Microstructures and mechanical properties of Ti-Mn alloys for biomedical applications produced by metal injection molding and cold crucible levitation melting

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1. Introduction

Titanium (Ti) alloys have been used in the biomaterials field as implant materials, from prosthesis to pins and metallic rods. Among the most common titanium based materials for such applications are commercially pure Ti (CP-Ti) and Ti-6Al-4V ELI (Ti-64 ELI)⁶. However, these materials are not ideal for such applications due to diverse factors: mechanical strength of CP-Ti is not high, comparatively; Ti-64 includes the element vanadium (V), which has been proven as cytotoxic⁷; both materials possess Young’s moduli much higher than that of the human bone, inducing stress shielding effect which leads to bone absorption⁸. In this regard, efforts have been made to develop new β-type Ti alloys such as Ti-29Nb-13Ta-4.6Zr (TNTZ)⁹, TNTZ alloy offers a great improvement to the high Young’s modulus issue⁹ while avoiding chemical elements toxic to the human body. However, the low availability of alloying elements niobium (Nb) and tantalum (Ta) makes harder the wide-spread use of such alloy.

With consideration towards mechanical properties, low toxicity and availability, the alloying element manganese (Mn) was chosen for this study. Manganese is a proved β-stabilizer element for Ti⁹, which could provide attractive mechanical properties for such application. Even though it’s not completely harmless⁹, Mn is an important element in the human body and most living organisms⁹. Also, it is a very abundant element in the Earth’s crust⁹, making it an excellent candidate for the established parameters.

In order to investigate the mechanical properties of Ti-Mn alloys, two methods of production have been chosen: metal injection molding (MIM) and cold crucible levitation melting (CCLM). Metal injection molding provides good control over the balance of mechanical properties and density. Cold crucible levitation melting was chosen as a comparative production method, and it can cover some of the possible shortcomings of MIM, such as contamination from binder.

In this study, Ti-Mn alloys with varying Mn content (from 6 to 20 mass%) will be evaluated from its

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microstructure and hardness. Microstructure analysis was conducted through optical microscopy (OM), X-rays diffractometry (XRD) and transmission electron microscopy (TEM).

2. Experimental Procedures

Rectangular MIM ingots with nominal 8, 10, 12, 14, 16, 18 and 20 Mn mass% were used. The ingots with dimensions 69 x 3.8 x 7.9 mm were produced from gas-atomized Ti powder with low oxygen (0.16O mass%) and fine Mn powder (0.77O mass%), both with particle size smaller than 45 μm. The material was sintered at 1373 K for 28.8 ks in vacuum atmosphere.

CCLM ingots with nominal 6, 10, 14 and 18 Mn mass% were produced. The ingots were produced from CP-Ti and CP-Mn chips, and had a hazelnut shape due to the crucible shape. Prior to melting, the oxide layer of the Mn chips was removed with HNO3. All chips were washed with acetone, ethanol and then dried before being inserted into the crucible. The ingots were later homogenized at 1273 K for 21.6 ks in argon atmosphere. All MIM and CCLM specimens were subjected to solution treatment at 1173 K for 3.6 ks in vacuum atmosphere followed by water-quenching.

The specimens for OM measurement were etched with a 1 % HF + 0.5 % HNO3 solution for a time of 15 s. The TEM observations were performed at an accelerating voltage of 200 keV. Hardness measurements were taken with a Vickers hardness testing machine. A force of 9.807 N was applied for 15 s on each measurement. At least 10 measurements were taken for each specimen.

3. Results and Discussion

Figure 1 shows the typical OM for both MIM and CCLM specimens. The apparent single phase structure of each alloy has been confirmed through XRD analysis as single β-phase, as shown in Fig. 2. However, further analysis of MIM specimens with TEM (Fig. 3) pointed the existence of ω-phase. Very intense ω diffraction peaks were observed in Ti-8Mn alloy, gradually decreasing in intensity up to Ti-14Mn alloy, but still visible (and apparently stronger) in Ti-20Mn alloy.

![OM images of (a) MIM and (b) CCLM Ti-14Mn alloys.](image)

Fig. 1 – OM images of (a) MIM and (b) CCLM Ti-14Mn alloys.
Fig. 2 – XRD profiles of (a) MIM (b) CCLM specimens.

Fig. 3 – SAD patterns of selected MIM specimens.

Fig. 4 – Vickers hardness of MIM and CCLM specimens.
The small hardness variation observed between different MIM samples is related to the presence of \( \omega \)-phase and the solid solution strengthening (SSS) effect. The higher volume of \( \omega \)-phase makes the sample harder, thus the hardness decreases from the Ti-8Mn (strong \( \omega \)) up to about the Ti-16Mn, when it increases again because of the SSS effect.

Hardness values of CCLM specimens are comparable to those of Ti-64 ELI\(^5\) and other Ti alloys. The comparatively lower values on MIM specimens can be explained by the presence of pores in MIM specimens as observed in the OM images on Fig. 1. During the hardness data acquisition on MIM specimens, care was taken to avoid superficial pores directly in the indentation area but it was not possible to avoid the occasional sub-surface pore and its stress concentration field. The larger grain size (up to a couple centimeters) of CCLM specimens can explain the difference observed in the error bars between MIM and CCLM.

4. Conclusions

- Ti-Mn Alloys produced by MIM and CCLM are mainly consisted by \( \beta \)-phase. However, \( \omega \)-phase exists on the Ti-Mn alloys produced by MIM.
- The hardness of Ti-Mn alloys produced by MIM shows small variations between the various Mn contents and is comparable to those of other Ti-based materials used in biomaterials applications, having the highest value in Ti-20Mn (324 HV) and lowest in Ti-16Mn (289 HV).
- Hardness of Ti-Mn alloys produced by CCLM is slightly higher (336 HV on Ti-18Mn) than that of MIM-produced alloys.
- The existence of pores evidently caused the MIM samples to have an average hardness lower than that of CCLM samples.

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6. References