Synthesis and Characterization of Ti-foam Using NaCl as Space Holder

A thesis submitted in partial fulfilment of the requirements for the degree of

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In

Biomedical Engineering

Submitted By

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CERTIFICATE

This is to certify that the thesis entitled "**Synthesis and Characterization of Ti-foam using NaCl as space holder"** submitted by **MR. AMBER CHOUHAN** in partial fulfilment of the requirements for the degree of **Bachelor of Technology** in **Biomedical Engineering** embodies the bonafide work done by him in the final year of his degree under the supervision of the undersigned. The thesis or any part of it has not been submitted earlier to any other University / Institute for the award of any Degree or Diploma.

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Amber Chouhan

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ABSTRACT

Titanium and its alloys are widely used in medical implant industries due to their unique structure, excellent mechanical properties, low density, high chemical resistance and excellent biocompatibility. Porous titanium inherits the excellent mechanical and biological properties of titanium. Porous titanium i.e. Ti foams potentially use as functional and structural material for making implants as this structure provides lower young modulus and provides better cellular attachment. In the present studies, titanium NaCl syntactic foam was prepared by varying the size of NaCl particles by powder metallurgy route. In order to ensure sufficient handling strength in cold compacted pallets, 5 wt % of PVA solution (10 wt % PVA dissolved in water) was mixed with the mixture of Titanium and NaCl particles prior to cold compaction. Pressure less conventional sintering was carried out at 800 ºC and 1200 ºC for 2, 4 and 6 hours. The microstructural and morphological analysis was done by scanning electron microscopy (SEM) and phase purity by X-ray diffraction analysis (XRD). The effects of NaCl particle size, sintering time and temperature were also studied in details. The Ti-NaCl syntactic foam thus produced in this process is found to be an effective process for implant material fabrication.

Keywords- Biocompatibility, Porous, powder metallurgy, cold compaction, microstructural , X-ray diffraction analysis (XRD)

CHAPTER 1

INTRODUCTION

In recent years metal foams have been emerged as new materials for both structural and functional applications. For years, researchers have been trying to prepare these materials in an attempt to emulate naturally occurring porous materials, such as bone, coral and cork. The history of metal foam fabrication dates back in 1948 when Sosnik [1] filed a patent for the fabrication technique of aluminium foam by inducing gas into molten metal. However, Surge in the research and development of metal foams has been started in 1980s, and thus they are considered as new materials. This is due to the fact that applications of metal foams have been discovered in the past two decades. The characteristics of metal foams which establish them as a different class of materials are the combined properties of metals and foams. Metals are tough, thermally and electrically conductive and strong. Foams have low weight and adjustable density [2]. Combined properties of metals and foams make metal foam suitable for many structural and functional applications. They offer opportunities to use them for a wide range of applications, such as shock and impact energy absorbers, dust and fluid filters, engine exhaust mufflers, porous electrodes, high temperature gaskets, silencers, flame arresters, heaters, heat exchangers, catalyst supporters, construction materials and biomedical implant[3]. There are two fundamental strategies for fabrication of metal foams. Direct foaming methods start from a specially prepared molten metal containing uniformly dispersed non-metallic particles as stabilising agents to which gas is passed to form bubbles to create foam. Indirect foaming methods start from a solid precursor which consists of a metallic matrix containing uniformly dispersed blowing agent particles, mostly titanium or zirconium hydride. Upon matrix melting, this precursor expands and forms foam [4]. The methods for metal foam fabrication can further be classified into four groups according to the physical state of starting metal: liquid, solid, gas and aqueous solutions.

Titanium foams have been mostly studied as materials of biomedical importance as Titanium is one of the metals that have been used as bio implants in human body as it offers excellent biocompatibility. Researchers have been working to obtain Ti implants with low density, reduced Young's modulus to reduce stress shielding effect which causes bio implant loosening, and porous structure for better anchoring by tissue in growth. However, outstanding mechanical properties, low density and high chemical resistance of titanium make titanium foam a suitable material for structural applications, as in sandwich core for aerospace or submarine vehicles, taking advantage of its low density combined with good strength, stiffness and excellent corrosion resistance. Also, Titanium has high melting point that makes titanium foam suitable to be used at elevated temperature as in heat exchangers and catalysts substrate, but limited to 400 C due to low oxidation resistance of titanium [5]. Titanium foams have been now widely studied for a number of applications, and becoming popular materials for many applications, such as such as shock and impact energy absorbers, dust and fluid filters, engine exhaust mufflers, porous electrodes, high temperature gaskets, silencers, flame arresters, heaters, heat exchangers, catalyst supporters, construction materials[6][7][8][9].

Research in fabrication of Titanium foam has achieved great success in recent years. A number of techniques for the Ti foam fabrication, such as space-holder, replication, loose powder sintering, hollow Titanium powder sintering, freeze casting and Argon gas expansion are important to be noted [10]. Unlike the aluminium processing of Titanium in to foam in, liquid state is very difficult. This is due to the fact Titanium has very high melting point (1668 C) and also it has high reactivity with gases like oxygen and nitrogen at elevated temperature. This also explains the fact that aluminium is widely used for foaming purpose as it can be processed in to foam in both liquid and solid states.

