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LCA of titanium powder: empirical evidence vs data from patents, possible future applications

Daniele Landi^{a,*}, Christian Spreafico^a, Davide Russo^a

^aDepartment of Management, Information and Production Engineering, Università degli Studi di Bergamo, Via Pasubio 7/b, 24044 Dalmine (BG), Italy

* Corresponding author. Tel.: +39-035-2052083. E-mail address: daniele.landini@unibg.it

Abstract

The recent increase of interest in manufacturing techniques using metal powders, including additive manufacturing (AM), metal injection moulding (MIM) and hot isostatic pressing (HIP), has made methods for manufacturing alloyed metal powders especially iron-, nickel and cobalt-based alloys, a topic of much increased importance. The ‘classical’ PM sintered parts business did not attract much research interest, but the last twenty years have seen first, the advent of MIM and HIP and, more recently, AM or three-dimensional (3D) printing. These newer branches of PM make quite different demands on the metal powders that they employ. Metal powders can be produced by a range of techniques including solid-state reduction, electrolysis, atomization, chemical processes, and mechanical comminution. Among these methods, atomization and solid-state reduction are the most popular methods. Metal atomization powder production typically includes three steps: melting the raw materials, atomizing the intermediate products, and solidifying the resulting metallic powders. Although additive techniques are generally sustainable, the production of powders must be studied carefully. In this paper, the Life Cycle Assessment methodology has been used to assess the environmental impacts of titanium powder production in terms of both ReCiPe midpoints and endpoints. Then some solutions to minimize the environmental production impacts have been extracted from patents, following a systematic procedure, and have been reported and qualitatively assessed.

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1. Introduction

Since the industrial revolution, global greenhouse gas emissions have increased significantly by human activities in energy production, industrial manufacturing, and vehicle emissions, which induce the global climate and environmental changes [1]. Experts in climatology have expressed increasing concerns regarding the increasing rate and impact of global climate change since the 20th century. The emission of greenhouse gases, primarily carbon dioxide and methane, accelerate the global climate changes with a consequent increase of heavy rains, droughts, and expansion of

desertification [2][3][4]. It is therefore necessary to concentrate efforts on the design methods and tools for increase the product and process sustainability. In this context, the introduction of the metal powders in the industrials, civil biomedical, etc. process can be a good solution for reduce the environmental footprint in a circular economy perspective.

Metal powders can be derived from virgin raw materials, or from recovery chains. This aspect it is very important, therefore it is necessary to focus the attention of researchers on the development and production of metal powders. In the powders world, titanium and its alloys play an irreplaceable role in many fields due to their various outstanding properties.

High corrosion resistance and high strength levels at low density allow them to be widely used in chemical and aerospace industry [5]. The characteristics of non-toxic and fine biological compatibility enable them the perfect choice for medical care [6]. However, even if the interest of the last period is directed towards large-scale application [7], they are it is still difficult to realize due to two principal limits. The first one is high cost of titanium sponge, compared with other high-priced metals, the price level of titanium and its alloys is unreasonable considering its abundant raw material shortage. The second aspect is due to the large scraps generation from the different application. For instance, in the aerospace industry the scraps are larger than 80% [8]. In addition, more and more titanium parts and products are discarded and turned to titanium scraps with the increase of service time due to the slow and batch-type reduction in the current Ti smelting process, the Kroll process [9]. Nowadays, the titanium scraps have been recycled by remelting techniques. However, remelting has a number of limits, both regarding the different melting points contained in the alloys and the high oxygen content present after remelting. Then, titanium scraps with high production cost turns to down-graded titanium ingot or they are simply used as feed material for the ferrotitanium alloy production line [10]. It has been an extremely urgent a research and development direction for the entire titanium industry to develop a sustainable recirculation route for titanium scraps.

A practice that is already widespread is the reuse through pulverization of titanium (create a titanium powder), which can be recycled until the degradation process undergone is such as to lose the properties that allow to obtain a quality product. In particular, to develop sustainable powder producing technologies, the sustainable innovation proposed by an Italian company concerns the exclusive use of recycled titanium scraps as input of the process in order to reduce the consumption of resources.

