148 North Rd.
Bedford MA, 01730
781-888-8997
natalieb03@vt.edu

1005 Hillwell Road
Chesapeake VA, 23328
757-323-0048
austinc1@vt.edu
December 5th, 2022

Mrs. Christine Burgoyne
ECP Professor
Virginia Polytechnic Institute and State University
Holden Hall
Blacksburg VA, 24061

Dear Professor Burgoyne,

We are submitting the paper entitled *A Brief Analysis of Ti-64*. The technical paper is centered around Ti-6Al-4V and an analysis of its thermodynamic properties to determine whether it would be appreciated for use in aerospace applications. The paper is targeted towards those involved in research and development for aircraft parts due to the fact that the properties of a material define whether or not a material will be suitable for a specific application. By breaking up the titanium alloy into the subdivisions of structure, properties, processing, performance, and green engineering we are able to break down and analyze each aspect of the material and its pros and cons not only physically in terms of the material but environmentally and economically.

Respectfully,

Natalie Barney
Austin Cantrell
VT MSE 2025

A Brief Analysis of Titanium-64

Introduction

Materials scientists are often concerned with making a material more efficient and safe to use while also remaining economically viable. This is especially true in the sub-field of metallic alloys. Being able to produce steel at an efficient and cost effective rate is paramount to countless companies worldwide. However, it is also important to take into account how long steel can last before failure occurs and how the production of steel affects the environment around us.

Completing an analysis of an alloy that is known for its exceptional strength, durability and biocompatibility but is produced at high economic cost reflects the modern problems that materials science engineers face when working with metals and their prospective alloys. Titanium-64, a titanium alloy composed of titanium, vanadium and aluminum, is used extensively in the aerospace and medical engineering fields. It is widely used within the fields of medical, aerospace and defense engineering because of its extreme durability and strength [11]. Examples of applications of Titanium-64 include hip replacement components and turbine blades for jet engines [11]. The purpose of this critical review is to discuss and analyze the structure, processing, properties and performance of Ti-64, a well known alloy that has a variety of applications in the aerospace and medical industry. However, its increased susceptibility to corrosion makes it often difficult to work with. Corrosion can be generally defined as the breakdown or deterioration of a material due to repetitive wear from its surroundings. This paper will focus on analyzing Ti-64 as a base alloy and then discuss the current research to make it less susceptible to corrosive effects while also noting the cost effectiveness and carbon footprint of processing and utilizing Ti-64 in industry.

Structure of Ti-64

The composition breakdown of Ti-64 is described in its name. The main components of the alloy are titanium, aluminum and vanadium. Table I gives a detailed breakdown in weight percent of the components of several different samples of Ti-64 which were produced using electron beam fabrication (EBF) with the addition of hot isostatic pressing (HIP). Both of these processes are additive manufacturing processes [2] . This means they have a similar basic process to 3D printing. The data contained in Table I shows that the standard composition (basic components of the alloy in terms of natural elements) is between 3.5% and 4.5% aluminum and vanadium with the remaining composition being titanium and a small amount of impurities such as oxygen, nitrogen, iron and silicon that are introduced to the alloy through processing and handling.

Ti-64 presents itself in two different crystallographic structures based on processing technique. Structure is defined as the specific arrangement of atoms that occur at the atomic scale of a material. The first structure is alpha Ti-64 which has a hexagonal close packed structure. This type of structure can be visualized as repeating layers of hexagons made of atoms.. Beta Ti-64 has a body centered cubic structure. Body centered cubic structures are atomic based structures that make a cube where atoms can be located at the four corners and one in the center of the cube. The alpha and beta structure of Ti-64 has a significant influence on material density, Young's modulus, Poisson ratio and Rockwell hardness. The two secondary components of Ti-64 act as stabilizers for either the alpha or beta versions of Ti-64. The difference between alpha and beta versions are seen at the atomic level after the alloy is processed. Processing technique, temperature at processing and alloy composition all play a role in determining which version of Ti-64 is being produced. Aluminum tends to chemically stabilize the alpha version of Ti-64 while vanadium will act as the stabilizing component in the beta type.

