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Review

A Review of the State of Art of Fabrication Technologies of Titanium Aluminide (Ti-Al) Based on US Patents

Shawdon Huang [1,2], Yu-Chien Lin [1,3] and Ren-Jei Chung [1,4,*]

1 Department of Chemical Engineering and Biotechnology, National Taipei University of Technology (Taipei Tech), Taipei 10608, Taiwan; patent@shawdon.com.tw (S.H.); yuchien.lin91@gmail.com (Y.-C.L.)
2 Shawdon Intellectual Property Office, New Taipei City 24445, Taiwan
3 School of Materials Science and Engineering, Nanyang Technological University, Singapore 639798, Singapore
4 High-Value Biomaterials Research and Commercialization Center, National Taipei University of Technology (Taipei Tech), Taipei 10608, Taiwan
* Correspondence: rjchung@ntut.edu.tw; Tel.: +886-2-8772-8701 or +886-2-2771-2171 (ext. 2547); Fax: +886-2-2731-7117

Abstract: This article evaluates the fabrication technologies of titanium aluminide (Ti-Al) and its practical applications by comparing it with the well-known Ti-Al binary phase diagram and US patents. Meanwhile, by analyzing and discussing the various patented Ti-Al fabrication technologies and applications, this article discusses the applications of Ti-Al-based alloys, mainly in the aircraft field. The improved fabrication processes and new application technologies are under patent protection. These technologies are classified into six categories: basic research on Ti-Al-based alloys, powder metallurgy of Ti-Al-based alloys, casting and melting of Ti-Al-based alloys, PM and AM manufacturing methods for aircraft applications, other fabrication technologies by Ti-Al-based alloys, and self-propagating high-temperature synthesis (SHS) of Ti-Al-based alloys. By comparing the principles and characteristics of the above techniques, the advantages, disadvantages, and application fields of each are analyzed and their developments are discussed. Based on the characteristics of Ti-Al, new fabrication and application technologies can be developed, which can overcome the existing disadvantages and be used to form new aircraft components.

Keywords: titanium aluminide; powder metallurgy; casting and melting; coating

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1. Introduction

Conventionally, the turbofan engines of aircraft use nickel-based alloys in the low-pressure turbine blades and high-pressure compressor blades of the aircraft engine. Nickel-based alloys can withstand high temperatures ranging from 650 to 1000 °C [1]. However, the steady improvement in the engine performance and the decrease in the number of compressor and turbine stages have increased the strain on individual-stage blades. Nickel-based alloys have reached their limits, making further enhancements challenging [2,3].

Until now, the most important materials used in gas turbines include high-strength steels, titanium alloys, and nickel alloys. Usually, high-strength steels are used as gear components, compressor casings, turbine casings, and shaft components; titanium alloys are used as aircraft materials for compressor parts, such as turbine engine blades; and nickel alloys are used in some parts of airplane engines [4].

Fortunately, with the increasing industrial demand for titanium aluminide (Ti-Al) alloys [5,6], there is a unique opportunity to develop advanced materials that offer exceptional engineering properties suitable for a wide array of commercial jet engines [7,8] that are also suitable for automobile engines [9,10], but most target applications in this article still will be emphasized in the aircraft industry field. Ti-Al, also referred to as a titanium aluminide intermetallic compound, encompasses $TiAl_2$, $TiAl_3$, α_2-Ti_3Al [11–13], and γ-TiAl, as demonstrated in Figure 1, which presents the Ti-Al phase diagram. Also, the well-known Ti-Al binary phase diagram is the most important phase diagram of Ti alloys. Therefore, the question is, is it possible to evaluate the fabrication technologies of titanium aluminide (Ti-Al) and its practical applications by comparing them with the Ti-Al binary phase diagram and US patents?

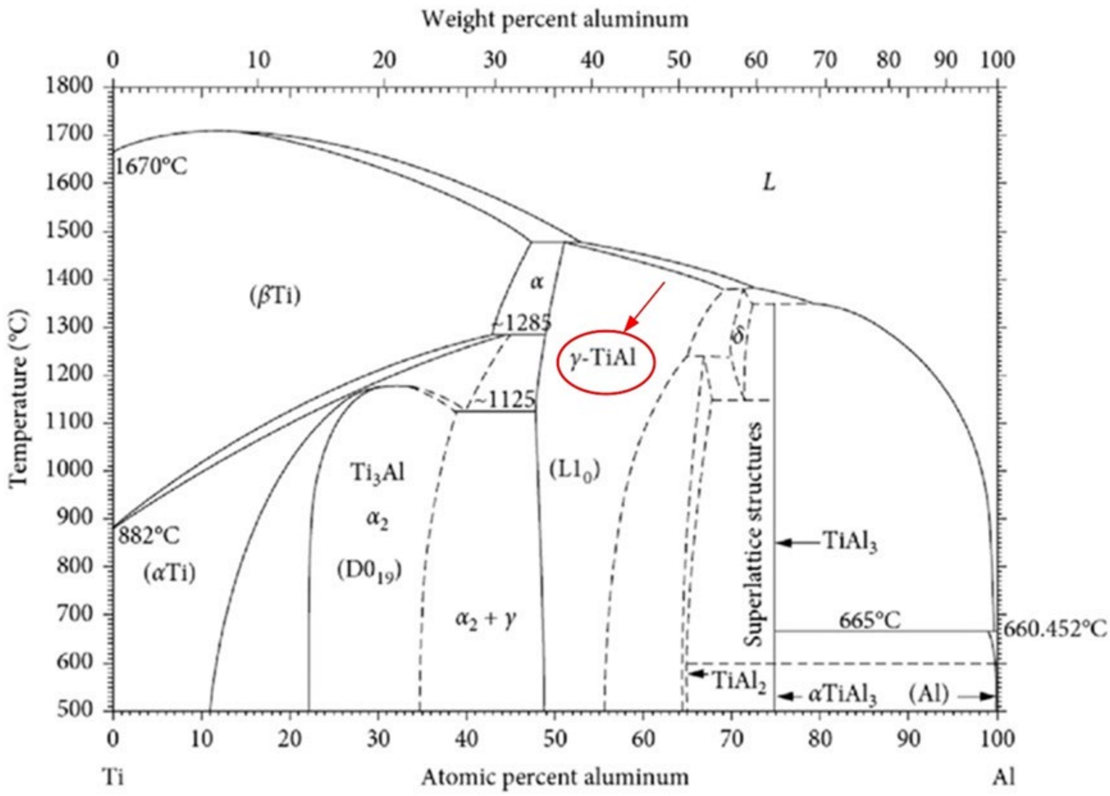

Figure 1. Ti-Al binary phase diagram.

There are two main reasons to focus on US patents in this article. The first reason is, according to the 2007 publication by the European Patent Office, which was named Patents for Researchers, there was the following sentence: "Patents contain detailed technical information which often cannot be found anywhere else: up to 80% of current technical knowledge can only be found in patent documents"; that is, "80% of technical knowledge found only in patents", which is also known to patent professionals in past decades. The second reason is the following: US patents are normally used as measurements for comparison at the 2023 IMD World Competitiveness Yearbook of the International Institute for Management Development (IMD) in Switzerland.

Since 2014, γ-TiAl has been employed in the gas turbine blades of the GEnx aircraft engine by the US General Electric Company [14,15]. Ti-Al-based alloys began to be applied to two types of gas turbine engines, including those used in the Boeing 787 and 747-8 aircraft. GE 48-2-2 [16] was chosen for the low-pressure turbine (LPT) blades of the GEnx engine, which is used in the gas turbine blade of the Boeing 787 aircraft, also, Ti-Al-based alloys help with weight reduction in the range of grams. The utilization of γ-TiAl in a commercial jet engine [17,18] marked a significant milestone. Ti-Al-based alloys entered service in 2011, representing the first large-scale use of γ-TiAl [19].