Among the fabrication methods of Titanium foam, powder metallurgical routes or powder compact foaming methods are promising due to their considerable advantages [11]. The most

significant advantages of these methods are low cost, better control over pore size and shapes, and the capability of near-net-shape production. In powder metallurgical methods perform is made by compaction of metal powder or hollow spheres of metals. It is followed by the sintering of perform.

Among powder metallurgical methods Space holder method is very promising to fabricate Ti foam. In this method, Ti powder is mixed with a space holder which actually reserves space for porosity in the titanium matrix. Ti powder and space holder must be mixed completely to assure the homogeneity of the mixture. Control over this process depends on how well the powders are mixed.

Depending on the type of space holder, thermal removable or solvent removable compaction is followed by either space holder removal or sintering. The selection of space holder is very crucial step in the process of making Ti foam through this technique. As space holder may contaminate Titanium foam which can make it unsuitable for a number of applications. For example, contamination of Ti foam by space holder materials with some bioactive compound. Magnesium, NaCl, carbamide have been successfully used as space holder materials [12] [13][14]. There is a separate category of metal foams which are made by space holder technique but spacers which are hollow spheres of inert materials are not removed rather remain in the foam.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction to porous materials

Porous materials are also described as cellular solid structures. Natural porous materials in the form of wood, cork and plant stem include prismatic, honeycomb-like cells, and are strong lightweight structures that are known to humankind from the very beginning[1]. These materials offer a unique combination of physical and mechanical properties such as good electrical insulating properties, good permeability for water and air, acoustic properties, low thermal conductivity, impact energy absorption capacity, high stiffness and very low specific weight. Manmade porous materials which are made from polymers and ceramics have been widely used for a long time now. Porous materials made from metal followed and a boost in research and development of metal foam has been seen after 1990[2]. These porous materials made from metallic, polymeric or ceramic structures can be divided in three types: Honeycomb, Open cell and closed cell foam [3].

2.2 Types of porous metals

The applications for permeable (metals having a vast volume of porosity, regularly 75-95%) and metal froths (metals with pores purposely incorporated into their structure through a frothing procedure) rely on upon their structures. Metallic froths can be separated in two classifications, in light of cell structure.

(a) Closed cell froths, which have gas-filled pores differentiated from one another by metal cell dividers, have great quality and are for the most part utilized for auxiliary applications.

(b) Open cell froths, which contain a ceaseless system of metallic struts and the encased pores in every strut edge are joined (by and large these materials are really permeable or cell metals), are weaker and are predominantly utilized as a part of practical applications where the consistent way of the porosity is abused.

Among the man made permeable metals or froth titanium and aluminum based froths have been generally utilized as a part of numerous auxiliary and utilitarian applications. Powder smaller softening procedure was produced by Fraunhofer-Institute in Bremen (Germany) [37-39]. The initial phase in this system is making of a forerunner or foamable metals. Metals powder, or amalgam powder is blended. Then blend is compacted to a thick, half completed item for further preparing. In the following step forerunner material is warmed close to the liquefying temperature of the framework material. Blowing specialists which is homogenously disseminated inside the grid decays. A very permeable structure is shaped as discharged gas on the disintegration of blowing specialists compels the antecedent material to grow. The time required for full extension relies on upon temperature. The span of the forerunner and reaches from a couple of seconds to a few minutes. The level of greatest extension, and consequently, the thickness of the strong metal froth, can be controlled by conforming the substance of blowing operators and a few other frothing parameters, for example, temperature and warming rates. Titanium or Zirconoium hydride is utilized to froth Zinc and Aluminum combinations. SrCO 3 [40] can be utilized to froth steel. Under 1 % amount of blowing operators is obliged in the event that it is a metal hydride. Aluminum froths made thusly have given exchange names ""Foaminal"" and "Alulight".

2.3.1 Casting methods

2.3.1.1 Casting around space holder materials.

In this strategy empty circles or granules which are made of natural or even inorganic materials are utilized. A permeable low thickness metal can be acquired by packaging liquid metal around these low thickness granules or essentially by consolidating these granules into the melt. Granules are later uprooted by draining in a suitable solvents or acids or by warm treatment.

