POSSIBILITIES OF RECYCLING Ti-6Al-4V AND ITS USE IN ADDITIVE MANUFACTURING

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Abstract

Titanium and its alloys offer a unique combination of properties (e.g. high specific strength, biocompatibility and corrosion resistance). The production volumes of titanium are lower compared to other metals, despite its excellent properties and relatively high mineral resources. It is all caused by the costly and ineffective production method, so-called Kroll process. A reduction in costs could lead to an increase in the use of titanium and its alloys. Recycling of titanium scrap is a potential solution. However, the recycling process might be problematic due to the contamination of scrap by gasses, cutting fluids, machining debris, oxide layer caused by titanium's high reactivity with oxygen etc. As a result, most of titanium scrap being used for production of a ferrotitanium (deoxidising element for steel) rather than being recycled into titanium alloys.

The suitable recycling method, which would allow to use titanium scrap for manufacturing of materials comparable to the primary alloys, could represent significant change for the titanium market.

The aim of this work is to evaluate the recycling process of Ti-6Al-4V alloy using the plasma arc melting (PAM) method and subsequently to assess the possibilities for its use in additive manufacturing. The purity, microstructure and mechanical properties of recycled alloy were analysed. The powder obtained from atomizing the same recycled alloy has been evaluated (distribution, morphology and chemical composition) and possibilities of processing this powder by two 3D printing methods, laser powder bed fusion (LPBF) and direct energy deposition (DED), were investigated.

Keywords: Ti-6Al-4V, recycling, PAM method, additive manufacturing

1. INTRODUCTION

Nowadays there is great demand for titanium and titanium alloys. However, it is known that the production of titanium by the so-called Kroll process is an expensive and inefficient process [1]. Therefore, the production of titanium is very limited compared to other metals (e.g. Fe or Al), despite the excellent combination of properties that titanium is characterized by. Recycling of titanium scrap (scrap pieces, machining chips, etc.) appears to be a potential solution. However, contamination of the scrap with unwanted gases, cutting fluids and materials from cutting/machining tools, as well as the formation of oxide layers due to titanium's high affinity for oxygen, makes recycling problematic. Most titanium scrap is not being recycled, it is instead used to produce ferrotitanium as a deoxidizing agent in steelmaking, due to the reasons mentioned [2].

The recycling of titanium alloys could significantly impact the titanium alloy market if a suitable method was developed to obtain materials comparable to primary alloys from titanium scrap. The recycling of titanium and its alloys is becoming increasingly prevalent worldwide. For instance, in the United States in 2004, out of a total consumption of 45,000 tons of titanium alloys, 25,000 tons were made up of titanium scrap, including machining chips, compact pieces of parts, powder, and 3D printing support [3]. This amount has continued to rise, reaching 50,000-65,000 tons of titanium scrap between 2017 and 2019 [4]. A global increase in demand for recycled titanium is also taking place. The authors of the paper [2] predict a rise in demand for recycled titanium, even in alloys with higher impurity contents. For instance, they suggest that the use of titanium in the automotive industry, which is constrained by the amount of titanium produced, may be one reason for this. They anticipate that the demand for secondary titanium alloys (higher impurity contents) will surpass that of ferrotitanium. The issue of finding a suitable and efficient recycling methodology remains crucial.

Tertiary metallurgy is a separate chapter, in this case the non-contact atomization of alloys into spherical powders for use in additive technologies. Modern engineering solutions require the minimization of raw material and energy consumption to achieve maximum benefit. The titanium industry can achieve this through the significant expansion of additive manufacturing (AM). As a result of the expansion of AM, raw material consumption, the number of production steps and final machining processes could be significantly reduced. The quality and final properties of additive manufactured titanium components are fundamentally influenced by the quality of the powders used. Strict requirements are set for the chemical composition and physical properties of titanium powder. Controlling the oxygen content of the powder, particularly fine powder, is a significant challenge in the production of titanium powders. Unfortunately, high-quality powders meeting these requirements are expensive and scarce, hindering the development of titanium for widespread applications using AM. Therefore, the industry needs to develop new ways to produce low-cost Ti alloy powders that meet all chemical composition and physical property requirements [5, 6].

The presented work is a preliminary study with two main objectives: firstly, to assess the recycling of the titanium alloy Ti-6Al-4V through the plasma arc melting process; secondly, to evaluate the production of powder from recycled alloy with a view to assessing the possibilities of 3D printing of this powder. Therefore, the experimental part does not compare the possibilities of 3D printing of pure primary produced alloy and recycled material, nor does it undertake a comparative analysis with alternative recycling techniques.

