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Facile mechanical alloying of titanium sponge

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ABSTRACT

The mechanical alloying of titanium with 3 wt% chromium was performed starting directly from Hunter or Kroll titanium sponge. A small quantity of calcium was added as a process control agent (PCA) to obtain a high process yield, uniform microstructure and homogeneous chemical composition.

The milled powder was then sintered using spark plasma sintering (SPS) at low temperature to achieve the best mechanical properties and a high-quality microstructure. Samples were also heat treated at high temperature to understand the behavior of the chlorine content of the titanium sponge.

The mechanical properties were tested by three-point bending. Depending on the kind of starting titanium sponge, high transverse rupture strength (TRS) and high plastic deformation were obtained for all of the alloys in both the as-sintered and heat-treated condition: the high TRS was correlated to the total interstitial elements content.

Tensile tests on samples obtained from Hunter titanium sponge yielded results comparable with those of wrought Ti6Al4V, and after high-temperature heat treatment, the samples obtained from the mechanical alloyed powders showed much better properties due to their much smaller grain size compared with that of Ti6Al4V.

1. Introduction

Titanium alloys possess many properties that make them highly attractive for industrial use, including relatively low density, exceptional corrosion resistance, high mechanical properties, biocompatibility, elevated strength-to-density ratio, high fatigue strength, and a low thermal expansion coefficient [1].

Nevertheless, their high cost and low cold workability limit the widespread use of titanium alloys; even after 60 years since their introduction, titanium alloys fill a market niche in the aeronautical and medical fields, where their high final cost is acceptable.

Powder metallurgy is a technological process by which alloys and parts with tailored microstructure and enhanced mechanical properties can be produced. In powder metallurgy, powder forming and sintering treatment are the main processes that are implemented to obtain the final product. Near net shape components that exhibit good mechanical properties and low cost or very high mechanical properties with a microstructure that would otherwise be impossible to obtain can be produced by adopting different techniques (e.g., pressing and sintering, hot isostatic pressing, powder extrusion, powder forging, spark plasma sintering, laser sintering, and electron beam melting) [2].

It is clear that the application of powder metallurgy techniques to titanium alloys could have many benefits, primarily, low-cost final products. Neglecting the technological and metallurgical problems associated with the production of sintered titanium alloys, there is another greater difficulty that must be addressed: powder cost [3–7]. Depending on purity and particle size and shape, powders are reported to cost between 30 $/lb to 180 $/lb; it should be noted that a bar/plate/foil of titanium alloy ranges between 20 $/lb and 40 $/lb; therefore, powders cost much more than semi-finished titanium alloys.

Part of the high cost of titanium powder originates from the process required to obtain metallic titanium. Briefly, titanium is mainly produced by the Kroll process, which induces the transformation of TiO_2 ores into $TiCl_4$ and then reduces the $TiCl_4$ with magnesium to yield metallic titanium and $MgCl_2$. This metallic titanium is called titanium sponge. Titanium sponge has a soft consistency and is the primary ingredient of all titanium alloys. Unfortunately, primary titanium sponge has quite a high level of chlorine, and double melting under high vacuum is required to lower the impurity content and homogenize potential alloying elements. After double melting, the titanium alloys are hot worked to produce bars, blooms, foils, etc. [8]. A variant of the Kroll process is the Hunter process, which uses sodium instead of magnesium: the result is a very soft and porous sponge, which still requires double remelting to lower a chlorine content that is even higher than that observed in the Kroll process. Therefore, the production of titanium powder mainly involves an atomizing

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process starting from castings or bars of titanium bulk alloys, which is the reason for the high cost of titanium powder.

From a scientific point of view, there is the possibility of producing titanium powder directly from TiO_2 ores, which would be a giant leap toward obtaining low-cost titanium alloys. In this respect, there are many new processes that have been developed, for example, the direct reduction of ores to produce high-purity titanium powder with good morphology [9–13]. However, the issues of purity, morphology and industrial scale-up remain unresolved.

Nevertheless, it is interesting to note that more than 60% of the cost of titanium alloys is represented by the transformation of titanium sponge to bulk alloy [14]. The cost of titanium powder could be greatly reduced by using titanium sponge directly to obtain titanium powder without the double remelting and the hot working process (e.g., extrusion, rolling, and forging).

Mechanical alloying is a solid-state process that consists in the repetitive and continuous plastic deformation of a powder to obtain new alloys or microstructures; the successive cold welding and fracturing of a powder yields a new powder with different features. Particle size, microstructure, and chemical composition can be modified by mechanical alloying [15]. The application of mechanical alloying to titanium alloys has been an interesting topic of research for many years due to its ability to produce new microstructures and compositions without expensive melting processes [16].

The use of titanium sponge in mechanical alloying presents two main problems: the low grindability of titanium sponge and high chlorine content.