However, despite the production process of titanium powders has been extensively studied, to date, the dedicated literature still suffers from two main shortcomings relating to:

- an environmental analysis including the whole process that can give an overview of the overall impacts of the process and their distribution among all the main constitutive phases;
- a broad-spectrum prospective analysis of the improvement interventions that could be implemented to improve environmental sustainability.

This study proposes two novelties with respect to the literature related to the study of the powder's titanium production:

- The determination of the environmental impacts of the entire powered process by applying the life cycle assessment (LCA) methodology.
- The discussion of the obtained results through the comparison with the data extracted from patents in order to provide an idea about the developments of the considered process that companies are working on and possible positive repercussion on the environmental sustainability of the process that could be obtained from their implementation.

This analysis and research approach can be applied to the analysis of other metal powders but also in other industrial sectors. Patent analysis as a discussion of the results of environmental analysis can become a best practice to be implemented in other sectors.

The document is organized in the following manner. In Section 2, different powered methods are briefly summarized and key literature references are provided. In Section 3 method and case study key characteristics are described. Section 4 summarizes the key results of the study. Finally, Section 5 concludes the article and presents the future work.

2. System description

Among the metal powder production methods, atomization, followed by solid-state reactor are the most popular [10]. For this reason, the first one has been considered in this study.

Atomization is the breakup of a liquid into a fine spray. If done on a molten material, the resulting spray commonly freezes into powder. There exist different techniques of metal powder development: gas atomization, water atomization, centrifugal atomization, plasma atomization, mechanical attrition, and alloying, melt spinning, rotating electrode process (REP), and a variety of chemical processes [11].

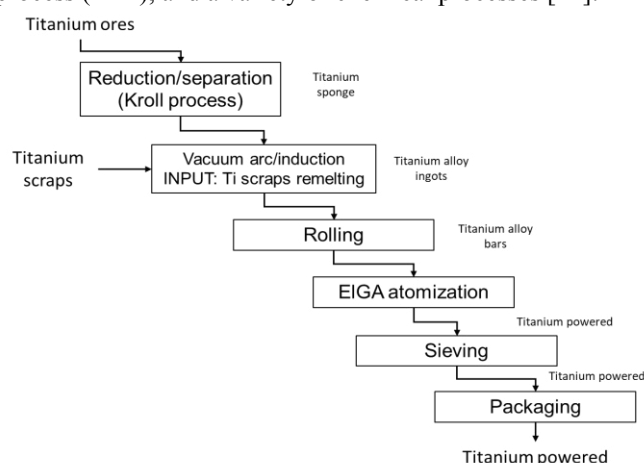


Fig. 1. Titanium powered process

For understand the advantages of this research, a titanium powered alloy material has been considered for the case study. The use of titanium alloy is strongly growing in different applications, automotive, aerospace, medical, etc.[13]. To produce high quality metal parts with titanium alloy powder it is necessary to have a low oxygen level, high purity, unique sphericity and fine particle size [14]. In the preparation process of titanium alloy powder, melting titanium alloy is the first step. What's more, at the high temperature, the molten titanium alloy is extremely easy to react with corundum crucible, oxygen, hydrogen and nitrogen, etc. In order to avoid the harm of crucible impurities and gaseous element, a non-contact smelting method should be applied, and high vacuum condition need to be maintained. So, Electrode Induction Melting Gas Atomization (EIGA) and Plasma Processing methods are the main ways to produce spherical titanium alloy powder, which combining

outstanding vacuum system with non-contact smelting technology. Moreover, the fine powder preparation rate of EIGA method is higher and the mean particle size distribution is narrower than the plasma [15] therefore, the EIGA method has become a significant technology to produce titanium alloy powders. Fig. 1 show the different phase for obtain the Ti powered with the EIGA process.

