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MANUFACTURING HIGHLY POROUS TI ALLOYS BY MOLTEN SALT SINTERING

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Abstract. *Titanium alloys are widely used in medicine and aerospace industries due to their unique high strength and corrosion resistance combination. Some titanium alloys like Ti-Nb and Ti-Ni alloys can present superelasticity. The addition of porosity in those alloys reduces their Young modulus, which makes it close to the human bone. Furthermore, pore addition can increase the vibration-damping capacity. Powder metallurgy is a suitable technology for manufacturing less ductile metals such as titanium alloys, it enables good control over the porosity, composition, and mechanical properties. However, the sintering of titanium alloys is a critical step due to titanium's high oxygen affinity. In general, a high vacuum furnace is required to avoid titanium oxidation. Recently, a new sintering route using molten a protective atmosphere was proposed for sintering titanium alloys. The molten salt avoided the contact of the part with oxygen without the need for a vacuum furnace. In this study, we applied the molten salt approach for sintering porous Ti, Ti-10Nb, and Ti-50Ni parts. For that, green parts were produced by warm compaction of metal injection molding feedstocks with the addition of a space holder. Microstructure, Hardness, and Young Modulus of sintered parts were evaluated.*

Keywords: *Titanium Alloys, Powder Metallurgy, Mechanical Properties, Microstructure, Microhardness*

1. INTRODUCTION

Titanium and its alloys have extensive applications in the mechanical and aerospace industries because of their high strength-to-weight ratio and excellent corrosion resistance. Thus, they can replace the most commonly used materials like Aluminum, nickel, and steel alloys in certain situations when it's needed to reduce weight, and space, higher corrosion resistance, or operate at high temperatures. Titanium and its alloys are also vastly used by medicine and odontology as implant material due to their well-established biocompatibility with the body, corrosion resistance, and mechanical properties. Barbosa *et al.* (2013) points out their potential as a suitable bone substitute. For that reason, good adhesion to adjacent bone tissue is necessary, this can be achieved by a more porous implant that can facilitate bone ingrowth. Furthermore, the pore can reduce the material's elastic properties closer to the bone's elastic properties. Yu, et al., (2011), in their study with porous titanium alloys, verified that biomaterials with porosity close to 30% help in the osseointegration process.

Boyer (1996) and Barbosa *et al.* (2013) both emphasize the importance and wide scope of applications of titanium and titanium alloys in various industries as well as highlight the characteristics that are of most interest to each. Signor *et al.* (2023) suggests the expansion in the use of TiNb alloys as material for implants as a substitute for Ti6AL4V, a widely used alloy for implants considering the presence of aluminum and vanadium, materials associated with toxicity and neurological diseases. In the meantime, the addition of niobium has shown an increase in the hardness and biocompatibility of the alloy. Following the same principle, da Silva *et al.* (2021) suggests that TiNi alloys have a wide range of applications, like aerospace and biomedical uses, considering that in addition to their high biocompatibility, they present superelasticity, which gives them the capability to endure large elastic deformations.

The biggest limitations to its even wider usage are the high cost of the material and its manufacturing. Lütjering and Williams (2007) suggests the use of near-net shape processes to drastically reduce the amount of material wasted by using processes like casting, laser forming, conventional sheet forming, or powder metallurgy.

Despite citing powder metallurgy as a good process for obtaining near-net shape components, due to the low cost of the process, low material waste, and high control of the alloy, they emphasize that the method has a limited range of potential applications when it comes to titanium alloys. Due to the reactivity of titanium with oxygen at temperatures above 600 ºC, it requires the use of a high vacuum or controlled atmosphere to guarantee the absence of oxygen during sintering, increasing the complexity of the process as well as the cost.