Figure 1 shows the binary phase diagram for Ti-Al alloys. The Ti-Al binary phase diagram is the most important phase diagram of titanium alloys. Aluminum is as important to titanium as carbon is to iron. Using different compositions of Ti and Al at various temperatures, Ti-Al-based alloys with different crystalline phases can be produced, which offer distinct mechanical properties for various applications [20]. Normally, the most concern area of the Ti-Al binary phase diagram ranges between 49 and 75 at% Al, and temperature between 900 and 1450 °C, which is almost in the γ-TiAl phase zone. The TiAl compounds are formed by peritectic transformations. In this article, the fabrication technologies of titanium aluminide (Ti-Al) and its practical applications are evaluated by comparing the Ti-Al binary phase diagram and US patents.

Ti-Al boasts a density of approximately 3.8 g/cm^3 [21]. Pure titanium has a density of 4.54 g/cm^3, aluminum has a density of 2.70 g/cm^3, and iron's density stands at 7.9 g/cm^3. This makes Ti-Al significantly lighter than steel, with approximately 43% less weight. Remarkably, despite its lower density, the mechanical strength of Ti-Al closely rivals that of steel.

Titanium constitutes a mere 0.44% of the earth's crust by weight, and the global supply of titanium ore currently exceeds 10 million tons. In comparison to aluminum ore, titanium resources are thus considerably scarcer. When considering the application of titanium in the development of Ti-Al materials, the following question arises: if aluminum alloys can be enhanced to deliver comparable results, could their reliance on titanium be significantly diminished? This, in turn, presents a promising prospect for achieving substantial reductions in material costs. Ti-Al materials exhibit a relatively low density and a high elastic coefficient of 165 GPa [22]. Notably, their toughness surpasses that of common ceramic materials. Among superalloys, Ti-Al materials stand out as the lightest with the most outstanding overall mechanical properties, particularly the latest-generation materials known as high Nb-TiAl [23,24]. Ti-Al materials have long been anticipated as the next-generation lightweight and heat-resistant structural materials for aircraft applications. After nearly four decades of research, development, and manufacturing–technology advancement, they have now become available for industry-wide implementation.

2. Review of Manufacturing Methods of Ti-Al-Based Alloys by US Patent Section

This section provides an overview of the US patents related to Ti-Al, presenting comprehensive insights and discoveries pertaining to particle topics from both theoretical and methodological perspectives. The US patents covered here are categorized into six distinct types, ranging from fundamental research to practical applications, with the final category focusing on advanced manufacturing processes.

2.1. Basic Research on Ti-Al-Based Alloys

In 1990, the inventor of US Patent No. 5098653A [25] found that three concentrations of aluminum, 46, 48, and 50 at%, were contained for γ-TiAl.

In 1990, the holder of US patent No. 5032353A [26] recorded that a powder mixture of titanium powder and aluminum powder was prepared, the proportion of titanium powder was 50 mol% and the proportion of aluminum was 50 mol%, and the mixture was sintered by hot isostatic pressing at a temperature of 1300 °C, which was pressed for 3 h and 200 MPa for the product of intermetallic compounds.

In 1990, the innovator of US Patent No. 5015305A [27] mentioned that the high-temperature hydrogenation of γ titanium aluminide was rapidly solidified, wherein approximately 45–55 at% aluminum was contained, which was for the Ti-Al alloy, by heating temperatures in the range of approximately 400–780° C.

In 1991, the holder of US patent No. 5205875A [28] found that according to the approximate formula $TiAl_{46–48}Cr_2Nb_2B_{0.1–0.2}$, the atomic ratio of titanium and aluminum was changed using an effective aluminum concentration, and chromium, boron, and niobium were added.

In 1991, the inventor of US Patent No. 5213635A [29] found that for γ-TiAl, its preferred component was $TiAl_{46–48}Cr_{1–3}Nb_{6–14.}$

In 1993, US Patent No. 5228931A [30] was found to be related to the component of the titanium–aluminum alloy, and its atomic ratio was approximately $TiAl_{45–50}Cr_{1–3}Ta_{1–8}B_{0.1–0.3}$.

In Table 1 as the abovementioned patents, including US patent numbers 5098653A, 5032353A, 5015305A, 5205875A, 5213635A, and 5032353A, the Ti-Al-based alloys would contain approximately 45–55 at% aluminum, according to US patent number 5098653A [31].

Table 1. Ti + Al composition.

US Patent Number	Ti + Al Composition	Other Composition
5098653A	Ti-46Al	none
5032353A	Ti_{50}-Al_{50}	Al_2O_3, Er_2O_3, TiC, or TiB_2
5015305A	Ti-$Al_{45–55}$	none
5205875A	Ti-$Al_{46–48}$	$Cr_2Nb_2B_{0.1–0.2}$
5213635A	Ti-$Al_{46–48}$	$Cr_{1–3}Nb_{6–14}$
5228931A	Ti-$Al_{45–50}$	$Cr_{1–3}Ta_{1–8}B_{0.1–0.3}$

2.2. Powder Metallurgy for Ti-Al-Based Alloys

Generally, the normal typical Ti-Al powder metallurgy process is presented in the following few steps:

(A) First, titanium powders will be mixed with aluminide powders in a stoichiometric ratio;
(B) Then, the die or mold is filled with the titanium and aluminide powders;
(C) Next, it is pressed;
(D) Then, sintering is performed.

In 1991, the holder of US Patent No. 5098650A [32] found a technique for the production of a titanium aluminide alloy. γ-TiAl alloy powder was taken, and then a mold or die with the powder was filled; the powder was solidified at a pressure of 207 MPa [30 ksi], and a temperature of approximately 70–95 °C was set. These steps were quite similar to the previous normal typical Ti-Al powder metallurgy process, except for the different composition powder. In the past, the mold or die was filled with the powder step, especially for examples of TiAl-based alloys, including Ti-50Al, Ti-48Al-1Nb, Ti-48Al-2Nb-2Cr, Ti-48Al-1Nb-IV, and Ti-48A-3Nb-2Cr-1Mn. At that time, this patent could probably be the first one mentioning the Ti-48Al-2Nb-2Cr composition and powder metallurgy technology [33].

Later, in 1993, the inventor of US Patent No. 5424027 [34] proposed that γ-TiAl alloy powder was obtained; the powder was filled into the mold; and the powder was pressed into the mold by hot isostatic pressing (HIP) at a pressure of 207 MPa [30 ksi] and at a temperature below the $\alpha_2 + \gamma$ eutectoid temperature. Ti-50Al, Ti-48Al-1Nb, Ti-48Al-2Nb-2Cr, Ti-48Al-1Nb-1V, and Ti-48Al-3Nb-2Cr-1Mn were included with consolidated titanium aluminum alloys [35].

In 1995, the inventor of US Patent No. 5580665A [36] pointed out that the volume ratio of voids was no more than 3.5%, and the mixture was sintered by the heating process.

In 1996, US Patent No. 5701575A [37] stated that when the mixture could be sintered, which was under the volume ratio of voids not exceeding 3.5%, it was very closed to the fabrication in the previous US Patent No. 5580665A.

In 1996, the holder of US patent No. 5768679A [38] pointed out a basic theoretical property of the mixture of sintered Ti powder and Al powder, and this patent was significantly different from the previous US Patent Nos. 5098650, 5424027, 5580665, and 5701575. In addition, it mentioned that the volume ratio of voids presented in the volume of the Ti-Al intermetallic compound, also known as the “void ratio”, would be approximately 0.2–0.4%, and the “maximum void size” would be less than 20 µm.

In 2000, the innovator of US Patent No. 2002/0184971A1 [39] proposed a method to produce Ti-Al. Firstly, an aluminum subchloride (AlCl) vapor stream was formed, which was then mixed with titanium chloride ($TiCl_4$), and the aluminum subchloride vapor and a chloride reactant reaction were produced. The aluminum trichloride vapor was then separated from the solid metal titanium-based reaction product.

In 2002, the holder of US patent No. 2004/0096350A1 [40] proposed the fabrication for a porous preform of an active powder alloy, including the α-TiAl alloy, γ-TiAl alloy, or any combination of multicomponent Ti-Al alloys by consolidation and sintering in a vacuum. Thermal consolidation was carried out by hot-pressing the preform. Additional sintering was performed at a temperature of 900 °C to consolidate the porous preform with a porosity of 25% by volume, or about 35–65% by volume, so that the active powder alloy, including the α-TiAl alloy, γ-TiAl alloy, or any combination of multicomponent Ti-Al alloys, was consolidated.