Properties

Table I

Table of percent weights of the samples [2]

Table I. Chemistry (wt %)

	Ti	Al	V	C	O	N	Fe	Cr	Si
Powder	Bal.	6.57	3.98	0.008	0.23	0.022	0.13	0.008	0.01
As Fab.	Bal.	6.01	3.87	0.009	0.23	0.023	0.12	0.007	0.009
Post HIP, Lot 1	Bal.	6.26	3.93	0.009	0.23	0.021	0.11	0.007	0.011
Post HIP, Lot 2	Bal.	5.92	3.89		0.25	0.022	0.10	0.006	0.009
Post HIP, Hor.	Bal.	6.2	3.97		0.26	0.023	0.14	0.007	0.013
ASTM F2924	Bal.	5.5-6.75	3.5-4.5	Max. 0.08	Max. 0.2	Max. 0.05	Max. 0.30	Max. 0.1	Max. 0.1

The properties of Ti-64 can be broken down into several subcategories including, thermodynamic, mechanical, and thermal properties. Many of the mechanical properties of Ti-64 are a result of the heat treatment the alloy goes through. Specific thermodynamic properties of the alloy that directly affect its performance include its specific heat, compressibility, and thermal expansion, while key properties affecting corrosion consist of ductility and brittleness. The necessary Joules to increase the temperature of a substance one degree of temperature is known as the specific heat [5]. Compressibility is defined as the capacity of something to be flattened or reduced in size by pressure [5]. Ti-6Al-4V's compressive strength, the amount of applied force when failure occurs divided by area of interest's cross section, is between 680 and 1.15e3 MPa [13][11]. "Thermal expansion is the increase in linear dimensions of a solid or in volume of a fluid because of rise in temperature" [6, p.1]. The thermal expansion coefficient of Ti-6Al-4V ranges from 8.27 and 9.8 µstrain/ºC. Other key properties that affect corrosion include the ductility and brittleness of the alloy. The ductility of Ti-6Al-4V is 2.0 with a tolerance of 0.5% and has also been found to not be brittle.

Processing & Performance

Use of Electron Beam Fabrication

The processing of Ti-64 is restricted to less conventional ways of alloy processing. Properties including thermal conductivity are the reason conventional methods of alloy processing cannot be applied to the titanium alloy. Thermal conductivity is the amount of heat that travels through a defined area with a specified thickness that will change a volume's opposing surface temperatures by one degree [5]. Ti-64 has a low thermal conductivity of 6.2 and 7.66 W/mK and a very high chemical reactivity making traditional metal casting and processes troublesome to complete. Thermal conductivity is a measure of how well a material can absorb heat during a certain time frame while high chemical reactivity means that the metal is more likely to react with its surroundings and change composition. The addition of high temperatures during manufacturing makes this even more likely. This leaves additive manufacturing as the most popular way to produce Ti-64. A primary interest in terms of additive manufacturing of Ti-64 is through electron beam fabrication (EBF) or electron beam deposition and the coatings that are added to the base Ti-64 alloy that increase its strength and wear resistance. As Taminger notes:

> "EBF employs a high power electron beam in a vacuum environment (1x10-4 torr or lower). Wire feedstock is used due to difficulties feeding powder in a vacuum, since the carrier gas used to assist powder delivery will be ionized in the electron beam" [4].

Wire feedstock can be thought of as a spool of material that is fed into the electron beam set up to be "printed". Figure 1 shows a basic EBF set up.

