sustainability

Review

Sustainable Recovery of Titanium Alloy: From Waste to Feedstock for Additive Manufacturing

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Abstract: Titanium and its alloys are widely employed in the aerospace industry, and their use will increase in the future. At present, titanium is mainly produced by the Kroll method, but this is expensive and energy-intensive. Therefore, the research of efficient and sustainable methods for its production has become relevant. The present review provides a description of the titanium recycling methods used to produce mostly aeronautical components by additive manufacturing, offering an overview of the actual state of the art in the field. More specifically, this paper illustrates that ilmenite is the main source of titanium and details different metallurgic processes for producing titanium and titanium alloys. The energy consumption required for each production step is also illustrated. An overview of additive manufacturing techniques is provided, along with an analysis of their relative challenges. The main focus of the review is on the current technologies employed for the recycling of swarf. Literature suggests that the most promising ways are the technologies based on severe plastic deformation, such as equal-channel angular pressing, solid-state field-assisted sintering technology-forge, and the Conform process. The latter is becoming established in the field and can replace the actual production of conventional titanium wire. Titanium-recycled powder for additive manufacturing is mainly produced using gas atomization techniques.

Keywords: titanium recycling; additive manufacturing; circular economy; sustainability

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1. Introduction

Titanium and its alloys are known for their lightweight, high specific strength, chemical and corrosion resistance, and favorable biocompatibility, making them suitable for a wide range of applications ranging from aerospace, biomedical, military, petrochemical, and automotive fields [1–3]. Despite being dispersed across the Earth's crust and being challenging to extract, titanium has the potential to emerge as the fourth generation of metal materials after copper, iron, and aluminum [4]. In recent years, the world's average production of titanium sponge, which is the porous intermediate product derived from the titanium ore (ore is a natural rock or sediment that contains one or more valuable minerals) used to produce titanium ingot (a piece of relatively pure material, usually metal, that is cast into a shape suitable for further processing), has been around 260.000 ton/year [5]. This is significantly less than the 1.88 billion ton/year [6] of crude steel and the 69 million metric ton/year of aluminum [7]. The global market growth of titanium sponge has been steady in recent years and is anticipated to maintain this positive progression until 2030. However, the high cost of this metal limits its applicability mainly in technically demanding sectors where its properties are essential, such as aerospace and aeronautic, military, and some industrial sectors (i.e., oil and gas, chemical processes, power generation, etc.). (Figure 1). The high cost of titanium sponge is due to (i) the numerous extraction and production steps; (ii) the high reactivity/affinity with elements such as oxygen and nitrogen; and (iii) the poor machinability caused by the low thermal conductivity. The price of titanium sponge varies greatly among different countries, depending on local demand, supply, and production costs. In recent years, the price of titanium has exceeded 10 €/kg [8]. Table 1 reports a cost comparison of titanium with other materials. The world's titanium sponge production is concentrated in a few nations, among which the main is China (Figure 2).

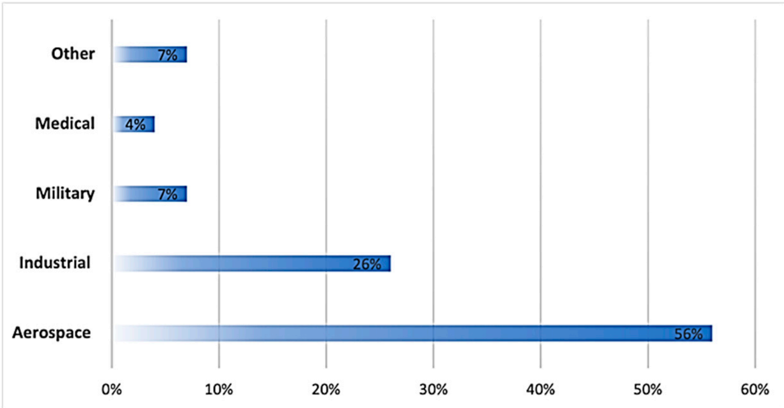

Figure 1. Titanium applications in 2018 [9].

Table 1. Comparison of the cost of titanium with other materials [8,10,11].

Material	€/Kg
Titanium sponge	10.27
Aluminum ingot	1.97
Stainless steel	2.18
Steel	0.25
Iron	0.105
Copper	7.85

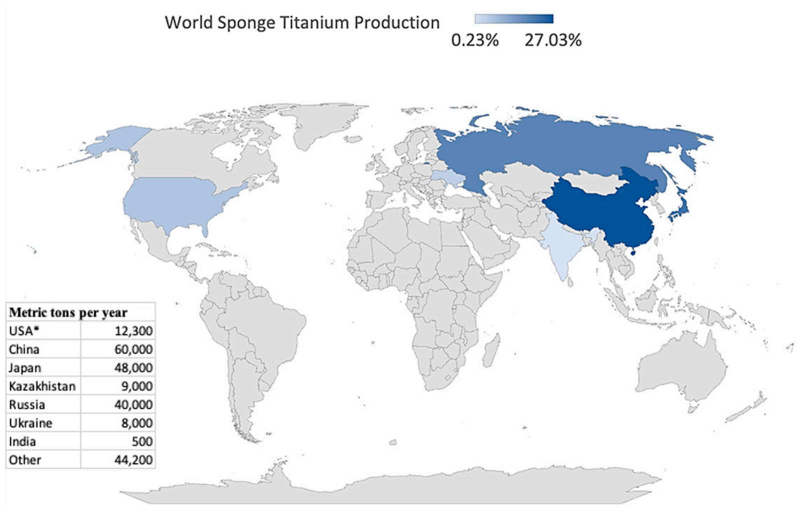

Figure 2. Production volume of titanium sponge worldwide in 2022 [5]; * The data relating to the USA are doubtful due to the lack of official documents.

The titanium sponge is used for the production of titanium ingot, which is manufactured on a large scale across the world by several different companies. Some of the leading companies that are entitled to be key players in the global metal market for titanium are: (i) VSMPO-AVISMA Corporation, which is the world's largest producer of titanium metal. The company processes the raw materials to produce high-grade titanium metal all over the world. It was incorporated in the year 1993, with its headquarters located in Russia; (ii) TIMET, Sigma Aerospace Metals, Admat Inc., KRONOS, Tronox Incorporated, Castle

Metals, ATI Specialty Metals, and Precision Castparts Corporation are key suppliers and manufacturers of titanium metal on a global scale, with headquarters located in the USA; (iii) Toho Titanium is a Japanese metal manufacturing firm that is mainly dedicated to manufacturing titanium on a large scale.

Titanium alloys with strong corrosion resistance are typically utilized in the manufacturing of heat exchangers, tanks, chemical processing, desalination, and power generation plants [12]. In the automotive sector, titanium and alloys are used to produce components for reducing weight and consumption, such as intake and exhaust valves and connecting rods [13]. Takahashi et al. [13] showed that a suitable surface treatment is necessary to minimize wear problems. As far as exhaust valves (exposed to high operative temperatures) are concerned, new alloys with higher heat resistance (close to 800 °C) need to be developed. The biomedical field is another expanding application of titanium alloys. Bombač et al. showed that pure titanium is effective for the production of dental implants and maxillofacial applications [14]. Elias et al. [1] used titanium alloys in the production of cardiac valve prostheses, pacemakers, and artificial hearts. Furthermore, Ti-6Al-4V alloy was used for hip and knee prostheses and trauma fixation devices such as nails, plates, and screws. However, Ti-6Al-4V has some disadvantages: (1) The V and Al elements are toxic to the human body; (2) the alloy has a higher elastic modulus (110 GPa) than that of the bone (18 GPa) [15]. For these reasons, it is necessary to: (1) substitute potential toxic elements (Al and V) with biocompatible alloying elements like Nb, Ta, and Zr; and (2) modulate the elastic modulus through appropriate treatments.

In the aerospace industry, titanium materials are widely used in engine and airframe systems. Its large employment is due to higher operating temperatures (instead of nickel alloys), weight reduction, and corrosion resistance (instead of steel) [16]. Pure titanium can be used for parts subjected to aggressive corrosion, while Ti-6Al-4V is used for parts subjected to high mechanical stresses.

As far as the aeronautical sector is concerned, the use of titanium (and its alloy) for commercial aircraft has increased in the last few decades. Until the development of the Boeing 777 in the mid of 1995 [17], commercial aircraft used mostly aluminum alloys as structural elements (>77 wt.%), with a use of titanium alloys of less than 7 wt.%. In the Boeing 787, a medium-size jetliner of the latest generation, titanium alloys were used in the construction of about 14% of the airframe to lighten it and save energy [18] (Figure 3). Because of this, long direct flights that previously required large-scale jetliners can now be approached by the Boeing 787.

