RECYCLING OF THE TITANIUM SCRAP BY USING OF PLASMA METALLURGY

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Abstract

The aim of this work is to design and define technological procedures enabling the use of titanium scrap in the form of chips or piece of material as an input raw material for the production of spherical powders suitable for powder metallurgy or additive technologies. In this work, plasma metallurgy in the horizontal and vertical furnaces under a high purity atmosphere of argon (5N8 purity) was used for remelting the commercial titanium alloys. The content of oxygen and hydrogen in titanium was measured by element analyser and changes in phase composition were studied by light optical and scanning electron microscopy supplemented by microhardness measurement. The results proved, that plasma arc melting can be used for recycling of titanium alloys in order to manufacture a material that not only corresponds in properties to the material produced by primary metallurgy but can also be used for the production of powder by atomization processes.

Keywords: Plasma metallurgy; titanium scrap; titanium alloys; recycling, microstructure

1. INTRODUCTION

Titanium holds a prime position in aerospace, biomedical, automotive, and chemical processing industries due to unique features: low density (60% of steel or super alloys density), higher tensile strength (higher than ferritic stainless steel and comparable to martensitic stainless steel and Fe-base superalloys), higher operating temperature (up to 595 °C for commercially available alloys and > 595 °C for titanium aluminides), excellent corrosion resistance (higher than stainless steel and biocompatible), forgeability and castability (mostly by investment casting) [1]. Cold hearth melting is a developing technique which uses either plasma arc (PAM) or electron beam (EBM) melting furnaces. Hydrogen plasma arc melting (H-PAM) of commercial Ti sponges (99.7%) was examined by Mimura et al. [2]. Commercial Ti sponges (99.7 wt% in purity) were used as a starting material. Experiments were carried out using a laboratory-scale plasma arc furnace equipped with a transferred arc type plasma torch. The plasma torch was a dc arc discharged type with a maximum power of 20 kW. Authors [2] used as inert gas a pure argon, argon with 10 % H_2 and Ar + 20 % H_2. The main impurities, such as Fe, Al and Mn in Ti sponges could be reduced more efficiently by H-PAM than by Ar PAM. This enhancement of removal degree (RD) in % was attributed to the increase in the surface temperature of molten metal due to the higher thermal conductivity of hydrogen plasma, and the enhancement of metal vapor transfer within the gaseous boundary layer by a dynamic interaction between hydrogen atoms and a metal vapor [2].

PAM using a horizontal hearth is emerging as a method for obtaining significant improvements in the quality of titanium alloys. A typical PAM furnace for industrial application is divided into three areas: a material feed system, the melting chamber and the ingot station. All three areas operate in an inert environment to minimize atmospheric contamination; oxygen and nitrogen being readily scavenged by titanium. To accomplish this, a series of vacuum pumps evacuate the system to 1.5 Pa and then the furnace is backfilled with helium to a pressure of 0.11 MPa or greater to enable the plasma torches to be started. During melting, the dynamic environment is set by a balance between the input plasma torch gas and the pumping rate or the pressure relief valve [3]. Hearths are constructed from copper or copper alloys and are water cooled. Production furnace in this case designs incorporate four torches with a total power capability of 2-3 MW. Authors prepared with using this PAM method Ti-6Al-4V and TiN alloys. Some problems of melting, casting and forging in titanium alloys described Mitchell [4]. Authors from the Republic of Korea [5] prepared button ingots using H-PAM, which enabled refining while suppressing the loss of alloy components as much as possible, in order to recycle Ti-Ni, Ti-Mo, and Ti-Al alloy scraps. When 20% hydrogen was added and the scraps were melted for 20 min, the weight losses were <1%, which is nearly no loss of components. The removal degrees (RD) of impurities for the Ti-Ni, Ti-Mo, and Ti-Al alloys were 82.6%, 86.2%, and 49.1%, respectively. The results confirmed that the scraps of each alloy could be recycled using the H-PAM.

This article describes experiences with a preparation of titanium alloys including chemical analyzes of the input and remelted material, an analysis of structural characteristics using light and electron microscopy and a measurement of selected mechanical properties.

