MICROSTRUCTURE OF COMMERCIALLY PURE TITANIUM AFTER CRYOGENIC MILLING AND SPARK PLASMA SINTERING

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Abstract

Commercially pure titanium was prepared by advanced powder metallurgy methods with the aim to produce the ultra-fine grained material. Cryogenic attritor milling was used as a first step to refine the microstructure at liquid argon temperatures to suppress recovery and dynamic recrystallization. Spark plasma sintering was subsequently employed to produce bulk material, exploiting its ability to achieve fully dense structure in short time and thus to reduce the grain growth. In order to understand the undergoing microstructural changes during the process, detailed investigation was performed after each preparation step. Powder morphology was changed significantly after milling, while particle fragmentation was only limited. Grain size after sintering was in micrometer scale, relatively independent of sintering conditions.

Keywords: Titanium, cryogenic milling, spark plasma sintering, microstructure

1. INTRODUCTION

Titanium is a promising material for many industrial applications, such as aerospace, biomedicine and advanced structural applications, where high specific strength or biocompatibility is required. However, the titanium production is expensive, resulting in high price of the metal. As a consequence, significant effort is made to reduce the material losses during machining. Powder metallurgy followed by an appropriate compaction method can avoid excessive machining by aiming on *near-net shape processing*, after which none or only little post-processing is necessary. Properties of the final material can be significantly influenced by the powder processing prior to compaction.

Ultra-fine grained (UFG) materials (with submicrometer grains) have higher strength than their coarse grained counterparts due to Hall-Petch strengthening. UFG materials can be prepared by application of *severe plastic deformation* (SPD) methods, when the material is severely deformed to achieve significant microstructure refinement. SPD is usually performed on bulk samples, however, there are methods such as ball milling which can process the powders in qualitatively similar way to bulk SPD methods. This is done by repetitive plastic deformation [1] during collisions of balls and powder. *Spark plasma sintering* (SPS) was selected for consolidation of powders, because it provides compaction in shortest processing time and at comparatively low sintering temperatures [2]. Limited sintering temperature and time are critical for retaining the UFG structure, which is inherently in a thermodynamically unstable condition.

The influence of milling parameters and evolution of powder properties during cryomilling of Ti was investigated in [3-5]. Liquid nitrogen (LN) was found unsuitable as a cooling liquid because Ti powders are prone to high nitrogen pick-up. The small grain size of approximately 20 nm was obtained after milling in [5, 6], but such refined microstructure was stable only due to high nitrogen contamination from liquid nitrogen. Spark plasma sintering was used for consolidation of commercially pure Ti, with minimum required temperature of 700 °C for successful compaction [7].

2. EXPERIMENTAL METHODS

2.1. Material preparation

Gas atomized commercially pure titanium (Grade 2) powder (20-60 μm) was supplied by TLS Technik, Germany with the composition as claimed by the supplier: 0.14 wt.% O, 0.08 wt.% Fe, 0.006 wt.% C, 0.004 wt.% N, 0.001 wt.% H and Ti balanced. The material was processed by wet cryogenic milling using Union Process 01-HD attritor in liquid argon (LAr) bath for 3.25 h at 650 rpm milling speed. Tungsten carbide (WC) balls of diameter 6.35 mm were used as grinding media, because of its high density of 15.6 g/cm^3 (compared to conventionally used stainless steel with the density of 7.8 g/cm^3). High density of balls leads to higher kinetic energy and impact energy, which results in more intensive deformation. Stearic acid was employed as a process control agent (PCA) to suppress cold-welding.

The spark plasma sintering was performed by SPS 10-4 furnace (Thermal Technology LLC) in a graphite die of 20 mm in diameter. The approximate batch size was 10 g, the samples 6 mm in height were produced. The milled powder was cleaned from the stearic acid by repeated washing in ethanol.

