International Journal of Mechanical and Materials Engineering (IJMME), Vol. 5 (2010), No.2, 244-250

DEVELOPMENT AND CHARACTERIZATION OF TITANIUM ALLOY FOAMS

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Received 27 October 2009, Accepted 30 June 2010

ABSTRACT

Titanium has excellent mechanical properties, a low density and bio-compatibility features. Titanium foam is an attractive material for structural and biomedical applications. Because of these properties and applications we have tried to produce titanium foam from titanium alloy (Al_3Ti). In this paper, the Slurry Method is selected to produce the titanium foam, in which sintering is the most critical process. The foam will be considered to have properties of titanium foam only after the sintering process. The titanium slurry is prepared by mixing Titanium Alloy Powder, Polyethylene Glycol (PEG), Methylcellulose and water. Then, the Polyurethane (PU) foam is impregnated in the slurry and dried at room temperature. This is later sintered in a high temperature vacuum furnace with different sintering temperature. The effects of sintering on the prepared titanium foam are quantified by measuring the sintering and soaking time as well as the rate of heating. All these parameters are fixed to make sure the results are consistent. The titanium foam is characterised by using a Scanning Electron Microscopy (SEM) and Carbon Hydrogen Nitrogen Sulfur (CHNS) element analysis. The range of pore size obtained is between 388μm to 1.07mm, with the strut size in the range of 59.4μm to 227μm. The element in the sample was only Carbon. In the present study, highly porous titanium foams with porosities up to 80% were produced by using slurry method. The highest compressive strength is 14.85 MPa for sample that be sintered at 1250^{o}C. This titanium foams can be use as the scaffold for bone tissue engineering or porous coating on implants.

Keywords: Metal foam, Slurry method, Porosity, Sintering and Mechanical properties.

1. INTRODUCTION

Metal foam has many beneficial physical and mechanical properties. These properties are from high impact energy absorption, high stiffness and strength to weight ratios, high gas permeability, and finally to high thermal conductivity. There are several applications of open-celled metal foam which are widely used as lightweight constructional materials, architectural materials, impact absorbers, silencers, filters, heat exchangers and implants. Metal and metal alloy foams containing up to 95% porosity are being explored for many applications. They offer many potential benefits for components that operate in extreme environments and at temperatures where conventional polymeric foams cannot be used (Degischer and Kriszt, 2002). They also promise cost advantages over conventional lightweight honeycomb structures and rib-stiffened panels used in many aerospace and ship structures.

Another benefit of metallic foams is that the Young's Modulus can be fine tuned to match the modulus of the bone in order to avoid stress-shielding effects which can lead to a high rate of bone resorption. The mechanical behaviour of a porous scaffold is dependent on the pore volume fraction and size distribution as this determines the size of the struts or walls between the pores which are bearing the load. Depending on the process used in making the foam, its micro/macrostructure can be tailored to optimise the biofactor delivery and mechanical properties by incorporating well-connected pores (Hollister, 2005). The metals that were used to produce foam are aluminum, zinc, lead, stainless steel and titanium. Aluminum is the most established metal to produce foam (Ashby et al., 2000). In this study, titanium alloy has been used to produce titanium foam. Titanium and its alloy are excellent

materials for lightweight applications at elevated temperatures and are widely used in aeronautical applications. Titanium is 60% heavier than aluminum but twice as strong (Callister, 2003). The density of titanium is roughly 55% that of steel. Titanium alloys are extensively utilised for significantly loaded aerospace components. Titanium is used in applications requiring somewhat elevated temperatures. The good corrosion resistance experienced in many environments is based on titanium's ability to form a stable oxide protective layer. This makes titanium useful in surgical implants and some chemical plant equipment applications. Porous titanium structures have an additional potential for weight reduction and could even be suitable for functional applications if the pore structure were open.