The input of the process is titanium ore. This metal is not found in nature in free form uncombined to other elements. The extraction of primary titanium, from the titanium ore, consist in a magnesium-thermic reduction/separation process of the $TiCl_4$ or also commonly called the Kroll process. The magnesium reduction, because titanium dioxide is reacted with chlorine to form titanium tetrachloride that reacts with magnesium to remove chlorine and create the metal pure. This reduction is carried out at temperatures of around 800-850 °C, with high energy consumption and high production costs [15]. This process, produce a significant amount of discarded material. The output of the Kroll process is the titanium sponge (starting point for create the ingots) which, combined with titanium waste, is the input for a Vacuum Arc process (or Induction Remelting). It is a continuous melting to produce metal ingots with high chemical and mechanical homogeneity [16]. To carry out this processing, it is necessary to use a copper crucible, arc furnaces and a vacuum with inert environment. It is important to ensure the consistency of this process in terms of output geometry and melting speed to have the best properties of the titanium alloy. In the rolling phase the titanium ingots are passed through pairs of rollers to reduce / uniform the thickness and increase the mechanical and technological properties. The output of this phase is the titanium bars, which will be the input for the atomization EIGA step. In this process, the material is melted using an inductive principle, using magnets to heat and melt the titanium bars. The molten alloy falls in a free flow, according to the gravity force, and whit a gas drop atomizer nozzle. is sprayed through a pump and falls in the form of droplets, under the action of gravity, which solidify become powdered.

In the sieving phase the product is cleaned from the granules and if the powdered have the correct characteristics is ready for the packaging phase. The not suitable powdered it is a waste and constituting the hazardous waste.

3. Methods

The general objective of this study is to define the environmental and potential impact of a titanium powdered process. Following ISO14040 and ISO14044 guidelines, the study defines the environmental impact using LCA methodology [17]. The scope of this study is to evaluate the current situation and propose a future and innovative prospective scenario. The functional unit for this study has been defined as “the production of 1 ton of titanium powdered with the EIGA atomization process”. The study is a “cradle to gate” type, this means it refer refers only to a specific step of the life cycle of the titanium powdered. All processes from the extraction of the raw materials to the realization of the final product (titanium powdered) have been considerate and describe in the previous section and in Fig. 1. For each

process, all inputs, outputs, and process inefficiencies have been considered. Through the patent search, the main innovations can be implemented in the different process step as indicate in the inventory phase. The impacts arising from the production of the machine, for the different step, have not been considered.

3.1. Life Cycle Inventory analysis

Life Cycle Inventory is a basic activity to assess the impact of the life cycle, allowing to quantify the flows into and out of the system boundaries. These flows include the use of resources (raw materials and energy), as well as releases into the air, water and soil associated with the system. During this phase, a list is produced containing the quantities of substances consumed and released into the environment and the quantities of matter and energy used. The primary data for process were collected at the company production site through direct measurement. The secondary data were extrapolated from the updated literature [18] and from the Simapro and Ecoinvent databases. The main material, resources and energy consumption to definite the functional unit are shown in Table 2. The study has been modelled in Simapro v 9.3 software and Ecoinvent 3.6 version database.

Table 1. Life Cycle Inventory data

Phase	Flow	Quantity
Kroll	Titanium ores	3,5 ton
	Mass loss in Kroll process	0,75
	Waste	2,369 ton
	Energy	2770 kWh/ton
	Natural gas	122 m ³ /ton
	Ti sponge	(1,097 ton)/0,97 = 1,131 ton/FU
Vacuum Arc	Ti scraps + Ti sponge	1,131 ton/FU
	Mass loss in VAR	0,03
	Ti sponge	0,77x (1,097 ton)/0,97 = 0,871
	Ti scraps	0,23x (1,097 ton)/0,97 = 0,260
	Waste	0,034 ton
	Ti-alloy ingots	(1,053 ton)/0,96 = 1,097 ton/FU
Rolling	Ti alloy ingots	1,097 ton/FU
	Mass loss in rolling	0,04
	Waste	0,044 ton
Transport	Ti-alloy bars	(1 ton)/0,95 = 1,053 ton/FU
	Ti-alloy bars with suitable size truck	1,053 ton/FU
EIGA	Transport	500 km
	Transported Ti-alloy bars	1,053 ton/FU
	Mass loss in EIGA atomization	5%
	Energy	8200 kWh/ton

	Water	340 m3/ton
	Argon	21,0512 ton
	Waste	0,05 ton
	Atomized powder	1 ton (FU)
Sieving	Power of the sieve	0,35 kW
	Throughput to the sieve	1008kg/h
	Energy use	(1000 kg x 0,35 kW):1008 kg/h = 0,347 kWh/FU
	Hazardous waste	10-15% of Atomized powder = 0,15 ton
	Sieved powder	Atomized powder - Hazardous waste = 0,85 ton
Packing	Sieved powder	0,85 ton
	Packed powder	0,85 ton
	Plastic mass	35 kg/ton x Packed powder