The sintering was done at temperatures of 700 °C, 750 °C, 800 °C and 850 °C. The program started with 1 min heating up to the temperature 50 °C below the desired sintering temperature (i.e. the heating rate varied from 625 °C /min to 775 °C /min). Such fast sintering can fully exploit the unique feature of SPS of attaining very high heating rates. Fast heating can be beneficial for preserving the UFG microstructure of the powder by reducing the total time of powder exposure to high temperatures. After this step, the sample was heated at 100 °C /min for 30 s to the desired sintering temperature. Limited heating rate in the final stage of heating was selected to avoid temperature overshooting. Isothermal sintering was subsequently performed for the time of 3 min. The cooling was uncontrolled with an approximate initial cooling rate of 200 °C /min. The pressure of 80 MPa was applied during the whole process.

2.2. Experimental characterization

The microstructure of samples was investigated using scanning electron microscopy (SEM). FEI Quanta 200F and Zeiss Auriga Compact FIB-SEM (microscopes both equipped by FEG electron source and EDS and EBSD detectors by EDAX) were used. For microstructure observations of the sintered samples, electron back-scattered diffraction (EBSD) was used.

The content of H, N and O in the cryomilled powder was determined by carrier gas hot extraction (CGHE) method.

3. RESULTS AND DISCUSSION

3.1. Powders

The SEM images of four different powders are presented in the **Figure 1** - the as-received gas atomized (GA) state and the milled powder. The originally spherical morphology of the gas atomized particles (**Figure 1 a)**) was significantly changed by cryogenic attritor milling. The as-milled particles have the shape of thin discs or plates as can be seen in the **Figure 1 b)**.

Only moderate fragmentation of powder particles was observed, with plastic deformation being the dominant mechanism during milling. This suggests that CP Ti remains ductile even at cryogenic temperatures. No signs of cold-welding were observed, which is a direct consequence of application of PCA.

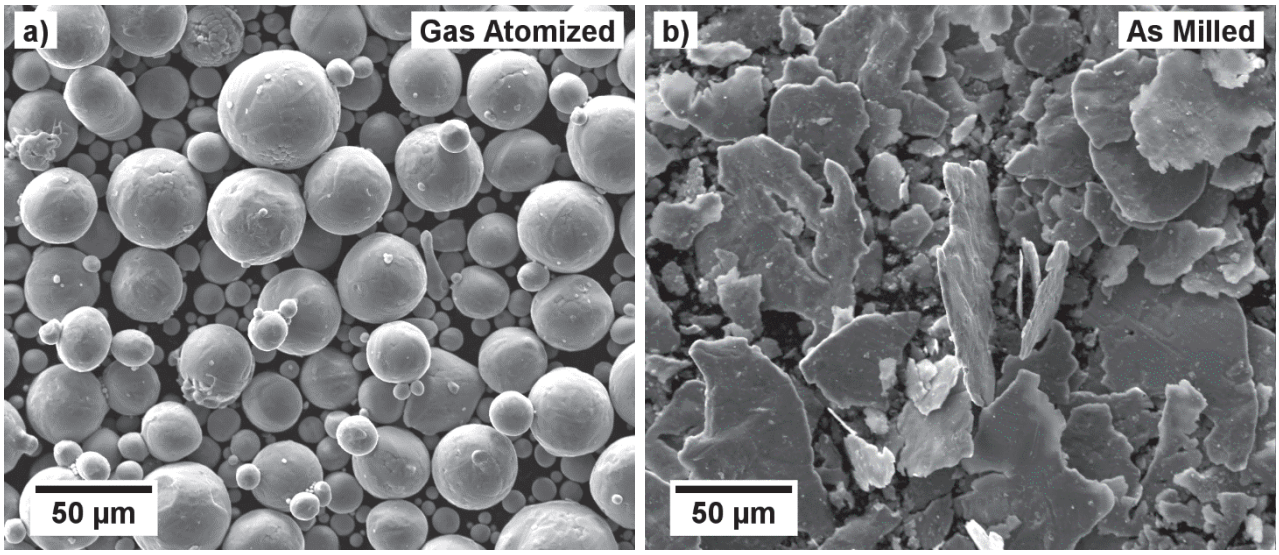

Figure 1 SEM micrographs of the powder particles before (a) and after (b) milling

Contamination by tungsten carbide balls (WC) is illustrated in the **Figure 2**. Micrometer sized WC particles detach from WC balls which become brittle at cryogenic temperatures and are embedded in comparatively softer Ti particles.