2. METHODOLOGY

Advanced Metal Powders (AMP) company has two PAM facilities, one with a horizontal and the other with a vertical crystallizer of 50 kW power, suitable for titanium waste processing. High-purity argon 5N8 was used as plasma-forming and inert gas. The process of plasma remelting of titanium and titanium waste requires observing a number of principles:

a) Remelting time. To ensure the lowest possible gas content, the shortest melting time is most advantageous, i.e. to use faster molten zone procedures and to keep the number of zones to the lowest possible minimum. On the contrary, longer melting times can have a favorable effect by reducing the content of iron, silicon and carbon.

b) Argon purity. When remelting titanium by plasma melting, the used argon purity plays a big role. By formed titanium remelting higher oxygen contents were achieved than by remelting titanium scraps, screws, nuts and targets. It was apparently due to imperfect cleaning of the surface of the titanium rods and the introduction of oxygen in the form of TiO_2. As a result, the dependences on melting time and argon purity were also not clearly manifested. An important role here is also played by traces of moisture that have not been completely removed, i.e. chemically bound water on the surface of remelted titanium pieces and also, in particular, moisture adsorbed on the surface of the cooled parts of the furnace space.

c) Conditions of experimental melting. The experiments were aimed at verifying the results and possibilities of titanium remelting with the aim of comparing its effect on the titanium purity. Physical properties of titanium are strongly dependent on the amount of dissolved or chemically bound gases and other interstitial elements. They are very sensitive to the furnace space atmosphere, especially in the case of reactive titanium and its alloys. Argon can also contain certain amounts of gases as impurities, namely oxygen, nitrogen, moisture and traces of hydrocarbons, which show high reactivity in the excited state, i.e. that they dissociate into monatomic gases in the plasma stream. These fall on a surface of the molten material and react to form compounds that form impurities, or inclusions.

d) Optimum melting conditions. The conditions that showed the lowest values of gassing and contamination with oxygen, nitrogen of the melted titanium alloys are: zone speed: 7-8 cm/min, current 750 A, argon purity 5N8.Before the melting process itself, the entire furnace space has to be evacuated several times. It can be stated that along with increasing the melting time, the content of gases in titanium increases.

Microstructural development was investigated using light optical microscope (LOM) Olympus DSX1000 and scanning electron microscope (SEM) JEOL JSM-7600F equipped with an Oxford X-Max detector for energy dispersive x-ray spectroscopy (EDXS) analyzes. Analyzes were done on metallographic samples in polished and etched state (etched by Weck's reagent: 100 ml H_2O + 5 g NH_5F_2). Changes in the hardness profile (HV30) were measured by Struers Duramin-40 hardness tester. The content of hydrogen and oxygen was measured by Bruker G8 Galileo element analyzer.

3. EXPERIMENT AND RESULTS

Titanium alloys Ti-64 (Ti-Al6-4V) and Ti-6242 (Ti-6Al-2Sn-4Zr-2Mo) were processed by plasma metallurgy. **Table 1** shows the nominal composition of both of the alloys according to the relevant standards.

Table 1 Nominal chemical composition of the Ti-6242 and Ti-64 alloy (wt%) [6,7]