An interesting alternative solution capable of simplifying and reducing costs and the need to vacuum or control atmosphere sintering was proposed by Dash *et al.* (2019), was that applying a molten salt atmosphere essentially shields the oxidation-prone material powder from oxygen. Signor *et al.* (2023) demonstrated that surrounding titanium alloys on molten potassium chloride can present mechanical characteristics similar to those of if sintered in a vacuum, which furthermore accentuates the feasibility of its application.

Metal injection molding (MIM) technology provides a simple and cheap route to obtaining near-net shape parts of smaller and medium dimensions. Engström (2017) provides a guide through the injection molding process; German (2013) makes an overview of the technique when applied to titanium powder and proposes four factors for process optimization: density, purity, alloying, and microstructure. Liu *et al.* (2023) and Dehghan-Manshadi *et al.* (2017) use this technique to obtain HDH titanium parts and analyze their properties.

Kennedy (2012) describes the main powder metallurgy-based manufacturing options, discussing their main aspects and characteristics. One of those is the space holder method, which is frequently combined with metal injection molding as a means to raise the porosity of titanium and titanium alloys since this combination presents excellent control of porosity with high reproducibility, simplicity, the possibility of having geometrically complex parts, and flexibility of materials. Neto *et al.* (2022) develops an overview of the production of highly porous titanium by combining the two techniques and performing a comparison on the main space holders used. Barbosa *et al.* (2013) utilizes MiM and space holder techniques to obtain net-shaped parts with controlled porosity that can be used as implants.

This article then proposes the manufacturing of porous commercially pure titanium, titanium niobium, and titanium nickel alloys by powder metallurgy, combining the warm compaction of metal injection molding (MIM) and space holder techniques to obtain the green parts and the molten salt sintering technique to determine the parts mechanical properties. It is expected that this study may be able to contribute to the dissemination of those techniques, improve the quality of the data available, help lower the costs of manufacturing those alloys, and provide reliable microstructural and mechanical property values.

2. MATERIALS AND METHODS

The procedure of this study was broken down into five phases of the manufacturing of the parts: feedstock production, warm compaction procedures, binder removal, sintering, and salt removal. The part characterization was also divided into apparent density determination, polishing process, composition characterization, microhardness test, and dynamic Young's modulus determination.

2.1 Materials

The materials used were commercially pure titanium powder, grade 2, with a density of 4,506 g/cm³ that was provided by Alfa Aesar Company, with a granulometry of approximately 45 μm and irregular morphology and shape. The niobium (Nb) powder, with 8,57 g/cm³ was provided by the Brazilian Metallurgical and Mining Company (CBMM), with a sieved to granulometry lower than 100 μm. Potassium chloride (KCl), which has a density of 1,98 g/cm³, and was sieved to a granulometry lower than 60 μm.

Furthermore, the materials used in the binder system were stearic acid (SA), with a density of 0,941 g/cm³, paraffin wax (PW), with 0,893 g/cm³ and high-density polyethylene (HDPE), with 0,955 g/cm³.

2.2 Methods

A combination of metal injection molding feedstock technique and space holder technique was utilized for the feedstock preparation. Where a mixture of the metal powder and binder was combined with the space holder that acts as a means for the introduction of porous. The composition of the titanium alloys in weight percentage in grams can be seen in Tab. 1.

Table 1. Feedstock's metal compositions

Feedstock	Ti (wt. %)	Nb (wt. %)	Ni (wt. %)
CP Ti	100	-	-
TiNb	90	10	-
TiNi	43.932	-	56.068

The paraffin wax-based binder is composed of paraffin wax, which acts as a low-viscosity material that gives the mixture good flowability; a high-density polyethylene (HDPE) polymer that acts like a high viscosity secondary binder and has a high melting point, providing mechanical stability after the removal of the space holder; and stearic acid (SA), which increases the mixture's fluidity by acting as a surfactant. The binder volume composition consists of 70% paraffin wax, 25% HDPE, and 5% SA.

The space holder used was potassium chloride (KCl), which doesn't contaminate the titanium, is available in multiple shapes of particles, has high solubility in water, a lower melting point, low cost, and is easy to obtain.

