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An Investigation of Sintering Parameters of Ti-6Al-7Nb Fabricated by Powder Injection Molding

Mehmet SUBAŞI[1,*], Asghar SAFARIAN[2], Çetin KARATAŞ[3]

[1]*Address – Technical Sciences Vocational School of Higher Education, Gazi University, Ankara, Turkey*
[2]*Address – Young Researchers and Elite Club, Maragheh Branch, Islamic Azad University, Maragheh, Iran*
[3]*Address – Department of Manufacturing Engineering, Faculty of Technology, Gazi University, Ankara, Turkey*

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Abstract

In this study, the optimized sintering parameters for a feedstock obtained by mixing the powder of Ti-6Al-7Nb and 31wt% binder system (comprised of high-density polyethylene, Polypropylene, PEG 20000, paraffin wax and stearic acid), were determined. In order to produce a component, Taguchi method was applied to obtain the optimum conditions. As a result of ANOVA, sintering temperature was proven to be the most effective one. It was also proven that for feedstock comprised of 69wt% Ti-6Al-7Nb powder, the suitable set of sintering parameters were as follows: sintering temperature of 1250 °C, dwell time of 60 min, heating rate of 1 °C/min, gas flow rate of 5 L/min.

1. INTRODUCTION

Ti-Al alloys are used extensively in biomedical applications in the skeleton and engine parts of aircraft and automobiles due to reasons such as low density, high temperature resistance, corrosion resistance and excellent biocompatibility [1-3].

Among the titanium alloys, Ti-6Al-4V, Ti-15Mo and Ti-6Al-7Nb are the most biologically compatible. Although the addition of some elements such as V, Ni and Al increases the strength of the material, it has been found that it reduces bone resistance and causes some health problems. As a result of the studies made, it has been found that the β-phase or semi-β-phase Ti alloys do not show such a feature. Niobium (Nb) is an important element acting as a βphase stabilizer and it simultaneously allows obtaining high biocompatibility. In addition, the alloy of Ti-6Al-7Nb is preferred because of good strength, high wear and fatigue resistance and good machinability. As a result, Ti-6Al-7Nb alloy is a very attractive material for implant applications such as dental roots, joint endoprosthesis, and surgical implant components for hip replacement[1-7].

However, the high cost of parts produced from titanium limits its application areas. The long production time is the main reason for such a high cost [8].

With Powder Injection Molding (PIM), production costs can be reduced and the structure of components used in many areas can be improved. PIM is an economical production method for components with small and complex geometry. In addition, the PIM application allows the production of many parts that cannot be obtained by other manufacturing techniques. These features of PIM result in higher desirability for production of components made of Ti and its alloys.

Recently, Powder Injection Molding has taken an important place in the production of components from titanium and its alloys. The principles of PIM production for Ti and its alloys are almost the same as other materials like stainless steel and ceramics.

*Corresponding author, e-mail: msubasi@gazi.edu.tr

However, there are considerable limitations in the parts produced by powder metallurgy from titanium, such as oxidation, purity and formation of various undesirable impurities. Oxidation is an undesirable phenomenon that reduces the mechanical properties. Since the Ti powders are prepared elementally and can react easily with oxygen during the sintering process, the sintering parameters should be selected optimally [4]. This increases the importance of all process parameters, primarily sintering. There are many titanium powder and feedstock suppliers in the market whose technical knowledge and data of binder systems, and injection molding and sintering parameters are mostly confidential.

According to the literature, production of parts from titanium and titanium alloys by PIM method is increasing. Obasi et al. investigated the effects of different production parameters on mechanical properties of Ti-6Al-4V components fabricated by PIM. Their results revealed that sintering temperature and dwell time had significant effect on specimens tensile strength [9]. Although for specimens with Niobium powder, the sintering process has been carried out at varying temperatures and dwell times, and has resulted in different tensile strengths, the process has not yet been efficiently optimized [7, 9-15].

The aim of this study was to determine the required optimum sintering parameters of PIM in biomedical applications to produce components of Ti-6Al-7Nb instead of Ti-6Al-4V which has potential of being harmful for human body due to vanadium toxic effects.

2. MATERIAL AND METHOD

2.1. Powder and binder

In this study, gas-atomized spherical Ti-6Al-7Nb powder with size of <25 μm and repose angle of 58° was supplied by TLS Technik GmbH company. The chemical properties of the powder used in the experiments are given in Table 1.

