

Production of spherical titanium alloy powders used in additive manufacturing from titanium scrap

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Abstract

The main materials for 3D printing of titanium are fine metal alloy powders from which produce final articles with required quality. These powders must have definite chemical compositions, physical/mechanical characteristics, and also necessary operational properties. Key parameters of titanium alloy powders are homogeneity of chemical compositions, microstructures as well as flow ability. Conventional atomisation methods for metal powders like GA, PREP, PA, etc, are complicated and sufficiently expensive. Alternative production route is usage of complex processing technology of titanium alloy scrap as initial raw material. Spheriodised powder manufacturing scheme which includes raw material preparation, preliminary and final treatments have been presented. At the first step titanium scrap was divided according to titanium alloy types, purified from contaminants and oxide films. Then prepared materials were converted to non-spherical powders with definite fractional compositions using hydrogenation/de-hydrogenation (HDH) method.

Experimental HDH equipment allows close cycle of hydrogen recovery almost without losses. Obtained non-spherical powders were treated in the plasma unit yielding spherical titanium alloy. Offered technical solutions permit production of raw materials for 3D printing from scrap with high actual yield of required fractional compositions.

Introduction

Modern solutions for technical assignments including their economics require the following: minimisation of raw material and energy consumption, concentration on the most important production directions with obtaining of maximum profit.

Resource and energy spending are based on the definite technological process and related equipment.

The above fully applies to metallurgical industry where the most important target is significant decrease in energy consumption for yielding of final metal products [1].

Application of additive manufacturing technologies (including titanium industry) allows significant minimisation for coefficient of material usage (more than 0.9) which is a weight ratio between final article and initial raw material (reciprocal of this factor is called "buy-to-fly" parameter) [2]. As a result, raw material consumption, number of production steps, and final machining processes will significantly be reduced. However, essential part for additive manufacturing is synthesis of titanium powders with required shapes and definite chemical compositions.

Titanium alloy powder manufacture with the above parameters is one of the costliest processes in non-ferrous metallurgy. Solution for this problem would greatly reduce production cost creating competitive technology.

The main method for titanium alloy (for example VT-6, TiAl-V) powder synthesis is pulverisation of melts [3]. This technology includes: titanium sponge manufacture, its mixing with master alloys, compacting of sponge block, its melting to ingot, ingot processing to required work piece, and finally work piece re-melting with pulverisation to metal powder.

The major problems in synthesis of titanium alloys are controlled addition of alloying elements, their even distribution in base metal, and also narrow size distribution of the powders. Concluding the above it is feasible to say that this technology is complicated and expensive.

The largest requirements are especially applied for key article parts. They include homogeneity of chemical composition and even distribution of mechanical properties. In addition, sufficiently high demands are introduced to particle shapes.

Required metal structure and its chemical homogeneity related to mechanical properties are directly bound to technology. Currently there is a number of additive manufacturing methods which differ in metal powder feeding into article formation zone and by applied energy type [4]. Each technique needs definite powder size and preferable particle shape. The former is defined by applied energy method (Fig. 1) For example, selective laser melting (SLM) has optimum particle size 20-45

microns. Usage of larger particles will yield significant increase in power of the laser unit. Quality problem for melted spherical particles will exist as well [5].

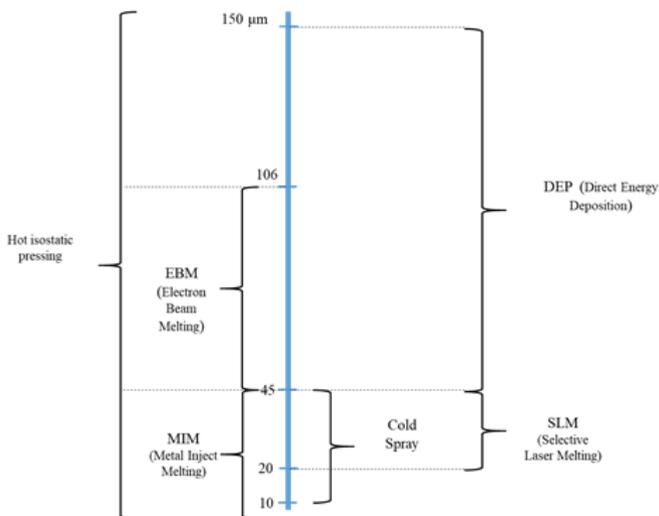


Figure 1 – Typical sizes of titanium alloy powders used in additive manufacturing processes

During electron beam melting powder particles with the size range below 45 µm might be blown away from reaction zone by intensive heat flows [6].