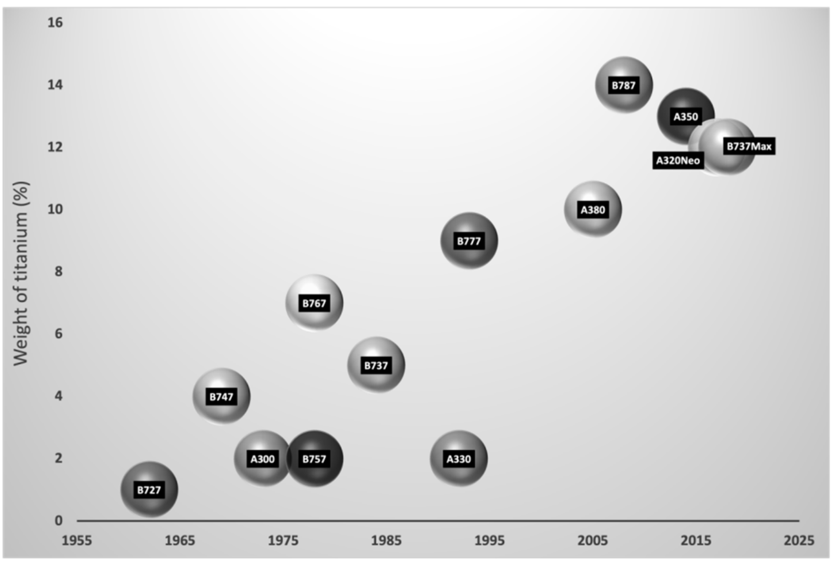

Figure 3. Titanium usage weight in commercial aircraft [19].

The total amount of titanium alloy utilized for aircraft structural materials is constantly rising. This, in turn, will increase the amount of titanium waste, so solutions to effectively boost the recyclability of scraps will be vital. From a general point of view, the reuse of secondary resources has a certain goal: to maximize the utilization of resources and, meanwhile, reduce potentially dangerous impacts on the environment and people. Recently, the introduction of additive manufacturing (AM) for titanium scraps has demonstrated the potential of these techniques in achieving 100% material usage and 0% waste production. This can significantly contribute to the reduction of costs and energy consumption. In this light, the goal of the current literature survey is to offer an overview of the current state-of-the-art for titanium recycling techniques utilizing additive manufacturing for aeronautical components. This paper is divided into three main parts. The first part describes the methods and processes for obtaining titanium sponge and its alloys. The energy consumption required for each production step is also illustrated. The second part focuses on the main additive manufacturing techniques used for titanium and its alloys. The last part concerns the current technologies for titanium recovery and the main additive manufacturing processes used for recycling scraps.

With the aim of monitoring the progress of the titanium recycling research, a bibliometric analysis was carried out. It was based on relevant articles obtained from the Scopus database and was carried out with the software program VOS Viewer 1.6.19. Using 'titanium', 'additive manufacturing', and 'recycling' as keywords, 78 papers (journal articles and conference papers) published between 2005 and 2023 were found. Co-occurrence analyses were performed, and a minimum number of keyword occurrences was 5, corresponding to 198 keywords. The obtained frame size, reported in Figure 4, reflects the relative number of publications; a larger frame size denotes stronger relevance. Furthermore, the distance between keywords reflects their relative co-occurrence. For instance, two keywords close to each other co-occur more frequently, but a significant distance between them denotes that they do not occur at the same time. Based on our analysis, it can be observed that no papers with the three keywords (i.e., 'titanium', 'additive manufacturing', and 'recycling') were published before 2005. Also, it can be observed: (i) a link between the keywords "powder recycling" and "additive manufacturing"; and (ii) only the keywords "selective laser melting" (SLM) and "electron beam melting" (EBM) appear as employed AM processes in this field of research.

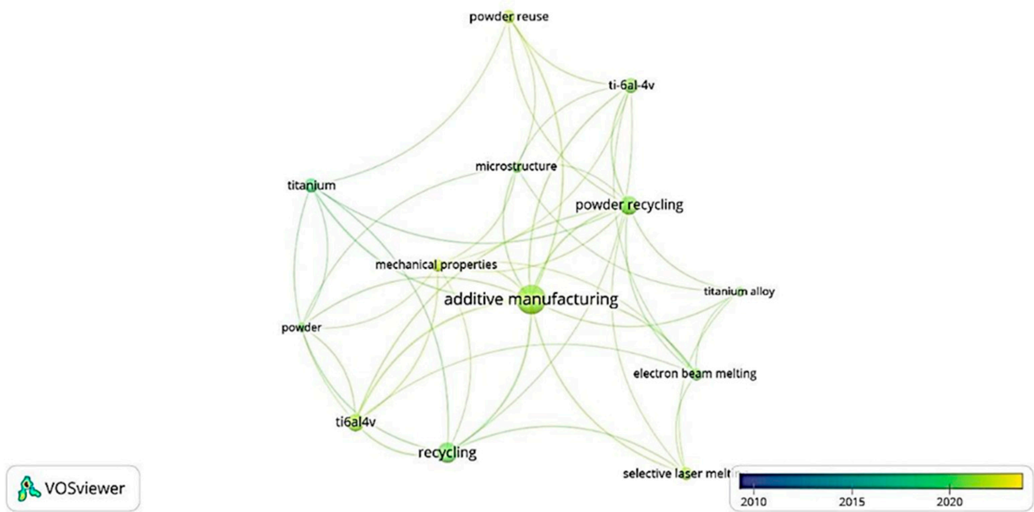

Figure 4. Mapping for co-occurring keywords for recycling of titanium for additive manufacturing from VOS Viewer.

2. Method and Process for Obtaining Titanium and Its Alloys

2.1. Titanium Resources

Titanium is the ninth most abundant element on earth's crust, with an estimated average amount of 0.6 wt.% [20]. Oxides are the prevalent minerals of titanium due to its great affinity for oxygen: ilmenite ($FeTiO_3$), leucoxene (highly altered ilmenite with a high amount of TiO_2), rutile (TiO_2), anatase (TiO_2), and perovskite ($CaTiO_3$). Currently, the principal source for the titanium industry is the ore, which contains rutile (TiO_2) and ilmenite ($FeTiO_3$) [21,22]. The titanium reserves of China rank first in the world, followed by Australia, India, Brazil, and other 9 countries (Figure 5). They account for about 97% of the world's total reserves [23]. At present, ilmenite deposits are mainly concentrated in China, Australia, India, South Africa, and Brazil, while rutile deposits are distributed in Australia, India, South Africa, and Sierra Leone. Considering the data from the United States Geological Survey, around 2 billion metric tons of titanium ore are available worldwide. They include 700 million metric tons of ilmenite resources and 49 million metric tons of rutile resources. Considering current mining rates of about 7 megatons per year, titanium deposits can last for more than six centuries [24].

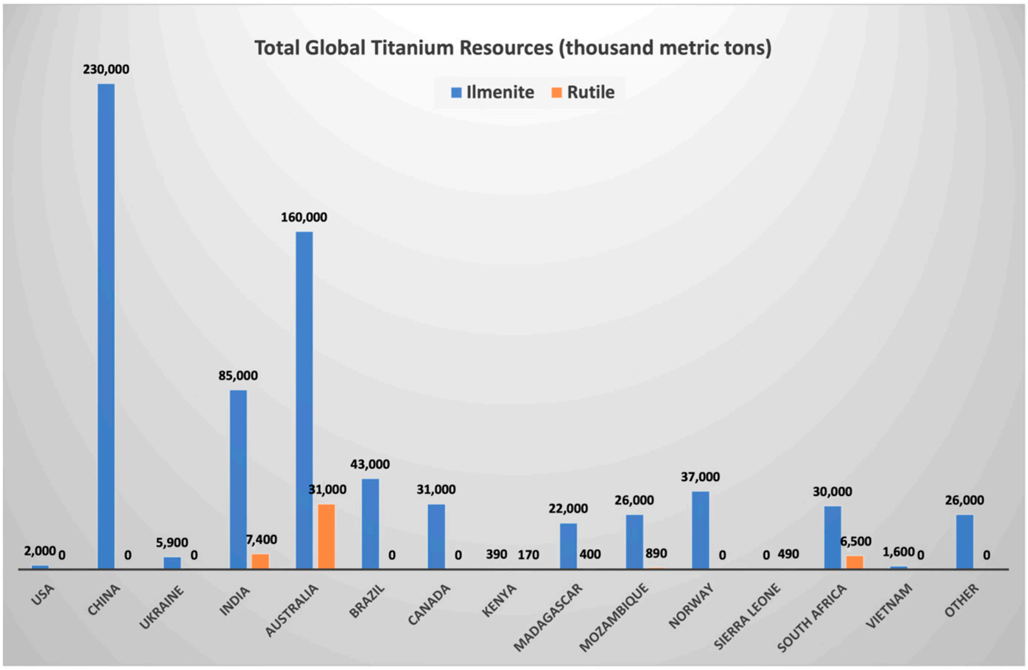

Figure 5. Total Global Titanium Resources [23].

In the ilmenite deposits, the mineral is found in layers as well as in disseminated patterns within igneous anorthosite rock complexes. It is often found coupled with hematite (Fe_2O_3), forming interposed lamella microstructures, which are characteristic of hemo-ilmenite minerals. Such a kind of mineral is present in Quebec (Canada) [25] or in Tellnes (Norway) [26,27]. The block flow diagram representing ilmenite extraction from Tellnes mines is displayed in Figure 6.