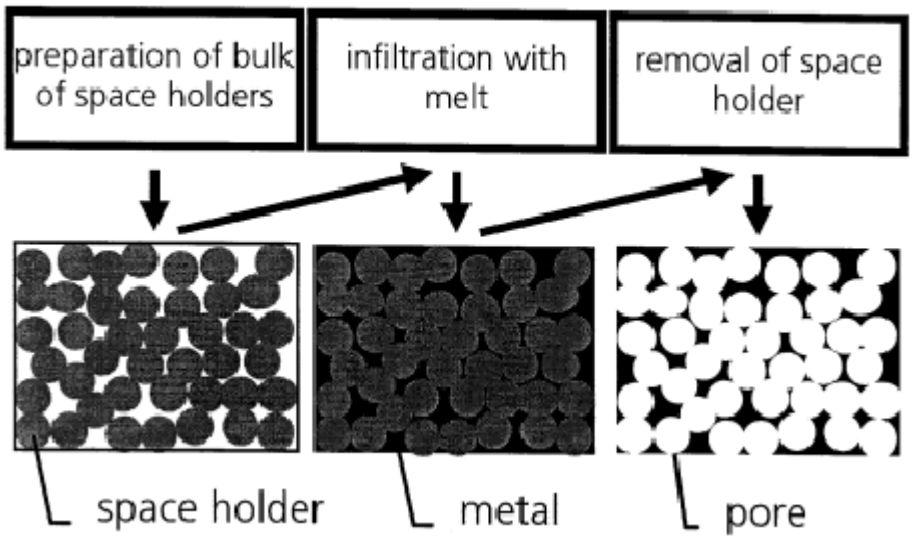


Figure 2.6. Schematic of casting around space holder method [41]

Cases of inorganic filler materials are Vermiculite or let go mud pellets [41], solvent salts [42], free majority of extended earth granules, frothed glass circles or aluminum oxide empty circles [43]. Polymer circles can be utilized as natural filler materials (figure 2.6). Untimely cementing of melt can bring about an issue. Additionally fragmented filling by liquid metal of voids between granules can be an issue as wetting edge of fluid metal and space holders is low. Utilizing prehated space holders and creating vacuum between granules or utilizing weight for invasion can be a reasonable answer for these issues. Various metals like Aluminum,

magnesium, zinc, lead, tin, and so forth can be handled by along these lines. A superior control over pore size and shape is the upside of this strategy.

2.3.1.2 Spray forming (‘‘Osprey process’’)

In spray forming a metal melt is continually atomised in to small droplets and deposit on to a substrate where it gets solidified in a dense film.

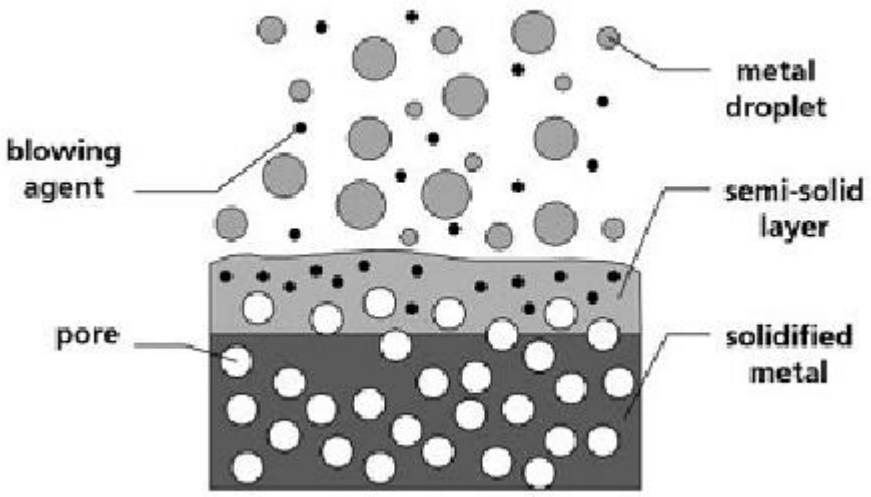


Figure 2.7 Spray forming method for manufacturing of porous metals [45]

There is one exceptionally intriguing plausibility of changing properties of store by infusing powders of oxides, carbides or immaculate metals into the splash and permitting them to respond with the liquid metal in the drops or be wetted by it and to be joined into the metal as it is kept on the substrate. In the event that the infused powders are substances which disintegrate upon contact with the liquid metal and discharge a lot of gas, they may create pores in the store (Figure 2.7). This impact can be utilized to make permeable metallic materials. Kelley et al. [44] have researched the development of porosity in CuSn6 composites by infusing BaCO3 powder. Banhart et al. [45] have made permeable steel by infusing silicon oxide or manganese oxide into a carbon steel splash, therefore making a lot of carbon monoxide in the

testimony zone in a synthetic response of the sort SiO2 + 2C ▶ Si + 2CO. By along these lines permeable materials with porosity up to 60% can be made yet pore morphology is non uniform.

2.3.2 Solid state processing of porous structure

Strong metal in powder structure can be utilized to make permeable structure. For this situation, metal stay strong in whole process and just experiences sintering methodology or other strong state operations. In this process no fluid metal is included so there is less risks of the arrangement of shut cell structure as just fluid metal tends to frame shut cell because of surface strain. So sintered permeable items demonstrate the average open morphology of confined, pretty much round particles associated by sinter necks.