The vast majority of 3D printers are using spherical titanium alloy powders [7]. These powders have better flow ability, allow channel feeding, and minimise active material surface. These materials might be obtained using different methods: atomisation of molten metal, centrifugal pulverisation, inert gas or vacuum spraying [8]. It were reported works related to usage of non-spherical powders for 3D printing [9,10]. Every described method for preparation of titanium alloy powders has own advantages and disadvantages (Table 1).

Table 1 –Key characteristics of methods for production of titanium powders

Method	Raw material	Particle size, µm	Advantages	Disadvantages
Gas atomisation (GA)	Titanium sponge, ingots, rods	<300	Wide range of alloys and produced materials	Satellites, porosity, significant material loss in gas flow
Plasma atomisation (PA)	Wire	<300	Small number of satellites, high actual yield of small fractions, high purity	Very expensive powders with high requirements
Centrifugal pulverisation (PREP)	Rod	<50-350	Absence of satellites, high purity, high quality shape	Low actual yield of small size fractions
Hydrogenation/dehydrogenation (HDH)	Titanium sponge, ingots, rods, waste, scrap	5-250	Wide range of alloys and produced materials, possibility of obtaining very small particles in required size interval	Non-spherical shape of particles, elevated concentration of hydrogen in powders

The most high-quality titanium alloy powders are obtained by centrifugal spraying. However, actual yield of these powders with the size below 80 microns is insufficient: only 20-30% [11]. The most effective method for small size material production is HDH. This technology generates non-spherical titanium alloy powders in wide interval of sizes (Fig. 2). In addition, hydrogenation/de-hydrogenation method enables manufacturing of high-quality titanium as well as its different alloy powders. Also, HDH technology allows usage of titanium alloy scrap and alloyed titanium sponge as raw materials [12]. This significantly decreases production cost.

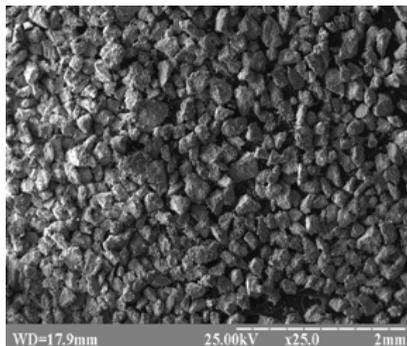


Fig. 2 – External view of titanium alloy powders produced by HDH method

For the implementation of this technology patented equipment with a closed cycle of hydrogen was developed [13]. Subject to the technology of hydrogen degassing process gas is directed to titanium hydrogenation unit standing together (fig. 3). At the first step titanium scrap was divided according to titanium alloy types, purified from contaminants and oxide films.

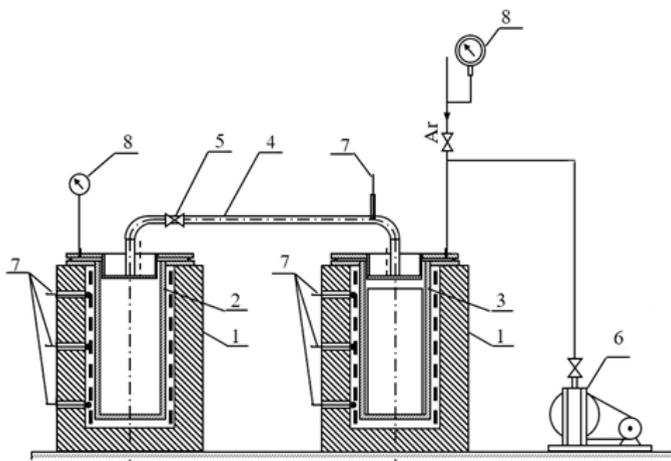


Fig. 3 - Hardware Diagram of HDH installation

1 - electric furnace; 2 - hydrogenation apparatus; 3 - degassing apparatus; 4 - gas pipeline; 5 - slide valve; 6 - vacuum block
7 - control device; 8 - vacuum gauge.

Prepared scrap of titanium alloys was subjected to saturation of hydrogen with the aim embrittlement. Then the hydrogenated metal was ground with ball mills in an inert argon atmosphere. After that hydride powder was placed into degassing apparatus to make dehydrogenation.