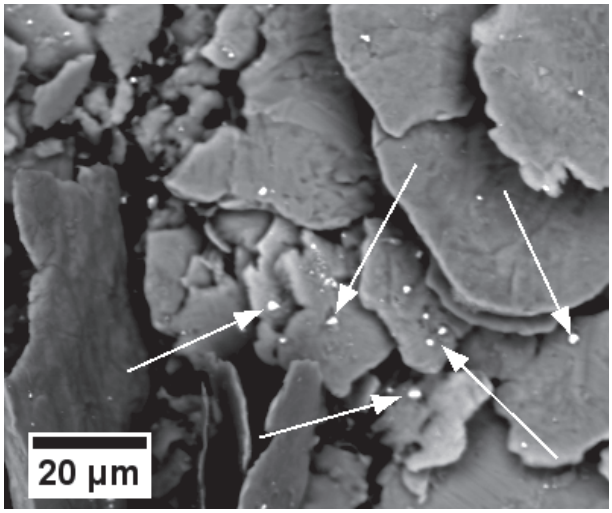

Figure 2 BSE image of Ti powder particle after milling by tungsten carbide (WC) balls. WC particles appear bright (marked by arrows)

The CGHE analysis revealed the increased contamination of powders (after cleaning): 0.594(2) wt.% of O, 0.082(1) wt.% of N and 0.029 wt.% of H. The adsorption of gasses is an inherent problem of mechanical milling because of large surface area of powders. The main source of hydrogen is SA used as a PCA, the main source of oxygen and nitrogen is the cooling liquid (LAr), which always contains some amount of these elements.

3.2. Sintered samples

The microstructure of sintered samples was investigated by SEM and EDS, the respective images can be found in the **Figure 3**. It was found that WC particles observed in the powder (**Figure 2**) are present also in the sintered samples (**Figure 3** on right), preferentially at grain triple points. Fe stabilized β-Ti precipitates were also found at grain boundaries.

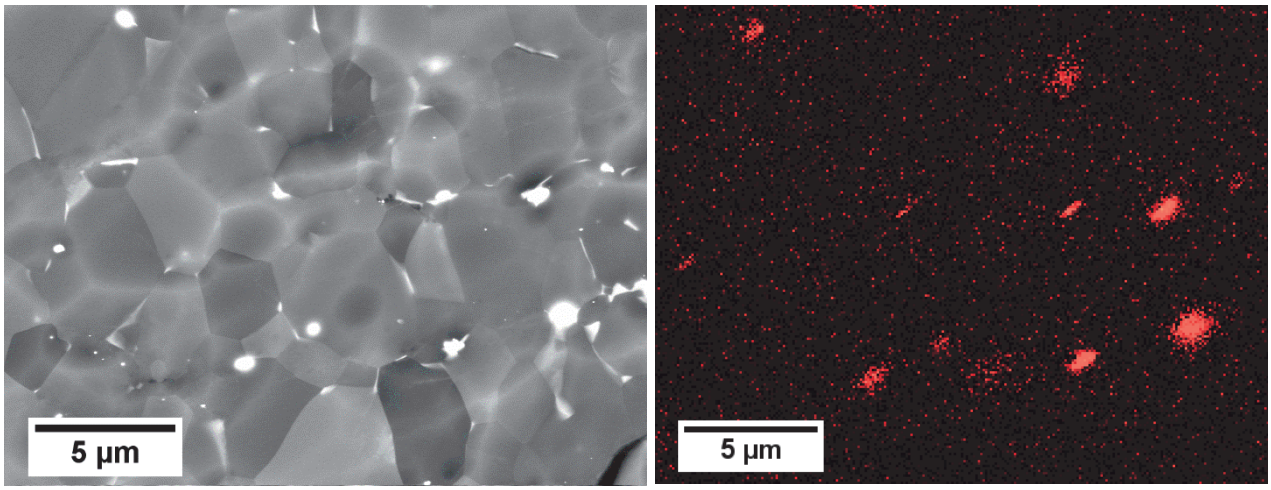

Figure 3 BSE image showing the microstructure of the sample sintered at 850 °C (left) with corresponding EDS map of W content (right). The white spots in the BSE image are WC particles. Brighter lines are artefacts from ion polishing.