The low grindability of titanium sponge is a consequence of the high toughness of the sponge and of the cold welding phenomenon. One way to solve these problems is to make the starting titanium brittle by introducing hydrogen at high temperature and pressure to obtain TiH_2. Titanium hydride is very brittle and can easily be ground to a fine powder. A subsequent vacuum annealing process removes all of the hydrogen and part of the chlorine content to yield pure titanium powder [17]. Alternatively, the TiH_2 powder can be directly sintered with alloying elements to obtain a bulk sintered titanium alloy [18–21]. However, some chlorine still remains in the alloys, and despite reports that show that to a certain extent, this process can provide the same advantage during sintering [22], it is normally undesirable: hydrogen and chlorine must be eliminated to make the alloys weldable [23,24]. Moreover, the use of TiH_2 can be dangerous due to its high flammability.

In a previous paper, the mechanical alloying of titanium powder using calcium, magnesium, or yttrium as process control agent (PCAs) was demonstrated to be easy and productive. It was shown that a high process yield, good mechanical properties, and high thermal stability can be obtained with the addition of as little as 0.25 wt% calcium as a process control agent [25].

Because titanium sponge is much cheaper than titanium powder and the mechanical alloying of titanium powder is feasible by adopting calcium as a PCA, the direct milling of titanium sponge to obtain titanium powder has been considered.

The use of calcium as a PCA is interesting because calcium has a higher affinity to oxygen and chlorine than titanium does; therefore, a scavenging effect could take place in a manner similar to that in the case of adding a rare earth element. In this respect, many authors have indicated that the addition of a rare earth element to titanium alloys involves the production of oxides, oxide-chlorine precipitates, and chloride, lowering the content of deleterious interstitial elements [26–33]. Calcium, instead of rare earth elements, has been used to maintain a low final cost, hopefully with similar effects.

As mentioned previously, titanium sponge can be produced in two different ways: by the Hunter or the Kroll process. Hunter sponge is easier to mill but has a higher level of chlorine than Kroll sponge. In this work, both types were used and compared to understand the effect of chlorine and the ease of milling.

Because $\alpha+\beta$ alloys were produced in this study, 3 wt% chromium was added to the titanium sponge. Chromium is a β-stabilizing element that promotes the eutectoid transformation, and it was selected because it is an inexpensive element that also provides significant benefits in terms of oxidation at high temperature [1].

2. Experimental procedure

As raw materials, Hunter titanium sponge (Honeywell, purity 99.8%), Kroll titanium sponge (Toho, purity 99.8%), pure chromium (Exotech Inc., $-150\ \mu m+45\ \mu m$, purity 99.9%), and calcium (Alfa Aesar, -16 mesh, purity 99.5%) were used. Both sponges were available in two particle sizes: standard size, -19.05 mm$+3.17$ mm, and fine size, -1.68 mm$+0.42$ mm.

The raw materials were weighed to obtain alloys with a composition of Ti3Cr0.3Ca. The different alloys were denoted by two letters: H or K depending on the kind of sponge and S or F depending on the sponge size (i.e., HS denotes Hunter sponge of the standard particle size and HF denotes Hunter sponge of the fine particle size).

Mechanical alloying was performed in a Fritsch Pulverisette 6 with a jar volume of 500 ml. A ball-to-powder ratio of 20:1, steel ball diameter of Ø15 mm, rotational speed of 500 rpm, and milling time of 80 min were the main parameters. The jar was evacuated to a low vacuum for reasons explained elsewhere [25]. After ball milling, the powders were cooled to room temperature in the jar over 2 h; the jar was always open to in air, and the powders were simply stored for days in bottles with air.

The powders were sieved to particles sizes below 355 μm, and the process yield was calculated as the ratio of the sieved powder to the amount of powder introduced into the jar.

Oxygen and nitrogen analysis was performed using a LECO TC400 system, and the chlorine content was obtained from the producer certificate of analysis. The powders were cold mounted and polished to verify the microstructure after the mechanical alloying step; Kroll's reagent was used to clarify the microstructure. The diffraction patterns were collected using a Cu kα ($\lambda=1.5418$) source and an image plate detector over the 2Θ range from 30° to 110° in reflection geometry. The experimental spectra were elaborated with the Rietveld method using the Materials Analysis Using Diffraction (MAUD) software [34]. Quantitative phase analysis (QPA) and line profile analysis (LPA) were performed to account for volume fraction and crystallite size.

The powders were sintered using spark plasma sintering (Sumitomo Coal & Mining, Dr. Sinter® 1050), maintaining a constant heating rate of 100 °C/min up to 900 °C. The heating rate was then reduced to 50 °C/min up to 950 °C, and the powders were held at the temperature for 1 min. The temperature was recorded by a pyrometer placed in a hole drilled into the graphite dies. The load was applied after the temperature reached 700 °C to achieve a pressure of 30 MPa until the completion of the sintering process.

Two sample shapes were obtained for the sintering process: cylindrical samples with a diameter of 20 mm and a thickness of 5 mm and dog-bone-shaped samples with a gage length of 20 mm, total length of 60 mm, and a thickness of 5 mm. On a few discs, heat treatments were performed in a metallic furnace in high vacuum (10^{-3} Pa) at 1300 °C for 1 h and furnace cooling to monitor the evolution of blistering, due to the presence of chlorine, microstructure stability, and the mechanical properties of the samples after the high-temperature treatment.