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Effect of titanium nitride nanoparticles on grain size stabilization and consolidation of cryomilled titanium

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ABSTRACT

In this work, titanium nitride (TiN) nanoparticles (~20 nm) were introduced during cryomilling of commercially pure titanium (CP Ti). Consolidation of cryomilled powders was performed using spark plasma sintering (SPS). Samples were analyzed and tested alongside cryomilled, SPS CP Ti not containing TiN nanoparticles. After cryomilling powders containing TiN nanoparticles and powders not containing TiN had a minimum grain size of ~20 nm. Microstructure analysis after thermal processing of both samples revealed that grain size retention occurred due to the presence of TiN nanoparticles in CP Ti microstructure. In consolidated samples containing 5 vol% TiN nanoparticles, the minimum average grain size was retained to ~250 nm, while in samples containing 0 vol% TiN nanoparticles, the minimum average grain size obtained was ~750 nm. Microhardness testing showed an increased hardness of samples containing TiN nanoparticles due to the retention of smaller grains and the presence of TiN nanoparticles.

1. Introduction

The production of nanocrystalline (nc) and ultrafine-grained (UFG) materials is gaining popularity amongst researchers because of the enhanced properties, such as strength [1,2] and corrosion resistance [3], that are exhibited by these materials compared to their coarse grained counterparts. Severe plastic deformation (SPD) is a class of techniques that is used to produce nc ($d < 100$ nm) and UFG (d~250 nm–900 nm) materials [4]. Of the various SPD techniques that exist, high pressure torsion [4,5], hydrostatic extrusion [6,7], and cryomilling [8,9] are capable of producing nc or near-nc materials. Of these techniques, cryomilling is advantageous [8] because cryomilling is a repeatable technique that can be used to produce large quantities of nc materials, and has been used on a variety of metals and alloys, including commercially pure Ti [10]. Cryomilling is a variation of conventional room temperature mechanical milling and involves mechanically milling a metallic powder in a cryogenic liquid medium, usually liquid nitrogen or liquid argon [8].

During high temperature consolidation, grain growth occurs due to heating. It was previously found [10,11] that during cryomilling in liquid nitrogen, nitrogen and oxygen react with the material during milling to form nanoscale nitrides and oxides, which have been shown to lead to grain size stabilization during heating. To enhance this effect, researchers [12–14] are now exploring the addition of nanoparticles during milling of materials. For example, Tang et al. [12] produced nanostructured Al-5083 with 6.5 vol% SiC particles (~25 nm in size). They found that after degassing at 400 °C for 20 h and HIPping at 400 °C for 2 h, the grain size was maintained as ~100–200 nm in certain regions where the particle concentration was 8 vol%. In addition, Maung et al. [13] recently produced cryomilled nc-Al with 1 wt% diamantine particles (< 5 nm in size). Grain size stability within the nc range was observed when the powders were heated to different temperatures between 150 °C and 500 °C.

For commercially pure (CP) Ti, it has been found that cryomilling of CP Ti in liquid nitrogen results in brittle consolidated samples due to the diffusion of nitrogen atoms into octahedral interstitial sites within the titanium crystal structure ($R_{N\ (65\ pm)}/R_{Ti\ (140\ pm)}=0.464$) [15]. Liquid argon is another choice for a cryogenic liquid medium and has been shown to be successful for milling of CP Ti. However, the formation of nanoscale oxides and nitrides were not observed in the microstructure of CP Ti after cryomilling in liquid argon [16]. As a result, grain growth stabilization is reduced within the material.

In this investigation, TiN nanoparticles were introduced during cryomilling of CP Ti powder in liquid argon in order to replicate the grain size stabilization effect of nanoscale particles during heating that accompanies the consolidation process. It is the purpose of this paper to report and discuss the results of the present investigation.

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Table 1
Parameters used for cryomilling.

Cryomilling parameter	Value
Quantity of Ti powder	500 g
Size of stainless steel balls	~6 mm in diameter
Ball-to-Powder Ratio (BPR)	30:1
Cryomilling medium	Liquid Argon
Temperature	$\sim -186 \pm 10$ °C
Impeller rotation speed	180 rpm
Time	8 h
TiN nanoparticles	0 vol% or 5 vol%
Stearic acid	0.05 wt% (with TiN)

Table 2
Chemical compositions of as-receive (AR) and cryomilled CP Ti powders.