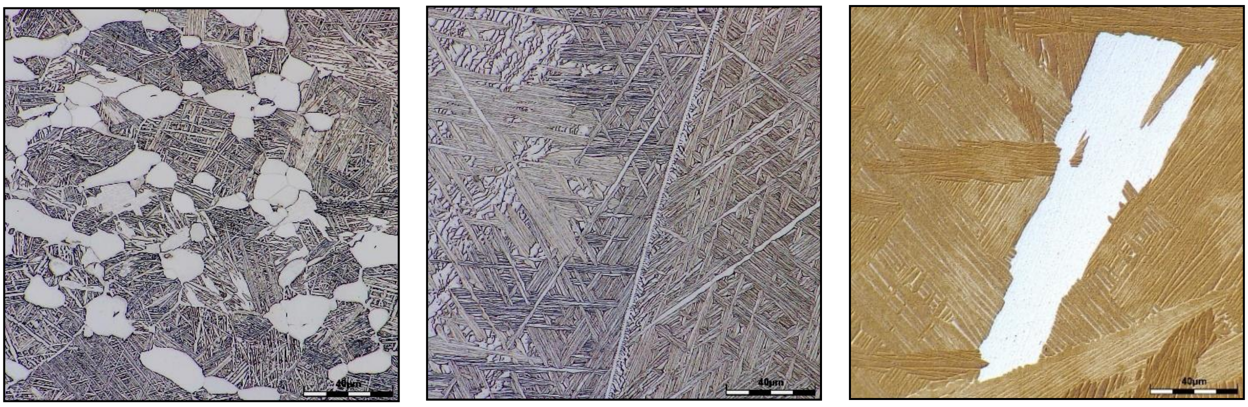
Material	Element	Al	V	Zr	Mo	Sn	Si	O	Fe	C	N	H	Y	Ti
Ti-6246	min.	5.50		3.60	5.50	1.80	0.06	---	---	---	---	---	---	bal.
	max.	6.50		4.40	6.50	2.20	0.10	0.15	0.10	0.05	0.05	0.0125	0.005	bal.
Ti-64	min.	5.50	3.50	---	---	---	---	---	---	---	---	---	---	bal.
	max.	6.75	4.50	---	---	---	---	0.20	0.3	0.08	0.05	0.015	0.005	bal.

Allowed oxygen contents are up to 0,2 wt.% for Ti-64 alloy, up to 0,15 wt.% for Ti-6242 alloy. The following **Table 2** presents the results of chemical analyzes of gases in the initial delivered material in a form of waste, after remelting in the plasma furnace with a horizontal crystallizer (H-PAM) and with a vertical crystallizer (V-PAM).The results show that the oxygen and hydrogen contents are lower than permitted by relevant standards.

Table 2 Oxygen and hydrogen content before and after plasma melting for Ti-64 and Ti-6242 alloys (wt.ppm)

Ti alloy	Ti-64			Ti-6242		
Element	**scrap**	**H-PAM**	**V-PAM**	**scrap**	**H-PAM**	**V-PAM**
O	1836	1775	1736	864	981	1041
H	189	99	49	17	27	44

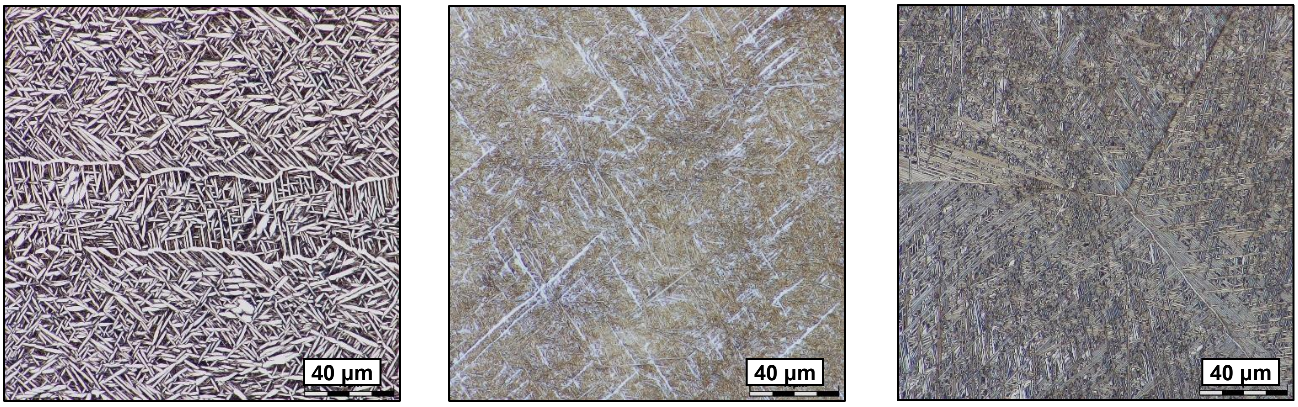
Figures 1 and **2** show the results of light microscopy.