Table 1. *The chemical composition of Ti-6Al-7Nb powder*

Element	Al	Nb	Fe	O	N	H	Ti
%	5.82	6.58	0.050	0.190	0.006	0.001	balance

The properties of the binder in the PIM are as important as the properties of the powder to be used. The required binder should shape powders in desired geometry and exhibit properties such as good packing and adequate strength of green and brown part before sintering; its hould also be completely extracted out of component after sintering. Powder and binder are mixed to form a homogenous feedstock.

The feedstock should be homogenous and have low viscosity so that it can be injected easily. These properties are provided by the aid of the binder system. The binder should consist of multiple elements which are needed to be gradually and sequentially extracted from the injected components. The binder system should be cheap and also possess some properties such as long shelf life, low thermal expansion coefficient. It should also be chemically neutral toward the powder [16, 17]. Accordingly, high density polyethylene, polypropylene, PEG 20000, paraffin and stearic acid have been used as the binder system in this study.

2.2. Injection process

ArburgAllrounder220S injection machine was used to perform the injection process. The standard tensile specimens were injected using a standard mold manufactured based on dimensions presented by Metal Powder Industries Federation [18]. The injection process was carried out based on parameters presented at Table 2.

Table 2. *Injection parameters*

Flow rate (cm^3/s)	Injection pressure (bar)	Holding pressure (%)	Injection temperature (°C)	Mold temperature (°C)
20	1300	60	140	60

2.3. Debinding process

Solvent and thermal debinding steps were applied to extract the binder out of injected components. Solvent debinding was carried out by immersing the components inside high purity heptane with temperature of 60°C for almost 20 hours. The specimens were then dried for 12 hours under the atmosphere of 60°C temperature. The thermal debinding process was completed in an atmosphere controlled furnace with high purity (99.999%) argon gas, passing through copper chips heated to 500 °C, to ensure its purity. The heating ramping was selected at three levels of 1-3-5 °C/min. Figure 1 depicts the sequences of thermal debinding process for heating ramping of 5 °C/min.

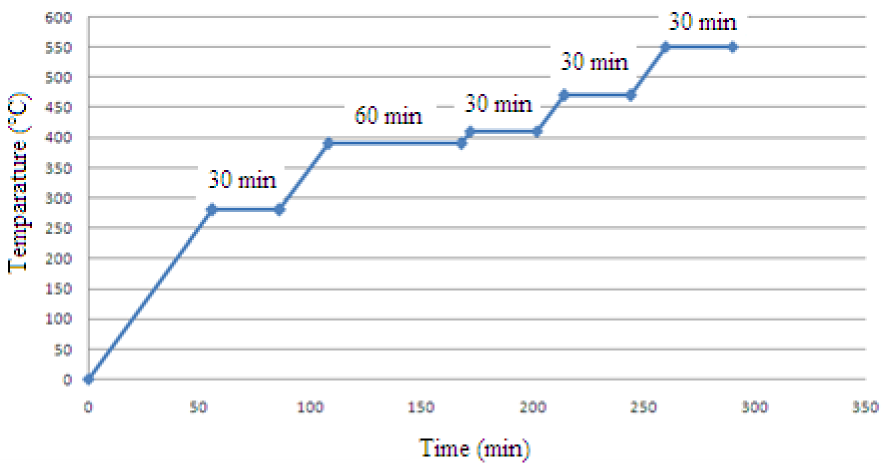

Figure 1. *The sequences of thermal debinding with heating ramping of 5 °C/min*

2.4. Sintering process

Sintering process was carried out after thermal debinding (pre-sintering step) in the same furnace and atmosphere. Sintering heating ramping was selected to be 3°C/min, reaching to sintering temperature of 1250, 1300 and 1350 °C. rate, with three levels of dwell time of 1, 2 and 3 hours. After sintering, the specimens were cooled slowly with cooling ramping of 5°C/min (Figure 2).