One of the most promising methods for manufacturing open porous titanium material is the sintering of compacted or extruded mixtures of powders and fillers that contain removable space holder materials. This method can produced 60% to 80% of porosity (Zhao and Monaghan, 2008; Lui et al., 2008; shimizu, 2005; Raush and Banhart 2002). For this study the method that been used is the slurry method or replication technique. This method can produce open celled and high porosity titanium foam (Li et al., 2002; Li et al., 2003; Cachinho and Correia, 2007). The investigation is focused more on the sintering process to make sure that the titanium alloy does not oxidize. We have also studied the elements present in the sample and the morphology of the titanium alloy foam after sintering. Characterisation of porosity and density of the sintered foam were also accomplished. The major limitation of titanium is its chemical reactivity with other materials at elevated temperatures (Callister, 2003).

2.0 MATERIALS AND METHOD

Titanium alloy powder has been purchased from TLS Technik GmbH & Co, Germany. The particles are spherical in shape and the diameters are less than 20µm. Water soluble materials, Polyethylene Glycol (PEG) and Carboxyl Methyl Cellulose (CMC) are used as binders. PEG and CMC are water soluble materials. Polyurethane (PU) foam is used as a scaffold. PU foam is cut into cylindrical shape with a 10 mm diameter and 20 mm height. This size is to be fixed with ASTM standard for compressive strength testing. Figure 1 shows the PU foam before dipping into the titanium alloy slurry.

2.1 Preparation of Sample

Initially, PEG and CMC are stirred in deionised water for one hour. Titanium alloy powder is subsequently added to the solution and stirred for two hours. The titanium alloy slurry is used to impregnate the PU foam. The PU foam is dipped into the slurry and the dipping and drying processes are repeated until the struts of the foam are completely coated with the titanium slurry. The excess slurry is then removed by pressing the foam under a roller.

The samples are dried in the oven for 24 hours at 30^{o}C. After the sample is completely dried, the PU is removed from the matrix by heating it at 600^{o}C for 60 minutes. Subsequently, the samples are sintered at 1250^{o}C with a holding time of two hours. The rate for heating is 1^{o}C/min. The sintering cycle is shown in Figure 2 whereas Figure 3 summarizes the titanium foam preparation process.

2.2. Samples Characterisation

The software Mettler Toledo Star^{e} System TGA 851e is used for the thermogravimetric analysis (TGA). It is to measure the thermal stability and composition of the material. It measures weight changes in the material as a function of temperature (or time) under controlled atmosphere. TGA is used to study the pyrolysis process of the polyurethane foam and to determine the burn off temperature of the PU foam. A *Philips XL30* Scanning Electron Microscopy (SEM) is used for morphological characterization of the samples after sintering. Furthermore, Carbon Hydrogen Nitrogen Sulfur (CHNS) element analysis is used to provide qualitative information on the elemental composition of the samples after the sintering process. *Bruker model D8 advance* X-ray Diffraction (XRD) Analysis is used to characterize the chemical composition and structure of the samples. XRD experiments are performed on both as received titanium alloy powder and the sintered samples. A liquid displacement method is used to measure the porosity and density of the samples. In this study, mechanical testing is used on the compressive strength. An Instron 4505 mechanical tester with 1.0 KN load cell is used for the compression mechanical test. The crosshead speed is set at 1.00 mm/min, and the load is applied until the titanium foam is cracked

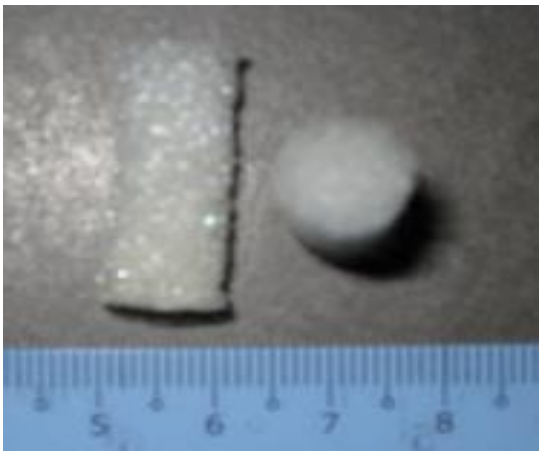

Figure 1 The Size of PU Foam After Cutting

Table 1 Chemical Composite (%wt) of Titanium Alloy (TLS Technik GmbH & Co, Germany 2008)