The metals and binder are weighed following the compositions mentioned, and into the metal powder mixture was added KCl as space holder in a proportion of 30% and 40% in volume for all three compositions (CP-Ti, Ti10Nb, and Ti51Ni). The binder mixture was heated up to 150 ºC until all materials reached a liquid state, at which point the metal/space holder mixture was gradually added under mechanical stirring until homogenization.

Next, the processes of warm compaction transform the feedstock into the green part by applying pressure and heat above the melting point of the binder system, which makes the feedstock mold into the die form.

A determined amount of feedstock was added to the 10 mm in diameter compaction die. The compaction die was placed in a hydraulic press. Then the die was heated up to 180 ºC and a pressure of 350 MPa was applied for 2 to 5 minutes. After cooling, the green part was removed from the die. The dimensions of the green part are presented in Tab. 2.

Table 2. Green part characteristics

Feedstock	Weight of feedstock (g)	Height (mm)	Diameter (mm)
CP Ti	4,300	20	10
TiNb	4,700	20	10
TiNi	5,120	20	10

Before sintering the green part, is important to remove the binders using a chemical solution that reacts with part of the binder, removing it. A second step of applying heat at a temperature equal to or close to the degradation temperature of the polymer, usually in the same furnace and cycle as the sintering step. By combining the two, the binder can be completely removed from the green part.

For the primary debinding, the green parts are immersed in a hexane bath and heated to 60 ºC for 24 hours, to remove the PW and SA. After this, the parts were heated to 60 ºC for two hours in an oven to ensure hexane evaporation. The secondary debinding occurs already in the sintering process, where the parts are heated to 500 ºC and maintained for 30 minutes before continuing the sintering process to degrade the HDPE polymer.

The sintering process uses heat to chemically bond the particles, increase their mechanical strength, and consolidate the structure of the part. The process was performed in a molten salt protective atmosphere to decrease oxidation,

The green parts were placed into a tubular crucible filled with potassium chloride (KCl) and closed. The crucible was then placed into a tube furnace that followed the heating rate shown in Fig. 1, with a sintering temperature plateau of 1200 ºC for 180 minutes.

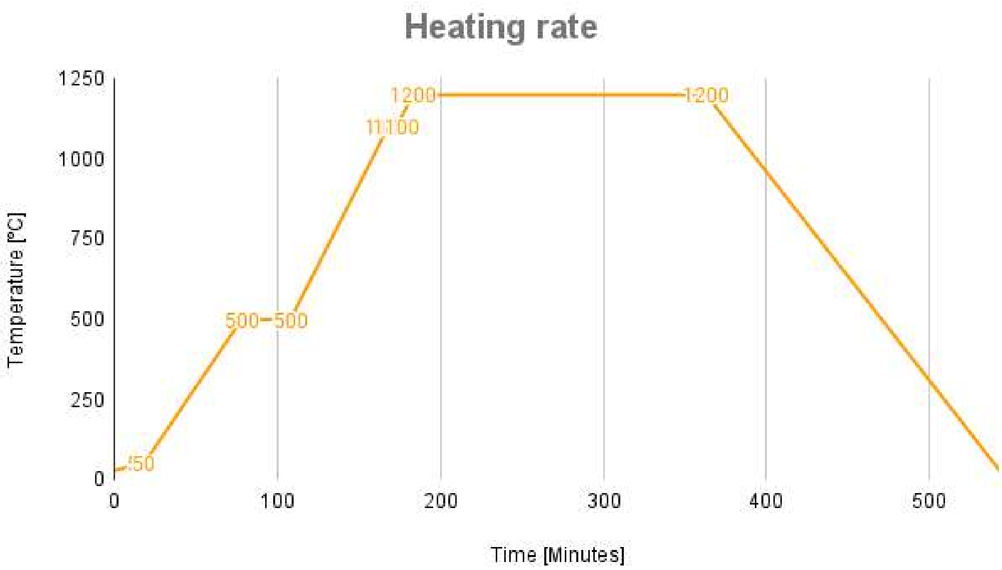


Figure 1. Sintering Heating rate.

