 specimen, with the location of the (1), (2) and (3) regions, revealed the fine plate-like precipitates (black) to be TiC ((a)-1), the needle-like (black) regions to be α titanium ((a)-2) and the Nb to have uniformly dissolved in the matrix as Nb-rich β titanium ((a)-3), respectively. It is reasonable to speculate that the niobium replaced the titanium atoms in the matrix. According to Takeuchi and Inoue indicated that the value of mixing enthalpy (ΔH\text{mix}) of the elements determines the level of reaction. In short, the elements tend to cause a reaction as they possess a lower ΔH\text{mix}. Furthermore, the negative mixing enthalpy (ΔH\text{mix}) in both elements lead to the overall reaction automatically. Thus, the element Carbon undergoes a combination reaction with Ti during the high-temperature sintering process, and a TiC is formed. Our study agrees with the previous finding.

As a result, fine plate-like TiC formed in the grain boundaries, while the niobium uniformly dissolved into the titanium matrix in the form of a solid solution and helped to strengthen the Ti-8Mo-6Ni-xNbC alloy. A comparison with the SEM image of Ti-8Mo-6Cr in Fig. 4(b) shows a refined and uniform Widmanstatten structure in the matrix. The EDS analysis of the Ti-8Mo-6Cr specimen shows that, noting the location of the (1) and (2) regions, the needle-like (black) regions were Ti-rich α titanium and the refined threadlike compounds (gray) were Mo-rich and Cr-rich β titanium, respectively. The needle-like (black) titanium surrounding the grains and the threadlike compounds (gray) were randomly dispersed within the grains. The results confirmed that α titanium precipitated needle-like at the grain boundaries of the β matrix and that the Ti-8Mo-6Cr materials formed α+β titanium alloys.

### 3.2 Effect of NbC content and sintering temperature on mechanical properties

Figure 5(a) shows the hardness test results of the Ti-8Mo-6Cr-xNbC specimens for the different sintering temperatures. The hardness of the Ti-8Mo-6Cr-xNbC specimens was obviously enhanced as the sintering temperature increased. However, the hardness slightly increased initially and then decreased as the added amount of NbC increased. The literature has indicated that decreasing the porosity and increasing the density of sintered materials can effectively enhance plastic deformation resistance and hardness.11,19) The results can be further compared with Figs. 1–3. The increase in porosity as the added amount of NbC increased could be a main factor affecting the hardness. When niobium elements were dissolved into the matrix, a typical β stable titanium alloy was formed as the added amount of NbC powders increased (>3%). As a result, the acicular precipitates disappeared, which was disadvantageous to the hardness. However, the hardness of the N1 specimens displayed a slight increase as compared with the Ti-8Mo-6Cr specimens. Significantly, the N1 specimen sintered at 1300°C possessed the highest hardness (66.5 HRA).

Figure 4(b) shows the TRS values of the Ti-8Mo-6Cr-xNbC specimens for the various sintering temperatures. The

<table>
<thead>
<tr>
<th>Elements (at%)</th>
<th>(a)-1</th>
<th>(a)-2</th>
<th>(a)-3</th>
<th>(b)-1</th>
<th>(b)-2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti K</td>
<td>85.52</td>
<td>91.53</td>
<td>84.84</td>
<td>94.99</td>
<td>86.49</td>
</tr>
<tr>
<td>Mo L</td>
<td>–</td>
<td>6.06</td>
<td>8.31</td>
<td>5.01</td>
<td>8.55</td>
</tr>
<tr>
<td>Cr K</td>
<td>–</td>
<td>2.41</td>
<td>5.14</td>
<td>–</td>
<td>4.96</td>
</tr>
<tr>
<td>C K</td>
<td>14.65</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Nb L</td>
<td>–</td>
<td>–</td>
<td>1.73</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Total</td>
<td>100.00</td>
<td>100.00</td>
<td>100.00</td>
<td>100.00</td>
<td>100.00</td>
</tr>
</tbody>
</table>

Fig. 4 The EDS analysis of the Ti-8Mo-6Cr-xNbC specimens (a) N1 specimen after sintered at 1300°C/1 h, and (b) the optimal sintered Ti-8Mo-6Cr specimen (non NbC added).