In 2004, the inventors of US Patent No. 2006/0037432A1 [41] mentioned that intermetallic alloy nanoparticles, such as Ti-Al, exhibited a variety of interesting structures and many electronic, catalytic, resistive, and magnetic applications. This powder could be produced by technology, including atomization, laser evaporation, and chemical techniques.

In 2004, the holder of US Patent No. 2006/0083653A1 [42] presented a process including the procurement of powder, manufacturing powders, creating components, heat-treating these components to form a predetermined microstructure, and processing HIP. This patented technology could be utilized with any material formed from rapidly solidifying powders, which was produced by powder metallurgy in an insoluble gas (i.e., argon or helium) that was thermally induced porosity in its consolidated and heat-treated form. The materials were made from powders produced by powder metallurgy in argon or helium, which often contained thermally induced pores after heat treatment because neither argon nor helium were soluble in metals, and when heat treated at high temperatures, these gases became mobile and precipitated as pores. Argon-atomized γ-TiAl powder was considered ideal because it presented a fine-grained microstructure with little chemical segregation.

In 2005, the inventor of US Patent No. 2007/0017817A1 [43] proposed that the parts were fabricated using the metal injection molding (MIM) process. These parts were processed on their surfaces through a precise electrochemical machining (PECM) process; therefore, there was no need for a heat-treatment process, and uniform quality was achieved. The volume composition of the metal powder reached between 50 and 70%, and the proportion of binder and plasticizer in the homogeneous mass was between approximately 30 and 50%.

In 2007, the innovator of US Patent No. 2010/0064852A1 [44] proposed a method by which powdered TiAl and Ti_3Al were added into a reaction device. Carrier substances were introduced to the TiAl and Ti_3Al powders to suspend the powder particles. Deoxidizing calcium vapor was provided to the reaction device to facilitate the reaction between the metal powder and calcium vapor; therefore, inclusions from both TiAl and Ti_3Al were removed.

In 2010, the inventor of US Patent No. 2010/0119402A1 [45] proposed that Ti-Al-based alloys are produced using metal droplets obtained from a Ti-Al metal melt through gas atomization. By exposing to halogen-containing gas, the metal droplets are enriched in halogen to obtain halogen-rich Ti-Al metal. The droplet forming the alloy was formed by HIP from halogen-rich Ti-Al metal droplets.

In 2015, the holder of US Patent No. 2016/0059312A1 [46] proposed a production method for titanium–aluminum alloy parts. The titanium–aluminum alloy powder was placed into capsules whose shape corresponded to the desired shape of the part, which was produced. Capsules containing the powder were closed by pressing the ends of the capsule together, and an HIP was performed. After heat treatment, the capsule was removed. The post-process part was contoured by removing material. The technology was particularly suitable for high-temperature titanium–aluminum alloy turbine materials, which were used as high-temperature blades.

In 2016, the innovator of US Patent No. 2017/0175834A1 [47] proposed a method for forming a vehicle brake disc by loading contents into a mold; subsequently, the contents of the mold were heated to the melting temperature, and the contents of the mold were densified by applying pressure to the mold.

In 2017, US Patent No. 2018/0016668A1 [48] stated that the α-TiAl alloy contained, in addition to titanium, 42–48 at% aluminum, 3–5 at% niobium, 0.05–1 at% molybdenum, 0.2–2.2 at% silicon, 0.2–0.4 at% carbon, 0.05–0.2 at% boron, and optionally, tungsten, zirconium and hafnium, as well as unavoidable impurities. Its room temperature microstructure contains, in addition to silicide precipitates, spherical clusters of α_2-Ti_3Al and γ-TiAl lamellae; however, the β phase was absent. Using the method for fabricating a part made of the α-TiAl alloy, the semi-finished product or heat-treated preform in the α phase temperature range was subjected to a second heat treatment at a temperature that was lower, rather than the γ solid solution temperature of the α-TiAl alloy. Material and influence of the γ-Ti were grained to form α_2-Ti_3Al and γ-TiAl lamellae, and the required lamella thickness or spacing was adjusted.

2.3. Casting and Melting of Ti-Al-Based Alloys

In 1994, the inventor of US Patent No. 5417781A [49] described a method for heat treating the alloy to preform at a temperature ranging from approximately Tα (the α-transus temperature) to Tα + 100 °C for about 0.5 to 8 h. The preform was formed at a temperature between Tα and Tα—30 °C so that the desired shape was produced. The obtained shaped article was aged at a temperature between about 750 and 1050 °C for about 2 to 24 h. Examples of such alloy compositions was included by Ti-46Al-2Cr-0.5Mn-0.5Mo-2.5Nb (at%), Ti-47.5Al-2Cr-1V-0.2Ni-2Nb (at%), Ti-47.3Al-1.5Cr-0.4Mn-0.5Si-2Nb (at%), Ti-47Al-1.6Cr-0.9V-2.3Nb (at%), Ti-47Al-1Cr-4Nb-1Si (at%), and Ti-(46–48)Al (at%).

In 1995, the holder of US Patent No. 5942057A [50] stated that Ti-Al intermetallic compound-based alloy material with Ti content of 50–53 at% and Al content of 47–50 at% were directly cast at a cooling rate of 103–105 °C/s.

In 2001, the innovator of US Patent No. 2004/0045644A1 [51] proposed a method for fabricating a flat plate type, which was similar to the intermetallic compound γ-TiAl-based alloy. A layered casting structure was composed of α_2-/γ lamellae and a near-γ structure, a dual-phase microstructure, or a fine-lamellar structure, in which the lamellar casting microstructure gradually was transformed into the other structures.

In 2002, the inventor of US Patent No. 2006/0230876A1 [52] proposed a method for producing metallic and intermetallic alloy ingots, which was achieved by continuous or quasi-continuous casting from cold-wall induction crucibles. Continuous casting of ingots (180 mm diameter and 2,600 mm length) for the production of γ-TiAl-based alloys with a composition of Ti-46.5Al-4 (Cr, Nb, Ta, B) (expressed in at%) was accomplished.

In US Patent No. 2003/0082311A1 [53], patented in 2002, the heating of a metal matrix was preformed with reinforcing fibers in a pressure vessel. The initial processing pressure was below the high-temperature zone, low-temperature zone, or medium-temperature zone of the plastic de-fabrication temperature of the metal matrix. This temperature was maintained for a predetermined preparation treatment time. Examples of such products included the Ti-41-52Al-X alloy (titanium and aluminum intermetallic compound; X was any additive, e.g., Ti-48Al-2Cr-2Nb), the Ti-25Al-10Nb-3V-1Mo alloy (super α_2), the Ti-14Al-19.5Nb-3V-2Mo alloy (Ti3Al intermetallic compound), and the Ti-24Al-11Nb alloy (Ti2AlNb).

In 2002, the innovator of US Patent No. 2004/0094246A1 [54] presented a method in two workpieces that was preheated to a welding temperature of about 927–1149 °C [1700–2100 °F] after they were electron-beam welded together at the welding temperature in a welding vacuum. The welded structure was subsequently annealed at about 982–1204 °C [1800–2200 °F] and was formed as a bonded structure. An example of the composition of a γ-TiAl alloy formed was in 48 at% aluminum, 2 at% chromium, 2 at% niobium, and the balance of titanium and minor impurities, totaling 100 at% (Ti-48Al-2Cr-2Nb) [55,56].

In 2015, the holder of US Patent No. 10570531B2 [57] proposed a process for the preparation of TiAl intermetallic compound single-crystal material. The alloy composition of the material was Ti_a, Al_b, and Nb_c $(C, Si)_d$, wherein $43 \leq b \leq 49$, $2 \leq c \leq 10$, a + b + c =100, and $0 \leq d \leq 1$ (at%). The lamellar orientation of the Ti-Al alloy was controlled through Bridgman directional solidification by changing the solidification parameters, the temperature gradient, and the growth rate. The primary phase was ensured to be a β phase; thereby, single-crystal grains were obtained during the solidification process.