After the sintering process, it is required to dissolve the potassium chloride that becomes solid in the crucible. For that, the crucible is placed under running water for 30 minutes and then kept in a beaker with water for another 12 hours.

After the potassium chloride is fully dissolved, the samples are removed from the crucible and placed in a beaker with water at 60 ºC for 24 hours, changing the water every hour for the first 5 hours, eliminating the KCl inside the samples due to the space holder technique.

With the parts obtained, a series of analyses were carried out in search of better characterizing the samples resulting from the manufacturing process. Firstly, the apparent porosity was determined using the Archimedes principle as suggested by Standard (2002).

The parts were then submitted to a vibroacoustic test to determine their dynamic Young's modulus. The vibroacoustic test was performed on 5 samples of each alloy, where 5 measurements were performed on each, using a load of 49 g. Next, the parts were cut in half of their height with a precision cutter machine with a diamond wet cutting disc, a Buehler Isomet 1000.

In sequence, the metallographic preparation of the cross-section of the samples was carried out, so the morphology and microstructure of the parts could be characterized by a scanning electron microscopy (SEM) equipped with energy dispersive X-ray spectroscopy (EDS), model JEOL JSM 6360 (Joel, USA). Lastly, the microhardness was determined using a Vickers microhardness (HMV-Shimadzu) considering the Standard *et al.* (2016). For each titanium alloy, 10 microhardness measurements were performed, using a load of 4.903 N for 10 s.

For the apparent porosity test using the Archimedes principle, the parts were weighted dry after they were submerged in distilled water for four hours, to be weighted submerged and weight damp. The test was carried out with ten parts of each alloy, the average of the apparent densities was then calculated, and the standard deviation of the samples of the same alloy was calculated, as shown in table 3.

3. RESULTS AND DISCUSSIONS

The combination of MIM feedstock with the space holder technique and the Molten Salt sintering approach proved to be effective as a process for manufacturing the porous titanium alloy components, where the parts (Fig. 2) presented effective sintering with good diffusion of the alloys.

Figure 2. TiNi Alloy Part After Sintering.

The results of apparent porosity calculated by Archimedes's principle are shown in Tab. 3.

Table 3. Apparent porosity.

Material	porosity (%)	Standard deviation (%)
CP Ti	25,28	3,16
TiNb	32,63	2,54
TiNi	23,27	2,47

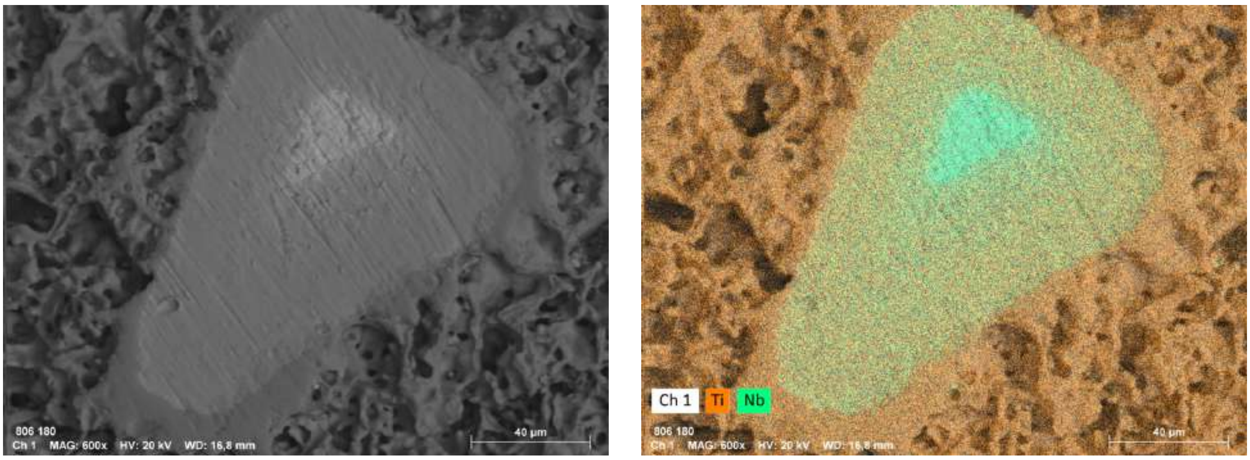
The parts show a high level of apparent porosity, indicating the effectiveness of the space holder addition in the feedstock. The values of porosity were similar to the amount of space holder added, indicating that the porosity can be adjusted by the amount of space holder added. The Ti10Nb alloy parts produced with the space holder addition present an apparent porosity 466% higher than the parts produced without space holder reported in the literature Signor *et al.* (2023).