a) input state b) H-PAM c) V-PAM

Figure 1 Microstructure of the Ti-64 alloy before and after plasma melting (cross-section)

The initial Ti-64 alloy is formed by a bimodal (duplex) microstructure, which consists of α phase polyhedral grains and transformed α needles in the primary β phase, which together form the Widmanstätten structure (**Figure 1a**). After remelting of H-PAM (**Figure 1b**) primary grains start to grow and the disintegration of α phase polyhedral grains occurs, while a part of the needles coarsen and transform into a basket-weave structure. At the boundaries of the primary grains we can observe bands of the α phase surrounded by fine polyhedral subgrains. The remelting of V-PAM (**Figure 1c**) also results in coarsening of the primary grains and creating a partially basket-weave microstructure, which consists of α phase lamellae embedded in β phase grains. In the regions of the β phase we can also observe segregated fine needles of the α phase, while the primary β phase consists of a lamellar structure.

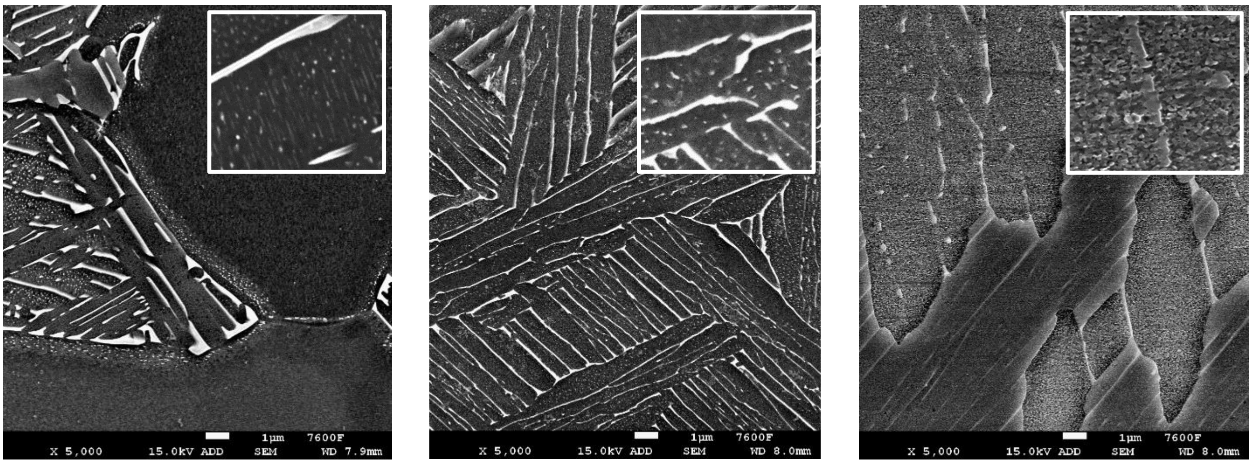


a) input state b) H-PAM c) V-PAM

Figure 2 Microstructure of the Ti-6246 alloy before and after plasma melting (cross-section)

The initial Ti-6246 alloy (**Figure 2a**) is formed by a fully basket-weave microstructure, which consists of α+β lamellae. After H-PAM remelting (**Figure 2b**), there is a coarsening of the primary grains and a partial transformation of the original basket-weave microstructure into a martensitic type structure, which consists of coarse and very fine needles/lamellae of the α phase embedded in the β phase. At the grain boundaries, envelopes of the original α phase remain and needles forming the Widmanstätten structure are visible in their surroundings. The original lamellae are transformed into rough α needles. Also, the remelting of V-PAM (**Figure 2c**) results in creating a martensitic microstructure and coarsening of the primary grains. However, the needles of the α phase are significantly finer compared to H-PAM and it is still possible to observe the original lamellae of the α phase to a lesser extent.

The results of the SEM analysis of the Ti-64 alloy are shown in the following figure (**Figure 3**).