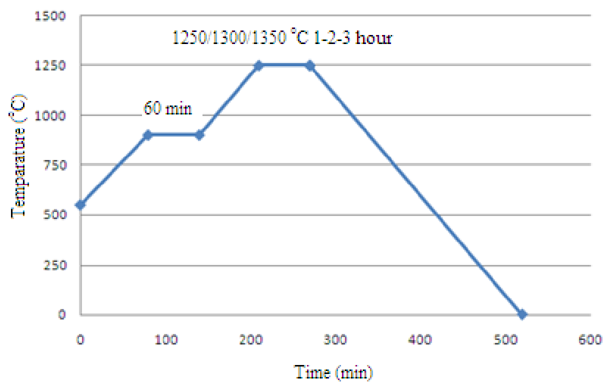

Figure 2. *Sintering sequence*

2.5. Design of experiment

Based on the literature review and some pervious experiments, the important sintering parameters, exhibited in Table 3, were selected to be studied [5,7,9,13,14]. The effect of sintering parameters on sintered components tensile strength was studied using Taguchi method.

Table 3. *The sintering parameters*

Sintering parameters	Sintering Temperature (°C)	Sintering dwell time (h)	Heating ramping (°C/min)	Gas flow rate (l/ min)
1	1250	1	1	5
2	1300	2	3	10
3	1350	3	5	15

2.6. Tensile experiments

The tensile experiments were carried out by 50kN Instron tensile machine, with cross-head speed of 1 mm/min, according to TS EN ISO 6892-1 standard.

2.7. Microstructural Analysis

Microstructure analyses of the samples were carried out in Gazi University Metallurgical and Materials Engineering laboratory, by LEICA optic microscopy, and JEOL JSM-6060LV scanning electron microscopy. In the course of the microstructure analysis, the samples were polished successively with abrasives of 400-600-800-1000-1200 (grit size) and then etched with Kroll solution (2 ml HF (Hydrofluoric acid) +10 ml HNO3 (Nitric Acid) +88 ml distilled water).

3. RESULTS AND DISCUSSION

As a result of our experiments, for specimens made of Ti-6Al-7Nb feedstocks with powder loading of 69%, the highest tensile strength reached was as high as 590 MPa. Table 4 illustrates the effect of input parameters in sequence, in which the lowest value of *Prob> F* presents the most effective parameter. Accordingly, sintering temperature showing the value of 0.0132 was determined as the most effective parameter (Table 4).

Table 4. *Input parameters effects on Ti-6Al-7Nb tensile strength*

Effect Tests S/N Ratio	
Source	*Prob> F*
Sintering temperature	0.0132
Sintering dwell time	0.1509
Heating ramping	0.6217
Gas flow rate	0.7673

In addition, optimum sintering parameters of specimens made of Ti-6Al-7Nb feedstocks were determined by Taguchi method. The optimum sintering parameters for feedstock Ti-6Al-7Nb; sintering temperature, sintering dwell time, sintering heating ramping, gas flow rate were 1250°C, 1 h, 1 min/°C and 5 l/min respectively. The highest tensile strength of 631 MPa was achieved in testing specimen sintered at optimized sintering parameters. The amounts of tensile strength obtained at different conditions were exhibited and compared in Table 5. Figure 3 depicts the tensile stress versus strain for specimen sintered using the optimized injection parameters.

Table 5.*The comparison of tensile strength values obtained in different conditions*

Feedstock	The highest value obtained in design of experiments based on Taguchi method (MPa)	The value obtained based on optimized suggested sintering parameters (MPa)	Wrought material tensile strength (MPa)
Ti-6Al-7Nb	590	631	900 (ASTM F1295-11)