Sample compositions measured by EDS are shown in Tab. 4. It shows the presence of contaminants like carbon (C) and silicon (Si) that can be attributed to the silicon carbide from the sandpaper that may have lodged in the pores, as well as the influence of the decomposition of the binder, which could have contributed to the carbon concentration. In addition to a very low presence of potassium (K) and chlorine (Cl) in the TiNi alloy coming from the KCl salt used in the manufacture. These results indicate that the desalination process was successful in CP Ti and TiNb parts, however, a higher timer is required to complete the desalination of TiNi parts.

Table 4. Alloy composition.

Alloy	Ti (wt. %)	Nb (wt. %)	Ni (wt. %)	C (wt. %)	K (wt. %)	Cl (wt. %)	Si (wt. %)
CP Ti	94,19	-	-	4,75	-	-	1,06
TiNb	79,23	15,95	-	3,74	-	-	0,25
TiNi	44,05	-	48,36	6,85	0,28	0,27	0,19

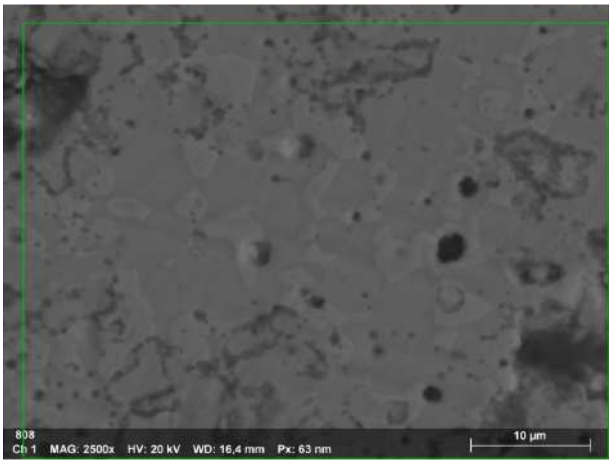
The images obtained from SEM and EDS mapping of the TiNb alloy can be seen in Fig. 3(a) and 3(b). They show a good diffusion of titanium and niobium. On the other hand, considering the coarse size of the niobium initial particle, it is well-defined with points where it has a higher concentration.



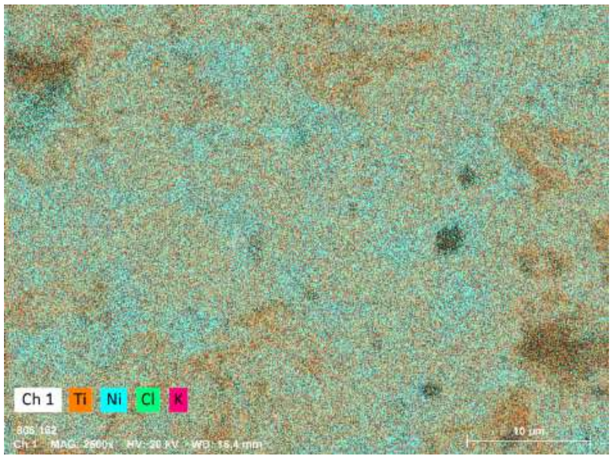
(a) (b)

Figure 3. TiNb Micrography TiN 600x magnification (a), EDS 600x magnification (b).