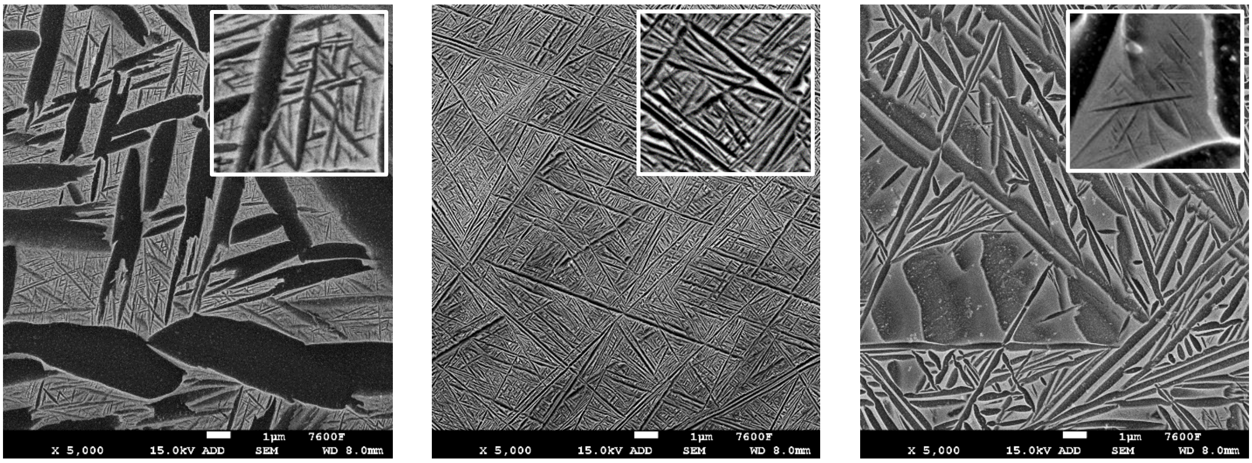


a) input state b) H-PAM c) V-PAM

Figure 3 SEM analysis of the Ti-64 alloy before and after plasma melting (cross-section)

It can be seen from the image of the initial alloy that the polyhedral grains of the α phase are surrounded by nanometric particles of the β phase, or these phases are segregated at the grain boundaries. Particles can also be observed in the Widmanstätten structure. In the areas where the α phase is regularly arranged in needles or lamellae (**Figure 3a**), the particles have a globular shape, while in the lamellae themselves the shape of needles prevails. In the case of H-PAM (see **Figure 3b**), nanometric particles of the β phase are present inside the primary and secondary lamellae of the basket-weave microstructure and are predominantly globular in shape. By remelting V-PAM (**Figure 3c**), the fine β particles disappear and the microstructure consists only of lamellae of the α+β phase.

In the case of the initial state of the Ti-6264 alloy (**Figure 4a**), it is possible to observe the primary and secondary lamellae of the α phase together with acicular needles α' in the basket-weave microstructure. Colonies of the Widmanstätten α/α' structure can be found in the vicinity of both of the phases. The structural phases are surrounded by the transformed β phase. In the case of H-PAM (**Figure 4b**), there is a transformation to an almost fully martensitic structure, which consists of acicular needles and colonies with a Widmanstätten α/α' structure. After V-PAM (**Figure 4c**), a significant coarsening of the present needles and the disappearance of the primary α lamellae are visible. The original basket-weave structure is still visible in the area of the coarse β phase.



a) input state b) H-PAM c) V-PAM

Figure 4 SEM analysis of the Ti-6246 alloy before and after plasma melting (cross-section)

The results of the quantitative and qualitative EDXS microanalysis of the alloys are shown in the following **Table 3**. From the results it can be seen that V-PAM shows a lower proportion of V and Al in the Ti-64 alloy compared to H-PAM.In the case of the Ti-6246 alloy there are no significant changes, with the exception of V-PAM, where the Al content is slightly higher. The chemical composition of both of the alloys corresponds to the nominal chemical composition. The quantitative EDXS analysis shows that in the Ti-64 alloy α phases are rich in Ti+Al, while the β phase consists of V+Fe+Ti. For the Ti-6246 alloy the α phase consists of Ti+Zr+Al+Si+Sn+Fe and the β phase consists of Ti+Mo+Sn+Fe. Furthermore, it has been confirmed that the chemical composition of individual phases remains preserved within H-PAM and V-PAM.