2.4. PM and AM Manufacturing Methods for Aircraft Applications

In 1999, the innovator of US Patent No. 6616408B1 [58] proposed a method for joining gas turbine blade components. A blade–body segment was procured, the end connection areas of the blade–body part were positioned, and another blade part was in alignment, the end connection area of the blade–body part and another blade part were surrounded, the main blade part was welded with the other blade part by energizing the inductor, and, finally, the main blade parts were welded to each other.

In 2002, the holder of US Patent No. 2005/0036893A1 [59] proposed that axially the hub of a Ti-Al turbine rotor was bonded to the preformed steel shaft of the rotor shaft assembly. The preformed steel shaft was axially mounted onto the hub of the press block of the rotor.

In 2002, the inventor of US Patent No. 2005/0036898 [60] proposed that the axial hub of a Ti-Al turbine rotor was bonded to a steel shaft of a rotor shaft assembly. A compacted block of the shaft with the steel powder mixed with a binder, which was axially mounted onto a compacted block of the rotor. The wheel hub contained Ti-Al powder mixed with a binder, and the mounted compact was de-bindered and sintered.

In 2012, the innovator of US Patent No. 2013/0287590A1 [61] described a method for producing gas turbine components; the low-pressure turbine blades were made of Ti-Al materials from powders locally and were selectively sintered in layers through the introduction of radiant energy through local confinement.

In 2012, US Patent No. 2014/0014639A1 [62] presented the fabrication of metallic, ceramic, or composite parts by flash sintering, which was the simultaneous application of uniaxial pressure, and devices with powdered component materials. Turbine blades were made of Ti-Al intermetallic alloys inside a mold or by flash sintering metal/silicide composites.

In 2012, the holder of US Patent No. 10100386B2 [63] proposed that an alloy is made as aluminum, cobalt, iron, iron–nickel, iron–nickel–cobalt, magnesium, nickel, and titanium. The precursor compound is prepared, the precursor compound is chemically reduced to form a metallic alloy, a precursor of the other additive constituent is added, the precursor of the other additive constituent is reacted, and the metallic alloy is consolidated.

In 2013, the innovator of US Patent No. 2015/0129583A1 [64] proposed that the low-pressure turbine blades were produced using Ti-Al materials. The steps included preheating partially produced low-pressure turbine blades through induction heating and performing laser-selective melting during production.

In 2013, US Patent No. 10604452B2 [65] described a microscale composite material, including a titanium matrix, grains, including a first volume fraction of a dispersion of intragranular titanium boride particles, and additional grains, including a second volume fraction of intragranular titanium boride particles.

In 2017, the inventor of US Patent No. 2017/0314402A1 [66] presented a method for producing a blade of a turbine. The blade root and one capsule were filled with metal and/or ceramic powder on a first platform area for producing a blade airfoil.

In 2018, the holder of US Patent No. 2019/0070665A1 [67] proposed a method for manufacturing turbine parts. Firstly, the casing was prepared from the intermetallic Ti-Al material. Then, the mold cavity was filled with a titanium alloy in the powder form. The cavity with the filled titanium alloy powder was sealed, and the inner shell housing the titanium alloy powder was tightly sealed via HIP.

In 2019, the inventor of US Patent No. 2019/0299288A1 [68] described the production of a part made of a Ti-Al alloy. Firstly, a powder of the Ti-Al alloy was procured, and the part with the Ti-Al alloy powder was additively manufactured. The powder was melted to separate the powder particles cohesively bonded to each other, the substrate, or a produced portion of the part. The powder particles were used to form the initial region, the powder particles were used to form the second region, and both were melted under different conditions, resulting in different chemical compositions of the deposited material in the first region and the second region.

In 2019, the innovator of US Patent No. 2019/0376170A1 [69] proposed a method for manufacturing γ-TiAl alloy parts. A forging blank made of a γ-TiAl alloy was made from the powdered material, and then it was reshaped into a semi-finished product. The reshaping degree of the entire forging blank was sufficiently high, and the structure was recrystallized during heat treatment.

In 2015, the innovator of US Patent No. 2023/0211418A1 [70] proposed a method for producing impact-resistant components in part via additive manufacturing methods using the powder material from which the component was formed, mainly from Ti-Al-based alloys. Powders of Ti-Al-based alloys and/or mixtures of powders of individual elements were used to form Ti-Al-based alloys, and about 43.5–48 at% aluminum content was used.

2.5. Other Fabrication Technologies by Ti-Al-Based Alloys

In 1994, the inventor of US Patent No. 5837387A [71] proposed that a coating method was able to protect Ti-Al alloys (including γ-TiAl + α_2-Ti_3Al) from oxidative attack and interstitial embrittlement at temperatures of 1000 °C. This protective coating was mainly composed of titanium, aluminum, and chromium. The atomic ratio was roughly Ti(41.5–34.5)Al(49–53)Cr(9.5–12.5), and the alloy was γ-based or a γ + Lavs alloy. The volume fraction of the TiAl(γ) phase was greater than 0.50, and the volume fraction of the Ti-Cr-Al (Laves) phase was less than 0.50.

In 1995, the holder of US Patent No. 5785775A [72] presented a process for welding γ-TiAl alloys. The articles were made from γ-TiAl alloys, any foreign matter was removed in the preselected area of the product to be welded, the product was brought to the welding temperature, and the temperature of the entire product was stabilized at the welding temperature; the preselected area released the stress, which was welded in the product.

In 2002, the inventor of US Patent No. 2002/0192470A1 [73] proposed a method for grinding and polishing diamonds, which used a grinder element as the main component. The grinder was included with Al, Cr, Mn, Fe, Co, Ni, Cu, Ru, Rh, Pd, Os, Ir, and Pt, intermetallic compounds, and one element was included with Ti, V, Zr, Nb, Mo, Hf, Ta, and W.

In 2008, the innovator of US Patent No. 2010/0038409A1 [74] proposed a method for connecting different parts in aircraft devices. The nano- or microstructured material was set between the first component and the second components, and an exothermic reaction was induced in the nano- or microstructured material to connect with the two components.

In 2013, the inventor of US Patent No. 2013/0143068A1 [75] mentioned that a layer of material was deposited on a workpiece made of a material with aluminum and titanium by localized heating of the workpiece; then, the workpiece was cladded after Ti-Al was deposited on the heated surface through build-up welding.

In 2017, the innovator of US Patent No. 2017/0335436A1 [76] described that parts were produced from Ti-Al alloys by layer-by-layer deposition of powder on a substrate, which was on a produced semi-finished product. The component was shown in aluminum.

In 2017, the inventor of US Patent No. 2021/0276094A1 [77] described a hydrogenation–dehydrogenation method for Ti-Al alloys by hydrogenating the Ti-Al alloy, and its phase was changed to the β phase. The hydrogen-treated Ti-Al alloy was subjected to dehydrogenation at a temperature of 1100–1600 °C.

In 2018, the holder of US Patent No. 11692273B2 [78] presented the preparation of a Ti-Al alloy matrix in which the γ phase accounted for 50% of the total composition of Ti-Al; then, the substrate surface was pretreated. The Ti-Al powder particles were heat treated at the temperature range of 600–1000 °C, and then the heat-treated powder particles were cold sprayed onto the substrate to form a Ti-Al layer. The Ti-Al layer was applied to the substrate, and then the Ti-Al layer was heat treated.

2.6. Self-Propagating High-Temperature Synthesis (SHS) for Ti-Al-Based Alloys

When Ti and Al powders were dry mixed and cold pressed to obtain a compact, which was subjected to heat treatment, such as sintering, a self-propagating high-temperature synthesis (SHS) reaction occurred. SHS is a natural reaction that produces inorganic and organic compounds through exothermic combustion reactions in solids of different properties. SHS was typically performed by heating one end of the reactant with an external heat source, such as a heated tungsten coil. The combustion wave was self-propagated to the other side of the reactants on its own without the need for another heating source [79,80].

For Ti-Al, the reaction mechanism was the following: the aluminum particles were melted, and then the solid titanium particles were dissolved in the molten aluminum pool. Ti and Al were undergoing an exothermic reaction to form Ti-Al, according to Ti + Al = Ti-Al [81].