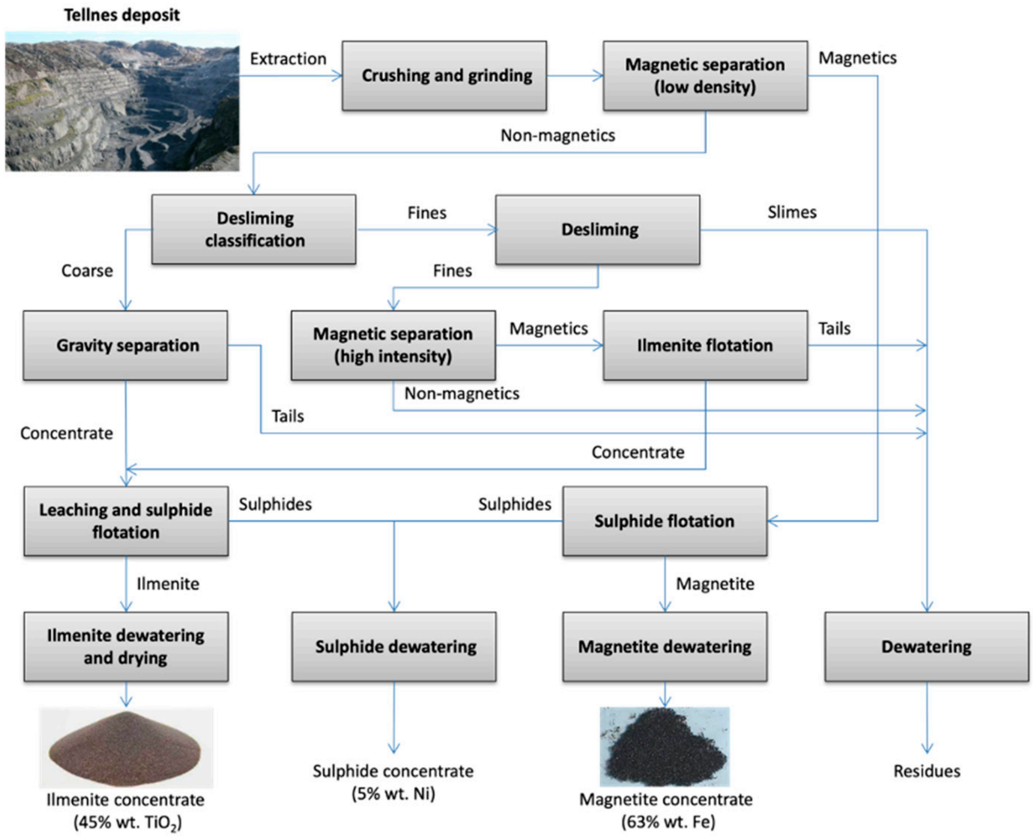

Figure 6. Block flow diagram of the extraction of Ilmenite from Tellnes mines (based on Kingman et al. [28]).

Depending on its geological history, ilmenite includes 40–65 wt.% of TiO_2 [29]. Conversely, natural rutile derives mainly from sand deposits and typically contains 92–96 wt.% of TiO_2. The main drawback of the rutile is its limited quantity and, consequently, its high cost. Sierra Leone is the region with the highest amount of sand deposits for rutile extraction [30,31].

2.2. Method and Process for Obtaining Titanium Dioxide

Commercial titanium metal is obtained by thermo-chemical reduction techniques, starting with $TiCl_4$. (see next paragraph.) In turn, $TiCl_4$ is produced by the chlorination of TiO_2. The major sources for the obtainment of TiO_2 are (i) natural rutile and (ii) ilmenite, from which synthetic rutile and titanium slag (i.e., the primary product of ilmenite smelting) can be obtained. When natural rutile is used, a series of concentrations of sands through gravity separation, electrostatic separation to remove non-conducting materials (i.e., zircon materials), and magnetic separation to separate ilmenite are conducted. The block flow diagram for the extraction of rutile from the sand deposit (from which ilmenite is also obtained) is shown in Figure 7.

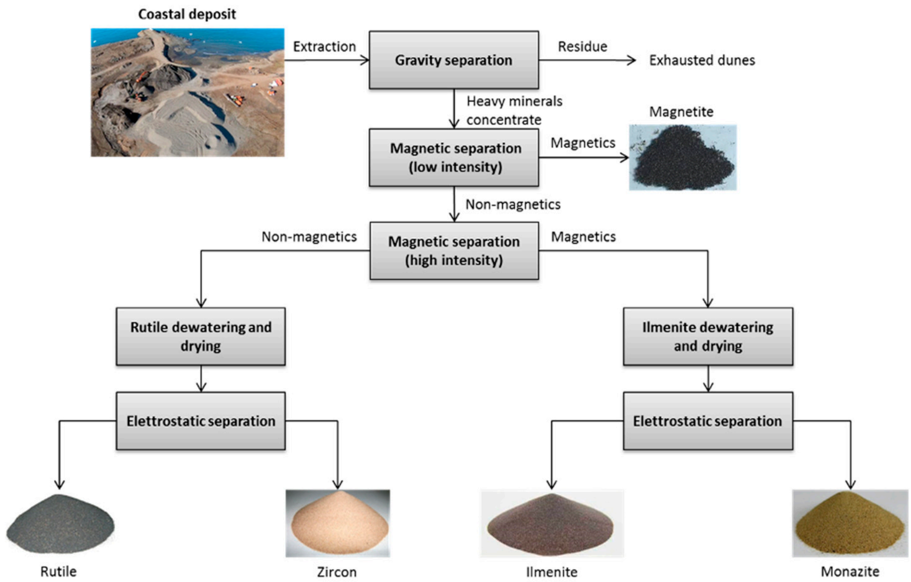

Figure 7. Block flow diagram of the extraction of Ilmenite from the sand deposit (based on Battle et al. [32]).

The rutile concentrate, containing about 95 wt.% of TiO_2, is directly used as a raw material [33]. Instead, synthetic rutile is obtained through a combination of thermal oxidation and reduction by roasting sand ilmenite, followed by leaching and physical separation steps for removing the iron. The final product typically contains about 92 wt.% of TiO_2. The two most common processes for obtaining this product are the Becher and Benelite processes. However, Murso and Austpac processes are also often used [34].

The Becher process was created and optimized in the late 1960s for the treatment of sand ilmenite in Australia [35], while the Benelite process [36,37] was developed in the United States during the 1970s. In the first one, ilmenite is reduced with coal, and metallic iron is rusted away [38]. In the second, ilmenite is reduced with carbon to convert ferric iron into a ferrous state, and hydrochloric acid is then used to leach the iron [39]. Presently, only two companies are using the Becher process, both operational in Australia, with a production of about 200.000 ton/year of synthetic rutile [40,41]. The Benelite process is rather costly and nowadays is used only in India, with a production of about 150.000 ton/year of synthetic rutile. Finally, high-quality titanium slag is obtained from ilmenite by melting it in an electric arc furnace. The titanium slag, which typically contains about 85–90 wt.% TiO_2, has a low percentage of impurities like MgO, CaO, and SiO_2. After this step, titanium slag can be processed using a variety of techniques to produce titanium dioxide, such as sulfuric acid leaching, hydrochloric acid leaching, fluoride leaching, ammonia decomposition, and magnetic separation. As reported by Liu et al. [42], almost 200 electric furnaces had been built in China by 2016, with a production of about two million ton/year of titanium slag. Around 60 kton/year of titania slag is also produced in Ukraine, Kazakhstan, Vietnam, and India [43].

The Murso method consists of the oxidation and reduction of ilmenite, followed by leaching with hydrochloric acid. Instead, the Austpac process involves roasting ilmenite ore to magnetize it, separating gangue minerals through magnetic separation, and then leaching with hydrochloric acid [34].

2.3. Titanium Production Process

The affinity of titanium for oxygen and the chemical stability of its mineral form are second only to those of some elements such as Al, Mg, Ca, and some rare-earth metals [44,45]. This makes it difficult and costly to extract and process it into commonly used alloys. In this section, the most commonly used and relevant processes employed for converting TiO_2 into titanium sponge are described. The commercial process used today for this conversion is the Kroll process®. The first titanium sponge was manufactured in

Japan by this process in 1952 (OSAKA Titanium Technologies Co., Amagasaki, Japan). The Kroll process can be divided into three main sub-processes [46,47]: (1) chlorination and purification where titanium minerals (that, as explained before, are generally natural and synthetic rutile) are chlorinated and distilled to produce pure titanium tetrachloride ($TiCl_4$) (reaction occurs at 1000 °C [48]); (2) reduction and vacuum distillation where titanium tetrachloride is reduced using molten magnesium to produce titanium sponge (reaction takes place in an argon atmosphere at 850–950 °C [48]). Residual magnesium and $MgCl_2$ are removed from the sponge by vacuum distillation; (3) electrolysis, where the magnesium chloride is decomposed into magnesium and chlorine gas. They are reused in the previous processes (reduction and chlorination).

The Kroll process has largely replaced a previous method of producing titanium, known as the Hunter process [49], which used liquid sodium as a reducer. The production of pure ductile metallic titanium was first achieved in industry by the Hunter process. It was invented in 1910 and is like the Kroll process, except for the substitution of sodium as a reductant. The primary obstacle to the Hunter process's use is the challenge of removing the generated NaCl from the titanium. The vapor pressure of NaCl is lower than that of $MgCl_2$, produced by the Kroll process. As a result, the NaCl is eliminated by aqueous solution leaching. The procedure of extracting the by-product (NaCl) from this aqueous solution needs more energy.