Titanium	Carbon	Ferum	Oxygen	Nitrogen	Hidrogen	Aluminum
89.691	0.005	0.043	0.185	0.004	0.002	5.99

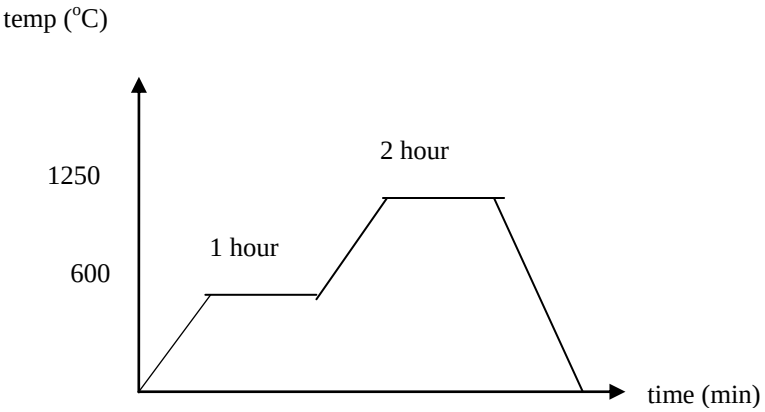

Figure 2 Sintering Cycle for the Preparation of the Titanium Alloy Foams

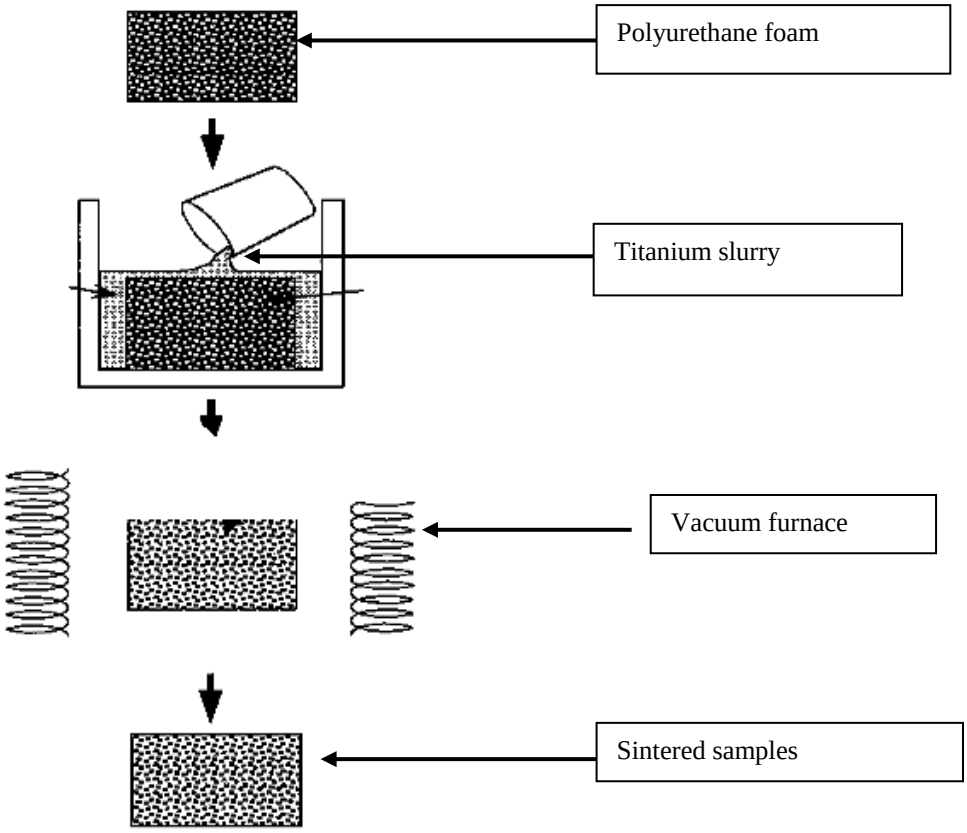

Figure 3 Schematic Illustration of the Production of the Titanium Foam

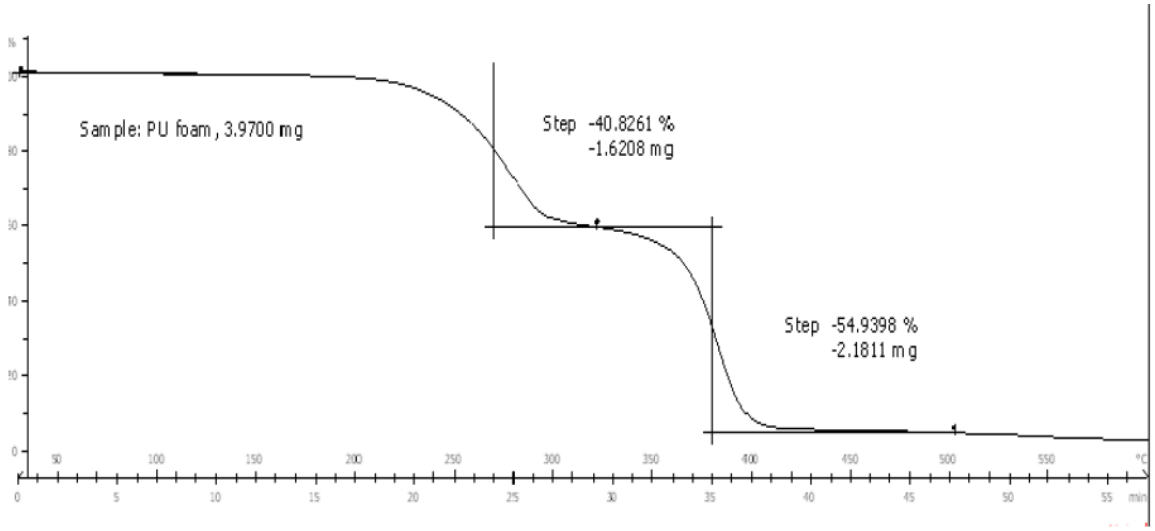

Figure 4 TGA Analysis of the polyurethane Foam

3. RESULTS AND DISSCUSSION

This section will be present the result for the analysis of titanium alloy before and after sintering process. Before that, the PU as a scaffold must be tested using TGA testing. The pyrolysis of the PU is critical in the sintering process especially for the polymer sponge method or slurry method (Ramay and Zhang, 2003). Sufficient time should be given to allow polymer burn out before sintering. This is to avoid cracks in the microstructure. In this research, the TGA is used to determine at which temperature the polyurethane foam is completely burnt. Figure 4 shows the weight change of the polyurethane foam versus temperature. It shows that the polyurethane foam is completely burnt at 600^{o}C. Thus, to allow ample time for the complete burning before the sintering starts, the heating rate is set to 1 ^{0}C/min up to 600^{o}C with a dwell time of 1 hour. Figure 5 shows the microstructure at different magnification of the sample after sintering at 1250^{o}C in the vacuum furnace. The pore size is found to be in the range of 500µm to 1.07mm. The strut is also show using SEM with 190X magnification in Figure 5. The size of the struts range from 59 to 100 µm, and the same residual porosity is revealed in the struts of the sintered body due to the pyrolysis of the polyurethane foam, which can reduce the mechanical strength of the structure. SEM result with a 300X of magnification show that titanium alloy was sintered to liquid phase sintering stage. It because of the alloying element in that sample; which is aluminum was melting and it wetting the particle of titanium alloy. The melting point for aluminum is at 660^{o}C (Callister, 2003) so all aluminum melts in this sintering process. The necking of particle was show in figure 6, 7 and 8. SEM result shown that more particles was contacting when the sintering temperature was increase 1250^{o}C. The neck growth between contacting particles and it can reduce the porosity for this sample (German 1996). With the increase of temperature or time, the diffusion of external atom of the particle and the stress induced by interfacial force make titanium atoms flow to the contact point of particles. Thus, point contact gradually expands to face contact and a great deal of small pores disappears (Li et al. 2008). Microspores and some ash also appear and it came from the PU foam. This ash will be analyzed using CHNS element analysis.