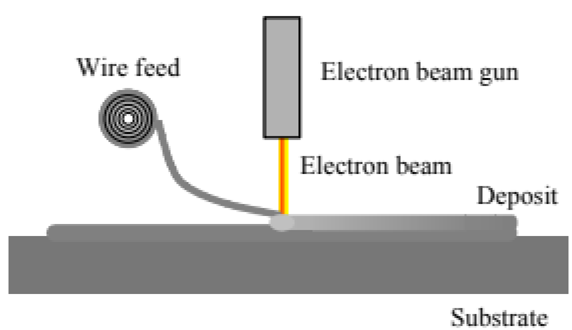

Fig 1. Schematic of the EBF process [4]

Electron beam fabrication is one of the most efficient processing techniques in advanced additive manufacturing according to Tamginger and Hafley some of the greatest advantages of

EBF include; repair and salvage of parts, reduced machining time, and reduced waste. Taminger specifically remarks:

> "SFF can be used to repair broken or out-of- tolerance parts at a fraction of the cost of remanufacturing. This can be particularly significant when there is a large investment, either in capital expenditures, high value materials, or large amounts of time already invested in a part" [4].

The previous statement is especially relevant because of the economic cost of Ti-64 which is about 29 USD/kg.

Hydrochloric Acid Treatment

Several coatings have been added to Ti-64 to enhance its properties. The first is a hydrochloric acid (HCL) and ruthenium (Ru) solution treatment to improve Ti-64's corrosion resistance. HCL acid treatment of Ti-64 Ru has been investigated using 10% HCL and 15% HCL acid at an extended amount of time. Using 10% HCL it was concluded "that density (2.492 × 10^-6 A/cm^2) of Ti-64-Ru alloy indicated higher corrosion resistance than that of Ti-55511-Ru alloy" [7, p. 11]. Wang and his associates highlight that:

> "Ru improved the passivation ability of titanium, and the passivation film consisted of TiO_2 predominantly. This is the direct evidence for Ru to improve the corrosion resistance of titanium alloys" [7].

Oxygen Boost Diffusion Hardening

Another process that has been investigated to improve the wear resistance of Ti-64 is oxygen boost diffusion treatments. Oxygen boost diffusion is done in two parts: "The first part involves the formation of a thick adherent oxide layer on the surface of the titanium specimen which will serve as an oxygen reservoir for the second step" [8, p. 1]. An oxide layer can be thought of as a thin film that develops on the surface of a material when exposed to oxygen. A rich oxygen filled environment is what defines an "oxygen reservoir". The oxidation is completed in an oxygen rich environment at a relatively high temperature [8]. After applying this process to Ti-64 it was concluded that oxygen boost diffusion increases the surface hardness of Ti-64 because after a 150 hour treatment several OBDH (oxygen boost diffusion hardening) samples "showed a higher resistance to wear than the untreated condition showing a decrease in volume loss after 2400m by 25%. "[8, p. 121].

Gas Nitriding

The third process that has been investigated to improve the wear resistance of Ti-64 is gas nitriding. Gas nitriding is a similar process to oxygen boost diffusion in that it is a heat treatment diffusion process except this technique uses a nitrogen based gas instead of oxygen. Heat treatment diffusion can be defined as when a material is placed in a heated environment where a gas is present and imbeds itself into a metal over a certain amount of time. Various studies were conducted to evaluate wear corrosion characteristics of Ti-6A1-4V. The wear and corrosion characteristics of the Ti alloy were observed to be improved after undergoing gas nitriding and a thin layer of TiN formed on the surface of the sample. [9]. The friction coefficient was indicated to be more stable in case of nitrided Ti-64-4V compared with Ti-A1-4V [9]. Wear rate and specific wear amount of nitrided Ti-6A1-4V specimens became smaller than that of Ti_Al-4V [9]. Friction coefficient can be thought of as a number value assigned to a material because of how "rough" the surface of that material is. Wear rate is the loss of material over distance during a set amount of time.

Green Engineering

It is important to consider the environmental impact of processing Ti, Al and V to create Ti-64 and its products. As discussed in the processing section, making Ti-64 with traditional casting tools results in an inferior alloy due to its high reactivity and low thermal conductivity. Electron beam fabrication continues to be the most efficient and cost effective way of producing Ti-64 [3]. By using the most efficient method of production this minimizes the energy consumption. Since the primary source of energy used by industry is still being produced in our world via fossil fuels, this minimizes the amount of carbon emissions that would be released into the atmosphere [12].

