HYDROGENATION PROCESS OF TITANIUM ALLOY FOR BIOMEDICAL PURPOSES

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ABSTRACT
The production of titanium is very expensive, so it is interesting to research technologies that require lower costs, such as the HDH hydrogenation-dehydrogenation process technology, which is used for cheaper powder production from the waste material of titanium alloys.
This paper presents the hydrogenation procedure of a recycled piece of the Ti6Al7Nb titanium alloy. Hydrogenation was carried out in a furnace for heat treatment at about 700°C in a hydrogen atmosphere. After hydrogenation, samples of the Ti-Al-Nb type alloy were mechanically crushed by the grinding process to a granulation below 120 μm.

1. INTRODUCTION

Titanium alloys are considered advanced and high-value materials due to their special properties and high production cost.
Titanium alloys are often used in the aerospace, automotive, and medical industries, due to their high strength/weight ratio, corrosion resistance, biocompatibility, and low thermal expansion characteristics. These alloys have a high strength/density ratio, and good mechanical properties at elevated temperatures up to 550 °C.
In addition to structural efficiency, Ti alloys are characterized by high corrosion resistance and do not cause chemical or immunological reactions in the human body. That is why they are successfully used for making implants and joint prostheses, but also for other purposes in surgery, dentistry, and other fields of medicine [1].
The disadvantage of using titanium alloys is the extremely high cost of raw materials, as well as the difficulties in machining this material into the final geometry. Thanks to techniques of "eliminating" machining, such as powder metallurgy, the loss of this relatively expensive material is reduced, and it is possible to obtain products with complicated shapes.

In this meaning, the HDH - hydrogenation-dehydrogenation process technology for obtaining titanium powder, which belongs to the range of recycling technologies, is of particular interest.

2. HDH TECHNOLOGY

The production of titanium powder is very expensive, so it is of interest to research technologies that require lower costs, such as recycling technologies. One such technology is the HDH process, which is used to produce powders from titanium alloy waste material that is not usable any more for medical purposes.

The HDH technology is based on hydrogenation and dehydrogenation processes based on a reversible reaction:

$$M + H_2 \leftrightarrow MH_2$$

The course of this reaction depends on the pressure of hydrogen gas. If the pressure is above the equilibrium pressure, hydrogen atoms enter the titanium materials and form a metallic hydrate, and if it is below this level, hydrogen atoms diffuse from the metal into the gas atmosphere [1,2].

Enrichment of materials based on titanium alloy with hydrogen by the hydrogenation process leads to an increase in the brittleness of the material, which can later be broken, that is, crushed to powder granulation under certain mechanical loads (usually with balls). The subsequent dehydrogenation process of the resulting powder aims to improve its properties, especially ductility.

The hydrogenation process is carried out by exposing titanium alloy waste to hydrogen gas at an elevated temperature. Hydrogenation is usually carried out in a furnace capable of operating with a protective atmosphere containing H_2. Titanium alloys can be hydrated at atmospheric pressure and temperatures lower than 800 ºC, forming titanium hydrides.

Titanium alloy waste is subjected to the hydrogenation process in a controlled hydrogen atmosphere in a chamber/furnace at a temperature between 550 ºC and 800 ºC from one to ten hours or longer, depending on the size of the pieces and the properties of the waste [1]. Operating conditions in the furnace should be adjusted to result in a hydrogen content in the waste between 1% and 2%. A higher hydrogen content than the above can be unfavorable. Also, the lower hydrogen content will not produce sufficient brittleness of the waste to enable easy and economical method by conventional milling processes. An example of an experiment for the production of powder by the HDH process is given in Figure 1.

