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Nanostructure in a Ti alloy processed using a cryomilling technique

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Abstract

A nanocrystalline Ti alloy with a uniform distribution of grains was synthesized using cryogenic mechanical milling. The effects of cryomilling parameters, such as milling time and ball to powder ratio (BPR), on the particle size, grain size, chemistry, and structure of cryomilled Ti powders were investigated using X-ray diffraction (XRD), scanning electron microscopy (SEM), and transmission electron microscopy (TEM). The experimental results show that nanocrystalline Ti powders with a grain size of about 20 nm can be prepared using the cryomilling technique. Compared to SPEX milling at room temperature, cryomilling led to lower contamination levels of oxygen, nitrogen, and iron in the cryomilled Ti powder. The average particle size initially increased from the original 55 μm to a maximum value of 125 μm after 2 h of milling, and then decreased to 44 μm after 8 h of milling. Both the average particle size and the grain size decreased as the BPR increased.

Keywords: Titanium alloy; Nanocrystalline; Cryogenic milling

1. Introduction

Nanocrystalline (nc) materials, characterized by a microstructural length scale in the range of a few tens to hundreds of nanometers, have been attracting much scientific and applied interest due to their unique combination of mechanical and physical properties, which are reportedly superior to those of their coarse-grained counterparts [1–4]. More recently, the cryogenic milling process has attracted considerable interest, primarily as a result of its ability to generate nanocrystalline and other nonequilibrium structures in large quantities. In addition, this technique has been widely used to synthesize nanostructured materials such as Ni, Al, Fe, and Zn [5–10]. Our current understanding of the mechanisms that govern the evolution of a nanocrystalline microstructure in single-phase materials during ball milling is summarized in the literature [4,6,11]. According to Fecht [4], the evolution of the microstructure or grain size refinement by ball milling includes three stages: (1) localized deformation in shear bands consisting of high density dislocation arrays; (2) dislocation annihilation and recombination that lead to small-angle grain boundaries separating individual grains; (3) development of completely random misorientations between neighboring grains.

The cryomilling technique possesses several characteristics that distinguish it from the conventional mechanical alloying process, including relatively high strain rates, large cumulative strains, and a cryogenic temperature. In related studies [5–7], it has been reported that the milling time required to reach the final grain size was significantly shorter for cryomilling than that for conventional milling performed at ambient temperature, which was attributed to the suppression of the recovery effect at cryogenic temperatures [6].

The nanocrystallization of titanium and its alloys has been studied with the aim of producing bulk materials using mechanical alloying at room temperature [11,12]. Recent investigations have also demonstrated that commercially pure titanium with an ultrafine grain structure in the nanometer range can be processed using severe plastic deformation methods such as equal channel angular pressing (ECAP) and high pressure torsion (HPT) [13–15]. One advantage of these methods is that they produce samples with no porosity; however, the structural evolution of Ti during warm ECAP plus cold rolling produces inhomogeneous grain/subgrain structures with sizes ranging from less than 100 to over 600 nm, leading to a hierarchy of nanostructures [13–15]. A previous study [16] showed that a nanostructured surface layer up to 50 μm thick was produced on commercially pure titanium

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Table 1
Chemical analysis of the cryomilled Ti powders

Milling time (h)	O (wt.%)	N (wt.%)	C (wt.%)	H (ppm)	Fe (wt.%)	Ball to powder ratio
As-received	0.190	0.0165	0.0030	204.5	0.013	
1	0.359	0.134	0.0149	260.9	0.066	30:1
2	0.394	0.494	0.0259	286.2	0.12	30:1
4	0.423	0.684	0.0129	280.6	0.11	30:1
4	0.467	1.53	0.0257	291.5	0.24	60:1
6	0.501	2.17	0.0183	300.5	0.083	30:1
8	0.453	2.02	0.0237	297.7	0.14	30:1

using surface mechanical attrition treatment (SMAT). However, the SMAT process can only be employed for producing a nanostructured surface on the order of a few to tens microns.