Also EBF, and additive manufacturing in general, has significant promise in the recyclability of its products. In a study where the *ProdSL* method was used it was concluded that "AM (additive manufacturing, also called 3D printing) products can be more sustainable where complex geometrical components are necessary" [10, p. 6].

The electron beam fabrication is a method of processing that lends itself to green engineering in the form of waste reduction from machining. When machining a metal via subtractive manufacturing (cutting down a sample to specific dimensions) chips are produced that then have to be recycled in order for them to be reprocessed. Reusing the chips produced by this manufacturing method shows the economic and environmental advantage to this process. This saves energy that would have been required to reprocess the material.

A case study was done using both conventional manufacturing (CM), also known as subtractive manufacturing, and additive manufacturing (AM) to compare their environmental indices [10]. The graph below shows the environmental sub-index score (measure of general sustainability as a product) for several different types of AM processes for a specific material. EOL is a type of EBF [10].

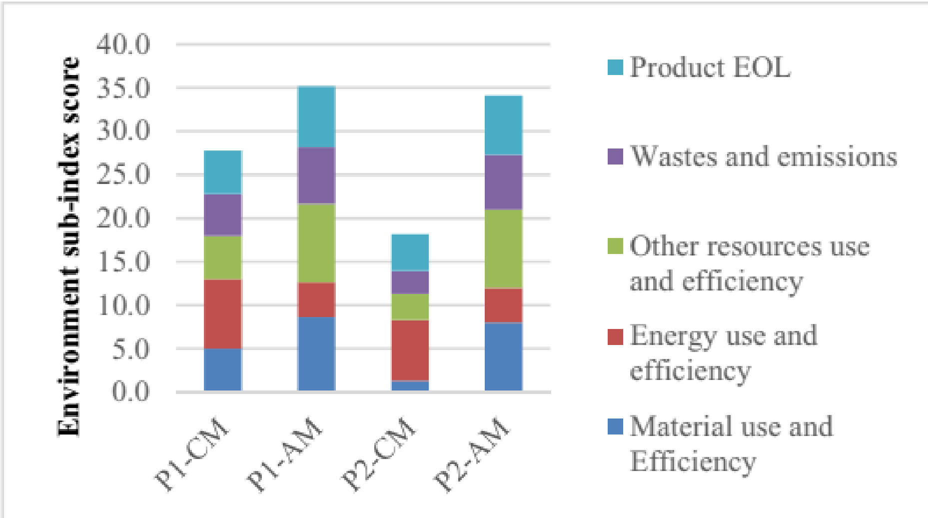

Figure 2. Environment sub index scores for each sample [10]

From the case study the scientists concluded that the additive manufacturing method had a better environmental sustainability performance since the additively manufactured samples had higher environmental sub-index scores in comparison to those of the conventionally manufactured samples [10].

Additional studies of additive manufacturing have shown that electron beam manufacturing consumes less energy per kilogram of material in comparison to even other forms of additive manufacturing [11]. The data collected by Dr. Kellens and their associates displayed the further breakdown of energy use during processing of titanium alloys [11]. From the data collected it is evident that not only is electron beam manufacturing an energy efficient method of manufacturing, but also that specifically Ti-6Al-4V has a lower requirement for specific kinetic energy making it more energy efficient to process.

Conclusion:

Ti-64 is a well known and popular metal in many parts of industry. Its formidable strength and durability makes it one of the most important alloys to date. However, its high production cost and vulnerability to corrosion has often made it troublesome to work with. There are several innovative processes that have been developed to improve Ti-64's anti-corrosive properties. These treatments include gas nitriding, oxygen diffusion and acid bath treatments. All of which have shown to improve Ti-64's anti corrosion properties. The use of AM has also aided in reducing the cost of production and improved the recyclability of Ti-64.Improved AM in the future may increase the sustainability of producing and processing of Ti-64 and its related products.