3.2. Life Cycle Impact Assessment

The assessment environmental impacts calculation has been realized by using Simapro tool as LCA software, equipped with the Ecoinvent 3.6 database. In a life cycle impact assessment (LCIA), there are essentially two methods: problem-oriented methods (mid-points) and damage-oriented

methods (end points) [19]. The first comparison has been made in terms of the 18 ReCiPe midpoints: (i) Climate change (CC), (ii) Ozone depletion (OD), (iii) Terrestrial acidification (TA), (iv) Freshwater eutrophication (FE), (v) Marine eutrophication (ME), (vi) Human toxicity (HT), (vii) Photochemical oxidant formation (POF), (viii) Particulate matter formation (PMF), (ix) Terrestrial ecotoxicity (MEP), (x) Freshwater ecotoxicity (FET), (xi) Marine ecotoxicity (MET), (xii) Ionising radiation (IR), (xiii) Agricultural land occupation (ALO), (xiv) Urban land occupation (ULO), (xv) Natural land transformation (NLT), (xvi) Water depletion (WD), (xvii) Metal resource depletion (MRD), (xviii) Fossil fuel depletion (FD). Fig. 2 provides a graphical comparison of the different powered production phases. Globally analyzing the obtained results, a general consideration can be derived: the most critical item of the life cycle is the EIGA atomization process. This is mainly due to two aspects: the high consumption of electricity and the consumption of argon. The Kroll process affects indicators of ecotoxicity and resource consumption. This is due to the consumption of electricity and natural gas during the Kroll phase and the impact of the raw material (in this case titanium sponge). The other processes account for less than 10% of the main indicators. In the vacuum arc phase, the treatment of titanium scrap produce a significative impact in term of terrestrial ecotoxicity and human non carcinogenic toxicity.

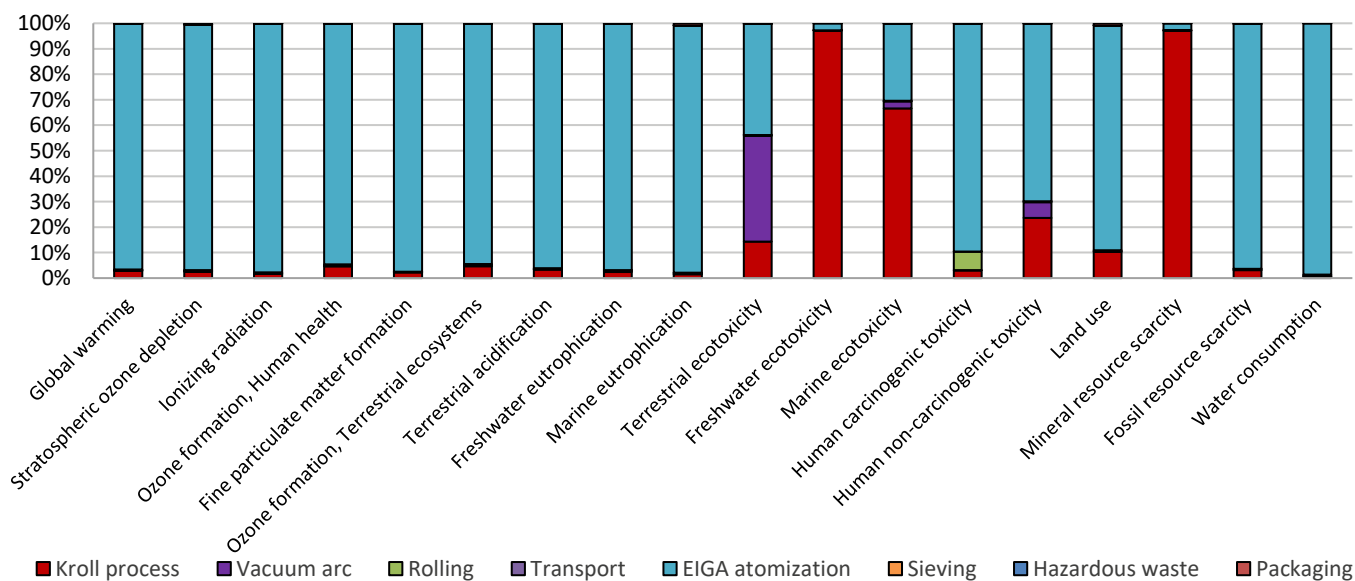


Fig. 2. Recipe mid-point powered production environmental impact

4. Discussion

4.1. Current situation

The LCA highlighted the preponderant role of the atomization phase in defining the total impacts of the powder process in almost all the impact categories, and secondly the Kroll process, which is preponderant only in certain categories of impact.