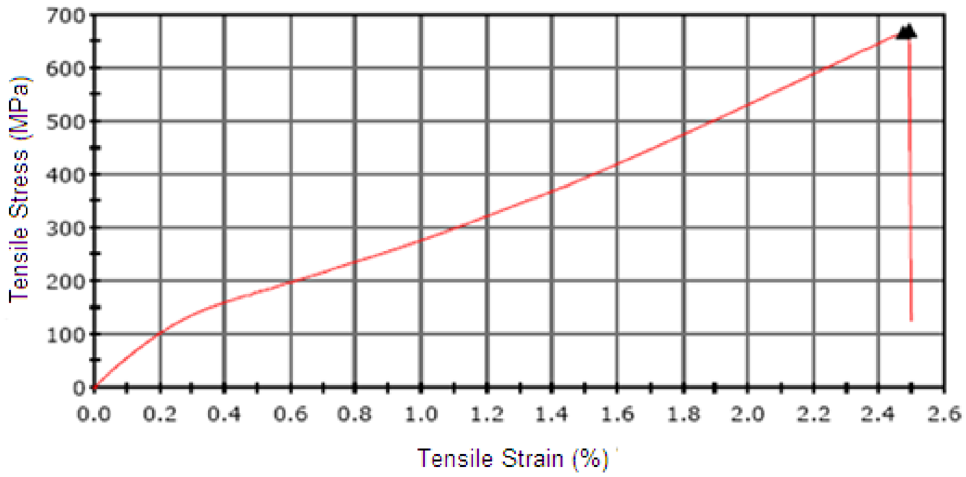

Figure 3. *Tensile stress versus strain for the specimen made of Ti-6Al-7Nb feedstock sintered with optimized sintering parameters*

As it is presented in Figure 3, by applying the tensile strength test, the sintered material behave like cast iron. Components made by powder metallurgy also be have like cast iron [19].

Limberg et al.[13] studied the tensile strength of Ti 45Al 5Nb 0.2B 0.2C made by PIM, and reported the highest value of 630 MPa for specimens sintered and then shot peened under argon gas with pressure of 800kPa. Haoming et al. [20] investigated the mechanical properties of Ti-45Al-8.5Nb-(W, B, Y) specimens which reached the tensile strength of 382MPa. Gerling et al.[21] have reported the tensile strength of Ti-47Al-4(Nb, Mn, Cr, Si, B) to be as high as 260 MPa for specimens sintered for 2 hours by HIP method.

Haoming [20] and Gerling [21] have pointed out that the main reason for low tensile strength of specimen was high structural porosity. They have also mentioned that the furnace atmosphere and its control have a noticeable impact on the amount of porosity inside. This is while Limberg et al.[13], who have utilized pressurized atmosphere and shot peening, have reported a tensile strength of 630 MPa. In the present study, the specimens were sintered without shot peening by normal atmosphere controlled furnace. The effect of shot peening on the mechanical properties of specimens is proven [22]. In this study, the tensile strength of 631MPa was developed without shot peening and with lower sintering temperature and dwell time (1250°C, 60 min) than those of other studies.

Zhao et al. [7] compared the mechanical properties of high purity titanium and its alloys consisting of Nb with varying percentages (10, 16 and 22%wt). As a result of their experiment, the Nb effect was determined. Ti-10Nb exhibited the tensile strength of 638MPa, whereas the amount for alloys Ti-16Nb and Ti-22Nb are 687 and 754MPa, respectively. It was concluded that Nb element increases the amount of tensile strength. Bidaux et al.[15] investigated the mechanical properties of Ti alloy with 17%wt Nb. The sintering process was carried out under the argon atmosphere with applied sintering temperature and dwell time of 1300°C and four hours, respectively, which resulted in the tensile strength of 749MPa.

Zhao [7] and Bidaux [15] determined the effect of Nb ratio on porosity of micro-structure. In both sintering and HIP processes, the amount of tensile strength increased when Nb ratio increased. In this study, the Ti alloy with 7% Nb was sintered at 1250°C for 60 minutes under argon atmosphere which resulted in a high tensile strength of 631 MPa. The tensile strength is however a little bit lower than the values developed by Zhao [7] and Bidaux [15]. This is due to using lower Nb (7%), and also lower sintering temperature, dwell time and a different atmosphere.

3.1. Evaluation of sintering parameters

3.1.1. Sintering temperature and dwell time

In addition to the injection parameters, there are other parameters namely sintering temperature, dwell time, heating ramping and sintering atmosphere which have effects on component mechanical properties [23]. The aim of most of the studies which have concentrated on sintering process is to reduce sintering temperature and dwell time. At high sintering temperatures, the rate of densification decreases, while the grain grows rapidly and therefore the mechanical properties of component deteriorate [24]. In our study, sintering was carried out at temperatures of 1250, 1300 and 1350 °C, and the highest tensile temperature was achieved for components sintered at 1250 °C, which was presented as the optimum sintering temperature. Sintering the components at a condition different from optimum sintering temperature and dwell time results in lower density of components. In such a condition the amount of porosity increases. Therefore, the structure is further densified with longer sintering dwell times[23, 24]. Sintering was carried out at three levels of dwell time, 1, 2 and 3 hours, resulting in highest tensile strength for dwell time of 1 hour. Components sintered at 1300 °C and dwell time of 2 hours exhibited the lowest tensile strength and maximum porosity of 3.28% (Figure 4).

