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The addition of a surfactant at regular time intervals in the mechanical alloying process

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ABSTRACT

The impact of regular additions of a surfactant (ethylene bis-stearamide; EBS) at different time intervals was investigated on the powder characteristics of a biomedical Ti–10Nb–3Mo alloy (wt.%). Ball milling was performed for 10 h on the elemental powders in four series of experiments at two rotation speeds (200 and 300 rpm). The addition of 2 wt.% total EBS at different time intervals during ball milling resulted in noticeable changes in particle size and morphology of the powders. The surfactant addition at shorter time intervals led to the formation of finer particles, a more homogenous powder distribution, a higher powder yield, and a lower contamination content in the final materials. Thermal analysis of the powders after ball milling suggested that differing decomposition rates of the surfactant were responsible for the measured powder particle changes and contamination contents. The results also indicated that the addition of surfactant during ball milling at 200 rpm caused a delay in the alloy formation, whereas ball milling at 300 rpm favored the formation of the titanium alloy.

1. Introduction

Mechanical alloying (MA) is a solid state powder process in which initial elemental powders undergo high energy collisions with milling balls in a container. The continuous collision of milling balls with the powder mixture results in repeated cold welding, fracturing and re-welding of powders, and thus promoting intimate alloying [1]. However, when the welding becomes dominant over fracturing (e.g. in case of ductile powders), the powder particles tend to agglomerate and severely adhere to grinding media. Consequently, the formation of atomically clean surfaces for further interdiffusion is impeded by excessive cold welding and the alloying process is suppressed.

One of the most frequently used techniques to minimize excessive cold welding during the MA process is introducing suitable organic materials that hinder the clean metal-to-metal contact necessary for cold welding [2]. These organic materials are often referred interchangeably as a surfactant or process control agent (PCA). The surfactant impedes clean metal-to-metal contact by being adsorbed onto the surface of powder particles, leading to the suppression of cold welding and an increase in fracturing rate of the powder particles, and between the powder particles and the grinding media.

Over the last few decades, a great deal of research has been conducted on the effect of type and amount of surfactants on the final characteristics and properties of mechanically alloyed powders. The required amount of surfactant is chosen by assessing possible interactions between the powder particles and surfactant components, which is usually about 1–5 wt.% of the total powder charge [3]. Stearic acid [4–6], ethylene bis-stearamide (EBS) [6,7], ethanol [8], methanol [9], hexane [10], and benzene [11] are among the most frequently used surfactants in the MA process. Most of these studies have been carried out based on the prior addition of surfactants to the powder system, in which the desired amount of surfactant is added to the powder mixture before the mechanical alloying is started.

All Surfactants, in solid state or liquid state, will suffer decomposition during milling and thus become less effective over time. While typically the surfactant is added before the MA commences, a few studies have also been conducted on the addition of surfactants during the milling process [12–15]. The later addition of surfactant is believed to diminish surfactant decomposition during the milling process, and hence, decrease the powder agglomeration. Lomayeva et al. [16] studied the presence of oleic acid as a surfactant on iron powders obtained by milling in a planetary ball mill in a liquid hydrocarbon environment (heptane). To compensate for

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surfactant decomposition during ball milling, the surfactant solution in heptane was renewed every 3 h. It was concluded that the presence of surfactant increased the dispersion of the ball-milled powders and changed the morphology and magnetic properties of the powders. In order to synthesize NiFeCuMo nanocrystalline soft magnetic powders, Neamţu et al. added benzene as a surfactant every 4 h for a total milling duration of 20 h. The later addition of benzene to powders compensated for the amount of benzene that evaporates during the milling process and hence, prevented the powders from agglomerating [17]. Deng et al. [13] reported that the addition of surfactant to the powder mixture after 20 h of ball milling and continuation of milling for a further 10 h would result in less agglomeration and narrower particle size distribution (PSD) than those of powders ball-milled without the addition of surfactant or those of ball-milled powders that the surfactant had been added prior to the milling process. Yao et al. [12] carried out three different experiments to fabricate an iron-based alloy by MA. In the first experiment, denoted as A_{50}, surfactant was initially added to the powder mixture and then milled together for 50 h. In the second experiment, denoted as A_0, MA was accomplished for 50 h without the addition of surfactant. And finally in the third experiment, denoted as A_2, surfactant was only added after 48 h of MA and milled together with powder for 2 h. The results indicated higher strength, more uniform grain, and higher density for the bulk alloy made of A_2 powders as compared to its counterparts.

Despite the above findings on the successive/cumulative addition of surfactants during MA process, no study has ever addressed the relationship between the time intervals of surfactant additions and the powder characteristics during mechanical alloying. The question arises whether splitting the desired amount of surfactant into smaller weight fractions and adding at regular time intervals during ball milling process can alter the characteristics and properties of the ball-milled particles. To this end, the current study aims to investigate the effect of total addition of 2 wt.% EBS, as a surfactant, at different time intervals during the 10 h ball milling process on Ti–10Nb–3Mo (wt.%, hereafter) powder alloy. The reason for selecting EBS as a surfactant in the present study lies in its high effectiveness in hindering excessive cold welding and imposing particle size reduction [4]. The presence of the two long hydrophobic tails in the EBS molecular structure, could give rise to its high lubricating effect. It was shown that the higher powder yield was obtained when EBS was used as compared to stearic acid [4]. The obtained powders were characterized using scanning electron microscopy, X-ray diffraction, mastersizer and thermal analyzer.