2.3.2.1 Sintering of metal powders and fibres

Titanium, super amalgams, bronze stainless steels are a few materials which are changed over into permeable structure by his technique. This technique fundamentally includes three stages: powder fractioning and planning, compaction or embellishment, and sintering [19]. By free pack or gravity sintering of bronze (Cu89Sn11) at 820 C a permeable structure with porosity extending from 20 to 50 % can be Making permeable structure from aluminum composites powder or granules is troublesome as aluminum is secured by thick oxide layer which keeps the particles from sintering together. This issue can be settled if powder mixture is disfigured before sintering. By disfigurement oxide layers are separated and metallic holding happens between powder particles. On the other hand, sintering guides, for example, copper, silicon or magnesium powders can be utilized. These sintering guides really frame a low liquefying eutectic combination amid sintering at 595- 625 ºC. There is an option approach to shape permeable structure by first changing over metals into metal fiber then sintering metal filaments to deliver permeable structure [20].

2.3.2.2. Gas entrapment technique

In this system metal powder is squeezed to thick minimal or antecedent material. Amid compaction some idle gas is permitted to be entangled in the material [21]. In second stride on warming the antecedent leads the metal development because of weight made by ensnared gas. This procedure can't be called as genuine faming as it happens in strong state however it’s an illustration of strong gaze drag process.

2.3.2.3 Porous metals based on space-holding fillers

In this system main part of space holding material is loaded with fine metal powder as opposed to being invaded with fluid metal. Metal powder is either documented into a dry majority of space holding materials, or a suitable dissolvable or even a natural dissolvable [22] can be utilized to blend metal powder and space holder particles. Space holder materials can be any of clay particles or empty circles, polymer grains or empty polymer circles, salts or even metals. The filled mass is then compacted either at room temperature or at hoisted temperature if filler material is adequately warm safe. At lifted temperature compaction impact is more declared as sintering techniques between the metal powders particles may begin. In both cases, a composite is acquired which comprises of a metal network with installed filler granules. On the off chance that the metal substance is adequately low, it is conceivable to evacuate the space holder material totally in a further process step in light of the fact that the system shaped by the filler material is interconnected. This could be possible by warm treatment, draining, or by utilization of a fluid dissolvable. Permeable material subsequently got can further be densified by sintering.

2.3.2.4 Metallic hollow sphere structures

In this method hollow spheres of metals such that copper, nickel, steel or titanium are used to make a highly porous structures by bonding the individual spheres together by sintering. There are many ways to make metallic hollow spheres:

- Combined chemical and electrical deposition of the respective metal onto polymer spheres which are removed in a following step [23],
- Or by coating polymer spheres (e.g., of polystyrene) with a binder/metal powder suspension and subsequently sintering the metal to obtain a dense metal shell while the polystyrene is removed [24].
- Or by blowing metal powder, metal oxide powder or metal hydride powder slurries up to micro-spheres using coaxial nozzles, dry the spheres in a drop tube, and then sinter or deoxidise these dried spheres [25, 26].
- Or by atomising metallic melts and under certain parameters so that hollow spheres [27] can be formed. Porous structures made of Ti-6Al-4V alloy hollow spheres contain 36% porosity outside the hollow spheres , 44% porosity in the sphere cavity and have a solid volume in the sphere walls of 20%, or overall density of 0.9 g/cm3

2.3.3 Electro-deposition technique

In this system beginning material is metal in its ionic state i.e. arrangement of metal particles in an electrolyte. Polymeric froth with open cells utilized as substrate on which metal is electrically saved. Later polymeric material is evacuated. For the most part polymer froths are not electric transmitter. In any case, electro testimony obliges some conductivity in polymer froths. Polymer froths can be made conductive by dunking the polymer froth into electrically conductive slurry, in view of graphite or carbon dark, by inundating the froth into an electro less plating arrangement, or by covering the polymer with a dainty conductive layer by cathode

sputtering [29]. Later, polymer is expelled from the metal/polymer composite by warm treatment. This system is especially suitable for nickel and nickel –chromium compounds however copper froths can likewise.

2.3.4 Vapour deposition

Vaporous metal or metallic mixes can likewise be utilized to deliver metallic froths. A strong forerunner which characterizes the geometry of froth to be delivered is needed. Polyurethane froth can be utilized for this reason. Metal vapour is created in a vacuum chamber and is permitted to consolidate on cool antecedent. The dense metal coats the surface of the polymer antecedent and structures a film of a certain thickness described by the thickness of the vapor and the introduction time. Bend vapour affidavit method can be utilized to complete this methodology. [30].

There is an option approach to make permeable structure by utilizing nickel carbonyl gas. On the decomposition of nickel carbonyl nickel gas and carbon monoxide is delivered at 120º ignoring nickel carbonyl gas polymer antecedent at such a temperature one can coat polymer forerunner by nickel. Froth framed by thusly is called in co-foam.