2. EXPERIMENTAL METHODS

The input material from Ti-6Al-4V alloy in the form of titanium waste (implants that were removed from the printing pad, printing supports, tensile bodies, and residual powder after 3D printing process) was recycled into rods using HPAM (horizontal plasma arc melting) method. Recycling was provided by Advanced Metal Powders s.r.o., where the chemical composition was also checked by X-ray spectrum analyser.

To assess the final properties of the recycled material, the input material and rods (HPAM) were analysed for the presence of undesirable gases (O, H) using a G8 Galileo elemental analyser. Metallographic samples from the input material and rods were prepared as well. These samples were ground using p280-p4000 grit and then polished with colloidal SiO_2. To reveal the structure, the samples were etched using Keller's solution (1 % hydrofluoric acid, 1.5 % hydrochloric acid, 2.5 % nitric acid, and 95 % distilled water). The microstructure was observed in the etched state using an Olympus DSX1000 light microscope and a JEOL JSM-7600F scanning electron microscope (SEM). Additionally, the hardness was measured using the Vickers method with a loading force of 30 kgf on a Struers Duramin 40AC3 automatic hardness tester. Ten impressions were made for each specimen, and the mean value and standard deviation were calculated.

Then the recycled rods were processed to the required cross-section for the subsequent atomization process. The ATO Lab atomizer used has a maximum diameter limit of 10 mm for circular cross-sections. The requisite cross-section was achieved by waterjet cutting, after which the rods were cleaned with isopropyl alcohol to remove any residual abrasive dust. Sample for monitoring microstructure from cut rod was prepared as indicated above. The microstructure was observed using a Neophot 32 light microscope.

Then the cut rods underwent an ultrasonic atomization process using an ATO Lab machine as the final metallurgical step. This process involved atomizing the molten metal into a stream of inert gas through ultrasonic oscillations. The resulting powder was evaluated for its morphology and chemical composition using a JEOL JSM-7600F scanning electron microscope and EDXS analysis. The powder was tested for its suitability for additive technologies, specifically the L-PBF method and the DED method. The L-PBF method was tested in collaboration with the Institute of Physics of the Academy of Sciences of the Czech Republic. Printing was performed on a TruPrint 1000 printer from TRUMPF using standard parameters for the Ti-6Al-4V alloy. DED printing was conducted on an InssTek MX-Lab printer, with parameters selected based on the available literature [7]. Metallographic sections of samples printed by the afore mentioned methods were prepared and evaluated using a Neophot 32 and Olympus DSX1000 light microscope.

3. RESULTS AND DISCUSSIONS

3.1 Purity of Recycled Alloy

Table 1 records the measurements of unwanted gases (O, H) present in the input material and the rod. The data indicates a minor reduction in oxygen levels and a more significant decrease in hydrogen levels. However, it is uncertain whether the recycling process refines the alloy or if the values are influenced by the sampling location.

Table 1 The content of unwanted gases before and after recycling process

Recycling stage	O (wt. ppm)	H (wt. ppm)
Input material	1836	189
Rod (HPAM)	1775	99
ASTM F2924-14 [8]	2000 ± 200	150 ± 20

The measurements aimed to predict the contamination of the alloy before atomization into powder for 3D printing, with a particular focus on the oxygen content. The ASTM F2924-14 [8] defines the oxygen content for Ti-6Al-4V alloy powder. **Table 1** shows that the limiting oxygen content is defined at 2200 wt. ppm, which is met in this case. Though, it should be assumed that further contamination with unwanted gases may occur within the atomization process and the limit value could potentially be exceeded for the prepared powder. This fact should be considered in future experiments.

3.2 Microstructure

Figure 1 shows the microstructure of both observed states. The input material exhibits a two-phase structure with primary α grains and lamellar α + β colonies (**Figure 1a**), which is typical for this alloy after undergoing heat treatment consisting of solution treating with rapid cooling and subsequent aging, as demonstrated in the paper [9]. The initial state appears to have a coarser grain size when compared to the literature. During the remelting step, the microstructure undergoes coarsening and transforms into a basket-weave microstructure, formed by colonies of α lamellae (**Figure 1b**). This structure is typical for higher solidification rates, as shown in the study [10].