The Kissinger–Akahira–Sunose (KAS) equation is as follows, as stated by H. Sina and S. Iyengar's article titled "Reactive synthesis and characterization of titanium aluminides produced from elemental powder mixtures" in the "Journal of Thermal Analysis and Calorimetry".

$$\ln \frac{\beta}{T_P^2} = \frac{E_a}{RT_P} + C, \tag{1}$$

where β is the linear heating rate (K/min), Tp is the reaction peak temperature (°C + 273.15), R is the universal gas constant (J/mol [°C + 273.15]), C is an independent constant, and E_a is the activation energy (J/mol) [82], and the formula for converting Kelvin to Celsius is °C + 273.15 = K.

3. State of the Art of the Results and Discussion according to the Review of Manufacturing Methods of Ti-Al-Based Alloys by US Patent Section

Section 2 reviews the manufacturing methods of Ti-Al-based alloys by US patent section, which provides results of classified US patents into six categories. Section 3 is the results and discussion, which are performed to analyze classified US patents; therefore, Section 3 is related to content such as comparisons with classified US patents in Section 2. Obviously, the resource of Section 3 is from Section 2, but the content in Section 2 is totally different than Section 3.

Table 2 presents the five main different research topics mentioned in the previous section.

Table 2. The five research topics.

Research Topics	Total
(1) Basic research on Ti-Al-based alloys	6
(2) Powder metallurgy of Ti-Al-based alloys	16
(3) Casting and melting of Ti-Al-based alloys	7
(4) PM and AM manufacturing methods for aircraft applications	13
(5) Other fabrication technologies by Ti-Al-based alloys	8
Total	50

Table 2 shows the developments in Ti-Al-based alloys from 1990 to 2021, which are analyzed in this work based on 50 collected patents. The technological development of Ti-Al-based alloys has been faster than before.

(1) Regarding the "Basic research on Ti-Al based alloys", the main parameters of composition, solidification structure, fracture strength, and heat-treatment temperature are analyzed based on six patents.
(2) In the "Powder metallurgy of Ti-Al based alloys" section, 16 patents are analyzed to obtain fabrication regarding the main parameters of stoichiometric, pressing, and high-temperature sintering techniques.
(3) In the "Casting and melting of Ti-Al based alloys" section, seven patents are studied to obtain the main parameters of stoichiometry and temperature.
(4) In the "PM & AM manufacturing methods for aircraft applications" part, 13 patents are studied to obtain the main parameters of materials and the application part.
(5) In the "Other fabrication technologies by Ti-Al based alloys" part, the main parameters of materials and their applications are studied based on eight patents.

In addition, because the abovementioned SHS is one type of natural reaction under high-temperature sintering during the synthesis of Ti-Al-based alloys, the following is not mentioned again.

"Powder metallurgy of Ti-Al based alloys" is the most focused-on research topic, with approximately 16 patents. The second topic is the "PM & AM manufacturing methods for aircraft applications", with approximately 13 patents. On the other hand, "Powder metallurgy for Ti-Al based alloys" is possibly the most important research development field for Ti-Al, while "PM & AM manufacturing methods for aircraft applications" is the most important application field for Ti-Al-based alloys.

According to Table 2, "Basic research on Ti-Al based alloys" is the early research development field, with approximately six patents. The "Casting and melting of Ti-Al based alloys" is the second most important research development field after "Powder metallurgy for Ti-Al based alloys", with approximately seven patents, and "Other fabrication technologies by Ti-Al based alloys" contains only approximately eight articles, which is very close to the value for "Casting and melting of Ti-Al based alloys".

3.1. Analysis of 2.1. Basic Research on Ti-Al-Based Alloys

Most of the patents are public and were disclosed in the early 1990s, i.e., from 1990 to 1993. Therefore, the basic knowledge of Ti-Al-based alloys is developed and is much more clearly understood during this period of time. Also, at this time, the technology for developing the components of the basic research on Ti-Al-based alloys from these six patents was selected by the casting and melting methods, and there were no more other technologies, such as powder metallurgy, used. It is worth knowing that the yield of the casting and melting methods could be easier than the yield of powder metallurgy, and the step of casting and melting methods is shorter than the step of powder metallurgy, and it is easy to observe the components of the production of casting and melting methods rather than and the production of powder metallurgy.

The most common compositions (at%) of the Ti-Al-based alloys are illustrated in Table 3 [83–85]. Therefore, Table 3 presents basic research data so that Ti-Al patents can be analyzed in terms of the solidification process by changing the Ti-Al-based alloy composition (at%), processing temperature, and mechanical properties.

The composition of Ti-Al-based alloys: owing to the small equiaxed crystals exhibited in US Patent No. 5098653, the microstructure of Ti-46Al could be the better crystal form in the castings, so that the "alloy composition (at%)" in the basic research for TiAl-based alloys is 46 at% and the "temperature" is about 1250 °C.

According to Table 3, also, referring to the Ti-Al binary phase diagram in Figure 1, all the different alloy compositions for the condition of basic research for TiAl-based alloys are collected and located from the γ-TiAl phase zone the red circle] of the Ti-Al binary phase diagram.

Table 3. Conditions of basic research on Ti-Al-based alloys.

Alloy Composition (at%)	Solidification Structure	Fracture Strength (MPa)	Heat-Treatment Temperature (°C)
Ti-43Al-12Nb (635)	fine equiaxed	703.8	1250
Ti-44Al-10Nb (635)	fine equiaxed	752.1	1250
Ti-44Al-12Nb (635)	fine equiaxed	662.4	1250
Ti-44Al-16Nb (635)	fine equiaxed	676.2	1275
Ti-44Al-2Cr-8Nb (635)	fine equiaxed	600.3	1275
Ti-46Al (635, 653)	large equiaxed	386.4	1250
$Ti_{54}Al_{46}$ (875)	none	910.8 (anneal)	1250
Ti-46Al-2Cr (635,653)	large equiaxed	365.7	1250
$Ti_{52}Al_{46}Cr_2$ (931, 875)	none	1173 (anneal)	1250
$Ti_{50}Al_{46}Cr_4$ (931,875)	none	738.3 (anneal)	1250
$Ti_{50}Al_{46}Nb_4$ (931,875)	none	1152.3 (anneal)	1250

Table 3. *Cont.*

Alloy Composition (at%)	Solidification Structure	Fracture Strength (MPa)	Heat-Treatment Temperature (°C)
Ti-46Al-10Nb (635)	equiaxed	683.1	1250
Ti-46Al-12Nb (635)	equiaxed	662.4	1250
Ti-46Al-2Cr-8Nb (635)	equiaxed	552	1250
Ti-46Al-2Cr-12Nb (635)	equiaxed	531.3	1250
Ti-46Al-2Cr-16Nb (635)	fine equiaxed	462.3	1250
Ti-47Al-2Cr-8Nb (635)	columnar	476.1	1250
Ti-48Al (635,653)	columnar	496.8	1250
$Ti_{52}Al_{48}$ (931,875)	none	1242 (anneal)	1250
Ti-48Al-2Cr (635,653)	columnar	414	1250
Ti-48Al-2Cr-6Nb (635)	large equiaxed	476.1	1250
Ti-48Al-2Cr-12Nb (635)	columnar	531.3	1250
$Ti_{50}Al_{48}Cr_2$ (931,875)	none	903.9 (anneal)	1250
$Ti_{48}Al_{48}Cr_4$ (931,875)	none	979.8 (anneal)	1250
Ti-48Al-6Nb (635)	columnar	476.1	1275
Ti-48Al-10Nb (635)	columnar	476.1	1275
Ti-48Al-16Nb (635)	equiaxed	420.9	1275
Ti-50Al (635,653)	columnar equiaxed	289.8	1250
$Ti_{50}Al_{50}$ (875)	none	634.8	1250
Ti-50Al-2Cr (635,653)	columnar equiaxed	414	1275
$Ti_{46}Al_{50}Cr_4$ (931,875)	none	959.1 (anneal)	1250
Ti-50Al-6Nb (635)	columnar	303.6	1325
Ti-50Al-12Nb (635)	columnar	345	1325
$Ti_{48}Al_{50}Cr_2$ (931,875)	none	841.8 (anneal)	1250

Huang Shyh-Chin, "653" for US Patent No. 5098653, "875" for US Patent No. 5205875, "635" for US Patent No. 5213635, and "931" for US Patent No. 5228931.