A primary selection of Ti–10Nb–3Mo alloy was made from our experimental results and those available in the literature on mechanical properties and cytotoxicity of its alloying constituents. Ti–10Nb–3Mo belongs to an advanced class of titanium alloys, known as β-Ti alloys. Traditionally, there has been a substantial interest in developing β-Ti alloys for biomedical applications. The β-Ti alloys are composed of non-toxic elements and have a good combination of mechanical properties, low Young's modulus (to inhibit bone resorption) and excellent corrosion resistance. The major alloying elements for β-Ti alloys are Nb, Mo and Ta, which are the elements that are considered to be very biocompatible [18].

2. Materials and methods

2.1. Preparation of Ti–10Nb–3Mo alloy by MA

Elemental metal powders of Ti, Nb and Mo (Atlantic Equipment Engineers, USA) were weighed according to the pre-determined stoichiometric composition of Ti–10Nb–3Mo alloy. The characteristics of the elemental metal powders are shown in Table 1.

Table 1
Characteristics of the elemental metal powders of Ti, Nb and Mo.

Elements	Purity (%)	Size (μm)	Morphology
Titanium (Ti)	99.70	⩽45 (−325 mesh)	Irregular
Niobium (Nb)	99.99	⩽45 (−325 mesh)	Irregular
Molybdenum (Mo)	99.99	⩽10 (−1250 mesh)	Spherical

The MA process was performed in a planetary ball mill (Vacon, Chinese ball milling system) using stainless steel containers and 10 mm steel balls at room temperature. Planetary ball mill is a frequently used machine for mechanical alloying. Since a very small amount of powder is required, the machine is suitable for research purposes in the laboratory. Using this machine, high impact energies can be achieved and the duration of the mechanical alloying can be shortened. The ball-to-powder weight ratio (BPR) was maintained at 20:1, and the ball milling was carried out at rotation speeds of 200 and 300 rpm. The powders were handled in a glove box chamber under argon gas to prevent atmospheric contamination. Four batches of Ti–10Nb–3Mo were prepared with 15 g total powder weight. The first batch (batch 1) was prepared without the addition of EBS. In batches 2, 3 and 4, a total amount of 2 wt.% EBS $[CONHCH_2CH_3(CH_2)_{16}]_2$, was added into the milling container as a surfactant both prior to and during the ball milling process. Intermittent milling was performed with time intervals of 2.5 h for a total of 10 h per batch. The ball milling process was stopped every 2.5 h for 30 min for all batches to both keep the temperature low and to add EBS to the container in batches 3 and 4. The ball milling procedure including ball milling time and the amount of EBS added at each time interval are listed in Table 2. At the end of the ball milling process, the powders were removed from the container inside the glove box chamber under argon gas, collected, weighed and kept in sealed glass vials for further experiments.

2.2. Characterization and evaluation of the ball-milled Ti–10Nb–3Mo alloy powders

The particle morphology, microstructures, and distribution of elements within the particles were examined using scanning electron microscopy combined with backscattered electron imaging (SEM-BEI) and Energy-dispersive X-ray spectroscopy (EDAX) (Zeiss Supra 55VP). Samples of each powder were characterized by PANalytical X-ray diffraction (XRD) using Cu Kα radiation (40 kV, 30 mA) at a scanning rate of $2° \min^{-1}$ over a 2θ angular range of 20–90°. The area of each peak was calculated from the pattern using X'pert Highscore Plus software. The mean particle size and particle size distribution were measured using a Malvern Instruments Mastersizer 2000 with a Hydro 2000S side feeder. Thermogravimetric analysis (TGA) was performed using thermal analyser STA 409 PC Luxx (Netzsch) to study the thermal decomposition of the surfactant during ball milling process via measuring the mass change of the samples as a function of temperature. For this analysis, 100 mg of loose ball-milled powders from each batch were put in alumina crucible under an argon (grade 4.2) flow with a heating rate of $10\ \text{k}\ \text{min}^{-1}$ and heated up to 800 °C. Each thermal measurement was repeated two times to ensure its reproducibility. The TGA data were analyzed using Proteus software (ver. 5.2.0) from Netzsch. Powder yield was evaluated by measuring the weight of loose powder extracted from the container. A digital scale was utilized to measure the weight of powders. In order to determine the presence of contaminants generated from the surfactant, chemical analysis was carried out by means of glow discharge atomic emission spectroscopy (Leco GDS850A) on bulk samples. For this purpose, disk-shaped samples with a diameter of 15 mm and thickness of 3 mm were prepared by consolidating powders in a H13 steel die with pressure of 750 MPa for 10 min. Subsequently, samples were sintered in a high vacuum furnace at 1150 °C for 3 h at a heating/cooling rate of $10\ °\text{C}\ \text{min}^{-1}$. The area used for excitation of the atoms was $4\ \text{mm}^2$ and an average of three measurements was used.

3. Result

3.1. Powder characteristics and alloying process

Fig. 1 shows the SEM images of the ball-milled Ti–10Nb–3Mo powders at the rotation speeds of 200 and 300 rpm without (Fig. 1(a and e)) and with the addition of EBS at regular time intervals (Fig. 1(b–d) and (f–h)). The powder particles are bigger in the absence of EBS, in comparison to powders ball-milled with the addition of EBS, as seen in Fig. 1(a and e). When EBS was added in 1, 2, or 4 intervals (batches 2, 3, or 4, respectively), the size of powder particles moderately decreased. It is clear that the addition of EBS at different time intervals can result in powder particles with different sizes and morphologies. The powders prepared in batch 4 (Fig. 1(d and h)) exhibited a relatively equiaxed particle morphology with a more uniform distribution of particle size compared to the other batches.