Table 3 Average chemical composition of the Ti-64 and Ti-6246 alloy (wt%)

Material	Process	Al	V	Fe	Ti	Si	Zr	Mo	Sn
Ti-64	Scrap	6.90	3.00	0.17	90.01	---	---	---	---
	H-PAM	6.30	3.47	0.17	90.09	---	---	---	---
	V-PAM	2.73	1.63	0.18	95.47	---	---	---	---
Ti-6246	Scrap	5.55	---	0.09	79.27	0.15	4.99	7.60	2.39
	H-PAM	5.77	---	0.03	79.57	0.12	5.01	7.09	2.41
	V-PAM	6.20	---	0.06	78.55	0.17	5.27	7.30	2.46

The results of the hardness measurement are shown in the following **Figure 5**. In the case of V-PAM there is a decrease in hardness for both of the alloys, where the decrease in Ti-64 is more significant compared to 6246 alloy. After H-PAM there is a slight decrease in Ti-64 alloy, while in the case of Ti-6246 the hardness increases compared to the initial state. Changes in hardness values correspond to structural transformations within the metallurgical manufacturing processes.

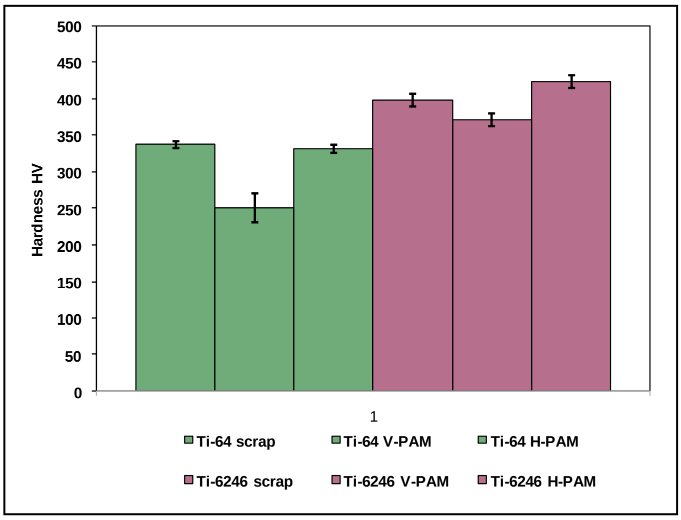


Figure 5 Vickers hardness values of Ti-64 and Ti-6246 before and after plasma melting

4. DISCUSSION

The obtained results imply that recycling of titanium scrap using remelting is possible and feasible. From the point of view of chemical composition there is no significant contamination and for the gas content it is possible to say that their contents remain below the limiting limits [6, 7]. In the case of V-PAM in the Ti-64 alloy lower Al and V contents are evident, however, this phenomenon may be related to the coarse-grained structure, local inhomogeneities of the chemical composition and the narrow analyzed area within the point EDX microanalysis. For Ti-6242 alloy, however, it is possible to notice that there was a slight increase in both oxygen and hydrogen content. Although their contents are still within the permitted limits, it is desirable that the oxygen content be kept as low as possible, since oxygen, as α stabilizer, can lead to undesirable problems in alloys containing β phases [8]. This is particularly related to the subsequent issue of atomization of recycled material and subsequent use for 3D printing [8], where increased contents of oxygen in particular (although meeting the standards of conventionally produced materials) could be an obstacle to the effective use. The gas content limit values for 3D printed metals are always defined by the gas content in the powder from which it is printed.

In terms of the microstructure the materials correspond to metallurgical processes and are satisfactory for the subsequent planned processing. The hardness values also range around the values that are common for the given alloys manufactured by primary metallurgy [9].