By this method were yielded titanium alloy powders of the different types, such as Grade 1-5 (ASTM B988 – 18), TA15 and TC8 (GB/T 3620-2016), VT-22, VT-6, VT-20 and VT-8 (GOST 19807 - 91) with different particle size (0-250 μm).

However, the majority of additive technology equipment manufacturers uses spherical powders since non-spherical ones have unsatisfactory flow ability. To make non-spherical “low-cost” powders more competitive in the market it has been suggested to do their spheroidisation [10]. Plasma treatment allows smoothing of sharp grain edges yielding more spherical appearance.

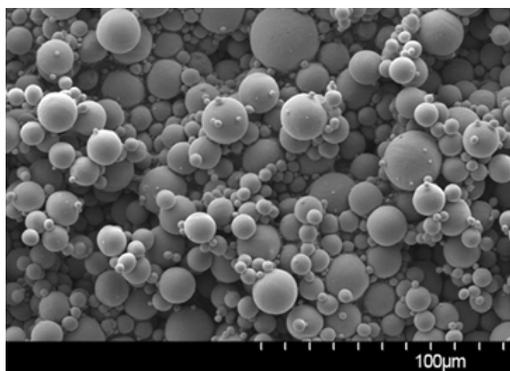


Fig. 4 – External view of HDH powders after plasma treatment

This significantly increases flow ability of the powder. It is important to say that in the majority of cases size range of HDH powders does not change after plasma treatment [14,15].

Table 2 –Spheroidisation of titanium powders in argon plasma

Properties	Before plasma treatment	After plasma treatment
Tap density	1.8 g/cm ³	2.6 g/cm ³
Production rate	-	5 kg/h at 80 kW
Particle size	- 120 + 35 μm	- 120 + 35 μm
Hall Flow rate, sec/50g	No flow	27.1

Table 2 shows that particle size has not been changed, powder density was increased 1.5 fold, and it has appeared measurable flow ability. Despite of the latter parameter is still lower compared to one of spherical powders it is sufficient for use in majority of industrial 3D printers. Considering all the above we have proposed technological scheme for production of spherical titanium alloy powders (Fig. 5). The powders are intended for usage in 3D printing industry. According to the proposed scheme titanium alloy work pieces are made from titanium scrap or sponge. Also, work pieces can be produced by VAR or EBM methods using titanium sponge mixed with master alloys or alloyed titanium sponge [10, 12].

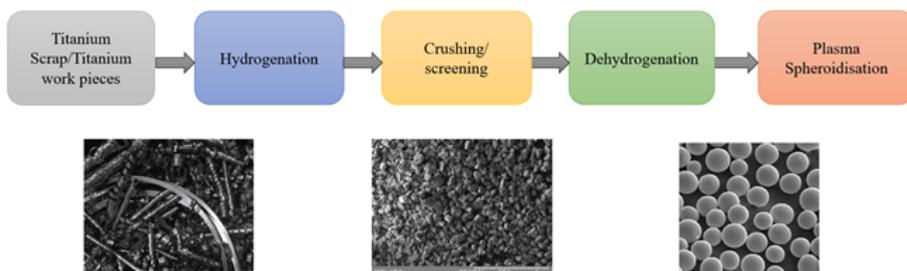


Fig. 5 – Technological scheme of manufacture titanium alloy powders for 3D printing industry

Titanium scrap with required chemical composition could also be used as raw material. This significantly decreases production cost. Hydrogenation is conducted with the objective for increasing titanium brittleness. As a result, percentage of small fractions (below 200 μm) could be more than 85%. Then non-spherical titanium alloy powders are treated by plasma. This operation yields partial melting of sharp grain edges and dendrite parts of the particles. Plasma treatment results spheroidisation of materials and also eliminates volatile impurities [15]. Such titanium alloy powders are suitable for usage in the majority of industrial and laboratory titanium 3D printers.

Conclusions

Obtaining of «low-cost» titanium alloy powders which fit majority of industrial demands for additive technologies requires complex technological scheme consisted as three stages:

- 1 –preparation of scrap or work piece for HDH process – titanium alloy ingot, alloyed titanium sponge or titanium alloy scrap;
- 2 – obtaining of titanium alloy powders with definite fractional composition by HDH method – hydrogenation, crushing /screening, degassing;
- 3 – plasma spheroidisation of non-spherical powders.

The offered technology produces spherical titanium alloy powders with required quality and competitive production cost.

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