The Hunter process was also modified to incorporate a two-stage reduction. In the first step, $TiCl_4$ and molten sodium react to form $TiCl_2$. After that, this mixture is added to a retort that has enough sodium in it to finish the reaction at a higher temperature. Since titanium subchlorides are soluble in NaCl, it is not feasible to separate the titanium by draining off the NaCl that is formed during the reduction. The final product in the retort contains a mixture of one part titanium and four parts of NaCl. Therefore, compared to a Kroll reaction of comparable size, the amount of titanium generated by the Hunter reaction is substantially less. An example of an effort to create a continuous process based on the Hunter process is the Armstrong process, which attracted a lot of interest and investment during the previous two decades. The Armstrong process uses sodium or magnesium vapor to reduce titanium tetrachloride and may offer advantages in terms of energy efficiency and lower operating temperatures. It has not yet been adopted due to various reasons, such as the need for specialized equipment and potential challenges in scaling up the process to meet industrial demands [29]. In the second half of the last century, many efforts have been conducted to improve the metallothermic reduction process of $TiCl_4$. Table 2 summarizes these attempts.

Table 2. Investigation of the titanium reduction process by metallothermic reduction.

Reference	Feedstock	Process News	Product
[50]	$TiCl_4$	Liquid Pb cathode without ceramic diaphragm	Dentrite
[51]	Na_2TiF_6	Utilizing Ti alloy melt	Liquid alloy
[52]	TiO_2	Electrolysis with plasma	
[53]	$TiCl_4$	Reaction with the use of a ceramic diaphragm	Dentrite
[54]	TiO_2	Al reduction and EB melting	Deposit
[55]	$TiCl_4$	$TiCl_4$ was injected into liquid Mg	Liquid
[56]	TiO_2	Calciothermic reduction with hot-spot cathode	
[57]	$TiCl_4$	Reaction of $TiCl_4 + Ti \rightarrow 2\ TiCl_2$	Sponge
[58]	$TiCl_4$	Reaction with the use of a ceramic diaphragm	Sponge
[59]	$TiCl_3$	Ti-coating and plate deposition	Plate
[60]	$TiCl_4$	$TiCl_4$ was reacted with aerosol Mg	Powder
[61]	$TiCl_4$	Pulse current and rotation electrode	Plate

These experiments aimed to establish high-speed and continuous responses, which are not present in the Kroll process. Unfortunately, titanium's high melting point and strong reactivity make such advancements technically challenging. Over the past two decades, alternative processes have been developed, including improved reactor design, omission of cooling steps in $TiCl_4$ reduction with vacuum distillation, and diaphragm-less electrolysis for $MgCl_2$ regeneration (Table 3).

Table 3. Recent developments for new titanium reduction processes [62].

Institution	Process News	Product
Aachen University [63]	Aluminothermic reduction of TiO_2	Liquid alloy
Armstrong (ITP company) [64]	Sodiothermic reduction of $TiCl_4$ vapor	Powder
BHP Billiton [65]	Reduction of TiO_2 by Ca in molten $CaCl_2$	Powder
CSIR in South Africa [66]	Electrochemical reduction of Ti slag (in CaF_2)	Liquid
DMR USA	Aluminothermic reduction of TiO_2	Liquid alloy
EMR/MSE Tokyo University [67]	Reduction of TiO_2 by liquid Ca alloy	Powder
ESR Toyohashi University [68]	Electrolytic reduction of TiO_2	Liquid
FFC Cambridge University [69]	Electrochemical reduction of a sintered TiO_2 electrode (in $CaCl_2$)	Powder
Gtt s.r.l. [70]	Electrochemical reduction of $TiCl_4$ in molten salt	Liquid
Idaho research	Reduction of liquid $TiCl_4$ by Mg or Ca	Powder
Idaho Ti technology	Reduction of $TiCl_4$ plasma by H_2	Powder
JTS (Japan Titanium Society)	Reduction of $TiCl_4$ by liquid Ca	Powder
MER Company	Reduction of TiO_2 at the anode utilizing the deposition of cathode	Powder
MIT	Electrochemical reduction of TiO_2 dissolved in molten salts	Liquid
OS Kyoto University	Reduction of TiO_2 by Ca	Powder
PRP Tokyo University	Reduction of TiO_2 by Ca vapor	Powder
QIT Rio Tinto	Electrochemical reduction of Ti slag	Liquid
SRI International	Reduction of $TiCl_4$ by H_2 in a fluidized bed	Powder
TIRO (CSIRO, Australia)	Reduction of $TiCl_4$ vapor by Mg vapor	Powder
University Sci. Tech. of Beijing	Reduction of TiO_2 by C	Powder
Vartech	Reduction of $TiCl_4$ vapor by H_2	Powder

A method that has come to the fore in recent years is the hydrogen-assisted Mg reduction (HAMR) process [45,71,72]. In this process, Mg reduction of TiO_2 is performed in a hydrogen atmosphere to form titanium hydride (TiH_2). Mg is chosen as the reducing agent for its cheapness compared to calcium or sodium. The reduction and deoxygenation steps are used to remove oxygen [73], while a heat treatment is carried out between the two processes to regulate the powder's specific surface area and particle size [74]. The aim of the last step is the removal of the exceeding hydrogen [75]. The HAMR process allows for an oxygen content lower than 0.15 wt.% in the final product. Figure 8 synthesizes the main steps of the HAMR process.

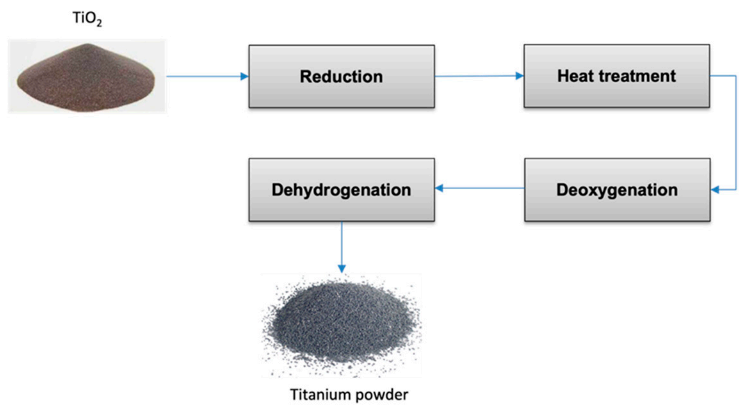

Figure 8. Block flow diagram of the HAMR process.

2.4. Main Production Method of Titanium Alloys

Based on their metallurgical properties, titanium alloys may be categorized into four main groups: α, near α, α–β, and β alloys [76,77]. The alloying elements are classified as neutral, α-stabilizers, or β-stabilizers, and they are used to stabilize the α and the β phases, respectively [78,79]. The α-alloys can be obtained from a α-phase single-solid solution. These alloys show good properties at high temperatures and are mainly used where deformability and corrosion behavior are required [12]. Near-α-alloys are composed of α-phase with less than 10 wt.% of β-phase due to the addition of 1–2 wt.% of β-stabilizers. These alloys, used to produce aeronautical engine components, have good strength and workability due to the presence of the β phase. However, they can be used at a maximum temperature of 500–550 °C [12]. β alloys consist of small quantities of α-stabilizers and 10–15 wt.% of β-stabilizers. The group of α-β alloys includes those that contain 4–16 wt.% of β-stabilizers. As far as the aeronautical field is concerned, the most important alloys are those in the α–β group. Among these, Ti-6Al-4V alloy is the most used, accounting for over 45% of the total titanium production [80]. Elements that raise the transformation temperature (α-stabilizer) are aluminum (Al), oxygen (O), nitrogen (N), and carbon (C). Al is a good α-strengthening element among them, active at both room temperature and elevated temperatures (up to 550 °C). Furthermore, the low density of Al is an important additional advantage. Elements that produce a decrease in the transformation temperature (β-stabilizers) can be divided into β-isomorphous and β-eutectoid elements. The first are molybdenum (Mo), vanadium (V), and niobium (Nb), and promote the stability of β phase along all the composition of the alloy; while the second are chrome (Cr), manganese (Mn), and hydrogen (H), and cause eutectoid transformations of β phase (Figure 9). These elements are soluble with β-titanium and progressively bring the β-to-α transformation up to ambient temperature [79]. While neutral elements, like tin (Sn) and zirconium (Zr), do not have a great influence on transus temperature, α-β titanium alloys are usually processed by conventional (α–β) forging. The first step of the process involves the pure titanium sponge being pre-densified in a hydraulic press to obtain a compact material [81]. Then, this titanium compact is assembled with an electrode for the melting step. α–β stabilizing elements (Al and V, the most common) are added to obtain specific alloy compositions. The pure titanium compact needs to be welded at low pressure with argon in a plasma-welding chamber because of its strong affinity for oxygen. During the process, an arc is ignited between the electrode and the self-consuming electrode, leading to the formation of an ingot. The melting temperature is computer-controlled, and the entire process is carried out in a vacuum. Materials are heated and processed at 40–50 °C below the β transus temperature [82]. The forged alloys have equiaxed microstructures that enhance ductility and thermal stability but reduce high-temperature properties and fracture toughness [82]. α–β alloys are also processed by β-forging processes. In this case, the materials are usually heated above the β transus, and the resulting forged materials have a lamellar microstructure (lamellar α in a transformed β matrix) with higher temperature creep properties, impact toughness, and fracture toughness. Lower thermal stability and ductility are a consequence of this development, though.