Residual porosity was also investigated in the sintered samples by image analysis of SEM micrographs (not shown here). The results are plotted against sintering temperature in the **Figure 4**. All samples exhibit low porosity < 0.5 %, proving that fast sintering program is capable of successful consolidation of Ti. Higher porosity of 0.33 % was observed only in the sample sintered at 700 °C. The porosity in the specimen sintered at 750 °C and higher is below 0.1 % and does not change (within the experimental error). The material can be therefore considered to be completely dense.

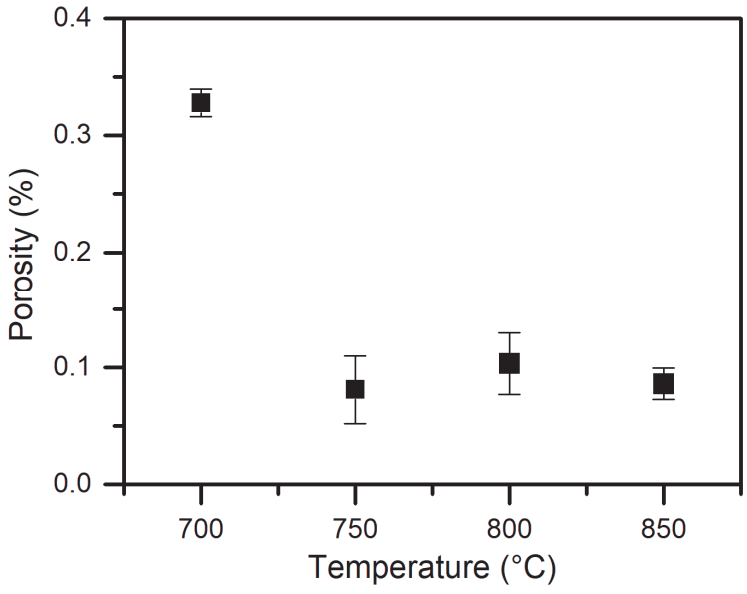

Figure 4 The porosity of the samples sintered at different temperatures

The grain structure of sintered specimens (in vertical plane) was investigated by EBSD. The resulting maps can be found in the **Figure 5**. The IPF maps show fully recrystallized microstructure with the mean grain size from 2.2 to 2.8 µm, relatively independent of sintering conditions. It was reported earlier, that titanium undergoes recrystallization at temperatures above 500 °C [8]. However, in this case, the microstructure was stabilized by WC particles present at the surface of powder particles (contamination from the milling, dispersed in the sintered samples) and by high oxygen and nitrogen content, which prevented the grain boundary

migration and coarsening of the microstructure [6]. As the result, grain size (given in the caption of the **Figure 5**) does not significantly increase with increasing sintering temperature.