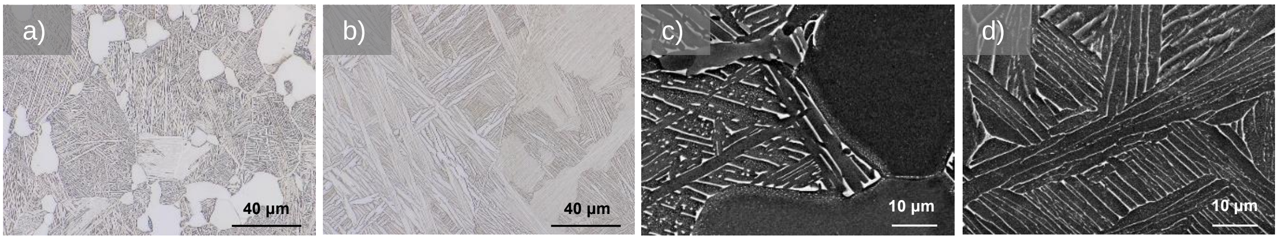

Figure 1 Microstructure from light microscope of a) input material, b) rod (HPAM) and SEM analysis of c) input material, b) rod (HPAM)

The SEM analysis (**Figure 1c, 1d**) confirmed the observations made through light microscopy but did not provide any additional information. This is mostly due to the coarse-grain nature of the microstructure.

The microstructure was also observed after cutting the rods and exhibited an unaltered basket-weave structure in accordance with expectations.

3.3 Hardness

For the Ti-6Al-4V alloy, the hardness value of the input material is 338 ± 5 HV30, likely due to previous heat treatment. The value of hardness after remelting by the HPAM method (332 ± 6 HV30) corresponds to the value of the input material. Despite the coarsening of the structure after remelting which would suggest a decrease in hardness, the growth of α + β colonies occurred resulting in an increase in hardness. Hence the hardness of the material is like that of the input material, despite its coarser structure. The result presented is consistent with the available literature [11] which indicates that the hardness of the Ti-6Al-4V alloy varies between 320 and 400 HV depending on the heat treatment and microstructure obtained.

3.4 Powder Evaluation

Figure 2 shows the SEM analysis and chemical composition of powder. The spherical particles appear to have a size range of 50 to 100 µm. It is important to note that this result may be influenced by the sampling of the powder. A more detailed analysis, for example, laser diffraction, would be required to confirm the distribution.

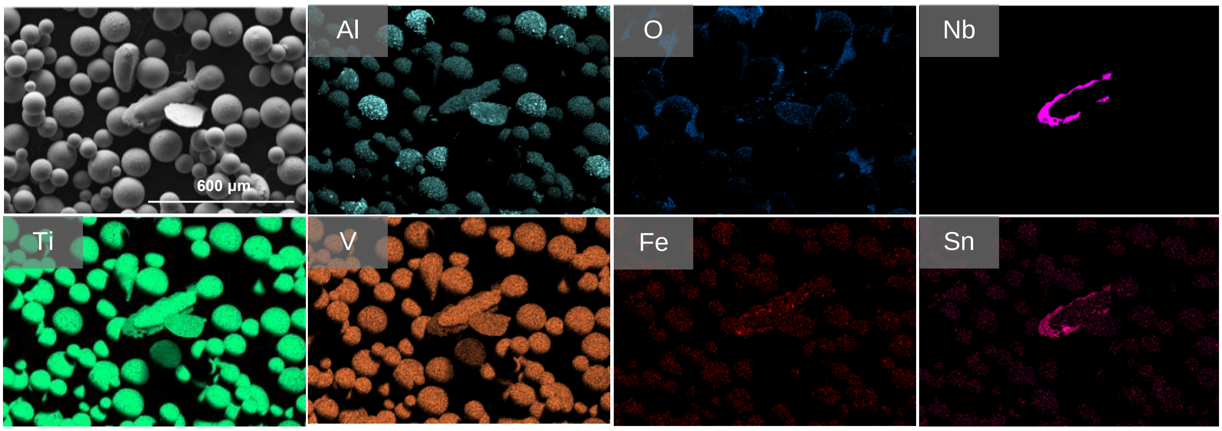

Figure 2 The SEM analysis and chemical composition of prepared powder

It can be seen, that one of the particles has a significant amount of niobium and tin. This contamination is probably due to inadequate cleaning of the atomizer during alloy replacement. Before the presented alloy, an alloy of Ti-Nb-Ta-Sn was atomized. The surface of some powder particles also appears to be oxidised. To verify that the oxygen content does not exceed the limit values stated in chapter 3.1, the experiment must be supplemented by an analysis of the unwanted gas content in the atomized powder.

