Preparation of TiMn alloy by mechanical alloying and spark plasma sintering for biomedical applications

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Abstract. TiMn alloy was prepared by mechanical alloying and subsequently consolidated by spark plasma sintering (SPS) technique for exploration of biomedical applications. The microstructures, mechanical properties and cytotoxicity of the TiMn alloys were investigated in comparison with the pure Ti and Mn metals. Ti8Mn and Ti12Mn alloys with high relative density (99%) were prepared by mechanical alloying for 60 h and SPS at 700 °C for 5 min. The doping of Mn in Ti has decreased the transformation temperature from α to β phase, increased the relative density and enhanced the hardness of the Ti metal significantly. The Ti8Mn alloys showed 86% cell viability which was comparable to that of the pure Ti (93%). The Mn can be used as a good alloying element for biomedical Ti metal, and the Ti8Mn alloy could have a potential use as bone substitutes and dental implants.

1. Introduction
Titanium (Ti) and its alloys are widely used as biomaterials especially for orthopedic implants in load bearing sites. Pure Ti was once used as biomaterial, but now Ti-6Al-4V alloy is preferentially in clinical use because of its better mechanical properties, corrosion resistance and biocompatibility [1]. However, the release of high toxicity Al and V ions could cause some side effects in the body during and after destruction of bioceramics coating on their surface [2]. Therefore, the exploration of new Ti alloys without Al and V for medical implants has gained great attentions in the past years and is still ongoing.

Manganese (Mn) is one of the trace elements in human body, thus the Mn ion should have less toxicity than Al and V. The Mn element has been incorporated to tri-calcium phosphate bioceramics and showed good cell compatibility [3]. The recent study in our group found that Mn incorporation into the Ti alloys could enhance the cell adhesion properties [4]. The TiMn alloys have been explored for aerospace and hydrogen storage applications already [5]; nevertheless, few studies were on its exploration for biomedical applications and they were generally fabricated by casting or traditional powder metallurgy techniques. In this study, the TiMn alloys with Ti8Mn and Ti12Mn compositions were prepared by mechanical alloying and spark plasma sintering techniques. The microstructure and properties were investigated for exploration of their biomedical applications. Pure Ti and Mn metals were also fabricated by SPS for comparison.

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2. Experimental and methods

The starting powders were high purity gas-atomized powders with average particle sizes of 100 µm (Fluka, Germany). Mechanical alloying was performed with a high energy PM400 planetary ball milling (Retsch PM400, Germany). Chromium hardened steel vials and balls were used as grinding media, with ball to powder ratio of 15:1. Wet-milling in hexane was performed for different hours at 250 rpm. Hexane was used as process control agent to prevent oxidation and excessive contamination from the grinding media.

The sintering was accomplished using a Model HPD-25/1 FCT spark plasma sintering system (FCT systeme GmbH, Rauenstein, Germany) at a temperature of 500–800 °C for various times. The powders were loaded into graphite die to sinter disc-shaped pellets (20 mm diameter, thickness 5-6 mm). The SPS experiments were conducted in vacuum (<6 Pa) under uniaxial pressure 50 MPa. The heating rate was maintained at 100 °C/min. X-ray diffraction (XRD, Bruker D8, Germany) was used to characterize the phase composition of the powders and sintered alloys. The phase transformation of the alloys was performed with a differential scanning calorimetry (DSC, Netzsch Pegasus 404C, Germany). Scanning electron microscopy (SEM, Zeiss Supra 25, Germany) was employed to analyze the microstructures of the powders and sintered alloys. The densities of the sintered alloys were determined by the Archimedes method, using water immersion. Hardness was measured by Vicker’s hardness tests under load of 10 Kg. The cytotoxicity of the alloys on human osteoblastic cells (cell line MG-63, ATCC-CRL-1427) was examined using MTS assay.

3. Results and discussions

The Ti8Mn and Ti12Mn powders were prepared by mechanical alloying method starting from mixing Ti and Mn powders. The mixtures were milled for 10, 20, 40 and 60 hours in the ball milling machine. By the XRD analysis, it was found that the 60 h milled TiMn powders had a good alloying effect where the pure Ti and Mn peaks were disappeared. Figure 1(a) shows the XRD results of the starting Ti, Mn powders and the 60 h ball milled TiMn powders. The pure Ti powder shows a hexagonal α-Ti phase and pure Mn shows a cubic α-Mn phase. The phase compositions in the mechanical alloyed Ti8Mn and Ti12Mn powders are mainly a tetragonal α-TiMn phase. Figure 1(b) shows the SEM micrograph of the Ti8Mn powders after 60 hours milling. The powders formed agglomerates with mean particle size about 5 µm in diameter with a narrow size distribution.