3.2. Analysis of 2.2. Powder Metallurgy of Ti-Al-Based Alloys

Powder metallurgy for Ti-Al-based alloys is the topic most focused on by researchers in the field of materials sciences. Powder metallurgy is a technology that continues to develop rapidly and covers most metal and alloy materials of various shapes, according to the introduction page of the European Powder Metallurgy Association. Powder metallurgy technology involves the following steps: (1) Mixing elemental or alloy powders; (2) compacting the mixture in a mold; and (3) heating or sintering the resulting shape in a controlled-atmosphere furnace to completely metallurgically bond the particles.

Powder metallurgy for Ti-Al-based alloys from these 16 patents is a much more complex technology than the casting and melting methods. Rather than the coating, there are more than some fabrication steps for powder metallurgy. However, since the melting temperature of the casting and melting methods could be higher than the sintering temperature of powder metallurgy, powder metallurgy could be a much more popular technology for developing Ti-Al-based alloys; one of the possible reasons is the pressing step, which can provide more solidification energy for combining the article as combination situation at the sintering step.

The "mixing elemental or alloy powders" step of powder metallurgy is clearly known by the void size, void ratio, and volume ratio of voids, according to these 16 patents.

Table 4 presents the conditions for "compacting the mixture in a mold" and "heating or sintering the resulting shape in a controlled atmosphere furnace, in order to metallurgically bond the particles for the powder metallurgy process", including the conditions for the "stoichiometric composition", "pressing", and "high-temperature sintering technique". All of the 16 patents were filed between 1991 and 2017.

Table 4. Conditions of powder metallurgy for Ti-Al-based alloys.

Patent Number	Stoichiometric Composition	Pressing	High-Temperature Sintering Technique
5098650	Ti-50Al, Ti-48Al-Nb, Ti-48Al-2Nb-2Cr, Ti-48Al-Nb-lV, and Ti-48A-3Nb-2Cr-lMn	207 MPa [30 ksi]	HIP; temperature not shown
5424027	Ti-48Al-2Nb-2Cr (atomic%)	207 MPa [30 ksi]	HIP; temperature 1290 °C, 1350 °C, and 1400 °C
5580665	Ti:Al = 83:17 to 10: 90(%), Ti:Al = 65.8%:34.2%	34.3 MPa [350 kgf/cm^2]	HIP; temperature from 600 to 1400 °C
5701575	Ti:Al = 83:17 to 10:90(%), 65:35 to 50:50 (%)	34.3 MPa [350 kgf/cm^2]	HIP; temperature from 600 to 1400 °C
5768679	Ti:Al = 65.8%:34.2%	34.3 MPa [350 kgf/cm^2]	HIP; temperature from 600 to 1000 °C, 1350 °C
2002/0184971A1	TiAl, Ti_3Al, and $TiAl_3$	NONE	temperature from 500 °C to 700 °C
2004/0096350A1	(1) 50 at% Ti and 50 at% Al (2) 40 wt% of the TiAl alloy, 30 wt% of the elemental Ti and Al powder blend, and 30 wt% of the hydrogenated TiAl alloy powder (3) Ti-48Al-4Nb-2Mn-0.5Si alloy reinforced with 1.2 wt% of TiB particles (4) layering titanium, Ti-6Al-4V alloy, Ti_3Al, Y-TiAl, Ti_3Al, Ti-6Al-4V alloy, and titanium powders	4.9 MPa [50 kgf/cm^2]–34.3 MPa [350 kgf/cm^2]	HIP; temperature in 1250 °C and 1350 °C
2006/0037432A1	TiAl compositions including 25–35 wt% Al and Ti-Al alloy powder	NONE	NONE
2006/0083653A1	Ti-46Al-3.7(Nb, Cr, Mo)-0.4(B, C)	NONE	HIP; temperature from 925 to 1320 °C
2007/0017817A1	Ti base alloy powder and TiAl alloy powder	NONE	NONE
2009/0311123A1	Al and TiO_2 powders	10–50 MPa, 200 MPa	700–800 °C
2010/0064852A1	69.6 wt% Ti-26.7 wt% Al-3.7 wt% O and 80 wt%Ti-10 wt% Al-5 wt% V-5 wt% O	50 kPa	1100 °C
2010/0119402A1	Ti-zAl-yNb-xB with 44.5 at% $\leq$ Z $\leq$ 47 at%, 5 at% $\leq$ Y $\leq$ 10 at%, and 0.05 at% $\leq$ X $\leq$ 10 0.8 at%, 0.1- 3 at% Mo	NONE	1320 °C
2016/0059312A1	TiAl alloy, one or more elements is selected by Nb, Mo, W, Co, Cr, V, Zr, Si, C, Er, Gd, Hf, Y, and B	NONE	HIP; temperature from 1100 to 1400 °C
2017/0175834A1	metal intermetallic, including TiAl, Ti_3Al, and $TiAl_3$	NONE	spark plasma sintering (SPS); temperature not shown
2018/0016668A1	Ti, 42–48 at% Al, 3–5 at% Nb, 0.05–1 at% Mo, 0.2–2.2 at% Si, 0.2–0.4 at% C, 0.05–0.2 at% B, 0–2.0 at% W, 0–3.5 at% Zr, and 0–0.3 at% Hf Ti, 43–45 at% Al, 3.5–4.5 at% Nb, 0.85–0.95 at% Mo, 0.25–0.35 at% Si, 0.25–0.35 at% C, and 0.05–0.15 at% B Ti, 43.5–45 at% Al, 3.5–4.5 at% Nb, 0.1–0.5 at% Mo, 0.4–1 at% W, 0.25–0.35 at% Si, 0.25–0.35 at% C, and 0.05–0.15 at% B Ti, 43.5–45 at% Al, 3.5–4.5 at% Nb, 0.85–0.95 at% Mo, 0.1–3 at% Zr, 0.25–2.2 at% Si, 0.25–0.35 at% C, and 0.05–0.15 at% B Ti, 46–48 at% Al, 3.5–5 at% Nb, 0.1–0.5 at% Mo, 0.4–1.8 at% W, and 0.1–3 at% Zr	NONE	temperature 900 °C

US patents 5424027, 5580665, 5701575, 5768679, 2004/0096350A1, and 2016/0059312A1 in Table 4 all show that the sintering temperature is almost around 1400 °C. Why is the sintering temperature quite close to the melting point at 1500 °C? Because at the powder metallurgy process, the sintering temperature normally would be two-thirds of the melting point; in other words, the sintering temperature could be 1000 °C or more than 1400 °C, which is too much in these previous six patents, and this could be an unknown shortcoming.

The "stoichiometric compositions" in the conditions of powder metallurgy for Ti-Al-based alloys are presented in Table 4, and according to these, the highest aluminum percentage in TiAl is about 42 to 50 at%.

The "pressing" condition for powder metallurgy of Ti-Al-based alloys is presented in Table 4. Only eight different pressing conditions are provided in these sixteen patents, which are calculated by 207 MPa [30 Ksi] in two patents, 34.3 MPa [350 kgf/cm^2] in three patents, 4.9 MPa [50 kgf/cm^2]–34.3 MPa [350 kgf/cm^2] in one patent, 10–50 MPa and 200 MPa in one patent, and 50 kPa in one patent. In another five patents, the pressing conditions are not clearly disclosed; therefore, it is assumed that the pressing conditions are not very important in the powder metallurgy process of Ti-Al-based alloys; on the other hand, the pressing condition is not seriously affected by the fabrication condition in the powder metallurgy process.

The conditions for the "high-temperature sintering technique" in the powder metallurgy of Ti-Al-based alloys are also presented in Table 4. Eight patents mention "HIP" only, with no other in the fabrication condition of the powder metallurgy process. The temperatures are mentioned in the patents at about 1350 °C in six patents, 1320 °C in five patents, and less than/equal to 1100 °C in four patents. Another four patents mentioned no temperature conditions. Therefore, more than half of the patents, including 11 patents, support the temperature for the high-temperature sintering technique condition being more than 1320 °C.