In particular, the main causes of the high impacts of these phases are the high amount of argon flow used within

the atomization Fig. 3 and Table 1 and the energy consumption of the electric arc used to melt the titanium ores in the Kroll process Fig. 4.

In turn, the flow rate of argon depends on its high speed to overcome the distance between the injector and the liquid titanium to be reached inside the reactor [20]. While high electricity is required to generate the electric arc in the Kroll process due to the low efficiency of the technologies currently available, when compared with more advanced systems, currently at the prototype development stage [21]

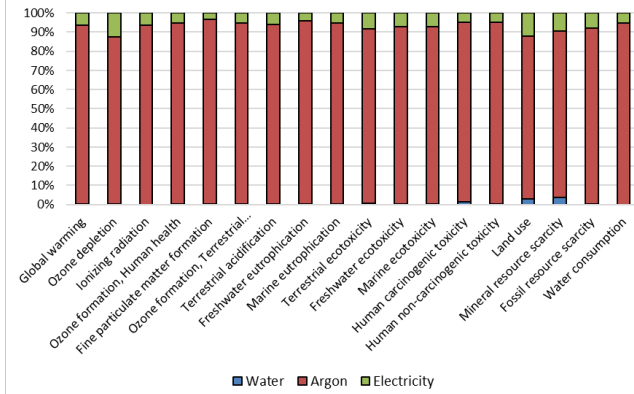


Fig. 3. Environmental impact of EIGA process

In the Kroll process, the electrolysis of $MgCl_2$ consumed the largest portion of energy, accounting for 35% of the total consumption. The second largest energy consumption came from the chlorination and refining process, accounting for 33% of the total amount. Fig. 4 also shows the incidence of the virgin ores titanium in the Kroll process. Produce titanium powder from scrap could lead to a reduction of the impacts in the kroll phase of about 30%. As describe in scientific literature, recycling of titanium technological scrap to produce new component components is feasible, it is necessary to provide a proper scrap selection and pre-treatment procedure [22]. Furthermore, if we consider the impacts of the titanium ores respect all impacts indicator of the powered titanium production an incidence of at least 10% on all indicators is highlight.

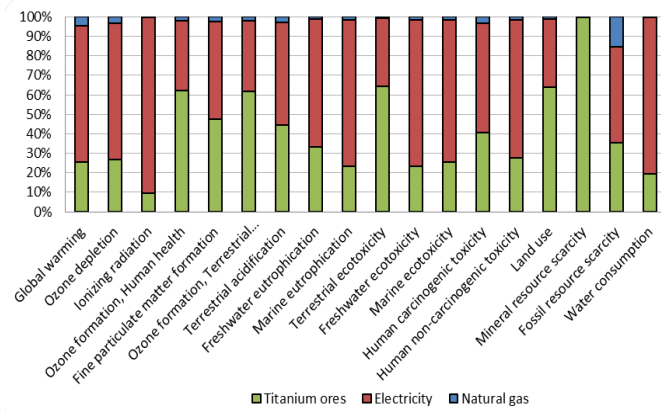


Fig. 4. Environmental impact of Kroll process

Fig. 5 show the environmental impact in term of end point with the related split of contributions for the three ReCiPe damage categories (Human Health, Ecosystems and Resources). It is evident that the damage to human health is the most important damage category for almost all processes. This is mainly due to the high consumption of electricity and e.g., argon for the atomization process. In the Kroll process, the impact of titanium ores it is significant damage with respect the resources and the ecosystem. From the results obtained by the end points it is important to improve the powder production process considering the human health categories.