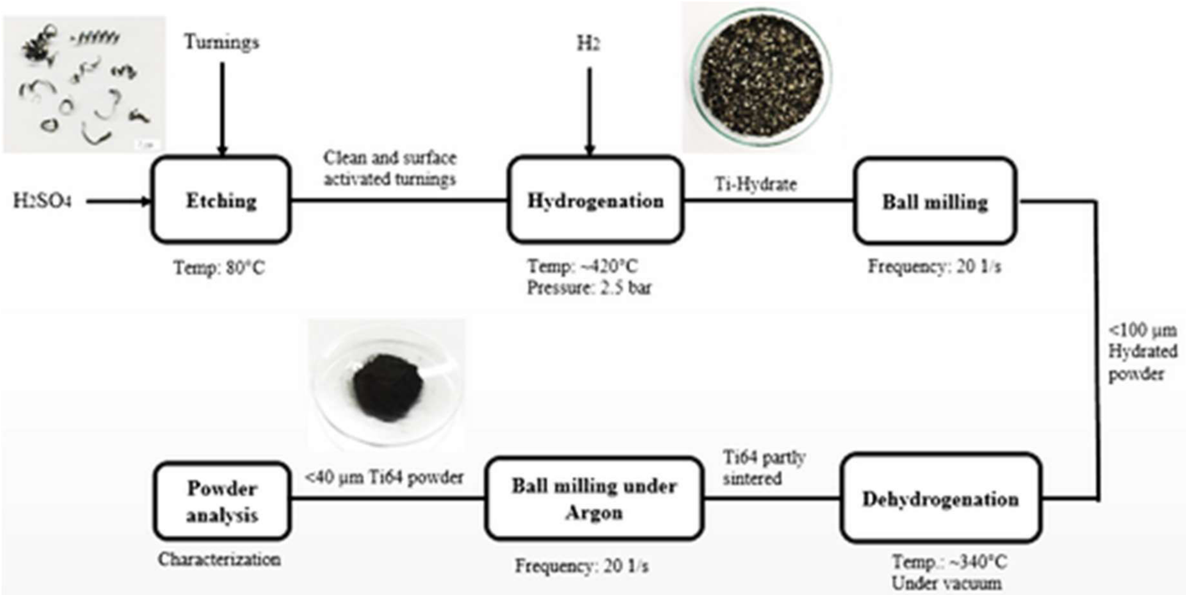

Figure 1. Example of an experiment for the production of titanium powder by the HDH process [2]

In the hydrogenation process, titanium alloy powder with unchanged chemical composition, with irregular particle shape, is obtained, Figure 2.

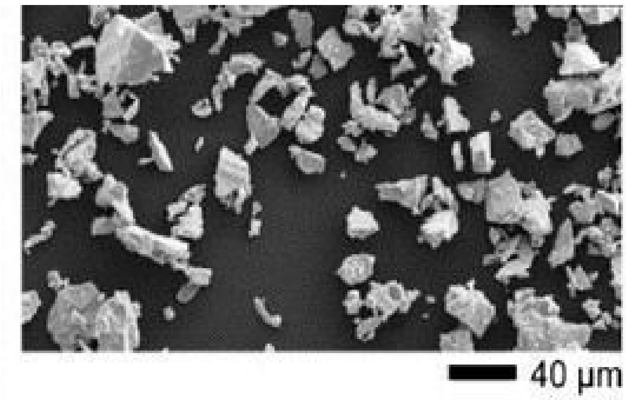

Figure 2.Titanium powder with irregular particle shape after the HDH process [2]

3. EXSPERIMENTAL PART

3.1. Titanium alloy type TiAl6Nb7

The Ti6Al7Nb type titanium alloy has the best corrosion resistance of all Ti-alloys. The alloying elements Al and Nb make the alloy more stable. This alloy in the presence of oxygen spontaneously forms a passive oxide film <1-2 nm thick of titanium oxide or mixed oxide TiO_2 (with Ti, Al, and Nb metal components). This protective layer is completely biocompatible and does not cause allergic reactions within the body or in contact with it.

The subject of the research is a titanium alloy of the designation EN, TiAl6Nb7/ASTM, F 1295, which was developed for medical use when the cytotoxic vanadium was replaced by niobium. This alloy has high strength, corrosion resistance, and exceptional biocompatibility. It does not cause chemical or immunological reactions in the human body and is widely used in medicine for the production of implants, prostheses, and their parts, Figure 3.