Sample Element	AR CP Ti powder wt%	Cryomilled CP Ti powder wt%	Cryomilled CP Ti powder with 5 vol%TiN wt%
O	0.229	0.94	2.22
N	0.016	0.34	1.96
H	0.0222	0.06	0.09
C	0.018	0.02	0.10
Fe	0.010	0.09	0.09
Residuals	<0.081	–	–
Ti	Balance		

2. Experimental procedure

Cryomilling and consolidation work were conducted at California Nanotechnologies, Inc. (Cerritos, Ca). The parameters used for cryomilling of CP Ti are listed in Table 1 and the chemical composition of the as-received CP Ti powder is listed in Table 2. Different concentrations of TiN nanoparticles (~20 nm in size) were used in separate cryomilling runs: 0 vol% and 5 vol%. During milling runs that included the addition of TiN nanoparticles, stearic acid was added as a process control agent (PCA) to prevent agglomeration of powder particles. This step was taken as a precaution because it was unknown if addition of TiN nanoparticles would affect agglomeration of particles during milling. Stearic acid was not added for the cryomilling run that did not include TiN because it was determined through previous milling runs that agglomeration of particles did not occur during cryomilling of CP Ti in liquid argon and that the presence of stearic acid during cryomilling did not affect the size and morphology of cryomilled powders. It should be mentioned, in their work on CP–Ti, in which a comparison was made between the mechanical behavior of cryomilled Ti using argon and that using nitrogen, Ertorer et al. [16] did not add a PCA during cryomilling runs involving liquid nitrogen as the powders did not agglomerate. After cryomilling, powders were degassed at 500 °C for 10 h at pressures no greater than 10^{-6} Torr.

Since cryomilling is a powder metallurgy technique, consolidation is required to produce bulk samples. Various consolidation techniques exist such as hot isostatic pressing (HIP) [17], quasi-isotactic pressing [18], and spark plasma sintering (SPS) [19]. In the present study, SPS is used to consolidate powders after cryomilling. During SPS, the material powder is packed into a die (usually made of graphite). A pulsed DC current is applied through the die and powder, resulting in heating of the die and powder. The temperature is monitored by a thermocouple placed in the center of the die wall. A pressure is simultaneously applied to the powder during heating, resulting in consolidation. SPS differs from other techniques because SPS involves internally heating the material powder by application of a pulsed DC current through the powder [20]. In other techniques, the powder is externally heated using an external heating source requiring longer times at elevated temperatures. Given this advantage in heating source, higher internal temperatures can be reached within the powders much more rapidly reducing the total time at elevated temperatures during SPS.

Cryomilled powders containing 5 vol% TiN were then spark plasma sintered using the parameters in Table 3 to produce samples labeled as 5volTiN1, 5volTiN2, and 5volTiN3. Cryomilled powders that did not contain TiN were not degassed and were directly spark plasma sintered using the parameters in Table 3 to produce samples labeled as 0volTiN1, 0volTiN2, 0volTiN3, and 0volTiN4. There are two reasons for not degassing 0volTiN. First, PCA was not added during cryomilling. Second, it was noticed that degassing the cryomilled 0 vol% TiN powder led to significant grain growth. For all samples, a heating rate of 50 °C/min was used and the sintering pressure was first applied when the sintering temperature was reached and held constant during sintering. Spark plasma sintered samples had dimensions approximately 1 in. diameter and 0.25 in. thick.

For microstructure analysis, powders were mounted in phenolic resin and mechanically polished. Transmission electron microscopy (TEM) specimens were prepared from these polished samples using the focused ion beam (FIB) in an FEI Quanta 3D FEG SEM. For each sample, slices were removed from the interiors of particles (as shown in Fig. 1) and thinned down using the FIB to form an electron transparent specimen. The specimens were analyzed in a Philips/FEI CM-20 TEM at 200 kV. Grain size measurements of 200 grains were performed for each sample using ImageJ software. Chemical analysis of the cryomilled powders was carried out by Luvak Inc., a professional chemical analysis company located in Boylston, MA.

Archimedes method was used to determine the porosity of the spark plasma sintered samples. For grain size analysis, samples

Table 3
Parameters used for SPS.

Sample	Pressure (MPa)	Sintering temperature (°C)	Sintering time (min)
0volTiN1	60	822	10
0volTiN2	85	750	5
0volTiN3	85	700	5
0volTiN4	85	600	5
5volTiN1	85	600	5
5volTiN2	85	600	10
5volTiN3	85	750	5

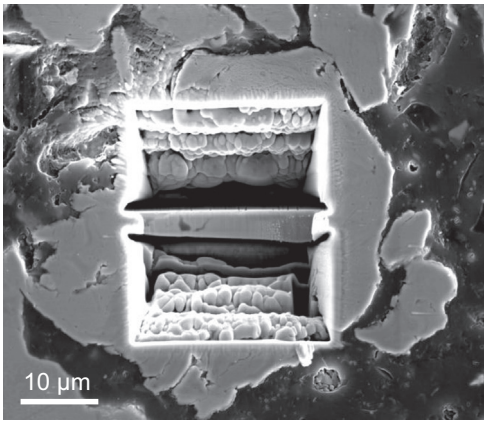

Fig. 1. SEM image of FIB cut powder particle during TEM sample preparation. A slice of materials was removed and further thinned using FIB to produce an electron transparent sample for examination in the TEM.