Solid-state reactions in mechanically milled and spark plasma sintered pure Titanium

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Highlights

- The Vickers microhardness of the pure titanium powders with process control agent (PCA) 0.25 g increased sharply from 189 HV to 513 HV after 8 h of the MM process.
- Formation of TiH_2 as the solid-state reaction product occurred in the MMed powder during 4 and 8 h of the MM process.
- The near full density was obtained for the SPS materials under the condition of an applied pressure at 49 MPa with a sintering temperature at 1073 K for 0.5 h.
- The Vickers hardness of the SPS material fabricated from 8 h MMed powder with PCA 0.50 g exhibited a maximum value of 1253 HV.

1. Introduction

Titanium alloys exhibit an excellent combination of attractive functional and mechanical properties, such as high hardness, low density, good corrosion resistance, and excellent biocompatibilities. Among titanium alloys, Ti-6Al-4V (mass%) alloys are generally used and showed the tensile strength of 931 MPa at room temperature. However, typical high strength titanium alloys generally contain rare earth metals, such as V, Ta, Nb, that are relatively expensive compared with ubiquitous elements, such as Fe, Si, Mg. On the other hand, pure titanium exhibits only the tensile strength of 552 MPa even though the maximum level of impurities, such as 4th grade of pure titanium. The most promising approach to strengthening the titanium is to either add such the elements and/or apply heat treatments. However, such the approaches have been limited to break through highly demanded properties. In this research, powder metallurgy process was applied to produce bulk materials exhibiting high hardness and strength. In addition, alloy elements were not added to matrix in order to reduce the materials costs.

In powder metallurgy process, a high level of dislocations due to cold working by mechanical milling (MM) process can be introduced into pure metal powder. The MM processing technique can also be used to obtain nanoparticles in titanium by milling in the presence of a process control agent (PCA) which enables a balance between fracture and welding to be established enabling refinement of the powder particle size. The role of the PCA, however, can be two folds; one is preventing the occurrence of excessive welding of the titanium powder particles: the other is reacting with the titanium during milling or subsequent heat treatments leading to the formation of second phases. Thus in order to produce composite powders and/or nanoparticles prior to particle-reinforced bulk composite materials, mechanical milling is one of effective techniques. Spark plasma sintering (SPS), known as the field-assisted sintering technique, is a comparatively novel sintering process that allows the nano and/or composite powders produced by MM process to be consolidated into bulk materials at low temperatures, with short heating, holding and cooling time compared to that used in conventional sintering and powder metallurgy techniques.

The aim of the present work was thus to investigate effects of mechanical milling times and amounts of PCA on solid-state reactions and mechanical properties of MMed powders and their bulk materials fabricated from the MMed powders by SPS process.

2. Methods

The starting material was hydrogen de-hydride 99.5% pure titanium powders with an average diameter of 45 μm. The pure titanium powder contains 0.31 mass% of oxygen and 0.028 mass% of iron which are corresponded to the grade Ⅲ type of pure titanium. Stainless steel balls of 7 mm diameter together with 10 g of the pure titanium powder mixture and stearic acid as a PCA were sealed in a hardened steel vial using a glove box filled with argon. The amount of PCA was varied from 0.25 g to 1.00 g. The ball to powder mass ratio was approximately 7:1. The MM process was performed at room temperature using an SPEX8000

mixer/mill, and the MM processing time was 4 h or 8 h. The scanning electron microscopy (SEM) was applied to observe particle size and appearance of the MM powders. The average Vickers microhardness of the MMed powders was determined from 15 particles per sample with a microhardness tester using an applied load of 98 mN.

The MMed powders were consolidated into bulk materials by a Sumitomo Coal, Dr. Sinter SPS-1050 SPS apparatus. Seven grams of MMed powder was placed into a graphite die of 20 mm in diameter and heated at 1 K / s under vacuum with an applied pressure of 49 MPa at 1073 K for 1.8 ks. The Vickers hardness of the SPS materials was measured using an applied load of 9.8 N. X-ray diffraction (XRD) analysis was performed on both the MMed powders and SPS materials.

3. Results and discussion

XRD patterns of the 4 h or 8 h MMed powders with the addition of 0.25 g of PCA clearly indicated that solid-state reaction between titanium and stearic acid in all the different MM time was detected, and diffraction peak corresponded to TiH_2 was observed as increasing MM time. This is due to occurrence of solid-state reaction between titanium and hydrogen in stearic acid during MM process.

The hardness of the pure titanium powder before MM was approximately 189 HV. The hardness of the MMed pure titanium powders with 0.25 g of PCA increased dramatically to over 500 HV after 8 h of MM. It should be emphasised that these hardness values of the pure titanium powder after 8 h of MM were significantly higher than that of typical high strength titanium alloys, such as Ti-6 Al-4V (mass%) alloys. It can be thought that these hardness values are attributable to not only large strain introduced by MM, but also formation of TiH_2 intermetallic compound as a solid-state reaction product during MM process. A novel technique, such as inducing solid-state reactions, using PCA during MM process suggests a relatively low cost method to enhance hardness and strength of pure titanium without an adding alloy elements method.

In the case of the bulk SPS materials fabricated from 4 h and 8 h MMed powders with a presence of 0.50 g of PCA, the diffraction peaks corresponding to α- titanium together with new diffraction identified as TiC were observed suggesting that solid-state reaction was promoted by a combination process of strain induced by MM and subsequently heated during SPS. Titanium is well known as a relatively active metal to be oxide, carbonate or nitride easily in the adequate atmospheres. However, no such the reaction between titanium and stearic acid added as PCA in the present research has been reported. It is interesting to note that the diffraction intensity of the TiC peaks in the SPS materials also increased when the MM time increased, suggesting the promotion of a solid-state reaction.

The near full density was attained for the SPS materials consolidated from the various MMed titanium powders under an applied pressure of 49 MPa at 1073 K for 0.5 h. The titanium SPS material produced from 8 h MMed powder with 0.50 g of PCA exhibited the highest hardness value of 1253 HV at room temperature due to a combination of strengthening mechanisms; strain hardening in the starting MMed powder, refinement of grain size and dispersion of solid-state reaction products in the SPS materials.

4. Conclusions

The solid-state reactions in the pure titanium powders with the presence of stearic acid occurred to form TiH_2 during MM process. As the result of the solid-state reactions together with strain induced by the MM process, a hardness increase of the MMed powders was observed. The near full density was attained for the SPS materials consolidated from the various MMed titanium powders under an applied pressure of 49 MPa at 1073 K for 0.5 h. The titanium SPS material produced from 8 h MMed powder with 0.50 g of PCA exhibited the highest hardness value of 1253 HV at room temperature due to a combination of strengthening mechanisms; strain hardening in the starting MMed powder, refinement of grain size and dispersion of solid-state reaction products in the SPS materials.

Keywords
Solid-state reaction; Mechanical milling; Spark plasma sintering; pure titanium