2.4 Titanium

Titanium has been utilized for various application, for example, aviation and boat businesses after its revelation. It was initially found in 1791. In the period of innovative progression Titanium and its combinations are being utilized as a part of new and energizing fields. Economically, Titanium with 99.9% immaculateness is delivered. It contains minor measure of debasements like carbon, iron and oxygen. Unalloyed Titanium is partitioned into 4 distinct evaluations. The evaluations are requested on the premise of relative consumption resistance, malleability and quality prerequisites for a particular application.

Grade 1 has the most noteworthy consumption resistance and malleability and lower quality. Grade 4 has most noteworthy quality and moderate formability. Pollutions of oxygen, carbon and nitrogen reinforce the titanium by framing a strong arrangement. A strong arrangement is shaped by the dispersion of a component into the lattice of others and development of strong arrangement influences the properties, for example, yield, pliable, exhaustion quality, of grid material. The yield quality of titanium is between 485-1030 MPa, elasticity 760-110 MPa and Young's modulus is 110 GPa.

2.5 Development of porous titanium

Titanium cannot be foamed in liquid state as the high melting point (1668 ºC high affinity of it with atmospheric gases (oxygen and nitrogen) make it practically difficult to foam titanium by liquid state processing. Though Titanium foam can be produced by many other processing techniques but powder metallurgy route offers a viable technique to fabricate titanium.

2.5.2 HIP method backfilled with argon gas

In this method powders are first filled into a steel canister which is evacuated and then backfilled with argon gas. In further process densification takes place by hot iso static processing. Since argon cannot react with titanium powder, it is entrapped in the matrix of titanium powder as isolated, micron sized and high pressure gas baubles. In final steel after the removal of steel canister titanium billet is heated at elevated temperature under vacuum. At elevated temperature reduced strength of titanium matrix allows expansion of high pressure argon bubbles. It results n the formation of porous titanium structure. . Thelen et al. [30], Spoerke et al. [31], Davis et al. [32] and Shen et al. [33] used hot isostatic pressed method backfilled with argon gas to produce pure titanium foam and Ti-6Al-4V foam. In their experiment, compressed bubbles of Argon have been used. They have also elongated the pores

by a tensile load during the process. Pure titanium foam was made by pressing titanium powder in the existence of argon gas.

2.5.3 Plasma spray method

M. Takemoto et el. [34] produced bioactive porous titanium by plasma spray technique and subsequent chemical and thermal treatment in a 5M aqueous NaOH solution at 60 ºC immersion in distilled water at 40 ºC strength and yield strength of 280 MPa and 101 MPa, respectively.

2.5.4 Directional freeze casting technique

Chino and Dunand [34] produced titanium foam through freeze casting of aqueous slurry of titanium powder with 57–67% porosity. It was found by these investigators that the size of Ti-powder plays an important role to the synthesis of Ti-foam. The strength of these foam ranges between 40 and 60 MPa, which are equivalent to that of human bone.Advantages of each of above techniques, are summarized in table.

Table2.1. Advantages of different production techniques of titanium foam.

Production technique	Advantages
Plasma spray method with chemical and thermal treatment [4]	• Homogeneous bioactive surface • Small change in surface morphology
Plasma rotating electrode process(PREP) [5]	• Good packing and flow characteristics • High quality and near net shape
Directional freeze casting technique [6]	• High compressive strength due to high powder oxygen content
Hot isostatic pressed method backfilled with argon gas [7],[8],[9]and[10]	• Faster forming rates, good strength and high porosity

2.5.5 Sintering of powder

2.5.5.1 Sintering of uniform powder

Among all methods of titanium foam production, powder-sintering method is most viable and widely used. Partial sintering of a porous perform of titanium powder is simplest technique of titanium foam production. Crincione et al. [23] produced foam with porosity 41-55 % by sintering loose Ti-6Al-4V powder for 0.5 to 24 h at 1000 C. It was found that at porosity of 49 %, foam produced is of maximum compressive strength of 55MPa. Amount of necking between powder particles determines strength of foam. Oh et al. [23] used unalloyed titanium powders, sintered with, and without pressure, achieved 5- 37 % porosity. With the increasing amount of porosity Young's modulus and strength decreased and at 30 % porosity, stiffness of porous titanium was close to that of human bone (20 GPa). Theime et al. [23] observed that sintering of coarse powder particle could be accelerated by addition of 1.5 wt % silicon to titanium powders which produced a transient liquid phase, with no measurable decrease in foam strength after processing. Theime et al. also sintered a stack of three powder layers with different particle size and silicon content. For finer powder layer volume fraction and pore size were reported as 22% and 48 μm, while for coarser powder layer volume fraction and pore size were 45% and 200 μm. Gradient in elastic property was also found. One of the limitations of powder sintering method is, the size and shape of pores depend on the size and shape of titanium powder. For spherical powder, porosity is limited to 50 % and highly non-spherical pore shape. Pores are cusped at the sintering necks between powder particles, at these points cracks can initiate under fatigue conditions. One of the solutions of this problem is, use of hollow powders. In that case, porosity consists of space within the powder particle and between the powder particles; Sypeck et al. [41] used this technique and produced foam with 73 % porosity by sintering of 0.5mm-1.4mm diameter hollow spherical particles of Ti-6Al-4V for

24h at 1000 ºC. Due to weak bonding between spheres of large size, Strength of foam produced by them was not good, and was 6.2MPa.