Therefore, the stoichiometric composition and high-temperature sintering technique conditions presented in Table 4 indicate that the aluminum percentage in Ti-Al is about 42–50 at%. Therefore, sintering through HIP is at high temperatures above 1320–1350 °C.

According to Table 4 and referring to the Ti-Al binary phase diagram in Figure 1, all the different alloy compositions for the condition of basic research for Ti-Al-based alloys are collected and located from the γ-TiAl phase zone [the red circle] of the Ti-Al binary phase diagram as Figure 1.

3.3. Analysis of 2.3. Casting and Melting of Ti-Al-Based Alloys

Generally, casting and melting is a manufacturing process in which a liquid material is poured into a prepared mold containing a cavity of a desired shape and is solidified. Even though powder metallurgy can solve many engineering problems, such as material densification, the wide range of complex applications require various degrees of casting and melting methods [86]. Different requirements can be met by adding different chemical elements or different process temperatures, thus necessitating advanced research on the different casting and melting methods. This paper reviews the methods for improving the workability of the casting and melting methods by adding different chemical elements and changing the process temperatures.

No doubt, the casting and melting methods from these seven patents are quite a long conventional technology for the metal industry, and the appeared time could be longer than the powder metallurgy process; there are fewer fabrication steps than powder metallurgy. However, the single-crystal production for the gas turbine of aircraft still relies on the casting and melting methods made, in particular, US patent 10570531B2, which was named the TiAl intermetallic compound single-crystal material. The preparation method, which belongs to the casting and melting methods, is the only key-point technology for fabricating the single crystal of the blade component; there is no other mature technology replaced. On the other hand, when there is no casting and melting, there is no blade component.

Table 5 presents the different conditions for the casting and melting process. All the patents reviewed are from 1994 to 2015. However, the public development of these patents on the casting and melting processes for Ti-Al is quite less than that in the powder metallurgy field.

The "stoichiometric composition (at%)" conditions in the casting and melting of Ti-Al-based materials are presented in Table 5, according to which the Al percentage in Ti-Al-based materials is about 44–53 at%.

Table 5. Conditions for the casting and melting of Ti-Al-based alloys.

Patent Number	Stoichiometric Composition	Temperature
5417781	Binaries: Ti-(45–49)Al(at%) Multicomponent alloys: Ti-(45–49)Al-(1–3)x-(2–6)Y, where X is Cr, V, Mn, W, or any combination thereof, and Y is Nb, Ta, or any combination thereof (at%); above alloys with additions of small amounts (0.05–2.0 at%) of Si, B, P, Se, Te, Ni, Fe, Ce, Er, Y, Ru, Sc or Sn, or any combination thereof	1360–1400 °C
5942057	Ti-Al(Ti: 50–53 at%, Al: 47–50 at%)	800–1100 °C
2004/0045644A1	Ti-Al$_{(44–48)}$(Cr, Mn, V)$_{0.5–5}$(Zr, Cu, Nb, Ta, Mo, W, Ni)$_{0.1–10}$(Si, B, C, Y)$_{0.05–1}$ (in at%).	900–1400 °C

2006/0230876A1	Ti_xAl_y(Cr, Mn, V)$_u$(Zr, Cu, Nb, Ta, Mo, W, Ni)$_{v,}$ (Si, B, C, Y)$_w$ with the concentrations in the following ranges (in at%):
	x =100 – y – u – v − w 0026;
	y = 40–48, preferably 44–48;
	u = 0.5 to 5;
	v = 0.1 to 10;
	w = 0.05 to 1
		1400–1750 °C

2003/0082311A1	Ti-41-52Al-X alloy (titanium and aluminum intermetallic compound: X is any other additive, such as in Ti-48Al-2Cr-2Nb); Ti-14A1-19.5Nb-3V-2Mo alloy	500–700 °C; preferably 600 °C
2004/0094246A1	Ti-48Al-2Cr-2Nb	982–1204 °C [1800–2200 °F]
10570531B2	$Ti_aAl_bNb_c(C, Si)_d$, wherein $43 \leq b \leq 49$, $2 \leq c \leq 10$, a + b + c + d = 100, and $0 \leq d \leq 1$	1250–1350 °C

The "temperature" conditions for the casting and melting of Ti-Al-based materials are also presented in Table 5, according to which the suitable temperature is estimated to be approximately 1350 °C.

Therefore, according to the stoichiometric compositions, the most suitable aluminum percentage in Ti-Al-based materials is about 44–53 at%, and the temperature is between 1250 and 1350 °C. The conditions for casting and melting are collected and are located in the γ-TiAl phase zone of the Ti-Al two binary phase diagram presented in Figure 1.

3.4. Analysis of 2.4. PM and AM Manufacturing Methods for Aircraft Applications

The aircraft gas turbine is a continuous-flow internal combustion engine that uses compressed gas to rotate and generate kinetic energy for use in aircraft or jet engines. The turbine blade is defined as a radial airfoil located at the edge of the turbine disk of the gas turbine, wherein each disk holds many turbine blades that generate the Ti-Al force that causes the turbine rotor to rotate. Single-crystal alloys are widely used in the fabrication of gas turbine blades of aircraft, owing to their excellent high-temperature properties.

Investment casting and forging are the conventional fabrication methods for gas turbine engine parts. High-stress gas turbine engine parts made from titanium, nickel, or high-strength steel, such as compressor parts, are forged parts. In contrast, turbine parts are manufactured as investment cast parts for gas turbine engines made of titanium.

Table 6 presents the conditions for aircraft applications. The patents are proposed between 1999 and 2023. Many low-pressure turbine blades for gas turbines or aircraft turbine components are made using Ti-Al-based alloy materials.

Table 6. Conditions for PM and AM manufacturing methods for aircraft applications.

Patent Number	Applied Materials	Application Part
6616408B1	TiAl through powder metallurgy	blade and rotor of gas turbine
2005/0036893A1	TiAl powder	rotor shaft assembly
2005/0036898	TiAl powder	rotor shaft assembly
2013/0287590A1	TiAl	aircraft turbine components
2014/0014639A1	An "alloy based on TiAl", which is an alloy including 40%, preferably 45% of Ti and 40%, and preferably 45% of Al	turbine blade of near-finished dimensions
10100386B2	Ti, Al, Fe, Ni, Co, Fe-Ni, Fe-Ni-Co, and Mg	gas turbine compressor blade
2015/0129583A1	TiAl powder	low-pressure turbine blade
10604452B2	Ti-base composition, B, and a stable-oxide-forming additive element	aircraft gas turbine engines
2017/0314402A1	γ-TiAl alloy including W, Mo, Nb, Co, Hf, Y, Zr, Er, Gd, Si, and C	turbomachine blade
2019/0070665A1	TiAl intermetallic material	turbomachines
2019/0299288A1	powder made of the TiAl alloy	gas turbines; aircraft turbines
2019/0376170A1	γ-TiAl powder with a composition including 43.5 at% Al, 4 at% Nb, and 1 at% Mo, along with Ti	turbomachine, a blade, or a blade segment
2023/0211418A1	TiAl alloy including 43.5–48 at% Al, 4–6 at% Nb, and any of elements Mo, W, Zr, Si, C, and B in total up to 2 at%	turbomachine

The "applied materials" in the PM and AM manufacturing methods for aircraft applications are presented in Table 6, along with the "application part". According to these, the conditions for the PM and AM manufacturing methods for aircraft applications are used for producing gas turbine parts, including the turbocharger, turbine blade, turbomachine, blade of the gas turbine, rotor of the gas turbine, gas turbine compressor blade, the low-pressure turbine blade, compressor blades, and fan-disk blades.

Again, powder metallurgy for Ti-Al-based alloys could be the much more popular technology for manufacturing the blades and rotors of gas turbines, turbine blades of near-finished dimensions, etc., such as 6616408B1, 2005/0036893A1, 2005/0036898, 2014/0014639A1, 2015/0129583A1, 2019/0299288A1, 2019/0376170A1, and 2023/0211418A1. When the complex parts of the gas turbine of the aircraft is increased in demand, powder metallurgy will be much more important to the aircraft than before.