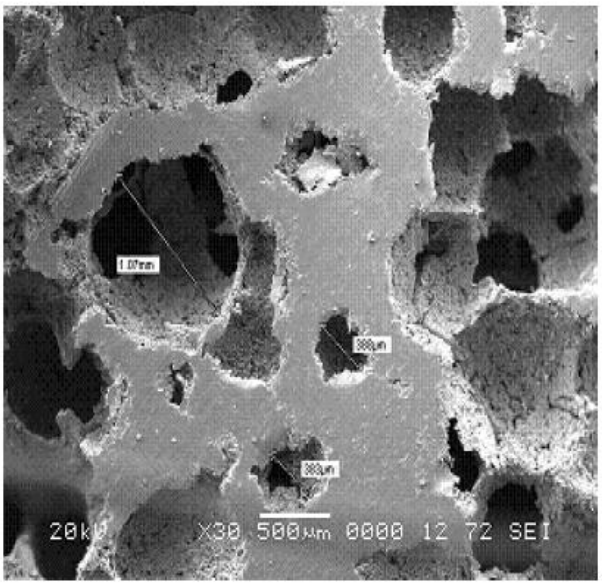

Figure 5 SEM Micrographs of Titanium Alloy Foam Sintered in the Vacuum Furnace. The Magnifications for these Samples are 30X.

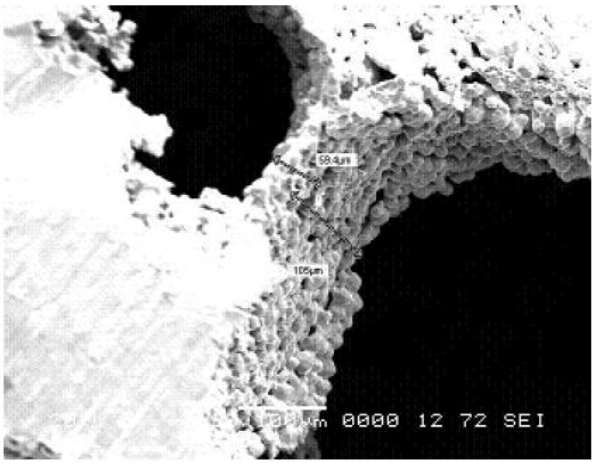

Figure 6 SEM Micrographs of Titanium Alloy Foam Sintered in the Vacuum Furnace. The Magnifications for these samples are 300X

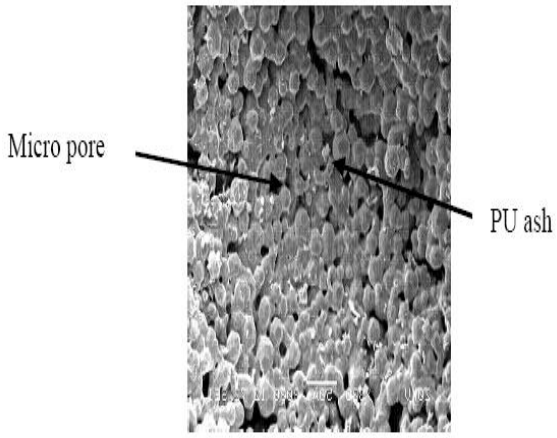

Figure 7 SEM Micrographs of Titanium Alloy Foam Sintered in the Vacuum Furnace. The Magnification for this Sample is 190X