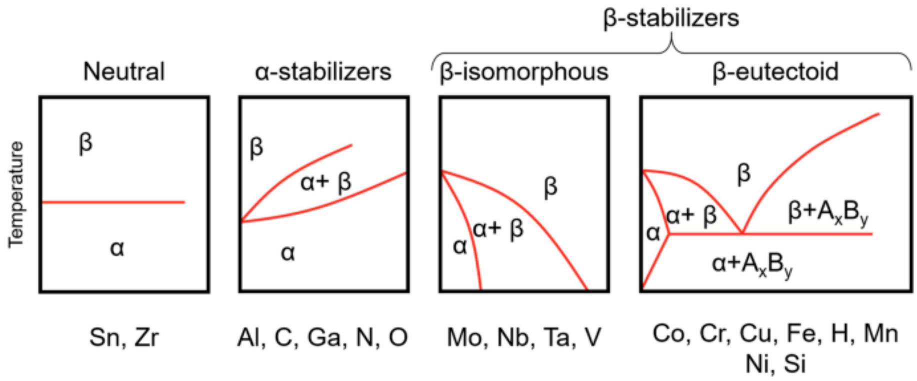

Figure 9. Phase diagram of titanium alloys [83].

In recent decades, new forging strategies have been explored to enhance the mechanical properties of titanium alloys in addition to conventional methods. For instance, advances in the development of dynamic plastic deformation methods to increase the strength of titanium alloys were made by Lu et al. [84] and Fang et al. [85]. Won et al. [86] controlled microstructure by deformation at cryogenic temperatures. Since the treated material's microstructure was ultra-finely grained, it gained significant strength without compromising its ductility. The production of multiscale structures in a hexagonal closed-packed titanium alloy using bulk nano-structuring has been reported by Zhao et al. [87], with notable improvements in tensile strength and ductility. Regretfully, these processing methods are difficult to successfully apply in real-world applications and are only useful in particular situations.

2.5. Energy Consumption for Titanium Preparation

The literature provides few details regarding the energy consumption of the titanium preparation steps from the perspective of efficiency. Significantly different values can be found for the same step in the processing of the titanium mineral until the Kroll process. Table 4 summarizes the different values for energy consumption as a function of the grade and source of the titanium mineral based on the work of Middlemas and Bradvard [88,89].

Table 4. Energy (MJ/kg) required for $TiCl_4$ preparation [48].

Raw Mineral	**Rutile (98% TiO_2)**	**Ilmenite Slag (90% TiO_2)**	**Ilmenite Slag (90% TiO_2)**	**Ilmenite Slag (90% TiO_2)**	**Ilmenite Slag (90% TiO_2)**	**Ilmenite Slag (90% TiO_2)**
Source	Beach sand (24% TiO_2)	Beach sand (1.4% TiO_2)	Rocks (20% TiO_2)	Rocks (35% TiO_2)	High Alumina Clay (5% TiO_2)	Soil (0.2% TiO_2)
Drilling, dredging, and blasting	0.20	1.50	0.07	0.05	0.56	13.25
Crushing	0.20	0.40	0.45	0.30	0.80	19.10
Gravity concentration	0.06	0.70	0.10	0	0.70	6.20
Magnetic concentration	0.06	0.50	0.05	0	0.20	4.70
Magnetic separation	0.14	2	0.12	0	0.70	16.20
Roasting	0	0	0	0	7.50	9
Miscellaneous	0.14	1.15	0.10	0	0.97	15.50
Melting of slag	0	18.70	19.45	24.85	23.40	23.40
Chlorination	2.10	3.60	3.60	3.60	3.60	3.60
$TiCl_4$ purification	7.20	7.90	7.90	7.90	7.90	7.95
Total	10.20	36.50	31.85	36.70	46.40	118.80

Additionally, there is disagreement on the amount of energy needed for each stage of the Kroll process. Peter et al. reported a value of energy consumption for the Kroll process of about 77.4 MJ/kg [90], whereas Kohli et al. fixed this value in the range between 55.44 and 174.24 MJ/kg [91]. By analyzing the individual steps of the Kroll process, it was found that the results are strictly affected by the process condition, the temperature, the efficiency of the used plants, the vacuum level of the distillation, and the required final size of the sponge. For example, the chlorination and purification of $TiCl_4$ require about 3.6 and 7.9 MJ/kg, respectively. The Mg reduction process requires about 36 MJ/kg [91], the vacuum distillation process accounts for values ranging from 64.8 MJ/kg [92] to 133.2 MJ/kg [93], and the electrolysis during magnesium regeneration ranges from 36 to 47.52 MJ/kg [94,95]. Moreover, considering that during the production only 10–50 wt.% of Mg is required to complete the reduction of $TiCl_4$ [96,97], the energy consumption due to the Mg loss is estimated at around 30 MJ/kg [98]. Because of the contamination due to the stainless-steel vessel, a small part of the sponge cannot be employed. It is estimated that there is a residue of 10–20% of titanium sponge in each production [99], causing an energy consumption of 42.96 MJ/kg.

Based on the literature, it is possible to derive an average value of energy consumption f of the whole process of about 258 MJ/kg. This is due to the energy for: the feedstock $TiCl_4$ (129 MJ/kg); the regeneration and loss of the reducing agent (73.2 MJ/kg); Mg reduction (0.9 MJ/kg); vacuum distillation (11.7 MJ/kg); and sponge loss (42.96 MJ/kg). Figure 10 shows the cradle-to-gate lifecycle energy consumption for titanium production.

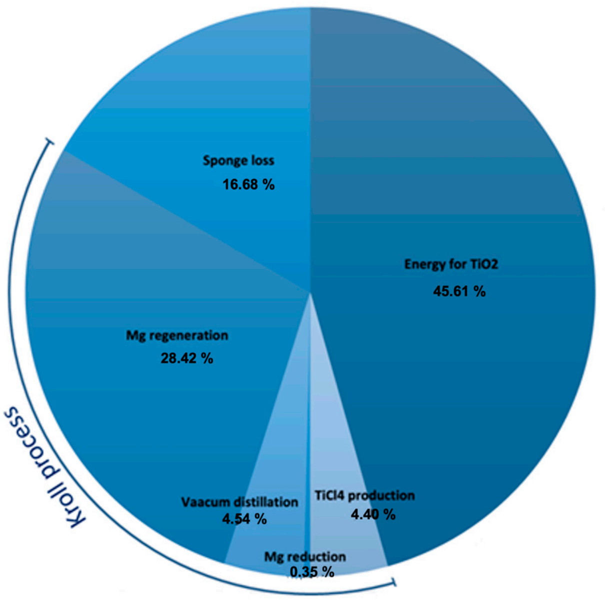

Figure 10. Pie chart for the energy consumption break-down of the titanium production.

The literature does not report extensive data on the energy consumption for other processes of titanium production. In the work of Xia and co-workers [48], the energy consumption of Kroll and HAMR processes was compared step by step. The results indicate that the HAMR process could have a lower consumption of about 25% than that of the Kroll process. Furthermore, in the HAMR process, Mg can be commercially purchased instead of being regenerated. When Mg regeneration is separately considered, the value of energy savings for the HAMR process reaches up to 65%. Regarding the production of titanium alloys, again, few data can be found in the literature. The conventional production of a plate in Ti-6Al-4V alloy requires energy consumption between 582 and 643 MJ/kg [100].

3. Additive Manufacturing of Titanium and Its Alloys

The ASTM F42 Technical Committee defines AM as the "process of joining materials to make objects from three-dimensional (3D) model data, usually layer upon layer, as opposed to subtractive manufacturing methodologies" [101]. This concept includes all those technologies that can build 3D geometries from raw materials [100]. AM has been hailed as a significant industrial technique in recent decades since it may reduce material waste and shorten the manufacturing cycle time. The technology is utilized in various industries like medical, aerospace, military, automotive, oil and gas, and tooling. This is due to its performance gains and ability to fabricate complex net shapes directly from 3D models [102–106].

Production of titanium aircraft obtained by traditional manufacturing has a "buy-to-fly" ratio (the ratio between the mass of the raw material employed to produce a component and the component mass itself) of (12–25):1 [107] with respect to (3–12):1 generally used for AM titanium components [108,109]. This allows faster product development and more efficient use of the raw material. Several additive manufacturing techniques are available, which are classified into different categories based on ASTM [110] standards. Direct energy deposition (DED) and powder bed fusion (PBF) are two of the main methods of AM and are characterized by the way the material is delivered into the fusion bath (Table 5).

Table 5. AM technologies suitable for titanium and its alloy processing [111].