2.5.5.2 Sintering of a non-uniform powder performs made with a gaseous blowing agent

Use of gas blowing agent within a preform consisting of titanium powder and small primary pores gives control over pore size and shape and in this case, pore size and shape are independent of titanium powder characteristics. Upon sintering primary pores are eliminated rapidly. Disadvantages of this method include large size of secondary pores, contamination due to binder used and residual primary porosity due to incomplete sintering. Jee at al. [28] used C02 based blowing agent to form large secondary pores in a titanium preform. They formed reticulated foams with 90-95% porosity and cell size 0.4 mm. Hurysz et al. [23] combined above two techniques- use of titanium hollow spheres with blowing agent titanium hydride and formed foam with porosity of 86 %.

2.5.5.3 Sintering of metal or alloys powder deposited on a fugitive scaffolds

In this technique a polymeric scaffold is repeatedly coated with a mixture of titanium powder and binder, after removal of binder and scaffold and subsequent sintering of remaining titanium powder, a reticulated open cell foam with hollow titanium struts results. Li et al. [24] used this technique to fabricate Ti-6Al-4V foam with 88 % porosity and 10 MPa compressive strength by using polyurethane scaffold foam.

2.5.5.4 Sintering of a non-uniform powder preforms containing a space holder

Many of the techniques discussed above have shortcomings of limited porosity and highly irregular pore size and shapes. A simple development of standard PM, incorporating a volume

of space holders offers a precise control over pore size and morphologies. The space holder technique was first used by Zhao et al. [20] to fabricate Aluminium foam. They used NaCl as space holder.

Space holder technique generally consists of 5 steps as shown in the figure.

- **Powder selection**

  The selection of space holder for a particular metal is a most crucial step as most of the properties of final foam such as the cell shape, size and porosity depend on the space holder.

- **Mixing**

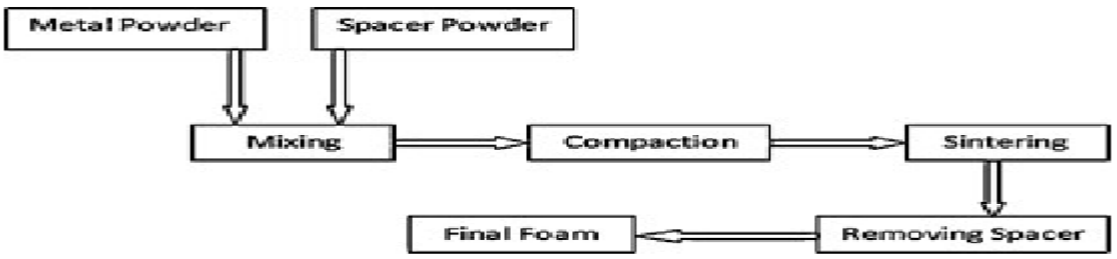
  After selection, metal powder and space holder must be mixed completely to assure the homogeneity of the mixture. Control over this process depends on how well the powders are mixed.

- **Compaction**

  In this step powder mix is compacted into a mold under controlled pressure conditions.

- **Sintering and spacer holder removal**

  Depending on what kind of space holder is used in the process, the next step can be either sintering or removal of the space holder.



2.6 Space holder

Generally, space holder is a solid material, which can be removed at low temperature without excessive contamination of titanium. Some of the commonalty used space holder materials are sodium chloride, sodium fluoride, carbamide, ammonium hydrogen carbonate, titanium dihydride, magnesium and even tapioca.

2.6.1 Types of space holder

Generally there are three types of space holder.

- Thermally removed
- Removed by solvent
- Micro ballons / NaCl /Hollow balls are used to fabricate syntactic foam

In this method titanium powder is mixed with space holder materials and then compacted, later space holder material is removed either in sintering or after sintering by dissolution or thermal degradation, leaving porosity. Also, porosity can be easily controlled by varying titanium/ space holder volume ratio. In one of the early approaches, Wheeler et al. [45] sintered Ti or Ti-6Al-4V at 1400 ºC, earlier to sintering they used Magnesium as space holder material, which was evaporated at 1000 C. Foam exhibited 25-82% porosity, strengths of 15-607 MPa, and Young's Moduli of 3-9 GPa. Bram et al. [41] produced titanium foam with porosity in the range of 60-77 % and pore size in the range 0.1-2.4mm.they used carbamide as space holder, which was removed below 200 ºC, and after that sintering, was done at 1400 ºC for 1 hour. Porosity and pore size were controlled by volume and particle size of carbamide. Dizlek et al. [75] prepared Ti6Al4 V foam with 60% porosity and pore size between 315 and 500 μm, and observed that biomodal particle distribution provides higher strength and stiffness as compared

monomodal particle distribution. They also found that strength and stiffness increase with increase in sintering temperature. Wen et al. [33] produced foam with porosity of 78 %, compressive strength of 35MPa.