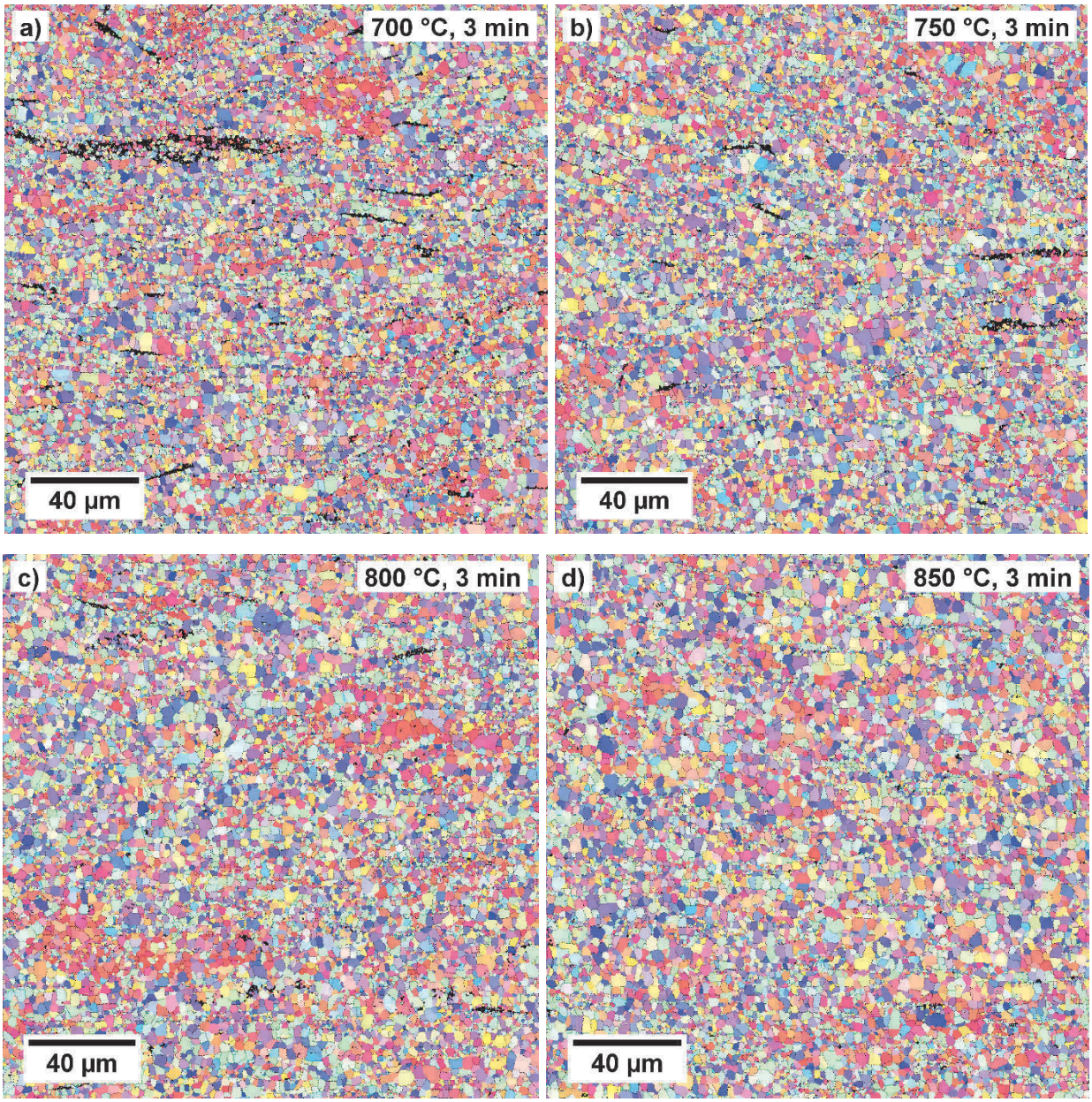

Figure 5 IPF maps of the sintered samples. Step size 0.4 µm, high-angle grain boundaries (HAGB) are marked with black lines. Only the well indexed points are shown. The mean grain size: a) 2.2 ± 1.0 µm, b) 2.4 ± 1.1 µm, c) 2.6 ± 1.2 µm, d) 2.8 ± 1.2 µm.

4. CONCLUSIONS

Commercially pure Ti was prepared by cryogenic attritor milling and spark plasma sintering. The microstructural investigations of both powder and bulk materials were performed with the following results:

- Cryogenic milling with the use of process control agent results in significant flattening of powder particles without apparent fragmentation.
- Powder milled by tungsten carbide (WC) balls is contaminated by WC fragments.

- WC fragments leads to stabilization of fine grained structure after sintering with the average grain size from 2.2 to 2.8 μm.
- Cryogenic milling followed by fast spark plasma sintering proved to be a suitbale combination of techniques for manufacturing of fine grained commercially pure Ti.

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