A recycled piece of titanium alloy - screw-type consumable raw material, Figure 4, was hydrogenated in a specially modified heat treatment furnace with a protective atmosphere at the "Center for Advanced Materials" in Sarajevo.

Figure 3. Schematic representation of the application of titanium alloys for medical purposes [7]

Figure 4. Recycled piece of titanium alloy for hydrogenation [7]

3.2.Chemical and mechanical properties of the alloy TiAl6Nb7

The chemical composition of the TiAl6Nb7 alloy is presented in Table 1.

Table 1. Chemical composition of TiAl6Nb7 alloy, in mass. %

C	Al	Nb	Fe	Ta	O	N	H	Ti
max.0,08	5,5-6,5	6,6-7,5	maks. 0,25	maks. 0,50	maks. 0,05	maks. 0,009	maks. 0,5	ostalo

The mechanical properties of the TiAl6Nb7 alloy are presented in Table 2.

Table 2. Mechanical properties of TiAl6Nb7 alloy

Parameter	Tensile strength	Yield stress	Elongation
Value	≥ 900 MPa	≥ 795 MPa	≥ 10%

4. RESULTS OF THE HYDROGENATION PROCESS

Hydrogenation, that is, temporary alloying with hydrogen, was carried out at a temperature of about 700 °C in an electric resistance furnace. The sample was treated in an atmosphere of nitrogen and hydrogen. Figure 5 shows a heat treatment furnace with a protective atmosphere that was used to simulate the hydrogenation process at the "Center for Advanced Technologies" in Sarajevo.

After hydrogenation, samples of the TiAl6Nb7 type alloy were mechanically crushed by the milling process, Figure 6, to a granulation below 125 µm, that is, with a greater proportion of granulation below 60 µm, Figure 7.

In this process, the titanium alloy powder is obtained, with an irregular shape of particles, but extremely favorable granulations, with a significant share of

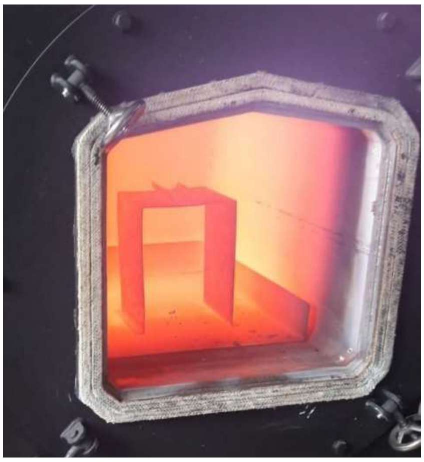

Figure 5. Hydrogenation process in a heat treatment furnace with a protective atmosphere [8]

Figure 6.Milling of hydrated TiAl6Nb7 titanium alloy

Figure 7. Titanium powder after hydrogenation and milling of TiAl6Nb7 titanium alloy

particle sizes below 60 µm, which means that a "low-cost" high-value powder based on titanium alloy can be obtained.

The hydrogenation process carried out was successful because the hydrated sample could relatively easily be mechanically crushed to the powder. and to use in the dehydrogenation process and obtain titanium powder with a satisfactory chemical composition.

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5. CONCLUSION

- The process of hydrogenation of TiAl6Nb7 type titanium alloy formed intermetallic compounds of metal and hydrogen, so-called hydrides by absorbing a considerable amount of hydrogen. The formed compounds led to the brittleness of this alloy, as it was required.
- In this experiment, the necessary parameters for the hydrogenation process were established according to the size of the recycled product, related to thermal treatment.
- The developed hydrogenation process was successful and the result was a hydrated sample that could be crushed mechanically.
- Favorable particle sizes, mostly below 60 µm, were achieved by milling the hydrated sample.
- The results obtained in this research indicate the possibility of developing the HDH procedure as an economic procedure for the production of "low-cost" high-value powder based on titanium alloy.

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