3.5. Analysis of 2.5. Other Fabrication Technologies by Ti-Al-Based Alloys

So far, this article provides an overview of the production and utilization of Ti-Al-based alloy materials, with a particular focus on applications in gas turbine components, such as blades, rotor-shaft assemblies, and aircraft turbines; therefore, Ti-Al-based alloy materials can be widely applied to some other fabrications, including coating, grinding and polishing, the joining method, surface enhancement, hydrogenation–dehydrogenation, etc., as shown in eight patents, and this could be one of the advantages of Ti-Al-based alloy materials.

Table 7 presents the other fabrication technologies by Ti-Al-based alloys; these patents were applied between 1999 and 2022.

The applied materials and the application field of the other technologies for Ti-Al-based alloys are presented in Table 7. The other fabrication technologies by Ti-Al-based alloys are selected and located in the surface enhancement technologies field, including coating [87], welding, grinding and polishing, joining, hard facing, repair, creating parts of Ti-Al-based alloys as raw materials using layer-by-layer deposition, hydrogenation–dehydrogenation, and coating of Ti-Al-based alloys [88] on the substrate by applying powder on the substrate and/or the prepared semifinished products, which all are widely used in some technical fabrications and application fields.

Table 7. Conditions for other fabrication technologies by Ti-Al-based alloys.

Patent Number	Applied Materials	Application Field
5837387	Ti-47Al-2Cr-4Ta, Ti(41.5–34.5)Al(49–53)Cr(9.5–12.5)	coating
5785775	Ti-48Al-2Cr-2Nb	welding
2002/0192470A1	Ti-Al intermetallic compound polishing grinder, TiC, TiAlC, and TiAICN	grinding and polishing
2010/0038409A1	TiAl, Ti_3A1, or $TiA1_3$	joining method
2013/0143068A1	TiAl	surface enhancement
2017/0335436A1	TiAl alloy	TiAl alloy produced by layer-by-layer deposition of powder on a substrate
2021/0276094A1	TiAl alloy	hydrogenation–dehydrogenation
11692273B2	TiAl alloy	TiAl alloy on a substrate

In the section on the "basic research on Ti-Al based alloys", the analysis of the basic research on Ti-Al-based alloys showed that Ti-Al-based alloys mostly contained approximately 43–50 at% aluminum. Moreover, the crystal of Ti-46Al is found to be formed in castings, with a preference for small equiaxed crystals, which could be achieved at high temperatures of approximately 1250 °C. The optimal alloy composition (at%) is estimated to be 46 at%. Referring to the Ti-Al binary phase diagram in Figure 1, the most concerning area of the Ti-Al binary phase diagram ranges between 49 and 75 at% Al, and temperature between 900 and 1450 °C, such as the γ-TiAl phase zone, so the main conditions obtained during the "basic research on TiAl based alloys" are selected and located in the γ-TiAl phase zone [the red circle] of the Ti-Al binary phase diagram in Figure 1.

In the section on the "powder metallurgy process of Ti-Al based alloys", the operating procedures of the various powder metallurgy process are explained, emphasizing the different steps and conditions of the method. According to the stoichiometric composition, the most preferred aluminum percentage in TiAl is about 42–50 at%, and the preferred sintering temperature for HIP is 1320–1350 °C, such as the γ-TiAl phase zone, so the main conditions obtained during the "powder metallurgy process of Ti-Al based alloys" are selected and located in the γ-TiAl phase zone [the red circle] of the Ti-Al binary phase diagram in Figure 1.

In the section on the "casting and melting of Ti-Al based alloys", according to the stoichiometric composition, the most preferred aluminum percentage in TiAl is about 44–53 at%, and temperature is from 1250 to 1350 °C, such as the γ-TiAl phase zone, so the main conditions obtained during the "casting and melting of Ti-Al based alloys" are selected and located in the γ-TiAl phase zone [the red circle] of the Ti-Al binary phase diagram in Figure 1.

As is well known, the Ti-Al binary phase diagram is the most important phase diagram of Ti alloys; at this time, a new evaluation is necessary using more accurate practical work, especially new categories based on the US patent database.

In the review of the PM and AM manufacturing methods for aircraft applications based on the applied materials and application parts, the conditions for the PM and AM manufacturing methods for aircraft applications are collected and are located for Ti-Al-based alloys, most are TiAl, so the main conditions obtained during the "PM & AM manufacturing methods for aircraft applications" are selected and located in the γ-TiAl phase zone [the red circle] of the Ti-Al binary phase diagram in Figure 1. Ti-Al-based alloys are commonly used for producing gas turbine parts, including the turbocharger, turbine blade, turbomachine, blade of the gas turbine, rotor of the gas turbine, gas turbine compressor blade, the low-pressure turbine blade, compressor blades, and fan-disk blades.

In the review of the "other fabrication technologies by Ti-Al based alloys", most are TiAl, so the main conditions obtained during the "other fabrication technologies by Ti-Al based alloys" are selected and located in the γ-TiAl phase zone [the red circle] of the Ti-Al binary phase diagram in Figure 1. The conditions of the other technologies for Ti-Al-based alloys are collected and are located on the surface enhancement technologies field, including coating, welding, grinding and polishing, joining, hard facing, repair, creating parts of Ti-Al-based alloys as raw materials using layer-by-layer deposition, hydrogenation–dehydrogenation, and coating of Ti-Al-based alloys on the substrate by applying powder on the substrate, i.e., all are widely used in some technical fabrications and application fields.

Even though the length of this article is quite limited, it is the starting basic research for a thorough review of Ti-Al-based alloys connecting the practical application industry field and the academic field.

Current advancements in the development and application of Ti-Al-based materials, coupled with subsequent patents, such as these 50 patents, are now eligible for broader protection covering other aspects that enhance these innovations. These follow-up patents, particularly in the aircraft field and surface-enhancement technologies field, can stimulate further research aimed at achieving safer and more efficient gas turbine products and more advanced surface technology.

Historically, Ni rarely appeared in previous patents; however, in future research on Ti-Al-based materials, the addition of nickel could become an important consideration that may pave the way for improved utilization. Also, the Ti-Al binary phase diagram is the most important phase diagram of Ti alloys. When Ti-Al is also a basic part of the Ti-Ni-Al [89] ternary phase diagram, it shall be used for the ternary phase diagram. At this time, a new evaluation is necessary using the more accurate practical work, especially new categories based on the US patent database.

4. Conclusions

According to the previous third section, the main conditions obtained during the "basic research on Ti-Al based alloys", "powder metallurgy of Ti-Al based alloys", "casting and melting of Ti-Al based alloys", "PM & AM manufacturing methods for aircraft applications", "other fabrication technologies by Ti-Al based alloys", and "other fabrication technologies by Ti-Al based alloys" are all selected and located in the γ-TiAl phase zone [the red circle] of the Ti-Al binary phase diagram in Figure 1.

It is worth noting that the practical industry has applied patents for the basic research on Ti-Al-based alloys in the 1990s only; however, there were more patents after the 1990s, except for patents for aircraft applications in the 1990s. On the other hand, the practical industry seems to only focus on the application field for Ti-Al-based alloys, which lacks the application of the basic research on Ti-Al-based alloys after the 1990s, which is worrying disadvantage.

In this article, indeed, evaluating the fabrication technologies of titanium aluminide (Ti-Al) and the practical applications by comparing the Ti-Al binary phase diagram and US patents is completely achieved. Even though the Ti-Al binary phase diagram has been intensively applied, the published patent database still should be critically analyzed before using the Ti-Al binary phase diagram for any practical applications.

In addition, in the past few decades, modern wind turbines have been developed. Wind turbine blades should satisfy the highest requirements in terms of durability, performance, reliability, lightness, and economic efficiency, and achieve a high degree of technical completion. Therefore, Ti-Al-based materials can be the better-selected materials for the next-generation wind turbine blades.

In fact, this article provides an overview of the state of the art for the production and utilization of Ti-Al-based alloys based on US patents only. Also, it is believed that this article has well-gathered information on US patents regarding the fabrication processes for Ti-Al alloys, which seems beneficial to researchers in the relevant research field.

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