Young's modulus of 5.3 GPa. They used ammonium hydrogen carbonate as space holder, which was decomposed at 200 OC, and subsequent sintering at 1200 OC for 2 h gave them good quality Rausch and Banhart [12] produced foams with 55-80 % porosity by sintering at 1100 ºC- 1250 ºC with polymer granules as space holder, which was earlier removed chemically at 130 ºC. Foam with Young's modulus of 0.3-16 GPa was obtained. Bing and Dunand [78] prepared open cell Ti-foam using NaCl salt as space holder. They observed that porosity and strength depend on NaCl content and its size, compaction pressure and sintering temperature.

2.6.2 Syntactic foam

Syntactic foams are a special class of closed cell foams. In syntactic foam a porous structure is made by filling a metal, polymer or a ceramic matrix with hollow particles called microballons. In actual sense these microballons act as space holder but they are not removed out rather remain in the foam. Microballons are inert, lightweight and strong particles. Presence of these hollow particles results in foam with low density, high specific strength and good dimensional stability because of lower thermal expansion coefficient. A wide variety of microballoons are available, including NaCl, glass microspheres, carbon and polymer microballoons. Many Properties of syntactic foams depend on the choice of microballons. Volume fraction and wall thickness of microballons influence the properties of the syntactic foam. So by controlling these parameters one can tailor the foam properties.

CHAPTER 3

EXPERIMENT AND MATERIALS

Experimental details

3.1 Milling of Titanium

3.2 Fabrication of Ti-NaCl Syntactic foam

The powder metallurgy method has been used to fabricate Ti-NaCl syntactic foam. A detailed process to fabricate Ti-NaCl syntactic foam by this method is described in this section.

To produce Ti- NaCl syntactic foam powder metallurgy method is one of the most promising methods, as it doesn't involve any kind of melting of Titanium and thus avoids the possibility of extensive reaction of Titanium with gases like Oxygen and nitrogen. Also, this method offers a pore size, shape and volume fraction, as it closely depends on size, shape and volume fraction of NaCl space holder.

The fabrication of Ti- NaCl syntactic foam by powder metallurgy method uses Titanium powder and NaCl as starting materials. It mainly consists of 4 steps:

(1) Mixing of Titanium powder with NaCl and binder.

(2) Uniaxial compaction of the mix under closed control over applied load.

(3) Drying of cold compacted pellets for increasing handling strength of pellets and it also removes moisture. Drying is followed by Debinding where compacts or green pellets are heated at around 400 C for sufficient time to remove the binder, it is an optional step. In present study debinding is not carried out rather dibinding took place during the process of high temperature sintering.

(4) Sintering of the dried cold compacted pellets.

To obtain Ti-NaCl syntactic foam with desirable properties following should be controlled:

- **Powder properties**

  Size, shape and purity of Ti powder and NaCl particles.

- **Compaction parameters**

  Compaction time and pressure or load. For given volume fraction of Ti and NaCl, Compaction load should be well optimized as NaCl are very much fragile. These hollow particles can be easily crushed during compaction process. But very less amount of load can be insufficient for proper bonding between the particles. Generally compaction load for this purpose is used in the range of 4 ton to 5 ton. In this study compaction load of 4 ton is used. Compaction time of 1 minute is used for this study.