AM Process	Technology	Description
Directed Energy Deposition (DED)	Direct Metal Deposition (DMD)	Laser and metal powder for melting and depositing using a patented close-loop process
	Laser-Engineered Net Shaping (LENS)	Laser and metal powder for melting and depositing
	Direct Manufacturing (DM)	Electron beam and metal wire for melting and depositing
	Shaped Metal Deposition or Wire and Arc Additive Manufacturing (WAAM)	Electric arc and metal wire for melting and depositing
Powder Bed Fusion (PBF)	Selective Laser Sintering (SLS)	Laser and metal powder for sintering and bonding
	Direct Metal Laser Sintering (DMLS)	Laser and metal powder for sintering, melting, and bonding
	Laser Melting (LM)	Laser and metal powder for melting and bonding
	Selective Laser Melting (SLM)	Laser and metal powder for melting and bonding
	Laser CUSING	Laser and metal powder for melting and bonding
	Electron Beam Melting (EBM)	Electron beam and metal powder for melting and bonding

An energy source, usually an electron beam [112], plasma arc [113], or laser [114], is necessary for direct energy deposition together with wire or powder feedstock material. The final properties obtained by the DED method are dependent on the environment (ambient, inert gas, or vacuum), beam-material interactions, feedstock characteristics, and deposition parameters (laser powder, laser scan speed, hatch spacing, powder feed rate, and laser scan strategy) [115]. Among others, the wire and arc additive manufacturing (WAAM) technique is one of the most efficient and successful additive manufacturing processes. WAAM is a direct energy deposition process that utilizes wire feedstock and an electric arc as an energy source [116–118]. Many types of arcs, such as plasma arc welding (PAW) [119], gas tungsten arc welding (GTAW) [120], and gas metal arc welding (GMAW) [121], can be utilized as energy sources. WAAM parts often need to be machined to achieve the desired final dimensional tolerances and surface finishes. Studies have demonstrated that WAAM is still more cost-effective than subtractive machining when only an extra machining step is added. This is also linked to the fact that it produces less material waste [122]. Ti-6Al-4V components with mechanical characteristics similar to those obtained by traditional manufacturing procedures can be produced via the WAAM process [118]. However, the control of thermal behavior, which influences the material microstructure, oxidation, and defect generation, is still a challenging task [123]. While DED techniques use a single coaxial nozzle to dispense powder on a substrate, PBF involves spreading powder thinly across the substrate by selectively fusing it with the layer below [124].

The most used PBF processes right now are selective laser melting (SLM) and electron beam melting (EBM) [125]. In SLM, a high-energy laser beam is used to fuse and consolidate small layers of loose powder [126], while in EBM, a high-energy electron beam is used to heat, sinter, and melt the powder.

Compared to EBM, SLM materials tend to be harder and less ductile. Furthermore, unlike SLM machines, the EBM works in a vacuum, thus reducing the risk of oxidation. Another important difference is that the SLM technique can use only metal powder, whereas the EBM technique can use both powder and wire as feedstock material.

Metal wires are easier to find, less expensive, and safer to handle than metal powder. In addition, compared to powder-based systems and other types of metallic AM, wire-feed additive methods provide a greater deposition rate [116]. Nevertheless, it is important to not exceed the increase in the deposition rate because it can cause a reduction in resolution and surface finish.

Despite the disadvantages of the metal powder technique when compared with the metal wire one, it is worth underscoring that the utilization of powder as the starting material allows recycling a significant portion of the material itself, preventing the consumption of precious materials.

Indeed, hundreds of recycling steps are frequently carried out, and sieving operations are often conducted. However, the unmelted metal powder's form, size distribution, surface morphology, and chemistry may all be progressively altered by repeatedly heating and cooling it in a vacuum. Such deterioration can make powder recycling difficult because the manufactured parts do not meet quality standards. Different recycling approaches were described with the aim of reusing the powders 5 to >30 times [127]. They all concur that the mechanical quality of the printed object starts to decrease significantly after a certain number of recycling steps. Many factors can affect a powder's capacity to be reused, including:

(1) The chemical composition of the employed powder. For instance, ASTM F3001–14 [128] and ASTM F2924–14 [129] dictate the chemical composition of Ti-6Al-4V powder to be used in the AM process.
(2) Contamination of the powder employed. Reusing powder can result in the accumulation of several contaminants derived from manufacturing tools, gaseous elements present during AM, and humidity during storage and/or in powder removal systems.
(3) Physical characteristics such as density and flowability. The printing process may fail if the powder loses its flowability. The layer packing density of powder will decrease as a result of the growing porosity. This is caused by the keyhole effect or lack of melting, which will also affect the density of products [130]. Consequently, the mechanical properties of the components, such as tensile and fatigue properties, will be affected.

One of the main problems in both traditional and additive manufacturing is the control of the oxygen level, as titanium has a high affinity for it. At low oxygen concentrations, oxygen atoms enter into the octahedral interstitial sites of the α-phase, improving the properties of the solid solution. On the contrary, at high oxygen levels, embrittlement occurs, which reduces the tensile strength, ductility, and fracture toughness of Ti alloys [131]. One method for preventing air contamination is to process the material in an inert gas chamber, under vacuum, or with a localized inert gas shield. Titanium AM processes like EBM and SLM typically operate in vacuum or inert gas chambers, but preventing contamination remains a challenge for out-of-chamber processes like WAAM [132]. In addition to the oxygen contamination, the AM still has some challenges that need to be resolved, such as the high porosity, the high surface roughness, and the propagation of cracks/voids that impact the product quality. All these defects generally increase with increasing recycling numbers [133]. Moreover, the expensive initial investments required for building the industrial implant and the restricted use of large-scale construction are problems to be taken into account [134,135].

Because of these challenges, AM is not yet considered a fully alternative technique to the classical ones. Several studies reported different methods for improving the quality of metal components produced by AM. However, there is still no optimal direction to produce metal AM components. Recently, with the birth and development of artificial intelligence, new opportunities have been created to face the AM problems [136–138].

4. Titanium Secondary Resources: Recovery and Recycling Technologies

4.1. Recovery of Titanium: Current Technologies

The titanium recycling of post-consumer products is not widely conducted on an industrial scale. This is because titanium is mostly utilized in durable products, including the structural parts of airplane engines (lifetime of about 10 years) and/or biomedical implants (lifetime of about 20–30 years). The ratio of titanium scrap volume to primary titanium sponge production volume is known as the nominal recycling rate. It is less than 1%, which is significantly lower than the recycling rates of other materials such as steel (about 25%), aluminum (36%), and copper (30%). Despite titanium's expensive cost (around 10 €/kg), recycling of the metal is well-established in both the basic sponge melting process and the component machining sector. In this context, the real recycling rate is estimated to be very high (about 90%) compared to that of other metals. It is expected that, if the production cost decreased, titanium would partially replace stainless steel, leading to a severe increase in its demand. This, in turn, would also affect the current recycling status. In this light, there is a strong interest in the recycling and reuse of titanium scraps originating from different processes.

Scraps originating from the Kroll process are iron-contaminated and cannot be used for producing titanium or its alloys (10–20% of total sponge production) [139]. Indeed, during every melting process, iron (present in the steel reactor) diffuses into the titanium sponge, leading to the formation of impurities. The titanium sponge's sides and bottom have extremely high concentrations of iron, which prevent it from being utilized as a raw material. Their main uses are for ferro-titanium products (Fe-Ti alloy) [140] and in the steel industry (its global demand is about 60 kton/year).

Limiting the number of impurities in titanium and alloys, particularly iron, is crucial. In general, the impurity level is rigorously managed to be below some standard values (provided in Table 6) by strictly controlling the composition of commercial titanium and its alloys (and consequently, their price).

Table 6. Quality and levels of impurities in pure titanium and titanium alloys [141].

	Concentration of Element (Mass%)											
	Material	Ti	C (max)	H [BC] (max)	O (max)	N (max)	Fe (max)	Al	V	Sn	Res. [DEF], max each	Res. [DEF], max tot.
Pure Titanium	ASTM Gr. 1	Balance	0.08	0.015	0.18	0.03	0.20	-	-	-	0.1	0.4
	ASTM Gr. 2	Balance	0.08	0.015	0.25	0.03	0.30	-	-	-	0.1	0.4
	ASTM Gr. 3	Balance	0.08	0.015	0.35	0.05	0.30	-	-	-	0.1	0.4
	ASTM Gr. 4	Balance	0.08	0.015	0.40	0.03	0.50	-	-	-	0.1	0.4
α and near-α alloys	ASTM Gr. 6	Balance	0.08	0.015	0.20	0.05	0.50	4–6	-	2–3	0.1	0.4
	ASTM Gr. 9	Balance	0.08	0.015	0.15	0.03	0.25	2.5–3.5	2–3	-	0.1	0.4

Table 6. *Cont.*

Concentration of Element (Mass%)												
α-β alloys	ASTM Gr. 5	Balance	0.08	0.015	0.20	0.05	0.40	5.5–6.75	3.5–4.5	-	0.1	0.4
	ASTM Gr. 23	Balance	0.08	0.012	0.13	0.03	0.25	5.5–6.5	3.5–4.5	-	0.1	0.4

[B] Lower hydrogen may be obtained by negotiation with the manufacturer. [C] Final product analysis. [D] not be reported. [E] A residual is an element present in a metal or alloy in small quantities is inherent to the manufacturing process but not added intentionally. In titanium, these elements include aluminum, vanadium, tin, chromium, molybdenum, niobium, zirconium, hafnium, bismuth, ruthenium, palladium, yttrium, copper, silicon, cobalt, tantalum, nickel, boron, manganese, and tungsten. [F] The purchaser may, in his written purchase order, request analysis for specific residual elements not listed in this specification.