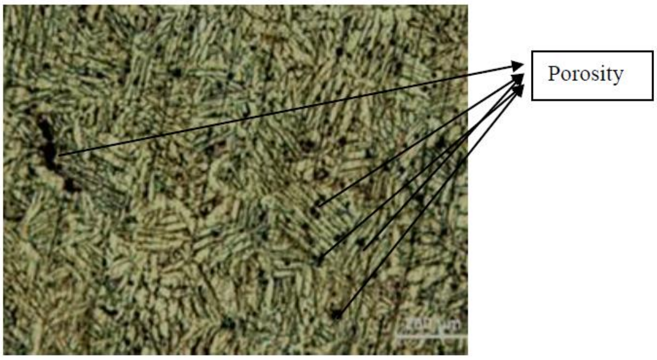

Figure 4.*Optic microscopic view for specimens with the lowest tensile strength of 210 MPa and density of 96.72%.*

Obasi et al.[9] pointed out that higher sintering temperature and longer dwell time cause grain growth which deteriorates the mechanical properties. Hoaming et al.[20] determined that increase of sintering temperature and dwell time will not result in components with full density. They also revealed that higher sintering temperature could result in warpage, while the longer dwell time could contribute to forming coarse lamellar structures. Our results are in line with the current literature and confirm fabricating components with the highest tensile strength sintered at low sintering temperature of 1250 °C and dwell time of 1 hour.

3.1.2. Heating ramping

The role of heating ramping is significant in the control of micro-structure development. In sintering at low temperatures, the surface diffusion is more dominant. It causes neck growth before densification, which contributes to higher densifications without grain enlargements [9]. Dominance of such a condition in micro-structure is related to heating ramping. In addition, it was determined that fast heating rates could cause some defects in components. For example, it causes faster heating of component corners which resulted in higher thermal stresses. Because of such thermal stresses, it was proven that some defects like cracks could exist [24]. Thian et al. [25] determined that to have defect-free Ti-6Al-4V components after thermal debinding, the heating rate should be as low as possible during debinding. German pointed out that in sintering of titanium above 350 ºC, there is possibility of reaction of titanium and binder system to form titanium carbide [24]. In addition to carbide formation, rapid debinding could also lead to carbon contamination, surface defects and color changes. In light of these explanations, it was proven that slow heating ramping is the most suitable method [24]. In the present study, heating ramping of 1, 2 and 3 °C/min were selected, among which the slowest heating ramping of 1 °C/min resulted in the highest tensile strength.

3.1.3. Sintering Atmosphere

Applied sintering atmosphere is dependent on sintering temperature and chemical composition of feedstock. During sintering, the atmosphere is not stable. The contaminants from feedstock are transmitted to sintering furnace. During heating, the contaminants change the composition of furnace atmosphere. Hence, not only the kind of atmosphere, but also the gas flow rate, sintering temperature, the powder and binder system which identify the composition of furnace inside atmosphere, should be taken into account [20]. The flowing gas inside the furnace is acting as contaminant sweeper and protective atmosphere. The cost of gas is also another important factor in sintering process [24]. Therefore, the amount of flowing gas during the sintering stage was optimized in our study. Three levels of 5, 10 and 15 L/min were selected as gas flow rate, among which the highest tensile strength was achieved in components sintered with flow rate of 5 L/min. With the increase of flow rate, the tensile strength was proven to decrease. The amount of tensile strength for specimens sintered with flow rates of 10 L/min and 15 L/min are 210 MPa and 214 MPa, respectively. Specimens with 210 MPa tensile strength exhibited more porosity inside (Figure 6). As illustrated in Figure 5, for Ti-6Al-7Nb specimens sintered at 1250 °C with dwell time of 1, 2 and 3 hours, and heating ramping of 1, 3 and 5 °C/min, it was determined that the tensile strength increases by decreasing the amount of dwell time, heating ramping and gas flow rate.