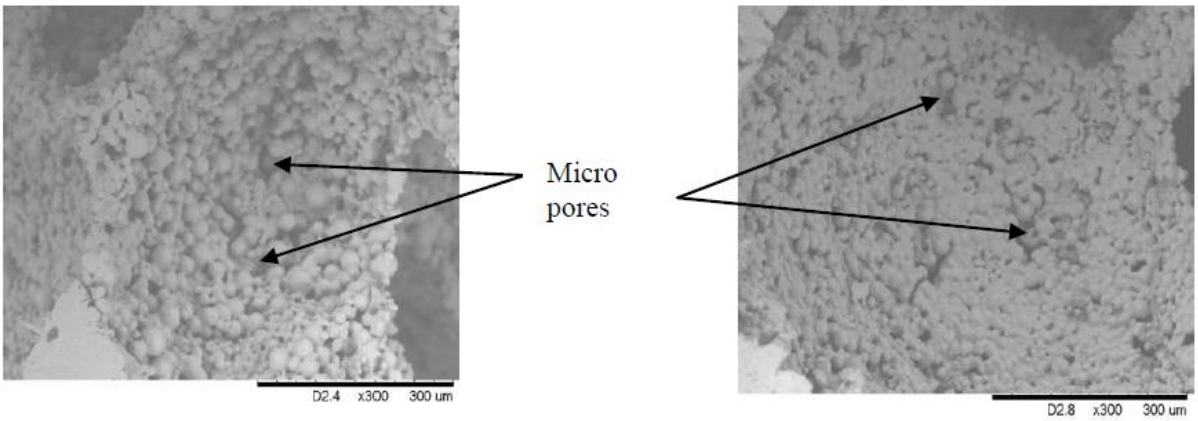

Figure 8 SEM Micrographs of Titanium Alloy Foam Sintered at 1200^{o}C (left) and 1250^{o}C (right) in the Vacuum Furnace. The Magnification for this Sample is 300X

Table 2 shows the percentage of element that exists in the PU and Titanium alloy before and after sintering process. Elemental analyses of the sintered titanium alloy foam are performed using Carbon Hydrogen Nitrogen Sulfur (CHNS) element analysis. It is believed that the carbon element came from the ash of the PU foam during sintering. Since PU is the resultant material from chemical reaction between poliol and polyisocyanate which has high carbon content, it is reasonable to assume that the carbon came from the PU ash. To prevent this problem, we can inflow argon or nitrogen gas in the furnace (Amaranan et al., 2008). In this study, the raw material was tested with XRD to make sure the compound that is present is the same to sample after the sintering process. This is to make sure the resulting sample does not oxidize. If the sample oxides, a different peak appears in the results of the sintered sample. XRD result for raw material follows the pattern of JCPDS 2007:00-052-0859, which is Aluminum Titanium (Al_3Ti). The highest intensity value for 2 theta is at 40.844. The peaks for the sample after the sintering process follow the pattern and the highest intensity is the same with the raw material. Other than that, the same low peak appears.

Lastly the result for density, porosity and compressive strength is shown in Table 3. From the literature review, the density is proportional with the compressive strength but diversely proportional to the porosity if the sintering temperature is increased (Li et al,. 2002). In this case we just compare with two different sintering temperature, 1200^{o}C and 1250^{o}C. From Lui et al, 2008 was sintered the sample at 1200^{o}C and Li et al, 2003 was sintered the sample at 1250^{o}C and their result was successful for density, porosity and compressive strength. We can see this trait followed the theoretical for this result (Shimizu, 2005). When sintering