3.5 Additive manufacturing

Lastly, the potential of 3D printing was evaluated. The cylindrical samples with a diameter of 20 mm were printed by the L-PBF method. The literature [9] indicates that powders with particle sizes in the low tens of microns are the most suitable for the L-PBF process. Although the presented powder is larger than the recommended particle size range in the available literature, it was used for printing by this method. As anticipated, the printed samples were non-compact (**Figure 3a**). The cracking was likely due to the fraction size being too large for the method and standard conditions used, resulting in significant stresses during printing. In addition to cracks, the microscopic observation of the section reveals significant porosity. Unmolten powder particles are visible in the pores in some areas. After etching the samples, a martensitic structure is visible (**Figure 3b**), as a result of the very high solidification and cooling rates, which is consistent with the available literature [12].

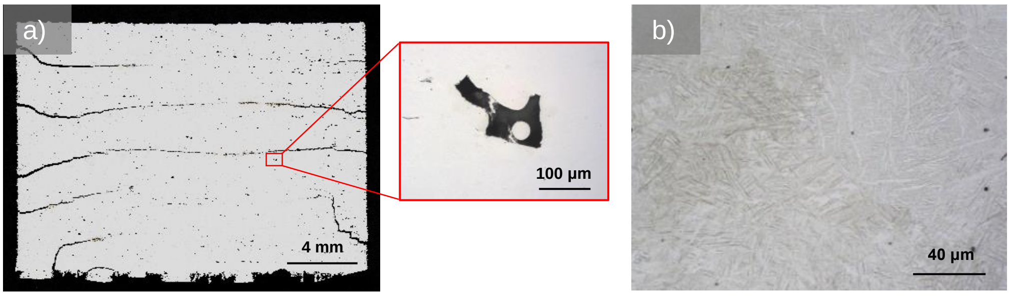

Figure 3 Macroscopic and microscopic observation of a sample printed by the L-PBF method

A cubic body with a side length of 5 mm was printed using the DED method. The printing parameters were chosen according to the paper [7], although the 3D printing machine used was different. Due to the different printing parameters and geometries of the printed bodies, it is almost impossible to compare the DED and L-PBF methods and the results obtained by these methods. However, in contrast to L-PBF printing, the DED method produces a compact body, making it more suitable for the tested powder morphologies. The resulting microstructure differs from that observed in the aforementioned literature, despite the use of the same parameters, and macroscopically does not resemble that of a 3D printed object (**Figure 4a**). There are no visible traces of printing, such as melt pools. However, a closer look at the etched structure (**Figure 4b**) reveals a martensitic structure, similar to the microstructure observed in the review [13] comparing microstructures after different 3D printing methods. In the future, it will be necessary to optimise the printing parameters to obtain the desired structure and mechanical properties.

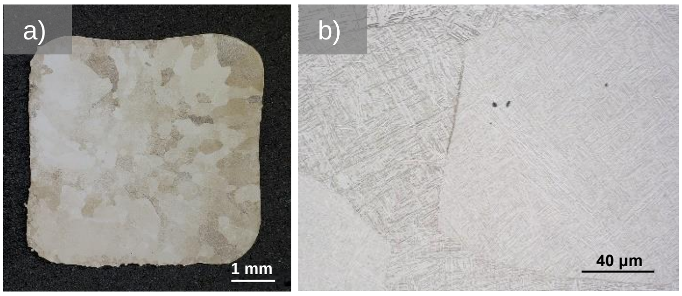

Figure 4 Macroscopic and microscopic observation of sample printed by the DED method

4. CONCLUSION

The presented work evaluated the properties of Ti-6Al-4V alloy after the recycling process provided by Advanced Metal Powders s.r.o., with the aim of predicting the contamination of alloy before further processing, namely atomization into powders for 3D printing, and finding the possibilities of 3D printing from such produced powders. The following was found:

- The oxygen content of the recycled material (rods after HPAM) meets the limits set by the standard. However, due to the further processing (cutting and atomization) it is necessary to check the resulting atomized powder for oxygen content.
- The recycled powder reported here cannot be processed by L-PBF 3D printing technology using standard parameters.

- DED method seems to be more suitable for presented powder. However, observed microstructure does not align with the expected outcome. It seems probable that further adjustments to the print parameters will be required in order to achieve the desired microstructure and mechanical properties.

Given the limited range of the presented work, an evaluation of the mechanical properties was not conducted. However, this will be addressed in subsequent experiments, thereby providing a more comprehensive assessment of the suitability of recycled alloys for use within the additive manufacturing.

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