5. CONCLUSION

By titanium scrap recycling it is possible to obtain alloys that, in terms of chemical composition, microstructure and hardness, have similar characteristics to alloys manufactured by primary metallurgy. They represent a suitable preliminary step for a subsequent atomization and the use in various methods of additive technologies. The critical factor that could hamper recycling possibilities the most is the oxygen content in the manufactured alloys. When recycling, it is also necessary to consider a smaller degree of contamination during atomization and especially storage of powders. The oxygen content in recycled alloys should therefore be as low as possible.

The goal of the activities of the research team is to develop and verify technological processes leading to the fully industrial production of Ti alloys in the form of a powder semi-finished product using waste.

It is necessary to emphasize that the key is designing suitable technological processes for sorting and separating usable materials. Because the materials used in the manufacture of implants are not only titanium alloys but also cobalt alloys or stainless steel. In the case of insufficient separation and especially non-compliance with work and technological discipline, a very small amount of impurities can chemically contaminate the alloy, thus devaluing it completely.

The proposed technological processes are used for the manufacture of ingots corresponding to semi-finished products for industrial atomization using inert gas - i.e. the contactless technology of atomization of reactive metals and the manufacture of products with a high degree of added value.

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REFERENCES

[1] SOUNDARARAJAN, S.R., VISHNU, J., MANIVASAGAM, G., MUKTINUTALAPATI, N.R. *Processing of beta titanium alloys for aerospace and biomedical applications*. [online]. Chapter in the book. 2018, 17 p. Available from: http://dx.doi.org/10.5772/intechopen.81899.

[2] MIMURA, K., LIM B, J.-W., OH, J.-M., CHOI, G.-S., CHO, S.-W., UCHIKOSHI, M., ISSHIKI, M. Refining effect of hydrogen plasma arc melting on titanium sponges. *Materials Letters.* [online]. 2010, vol. 64, pp. 411-414. Available from: https://doi.org/10.1016/j.matlet.2009.11.033.

[3] BLACKBURN, M.J., MALLEY, D.R. Plasma arc melting of titanium alloys. *Materials & Design.* [online]. 1993, vol. 14, no. 1, pp. 19-27. Available from: https://doi.org/10.1016/0261-3069(93)90041-S.

[4] MITCHELL, A. Melting, casting and forging problems in titanium alloys. *Materials Science and Engineering*. [online]. 1998, vol. A243, pp. 257-262. Available from: https://doi.org/10.1016/S0921-5093(97)00810-1.

[5] OH, J.-M., LEE, B.-K., SUH, CH.-Y., LIM, J.-W. Removal of metallic impurities from Ti binary alloy scraps using hydrogen plasma arc melting. *Journal of Alloys and Compounds*. [online]. 2013, vol. 574, pp. 1-5. Available from: http://dx.doi.org/10.1016/j.jallcom.2013.04.041.

[6] Titanium Alloy Bars, Wire, Forgings, Rings, and Drawn Shapes 6Al - 4V Annealed. 22. Warrendale, PA, USA: SAE International, 2017, 8 p. Available from: https://doi.org/10.4271/AMS4928W.

[7] SEFER, B. *Oxidation and alpha-case phenomena in titanium alloys used in aerospace industry: Ti-6Al-2Sn-4Zr-2Mo and Ti-6Al-4V*. [online]. Thesis. Luleå University of Technology. June 2014. Available from: https://www.researchgate.net/publication/305467167.

[8] WANJARA, P., BACKAMN, D., SIKAN, F., GHOLIPOUR, J., AMOS, R., PATNAIK, P., BROCHU, M. Microstructure and mechanical properties of Ti-6Al-4V additively manufactured by electron beam melting with 3D part nesting and powder reuse influences. *Journal of Manufacturing and Materials Processing*. [online]. 2022, vol. 6, no. 1. Available from: https://doi.org/10.3390/jmmp6010021.

[9] CARROZZA, A., AVERSA, A., FINO, P., LOMBARDI, M. A study on the microstructure and mechanical properties of the Ti-6Al-2Sn-4Zr-6Mo alloy produced via Laser Powder Bed Fusion. *Journal of Alloys and Compounds*. [online]. 2021 p. 870. Available from: https://doi.org/10.1016/j.jallcom.2021.159329.