Fig. 5 Comparison of the hardness and TRS of various mass% NbC added Ti-8Mo-6Cr-xNbC by the different sintering temperatures (a) hardness, and (b) TRS.
The fracture feature only presented larger cleavages and some of the brittle features resulting from grain coarsening. Taking the Ti-8Mo-6Cr-xNbC specimens sintered at 1250°C as an example, the pores, dimple features and small cleavages can be observed, with the small cleavages tending to a slight increase as the added amount of NbC increased, as shown in Figs. 6(a), (b) and 6(c). The fracture surface, as compared with that of the Ti-8Mo-6Cr specimen (Fig. 6(d)), showed that a suitable amount of NbC added to the matrix inhibited grain growth, thereby increasing the TRS of the Ti-8Mo-6Cr-xNbC materials. The fracture surface of the Ti-8Mo-6Cr displayed more smooth facets resulting from brittle features; this was ascribed to the larger grain size and brittle Cr in the Ti-8Mo-6Cr specimen. Besides, the fracture surface of the Ti-8Mo-6Cr-xNbC specimen was converted from a Widmanstatten (α+β) to a stable β structure as the added mount of NbC increased from 1% to 5%. Despite the fracture surface displaying no obvious variation, it was found that the grain size tended to decrease and the porosity increased slightly as the added mount of NbC increased. The fracture surface observations were in agreement with the SEM findings and provided verification that grain size and porosity had an important effect on the TRS value.

### 3.3 Effect of NbC content on corrosion resistance

Table 4 lists the results of the Ti-8Mo-6Cr-xNbC specimens sintered at 1250°C after the 1M H2SO4 corrosion test. Previous study has indicated that Ti-Mo alloys exhibit a passive behavior in 5% HCl solution, which is attributed to the passive film formation of a mixture of MoO3 and TiO2. In
In this work, all specimens possessed a slight passivation phenomenon after the corrosion test. However, the passivation layer could not completely form on the surface of the specimens. Although the Ti-8Mo-6Cr-xNbC alloy contained the Cr element, it was completely dissolved into the matrix and did not generate a precipitation phenomenon. Thus, the specimens did not possess a sufficient passivation layer.

Significantly, the polarization current in the N1 specimen had the lowest value. In an electrochemical reaction, the current value represents the diversification of the equilibrium constants in the oxidation reaction. A higher current value leads to an increase in the equilibrium constant and a fast oxidation. The increase in the added amount of NbC led to a significant corrosion current increase $(1.47 \rightarrow 1.54 \rightarrow 1.81 \times 10^{-5} \text{A cm}^{-2})$. The polarization resistance also needed to be considered. Higher polarization resistance usually means better corrosion resistance. The N1 specimens possessed the highest polarization resistance $(R_p = 3.61 \times 10^4 \text{Ω cm}^2)$ and the minimum corrosion current $(I_{corr} = 1.47 \times 10^{-5} \text{A cm}^{-2})$, as a result of their lower porosity. Previous study has indicated that internal pores can easily cause crevice corrosion. Table 2 shows that the porosity tended to increase as the added amount of NbC increased. Consequently, the corrosion resistance of the N1 specimens was higher than that of the N3 or N5 specimens. According to the above discussion and results, it could be stated that the N1 specimen has the optimal microstructure, corrosion resistance and suitable mechanical properties after sintering at 1250°C for 1 h.

4. Conclusions

According to the experimental results discussed in the previous sections, the following conclusions can be drawn:

(1) A small amount of refined NbC powders (1%) added to the Ti-8Mo-6Cr-xNbC alloys was helpful in filling the voids during the sintering process. Thus, the apparent porosity of the N1 specimens showed a significant decrease after the high-temperature sintering. These specimens also possessed the optimal corrosion resistance.

(2) NbC powders added to the Ti-8Mo-6Cr-xNbC alloys effectively inhibited grain growth. Particularly, niobium is an important β-phase stabilizer, and more niobium elements dissolved into the matrix to form a typical β stable titanium alloy as the added amount of NbC powders increased (>1%). As a result, the acicular precipitates (Widmanstatten structure) within the β matrix disappeared as the added amount of NbC was increased to 3%.

(3) For the N1 specimen, the lowest porosity (0.1%) and the highest hardness (66.5 HRA) were acquired after sintering at 1300°C for 1 h. However, due to the grain coarsening, the TRS value showed an obvious decrease as compared with that of the specimen sintered at 1250°C for 1 h. Consequently, the suitable TRS (1532 MPa) and hardness (64.0 HRA) were obtained for the Ti-8Mo-6Cr-xNbC alloys with an added 1% of NbC and sintered at 1250°C for 1 h.

(4) Although the Ti-8Mo-6Cr-1NbC specimens did not form an effective passive film during the corrosion tests, the lowest corrosion current and highest polarization resistance appeared in the N1 specimens after sintered at 1250°C for 1 h. These specimens also possessed the optimal corrosion resistance.

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REFERENCES