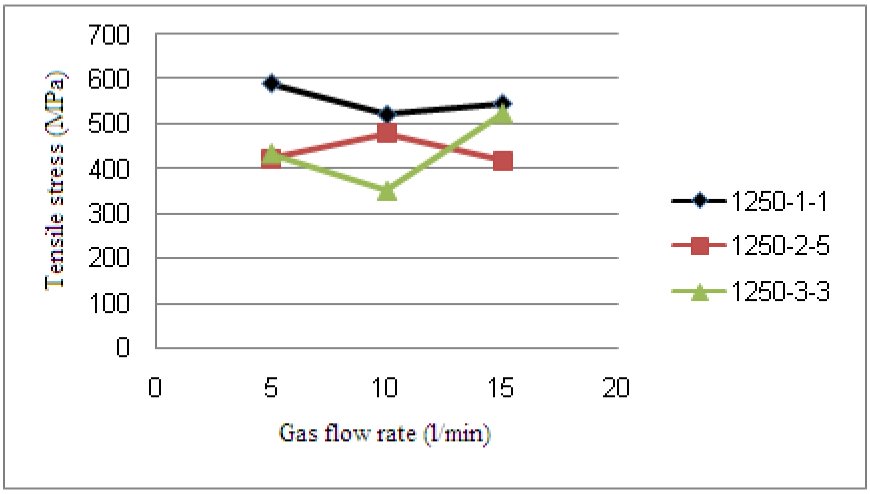

Figure 5. *The tensile strength of specimens sintered at varying dwell time and heating ramping*

3.2. Evaluation of the microstructure of specimens

The optic-microscopic views, SEM and tensile fracture surface views for sintered specimen Ti-6Al-7Nb are illustrated in Figures 6, 7 and 8, respectively. In the specimens with tensile strengths of 631 and 210 MPa, the phases of $\alpha+\beta$ were present in the structure. It should also be underlined that the amount of porosity is more in the specimen with lower tensile strength of 210 MPa. This higher level of porosity causes lower tensile strength. As it is graphically shown in the optic, SEM and tensile fracture surface view, the sintering occurred completely in specimen fabricated at optimum conditions.

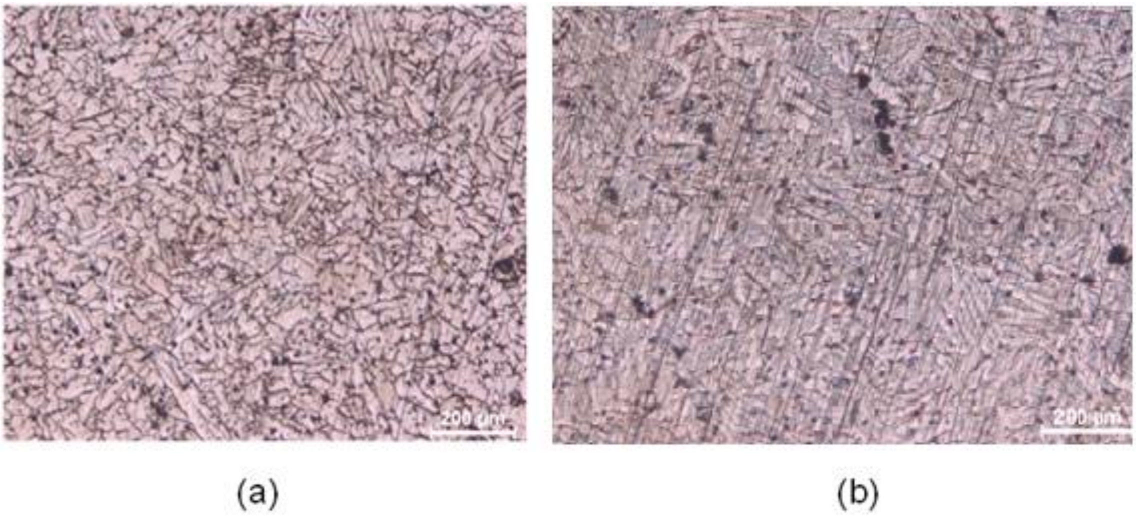

Figure 6. *Optic microscopic views of sintered Ti-6Al-7Nb; a) The specimen sintered at optimum condition (tensile strength of 631 MPa) b) The specimen with the lowest tensile strength of 210 MPa*