The ingot machining ratio of the titanium alloy parts is very high, and up to 90 wt.% can be turned into a swarf [142]. For example, 90–120 tons of titanium alloy are used for the airframe of the Boeing 787, and about 85 wt.% of this quantity is turned into swarf, which means that about 100 tons of titanium alloy waste are produced. In this case, the swarf must be collected and cleaned to remove impurities like oil and cutting tool pieces. Afterwards, they can be recycled by remelting. However, high-grade titanium ingots cannot be manufactured entirely from titanium scraps because the concentration of oxygen invariably rises after remelting. Remelting titanium scrap with a low-oxygen virgin titanium sponge reduces the oxygen content in practical manufacture. Most of the remelting methods used today, alone and/or in combination, include vacuum arc remelting, cold hearth melting, induction skull melting, and hydrogen plasma arc melting [143–147]. With these processes, it is possible to remove volatile impurities, whereas high melting points and non-volatile metals are difficult to separate. Currently, a large amount of titanium swarf is imported into different states/regions (i.e., the UK, USA, Japan, the Far East, and South Korea) [148,149], where there is a large industry for recycled ingot production. To achieve further progress in titanium recycling worldwide, more remelting facilities must be built. Moreover, new research studies are mandatory for improving the refining of titanium scraps. In fact, despite the high number of reported methods for reducing the oxygen level in titanium products, they are only at a basic stage. Table 7 reports the main studied methods. There are only two industrial processes of titanium refining: the calcium deoxidation of scrap [150] and the molten salt electrolysis (MSE) of titanium sponge [151]. The latter method, involving the electrolysis of $TiCl_4$, attracted high attention, motivated by the green and high-efficiency process developed for other metals. However, the presence of multivalent titanium ions (Ti(II), Ti(III), and Ti(IV)), the low solubility of $TiCl_4$ in molten salts, and unsuitable electrolytic cells [152] make this approach still to be refined. In this process, a low-purity titanium sponge is used as the anode material and chlorine salt mixtures as the electrolyte. The temperature is set at 900–950 °C. The metals with a reduction potential lower than that of Ti^{2+}/Ti ions remain in the bath, whereas those with a higher potential than that of Ti^{2+}/Ti ions remain at the anode [153].

Table 7. Studies of the refining process for titanium scraps [45].

Method	Advantage	Disadvantage
Deoxidation by Ca/CaO [154]	Effective deoxidation	Low or insufficient capability for deoxidation
VIM with $CaAl_2$ [155]	Short process time	Low or insufficient capability for deoxidation
Hydrogen plasma arc melting [156]	Short process time	Low or insufficient capability for deoxidation
Deoxidation of Ti alloy by HDH [157]	Simple process	Low or insufficient capability for deoxidation
Electrochemical deoxidation [158]	Ultra-high capability for deoxidation	Required a molten salt bath
Chlorination with reaction-mediating molten salt [99]	Applicable to most titanium alloys	Required a molten salt bath
FFC process [159]	Titanium production directly from oxides	The process time is too long

Table 7. *Cont.*

Method	Advantage	Disadvantage
OS process [65]	Titanium production directly from oxides	The process time is too long
Hydrogen-assisted magnesiothermic reduction [74]	Effective deoxidation	Multi-step process
Deoxidation during EB remelting with Al [160]	Short process time	Titanium with a high percentage of Al
VIM of TiNi with Ba in a CaO crucible [161]	Short process time	Required a Ba metal for the process
PESR with Ca and CaF_2 flux [162]	Short process time	A VAR process is required to remove residual Ca
Plasma arc melting with Si [163]	Inexpensive deoxidant	Titanium with a high percentage of Si
Leaching after hydrogenation [164]	Suitable for Ti-6Al-4V alloy	Toxic waste solutions are generated
Electrorefining in molten salt [165]	The process can remove almost all impurities	There is contamination from molten salt
Chlorination with $FeCl_x$ chloride waste [166]	It was possible to control impurities	High volatility of $FeCl_x$

4.2. Titanium Scrap Recycling

Despite the fact that machining has been considered an expensive and environmentally unfriendly process, nowadays it is widely used in the aerospace field for titanium component manufacturing. As already stated before, the amount of material scrap left after machining complicated shapes is very high, thus bringing economic losses and environmental issues [167,168]. The scrap recycling process requires energy-consuming techniques, the presence of an inert gas or vacuum, and can be used only for small volumes of materials. About 20 years ago, press-based recycling techniques, such as cold pressing [169], hot extrusion [170], and spark plasma sintering [171], were developed to address the drawbacks of traditional recycling.

Among the most promising methods for recycling metallic scrap, there is technology based on severe plastic deformation (SPD), such as equal-channel angular pressing (ECAP). Luo et al. [172,173], for example, used the ECAP method with temperatures between 400 and 600 °C and back pressure. During consolidation, the particles were forced to change shape, causing the fracture of the oxide surface. A fully dense (greater than 4.50 g/cm^3) bulk product (commercially grade 2 titanium chips) with a grained structure was obtained, possessing strength similar to that of commercially pure titanium. This demonstrated that ECAP can be considered a promising process for recycling the solid state of titanium machining scrap. However, it was observed that the surface of the oxide often did not change its microstructure, causing poor ductility. McDonald et al. [174] demonstrated how it is possible to dissolve the oxide layer by using a mill-annealing treatment after the ECAP process. This allowed us to achieve improved tensile strength and ductility. In these studies, the machining chips tested for the recycled process were prepared with dry milling to avoid complications, whereas lubri-coolants are in general used during machining, and the chip's shape and size change with the machining parameters (feed, speed, and cutting depth). Lui et al. [175] consolidated the recycling of various types of Ti-6Al-4V chips using ECAP with back pressure. They studied the influence of the initial scrap conditions on the microstructure and, in turn, on the mechanical parameters of the final product. The authors found that the obtained mechanical properties were independent of the initial chip conditions. Indeed, the recycled material generally possessed higher tensile ductility (i.e., >10%) and yield stresses (i.e., >900 MPa). These results satisfy the minimum ASTM standards for Grade 5 Ti-6Al-4V and are comparable to or even better than those indicated for commercial alloys. Furthermore, by increasing the number of ECAP passes, recycled material presented improved ductility. Shi et al. [176] also used Ti-6Al-4V chips for ECAP processing, obtaining a near-fully dense (~99.9%) recycled product. They preliminarily compressed the chips into a solid charge, and then they performed the ECAP process at temperatures between 400 and 500 °C with a back pressure between 50 and 250 MPa. They found that the relative density of the recycled product increased as the pressure increased.

The biggest drawback of ECAP is that it is not a continuous process, able to operate only on small samples [177], thus reducing its chances of being used on a large scale in industrial production.

Another technology for recycling titanium chips based on plastic deformation (PD) was proposed by Topolski et al. [178]. It was a direct extrusion synchronized with the cyclically rotating die [179]. The final grained structure was homogeneous with few voids, and the hardness was comparable with that of commercial titanium grade 2. Therefore, the recycled alloy can potentially be intended for similar applications, including the production of wires for additive manufacturing.

More recent research studies have demonstrated that titanium alloy scrap can be recycled using the solid-state field-assisted sintering technology (FAST)-forge process [180]. This technique, also called spark plasma sintering, combines the application of high temperature and uniaxial pressure to promote the solid-state consolidation of titanium powders [181].

Among the SPD processes, the technology that is becoming established in the field is the Conform process, described by Smythe et al. [182]. It is a continuous extrusion-forming process already used in the efficient continuous production of soft aluminum alloy rods as well as copper wires [183]. In this process, chips are fed into the extrusion wheel's profiled groove thanks to a coining roll. After, the groove is closed using a close-fitting shoe. An abutment prevents the continuing material from passing around the wheel. The high temperatures and pressures developed in the roll ensure the plasticity required for the material to pass through an extrusion die.

The wires obtained in the Conform process can be used in metal wire deposition additive manufacturing and fusion welding. This process is important since it can replace the conventional production of titanium wire, which is an expensive process involving numerous steps, i.e., titanium sponge production, vacuum arc melting, and multiple rollings and drawings. Using the Conform process, almost all the waste powder can be transformed into wire with a fine-grained microstructure. Moreover, after reaching the steady state, a relevant improvement in the mechanical parameters (tensile strength and hardness) as well as a reduction in porosity can be observed. Palan et al. [184] showed the possibility of obtaining ultra-fine-grained pure titanium wire using this process. Wilson [185] utilized the Conform process to obtain titanium alloy wire from powder at 900 °C in an argon environment. The typical tensile properties of the continuous extruded material from titanium powder matched those of titanium grades from 1 to 4.

However, depending on the intended application, it is often necessary for further processing to achieve the final desired microstructure. For example, the Conform process is often used in conjunction with ECAP in the literature [186], and their combination can increase the productivity of the ECAP process itself.