temperature increase, the value of density was increase and percentage of porosity was decrease nearly 10%. During sintering, the necks grow at the particle contact (German, 1996). This causes the elimination of pores and increase in density. Otherwise, compressive strength increase almost 100% after the sintering temperature increase. The higher sintering temperature and the longer sintering time can be higher compressive strength. Moreover, the contribution of sintering temperature to the increase of mechanical properties is more obvious (Li et al., 2008). The values for compressive strength still not enough for this application (Larminie and Dicks, 2003). Our application is to produce bipolar plate for Polymer Electron Membrane Fuel Cell (PEMFC). Other effects upon increase in sintering temperature may be greater shrinkage, grain growth, pore coarsening, less precision and higher properties (German, 1996).

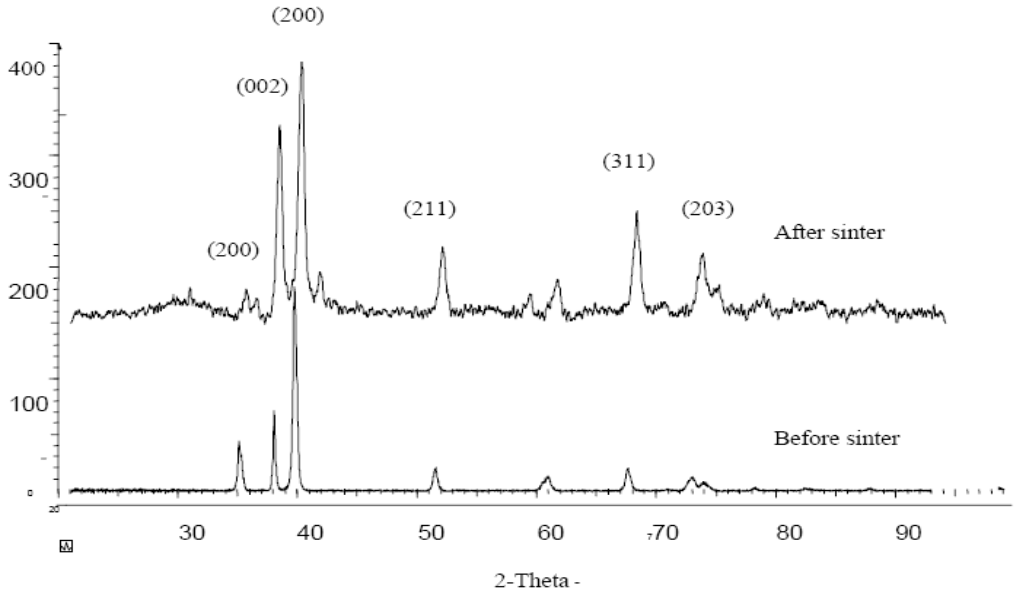

Figure 9 XRD Result for Titanium Alloy Foam Sintered in the Vacuum Furnace

Table 2 Results CHNS Elements Analysis for PU and Titanium alloy before and after Sintering Process

Elements	PU	PU ash (after sintering)	Titanium alloy	Titanium alloy (after sintering)
Nitrogen	7.9	1.51	0.004	0
Carbon	62.11	26.27	0.005	1.3131
Hydrogen	6.91	0.58	0.002	0

Table 3 Result for Density, Porosity and Compressive Strength for Titanium Alloy Foam

Sintering temperature (^{o}C)	Density (g/cm^{3})	Porosity (%)	Compressive strength (MPa)
1200	0.67	83.59	7.16
1250	0.88	72.76	14.85

4.0 CONCLUSIONS

Titanium alloy foam has been successfully produced by the slurry method without inducing oxidation on the samples. The titanium foam show pore sizes ranging from 1.07mm to 500μm and the strut from 59 to 300μm. The element that was found in this sample is only Carbon (1.313%). From the XRD result shows that the sample after sintering at 1250^{o}C did not oxide. The sintering parameters are found to play a critical part in forming the titanium alloy foam. For further research, the focus is to produce the stack for the PEMFC application.

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