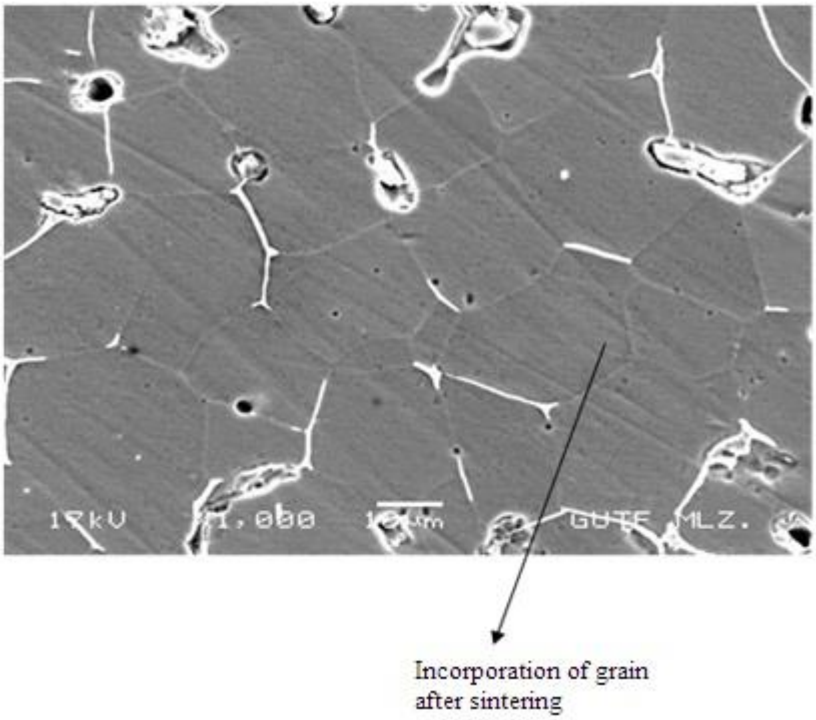

Figure 7. *SEM view of specimen sintered at 1250°C and dwell time of 60 min, giving the tensile strength of 631MPa*

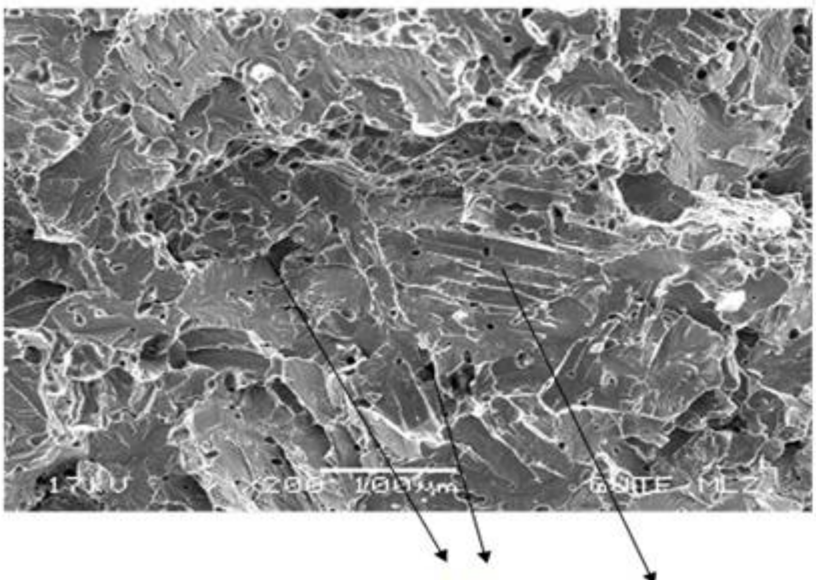

Figure 8. *Tensile fracture surface of specimen sintered at 1250°C and dwell time of 60 min, giving the tensile strength of 631MPa*

4. CONCLUSION

In this study, a feedstock was prepared using Ti-6Al-7Nb powders with powder loading of 69wt%. Using the prepared feedstock, standard tensile specimens were produced, and then sintering parameters were optimized. The results of our experiments can be summarized as:

- By optimizing the sintering process of Ti-6Al-7Nb feedstock, tensile strength of sintered specimens reached 631 MPa.
- Argon with high purity as a sintering atmosphere, passing through copper chips leads to sintered Ti specimens with high strength.
- The highest tensile strength was achieved in testing specimens sintered at 1250 °C and dwell time of 60 min.
- To have high strength Ti-6Al-7Nb specimens, it was determined that sintering heating ramping should be as low as 1 °C/min.

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CONFLICTS OF INTEREST

No conflict of interest was declared by the authors.

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