4.3. Titanium Powder Recycling

Many recycling processes need to start with titanium and titanium alloys in the form of powders that can be used for sintering or additive manufacturing. Nowadays, metal powder for additive manufacturing is mainly produced using the gas atomization technique [187]. The metal is melted by using a vacuum induction furnace operating at high temperatures, and then it is atomized by a high-pressure (between 0.5 and 4 MPa) jet consisting of an inert gas (i.e., argon and nitrogen) [188]. The entire process is energy-intensive [189] and produces harmful smoke during the metal melting. The most commonly used atomization processes are electrode induction melting gas atomization (EIGA) and plasma processing. They can produce spherical powder by combining a vacuum system with the technology of non-contact melting to avoid impurities. In the EIGA process, titanium scraps are combined with pure titanium sponge. The materials are melted, then fall in a free flow and, thanks to a nozzle, are sprayed in the form of droplets, which solidify into powder. In the plasma atomization process, three non-transferred arc argon plasma torch jets are used to continually feed the wire through their apex. At a temperature of around 10.000 °C, the wire starts to dissolve from the plasma and atomize into fine droplets. Landi et al. [190] evaluated the titanium powder production impact through life cycle assessment (LCA). The results showed that the atomization phase is predominant in terms of impact on global warming potential, water consumption, and acidification potential categories. The atomizer's large argon flow and rapid acceleration to bridge the gap between the injector and the reactor's liquid titanium are the primary reasons for this significant effect [191]. Despite the low sustainability associated with the atomization step, the production of titanium from scrap is still advantageous overall compared to the Kroll method (impact < of about 30%). Thus, titanium scrap recycling for producing high-quality components is feasible, but it is necessary to provide a suitable selection and pre-treatment procedure for scrap [147].

Titanium alloy powders can also be produced by the plasma rotating electrode process (PREP) [45]. In this process, titanium alloy-machined bars are used as the anode, rotating at about 15,000 rev/min while being melted by a plasma arc. The rotation of the anode allows the molten droplets to move away, thanks to centrifugal force. The molten droplets form a powder in a spherical shape spontaneously, minimizing surface energy. Roberts [192] obtained powder with particle sizes ranging from 50 to 350 μm by using a cooling rate of less than 100 °C s^{-1}. In recent years, Sun et al. [193] developed a new production method called granulation-sintering-deoxygenation (GSD). By particle sintering, titanium powders can be produced, forming spherical granules composed of fine titanium particles. The results showed that it is possible to obtain better granules when titanium particle precursors have dimensions lower than a few microns. Since the oxygen content of the powder depends strongly on the processing steps, deoxygenation is necessary. In the work, it was demonstrated that it was possible to maintain the oxygen content lower than 0.1 wt.%, which is a good value for many titanium applications.

Other processes to mention are the hydrogenation-dehydrogenation (HDH) process and ball milling. The HDH process is recognized as the most cost-effective way to produce titanium powders. HDH, coupled with the ball milling approach, was investigated as an alternative process for recovering Ti-6Al-4V waste. Gökelma et al. [194] utilized the powder produced from Ti-6Al-4V swarf as a feedstock for additive technology using the HDH method. They found out that the titanium particle size of the powder was lower than 45 μm. Additionally, the alloying element concentrations, like V, Al, and Fe, were within a standard-suitable range. The HDH step, however, is energy-intensive and requires maintaining specific conditions of pressure and temperature during the process. Furthermore, the shape of the particles is highly angular and unsuitable for additive manufacturing.

Umeda et al. [195] recycled the Ti-6Al-4V chips into fine powder using a ball milling atmosphere (Argon and H_2). With an average particle size of 120 μm, a fine titanium alloy powder was recreated. Ti-6Al-4V powders were produced from machining chips by Soufiani et al. [196] with planetary and shaker milling. They found that 40 h of planetary milling may yield particles as small as 25 μm. The effects of milling time and speed on the particle size, morphology, crystal phases, and oxygen concentration of Ti-6Al-4V powders were investigated by Dikici et al. [197]. They noticed that when the milling time and speed increased, the particle size decreased. Dhiman et al. [198] developed a clean process to transform Ti-6Al-4V swarf into powder feedstock by ball milling. The authors showed that the obtained powder has characteristics comparable to those obtained by gas atomization. Furthermore, LCA analysis revealed that the ball milling process consumed less energy (~59%) and was characterized by lower eco-cost (~82%) and lower global warming potential (GWP) (~68%).

To summarize, Figure 11 shows all the steps that are currently required for the recovery and recycling of titanium swarf.

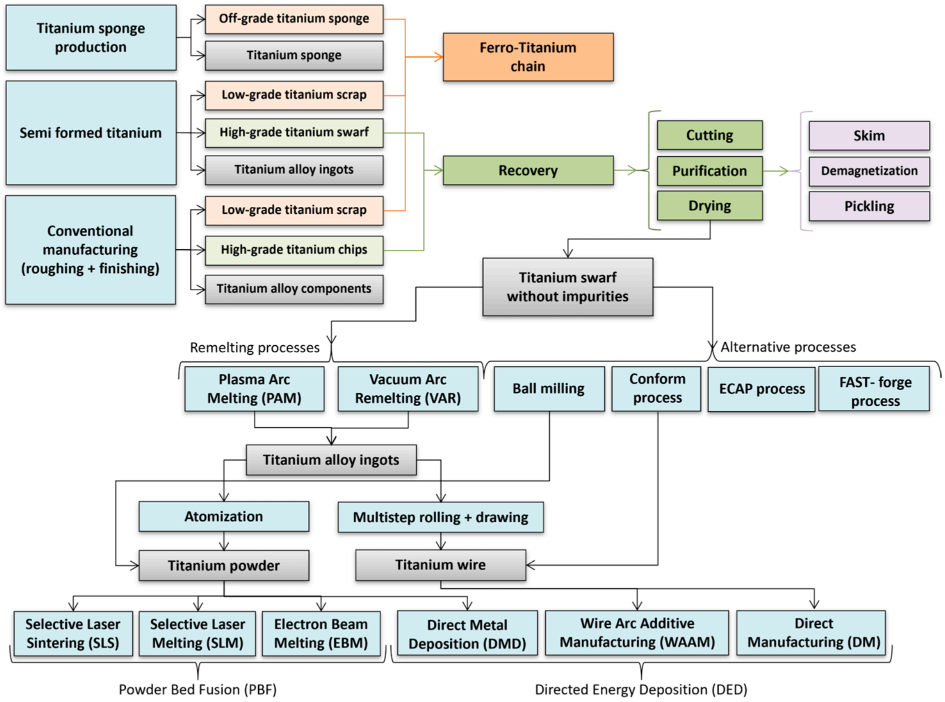

Figure 11. Block flow diagram for titanium recovery and recycling (Light blue—Processes; Light Green—Recyclable materials (Titanium chain); Green—Waste recovery processes; Light Orange—Non-recyclable materials (Titanium chain); Orange—Recycling low-quality materials; Grey—Products or raw materials; Purple—Waste purification processes).

5. Conclusions

The growth of the global titanium and its alloy market has been steady in recent years and is expected to maintain this positive progression until 2030. However, the high cost of this metal, resulting from its complex production, limits its applicability. As for the aircraft industry concerns, the use of titanium (and its alloys) has increased in recent decades. As a result, the amount of titanium waste is expected to increase, making solutions to effectively improve the recyclability of titanium scrap mandatory. Re-use of secondary resources implies better use of primary resources and a reduction of environmental impact related to the production process from the ore.

The main conclusions of this review are summarized as follows:

(i) Currently, the main industrial method used to produce titanium is the Kroll process. The reduction of $TiCl_4$ with the molten metal Mg to produce a titanium sponge is the fundamental step in the Kroll process. However, the process is expensive and energy-intensive;

(ii) Recycling industrial waste is a major issue in many sectors today, as waste poses a critical threat to the environment;

(iii) Despite the potential inherent benefits, titanium recycling of post-consumer products is not widespread on an industrial scale. In addition, subtractive processes, involving a high amount of scrap, are still widely preferred in the production of components for aircraft;

(iv) Additive processes based on both powder (EBM) and wire (WLAM) as starting materials are widely studied in the production of titanium and its alloys. The AM still has some challenges that need to be resolved;

(v) The most promising methods for recycling scrap metal are based on severe plastic deformation (SPD): Equal channel angle pressing (ECAP), solid-state field-assisted sintering (FAST) technology, and the Conform process. The latter has the potential to replace the current production of conventional titanium wire, which is an expensive and multi-step process. However, depending on the intended application, further treatment is often required to achieve the desired final microstructures.

(vi) When additive processes require powders, the gas atomization technique is usually employed, despite the low sustainability associated with the process. Anyway, the production of titanium from atomized scrap is still beneficial compared to its production from ore.

(vii) To realize a sustainable use of titanium scraps and powders, new strategies need to be studied. They should enable the separation of impurity elements from titanium and optimize processing conditions. Moreover, due to the broad range of potential elements in complicated scrap mixes (i.e., V, Al, Fe, Zr, and Cr), a new and broader alloy specification concerning the already established standards is essential. This would help in extending the application markets of the new recycled titanium products.

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