The primary objective of the present investigation is to study the synthesis of nanocrystalline titanium using the cryomilling technique and to perform structural evaluation on the synthesized materials using X-ray diffraction (XRD), scanning electron microscopy (SEM), and transmission electron microscopy (TEM). Particular attention is paid to the effects of cryomilling parameters, such as milling time and ball to powder ratio, on the synthesis and structure of cryomilled Ti powders, as well as on their chemistry.

2. Experimental

The samples were prepared from Ti powders with a chemical composition of 0.190 wt.% O, 0.0165 wt.% N, 0.0030 wt.% C, and 0.013 wt.% Fe, and with an average particle size of 55 μm. The mechanical attrition was performed using a modified Union Process 1-S attritor equipped with a stainless steel tank containing stainless steel balls (with a diameter of 6.4 mm), in a liquid nitrogen atmosphere. The titanium powders were cryomilled at a temperature of $-180 \pm 5\,^{\circ}C$ for 0.25, 0.5, 1.0, 2.0, 4.0, 6.0, and 8.0 h, respectively, with a ball to powder ratio (BPR) of 30:1 and an impeller rotation speed of 500 rpm. For comparison purposes, different BPRs (20:1, 30:1, 40:1 and 60:1) were also used to cryomill titanium powders. In addition, ball milling of Ti powders was also performed in a nitrogen gas medium at room temperature for 8 h using a SPEX 8000 mill (with a BPR 10:1). Chemical analyses (iron content) in the as-received and as-milled powders were carried out by Luvak Inc., a professional chemical analysis company located in Boylston, MA. The oxygen, nitrogen, hydrogen, and carbon contents were determined using a LECO TCH600 analyzer (Table 1).

X-ray diffraction (XRD) measurements were conducted using a Scintag XDS 2000 X-ray diffractometer equipped with a graphite monochromator using Cu Kα ($\lambda = 0.15406$ nm) radiation. A low scanning rate of 0.6 °/min and a step time of 2 s were used for phase identification and grain size measurements. The instrumental broadening was corrected using an annealed (200 °C/3 h) Ti sample. A COULTER LS particle size analyzer was used to determine the particle size distribution of the cryomilled powders. SEM observations were performed on a FEI XL-30SFEG microscope with a field emission gun in order to investigate the particle morphology and cross section microstructure of the cryomilled Ti powders. TEM observations were carried out using a PHILIPS CM20 microscope operated at 200 kV. The samples were prepared by embedding the powders in G-1 epoxy (Gatan Inc., Pleasanton, CA), following by mechanical polishing, dimpling, and ion milling.

3. Results and discussion

3.1. Chemical composition

The chemical analysis results of the as-received and cryomilled Ti powders are shown in Table 1. The results reveal an increase in the amount of nitrogen and oxygen, as well as increased amounts of iron and carbon during cryomilling. Powder contamination is an inherent characteristic of mechanical milling, and it may arise either from the processing media or the atmosphere. The Fe and C contamination stems from the wear of the stainless steel milling balls, tank, and shaft during cryomilling. The nitrogen is introduced into the powder during cryomilling because the milling was conducted in liquid nitrogen. With an increase of the milling time, the weight percentages of nitrogen increase. Oxygen contamination may be attributed to two sources: (1) as a result of leaking air if the container is not properly sealed during milling, and (2) as the Ti powders are transferred from the cryomilling container into the glove box.

In order to study the effect of cryomilling on the Ti powder contamination, a comparison of picked-up impurities (O, N, and Fe) after cryomilling at $-180\,^{\circ}C$ and SEPX milling at 25 °C is shown in Table 2. It is interesting to note that cryomilling at $-180\,^{\circ}C$ leads to a significant decrease in picked-up oxygen, nitrogen, and iron atoms in the milled Ti powders compared to SPEX milling at room temperature. The reduced oxygen and nitrogen contamination during cryomilling may be attributed to

Table 2
Pick-up of impurities in the Ti powders during cryomilling and milling at 25 °C

	O (wt.%)	N (wt.%)	Fe (wt.%)	Note
Cryomilling at $-180\,^{\circ}C$	0.263	2.01	0.127	BPR 30:1, milled in liquid nitrogen for 8 h
SPEX milling at 25 °C	0.643	3.85	3.61	BPR 10:1, milled in nitrogen gas for 8 h