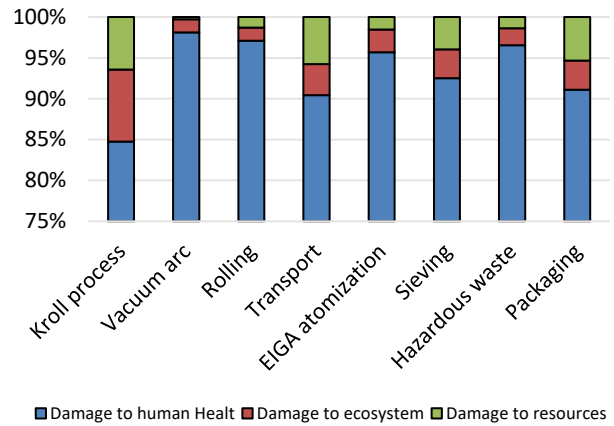


Fig. 5. Recipe end-point powered production environmental impact

4.2. Future perspectives

Fortunately, industry is developing several innovative solutions that can also improve the environmental sustainability of the atomization and the Kroll process, as evidenced by the related patent literature. These solutions work in different ways on the different impact sources, proposing the optimization or technological replacement of existing technologies, obtaining a performance increasing and environmental advantages. In the following paragraphs, three significant examples are present and discussed considering the repercussions on environmental sustainability.

Patent WO2022/174766 uses a laser system to provide energy during the Kroll process. The peculiarity is a selective path of the laser source, aimed to optimize the transmission of heat to the titanium ores. The advantages of this solution are different. The laser source is smaller and less energy-intensive than the normal Kroll process. Since the obtained titanium ingots have good mechanical properties, the input energy can be reduced by 50% and a plasma torch is used. The reduction of the environmental impacts arises from the production and use of the heat sources in Kroll process and atomization.

Patent CN112496278 uses a table electron beam cooling to provide energy to the titanium ores during the Kroll process. The advantage of this solution lies in its efficiency during the transmission of heat to titanium due the speed increase, which leads to a reduction in energy consumption, for the same heat supplied, up to 57%. At the environmental level, the impacts of this Kroll process solution are reduced, while the constructive and maintenance of the electron beam cooling table does not affect of additional impacts.

Patent CN112475309 increases the induction frequency of the thermal waves used to titanium transmit heat, in the atomization phase. In this way, the energy required to activate the reaction is reduced and consequently the gas flow rate introduced into the atomization reactor can be reduced by up to 90%. As indicate in the previously chapter, the gas used is one of the main causes of the high environmental impacts of atomization phase, then, the reduction produces benefits in term of sustainability,

compensating the increases in impacts due to the increasing of the power required by the radiative heat source for the raising the frequency of the waves. Table 2 shows innovations from patents with potential environmental benefits.

Table 2. Prospective patent innovation in Ti powered production

Patent	Process Phase	Environmental advantage
WO2022/174766	Kroll	Reduction of energy consumption and sustainability of manufacturing of the heat source
CN112496278	Kroll	Reduction of energy consumption through increased source efficiency
CN112475309	Atomization	Reduction of energy consumption and used gas flow rate

Conclusions

In this study, the LCA methodology have been applied to evaluate the environmental impact for the titanium powdered production. A result of the titanium powder production process from the ores have been presented.

The highest environmental impacts of the process arise from the atomization phase, in almost all the categories, such as global warming potential, acidification potential and water consumption, and from the Kroll process, which was particularly impactful as regards the ecotoxicity and mineral resource scarcity. The main causes of these impacts have been identified in the high consumption of argon in the atomization and in the electrical consumption for the generation of the electric arc in the Kroll process.

The analysis of the patent literature has highlighted interesting prospects for improving the environmental sustainability of the process, which can be obtained by implementing the innovations and technological optimizations claimed therein.

The results of this analysis, which can also be replicated for other case studies, have a double value. On the one hand they lay the knowledge bases for the construction of the prospective LCA of the process. On the other hand, the descriptions of the patented innovative solutions and their discussion in relation to environmental sustainability could be formalized in specific guidelines for the eco-design of the considered process.

The analysis of life cycle assessment, together with patent research can produce interesting prospective solutions that can be implemented in different industrial sectors in the coming years. this approach can be considered a true technological transfer of innovations, solutions, inventions from all over the scientific and industrial world.

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