![Fig. 1 XRD patterns (a) and SEM micrograph (b) of the mechanical alloyed TiMn powders.](image)

Then, the transformation behaviors of the TiMn powders were studied by using DSC. Figure 2 shows the transformation temperatures of the TiMn alloys in comparison with pure Ti. In the case of pure Ti, the transformation temperature from α to β phase occurred around 850 °C. In TiMn alloys, as
the amount of Mn increased, the transformation temperature decreased to relative lower temperature of 700 °C. The addition of Mn has decreased the transformation temperature from α to β phase in the Ti metal.

The Ti and its alloys are difficult to be sintered by traditional sintering techniques because of their stable surface oxide film (TiO$_2$) [6]. Thus, the SPS technique was incorporated to sinter the TiMn alloys in this study. Figure 3 shows the relative density of the pure Ti and TiMn alloys as a function of the sintering temperatures in SPS. With temperature increase from 550-750 °C, the relative density of the Ti metal increased from 68% to 98%. The TiMn alloys showed 99% relative density at 700 °C for 5 min. The Mn element doping has increased the relative density of Ti metal during SPS. By using the traditional sintering techniques, high temperatures of 1100-1300 °C were required to get a high density Ti metal and alloy [7]. The SPS has decrease the sintering temperature of Ti and TiMn alloys. Because the high reactivity of Ti metal above 1000 °C, the sintering of Ti avoiding the chemical reaction between Ti and die is difficult to be performed. The low sintering temperature used in the SPS allows the use of graphite dies in the present study. The low sintering temperature can be ascribed to the ionization of particles by local sparks during SPS, which melted the titanium oxide films and formed neck junctions among powder particles at a lower temperature [6].

Figure 4 (a) shows the SEM micrographs of the SPSed Ti8Mn and Ti12Mn alloys. There were few micropores on the fracture surface of the TiMn alloys. The grain size of the TiMn alloys is about 500-600 nm. The fracture mode of the alloy is primary intergranular. The XRD results of the Ti and TiMn alloys by SPS at 700 °C showed that the Ti retained α-Ti phase, but the TiMn alloys were mostly a β-TiMn phase with a small amount of α-TiMn phase (Fig.4b). The XRD results were corresponding to the DSC results in Fig.2 where the Mn doping has decreased the phase transitional temperature of Ti. The hardness values used to identify mechanical properties of TiMn alloys are shown in Figure 4 (c). The hardness value tended to rise with increasing Mn contents. The pure Ti showed a hardness of 160 HV$_{10}$, the Ti8Mn alloys had a hardness of 480 HV$_{10}$, Ti12Mn alloys exhibited a hardness of 550 HV$_{10}$. The hardness values of all TiMn alloys were significantly higher than that of pure Ti. The maximum increase in the hardness value versus pure Ti was about 340%. Figure 4 (d) shows the cytotoxicity of the pure Ti and TiMn alloys by MTS assay. The TCPS control was normalized to 100%. The pure Ti showed osteoblast cell viability of more than 93%. With increasing of the Mn contents, the cytotoxicity has been increased. However, the Ti8Mn alloys had a comparable cell viability of 86%. Small amount of Mn doping (<10 wt %) in Ti metal had little effect on the cytotoxicity but had great effect on the hardness increments; therefore, the Mn is a good alloying element for biomedical Ti metal and the Ti8Mn alloy has a potential use as bone substitutes and dental implants materials instead of the Ti6Al4V alloys.
4. Conclusions
The TiMn alloys were prepared by mechanical alloying and SPS techniques. High relative density (99%) TiMn alloys were prepared by SPS at 700 °C for 5 min. The addition of Mn in Ti has decreased the transformation temperature from α to β phase, increased the relative density, and enhanced the hardness of the Ti metal significantly. The Ti8Mn alloys showed a 86% cell viability which was comparable to that of the pure Ti (93%). The Mn is a good alloying element for biomedical Ti metal and Ti8Mn alloy has a potential use as bone substitutes and dental implants.

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