Figure 4(a) and 4(b) represent the SEM and EDS results for the TiNi alloy. They suggest a higher degree of densification of the part considering that the pore is much more rounded, as well as a great diffusion between the nickel and titanium. There is a higher concentration of nickel in the light areas of the SEM image that indicates the presence of an intermediate phase of Ni_3Ti Fig. 4(a).



(a)



(b)

Figure 4. TiNi Micrography 2500x magnification (a), TiNi Micrography EDS 2500x magnification (b).

The graph in Fig. 5 presents the mean value and standard deviation found for each of the alloys. It can be seen that there is a considerable reduction in the microhardness of both alloys compared to commercially pure titanium.

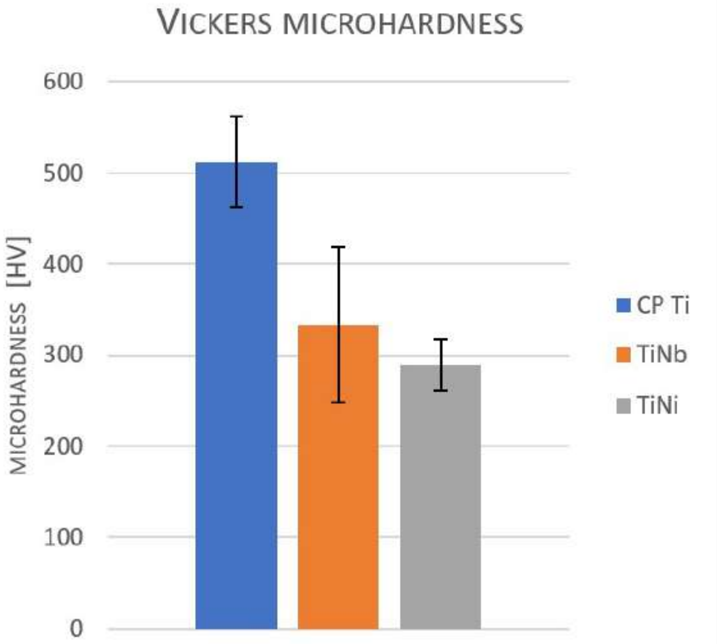


Figure 5. Vickers microhardness.

The reduction in microhardness in the samples can be partially explained by niobium's ability to increase the alloy's sintering temperature due to the high melting point of the element, which, despite creating necks, presents a less reflective face among the three studied alloys. And the fact that nickel is a low microhardness element, thus reducing that of the TiNi alloy.

The dynamic modulus of elasticity value and its standard deviation are shown in Tab. 5.

Table 5. Dynamic Young's Modulus.

Alloy	**E_d (GPa)**	**Standard deviation (GPa)**
CP Ti	8,28	0,62
TiNb	10,33	0,10
TiNi	10,96	0,42

All Ti alloy samples showed a low elastic modulus when compared to dense titanium (ca. 120 GPa), which is expected for porous samples. The technique of introducing porosity using a space holder combined with molten salt sintering seems to be efficient in reducing the elastic modulus of titanium alloys.

4. CONCLUSIONS

The results demonstrated the effectiveness of the proposed manufacturing process. The combination of MIM, space holder, and molten salt sintering enabled the production of porous titanium alloy components with good diffusion of alloys and without oxidation. The parts exhibited a high level of apparent porosity, indicating the successful incorporation of the space holder, which can contribute to bone ingrowth and adhesion in the case of biomedical implant applications. As expected the microhardness and dynamic Young's modulus values of the alloys were notably reduced compared to commercially pure dense titanium.

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