While the treatments of Ti-64 that are analyzed in this paper all seemed to improve the anti-corrosive properties of Ti-64 to some extent I think that more work should be done to look into laser shock peening of Ti-64 to improve its properties for two specific reasons. The first is that the three processes described in this paper all use extra material to strengthen Ti-64 while laser shock peening would not result in the use of any extra material. The second is that many of these treatments may use more total energy than laser shock peening does so from a green engineering standpoint I think this process of laser shock peening should be tested in the lab and compared to the three processes described in this paper.

References

[1] O. G. Klimova-Korsmik, G. A. Turichin, S. A. Shalnova, M. O. Gushchina, and V. V. Cheverikin, “Structure and Properties of Ti-6Al-4V Titanium Alloy Products Obtained by Direct Laser Deposition and Subsequent Heat Treatment,” *Journal of Physics: Conference Series*, vol. 1109, p. 012061, 2018. doi: 10.1088/1742-6596/1109/1/012061

[2] S. Draper, B. Lerch, R. Rogers, R. Martin, I. Locci, and A. Garg, “Materials Characterization of Electron Beam Melted Ti-6Al-4V.” Washington D.C., 16-Aug-2015.

[3] K. Kellens, R. Mertens, D. Paraskevas, W. Dewulf, and J. R. Duflou, “Environmental impact of additive manufacturing processes: Does AM contribute to a more sustainable way of part manufacturing?,” *Procedia CIRP*, vol. 61, pp. 582–587, 2017. doi: 10.1016/j.procir.2016.11.153

[4] K. M. B. Taminger, “ELECTRON BEAM FREEFORM FABRICATION: A RAPID METAL DEPOSITION PROCESS,” *Proceedings of the 3rd Annual Automotive Composites Conference, September 9-10, 2003, Troy, MI. Society of Plastics Engineers (2003).*, Sep. 2003.

[5] “Oxford languages and google - english,” *Oxford Languages*. [Online]. Available: https://languages.oup.com/google-dictionary-en/. [Accessed: 05-Nov-2022].

[6] “Thermal expansion definition & meaning,” *Merriam-Webster*. [Online]. Available: https://www.merriam-webster.com/dictionary/thermal%20expansion. [Accessed: 05-Nov-2022].

[7] L. Wang, C. Feng, H. Liu, D. Yi, L. Jiang, and Y. Feng, “Revealing the role of RU in improving corrosion resistance of titanium alloys in hcl solution,” *Heat Treatment and Surface Engineering*, vol. 1, no. 3-4, pp. 97–108, 2019. doi: 10.1080/25787616.2020.1743038

[8] R. Williams, *The improvement of the wear performance of the TI-64 alloy using the oxygen boost diffusion treatment*. 2010.

[9] A. Takakashi and Y. Kimura, “Evaluation of wear corrosion characteristics of Ti-6A1-4V in quasi-human body environment and improvement of wear corrosion characteristics by gas nitriding,” *Transactions on Engineering Sciences*, vol. 32, 2001. doi: 10.2495/CON010111

[10] B. Hapuwatte, K. D. Seevers, F. Badurdeen, and I. S. Jawahir, “Total life cycle sustainability analysis of additively manufactured products,” *Procedia CIRP*, vol. 48, pp. 376–381, 2016. doi: 10.1016/j.procir.2016.03.016

[11] *CESEdupack 2011 Edition*, Cambridge, 2011

[12] “U.S. Energy Information Administration - EIA - independent statistics and analysis,” *Use of energy in industry* , 13-Jun-2021. [Online]. Available: https://www.eia.gov/energyexplained/use-of-energy/industry.php. [Accessed: 06-Dec-2022].

[13] “Compressive strength,” *Compressive Strength - an overview | ScienceDirect Topics*. [Online]. Available:

https://www.sciencedirect.com/topics/materials-science/compressive-strength. [Accessed: 06-Dec-2022].