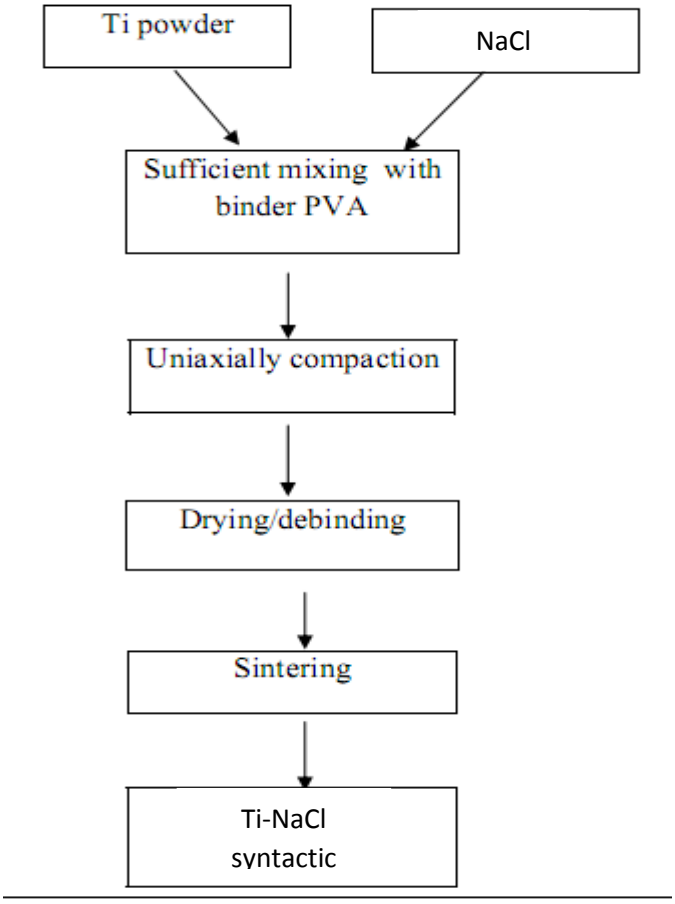


Figure 3.1 Schematic of processing of Ti-NaCl syntactic foam

- Sintering parameters

  To avoid oxidation of Titanium sintering is done in vacuum or inert atmosphere.

  To final properties of sintered materials mainly depend on:

- Sintering time
- Sintering temperature

  One of the main aims of this study is to understand the influence of above two sintering parameters on the properties of foam.

3.3 Materials

3.3.1 Titanium powder

The average size of Ti powder particles is 45 micron and morphology is irregular, while purity is 97 %. Colour of Ti powder was black.

3.3.2 Space holder: NaCl

3.3.3 Binder: PVA

Polyvinyl Alcohol (PVA) was used as binder. 5 wt% of PVA solution (10 wt% PVA dissolved in water) was used to provide sufficient green strength to compact.

3.4 Mixing

Titanium powder and NaCl were thoroughly mixed by using a pestle and mortar to ensure uniform distribution of NaCl and Titanium powder. This step is very crucial to ensure uniform properties such as porosity, density etc in the final foam material.

3.5 Cold compaction

Blended Ti-NaCl mixture is then cold compacted in a die made of high strength steel at a pressure of 100MPa at a crosshead speed of 0.1 mm/s. Pressure is applied for one minute in order to ensure effectively and uniformly pressing. Prior to compaction 2 or 3 drops of PVA binder were added in the mixture to ensure sufficient strength in green cold compacted pellets of Ti-NaCl.

As uniaxial pressure from top was applied to compressed powder mixture to form green compacts, so the green compacts will have heterogeneous density distribution because of the friction between die walls and powder mix and also between the powder particles. To lessen this effect lubricant, zinc stearate powder, was used to the die walls.

3.6 Drying of cold compacted pellets

The cold compacted pellets were characterized in terms of their dimension and density. Then cold compacted pellets were dried in a furnace at 200 C for 2 hours to remove moisture and increase handling strength.

3.7 Sintering of green compacts

Conventional sintering

Titanium is a highly reactive metal at elevated temperature. It readily reacts with atmospheric gases at elevated temperature. So to avoid undesirable reactions of Titanium with gases, thermal processing or sintering of Cold compacted green pellets was carried out in inert gas, argon environment. The argon gas used was 99.9% pure. In this process when green compacts are kept in a furnace at a high temperature, metallurgical bonds form between metal particles and densification process takes place.

For this study a tubular furnace was used. Cold compacted pellets were heated inside the furnace under argon atmosphere for sintering parameters described below to obtain desired samples for the study. During sintering cold compacted pellets were kept in the crucibles which were coated with alumina powder to prevent diffusion and sticking of Titanium to furnace walls.

Sintering parameters

- Time

  Three different holding times of 2, 4 and 6 hours were considered for the study.

- Temperature Two sintering temperatures of 1000 ºC and 1200 ºC were considered.

- Heating rate

  A heating rate of 5-7 C/minute was maintained.

3.8 XRD analysis

X-ray diffraction technique was used to identify the different phases present in green compact of Ti-NaCl, green compact of pure titanium and sintered pellets of Ti-NaCl or Ti-NaCl syntactic foam. XRD study was carried out in Bruker (ADVANCE D8) machine operated at accelerating voltage of 40 kV and current equal to 30 mA. Before XRD study, surface material of samples was removed by grinding to ensure removal of oxidized layer. The scans were performed using Copper Kα radiation (wavelength 1.541A0). The 2θ angle was varied from 20 to 110 and the scanning rate used was 5 per minute

3.9 Scanning Electron Microscopy (FE-SEM) analysis

The sintered samples were taken for microstructural Scanning Electron Microscope. Sample preparation for SEM analysis was carried out. Samples were first taken for grinding operation.

Samples were diamond polished to have scratch free surface. Before SEM analysis samples were thoroughly cleaned and dried for the removal of grease, dust etc.

Figure 3.2 Compaction Machine

Figure 3.3 Controller

Figure 3.4 Ball Milling

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Figure 3.5 Ball Milling

Figure 3.6 Weighing

CHAPTER 4

Result and Discussion

4.1 Morphological characterization

Figure 4.1 Shows the scanning electron micrograph of the compacted titanium composite after ball milling for two different time duration at different magnifications.

(a) Titanium powder ball milled for 20 hours at 300 rpm.

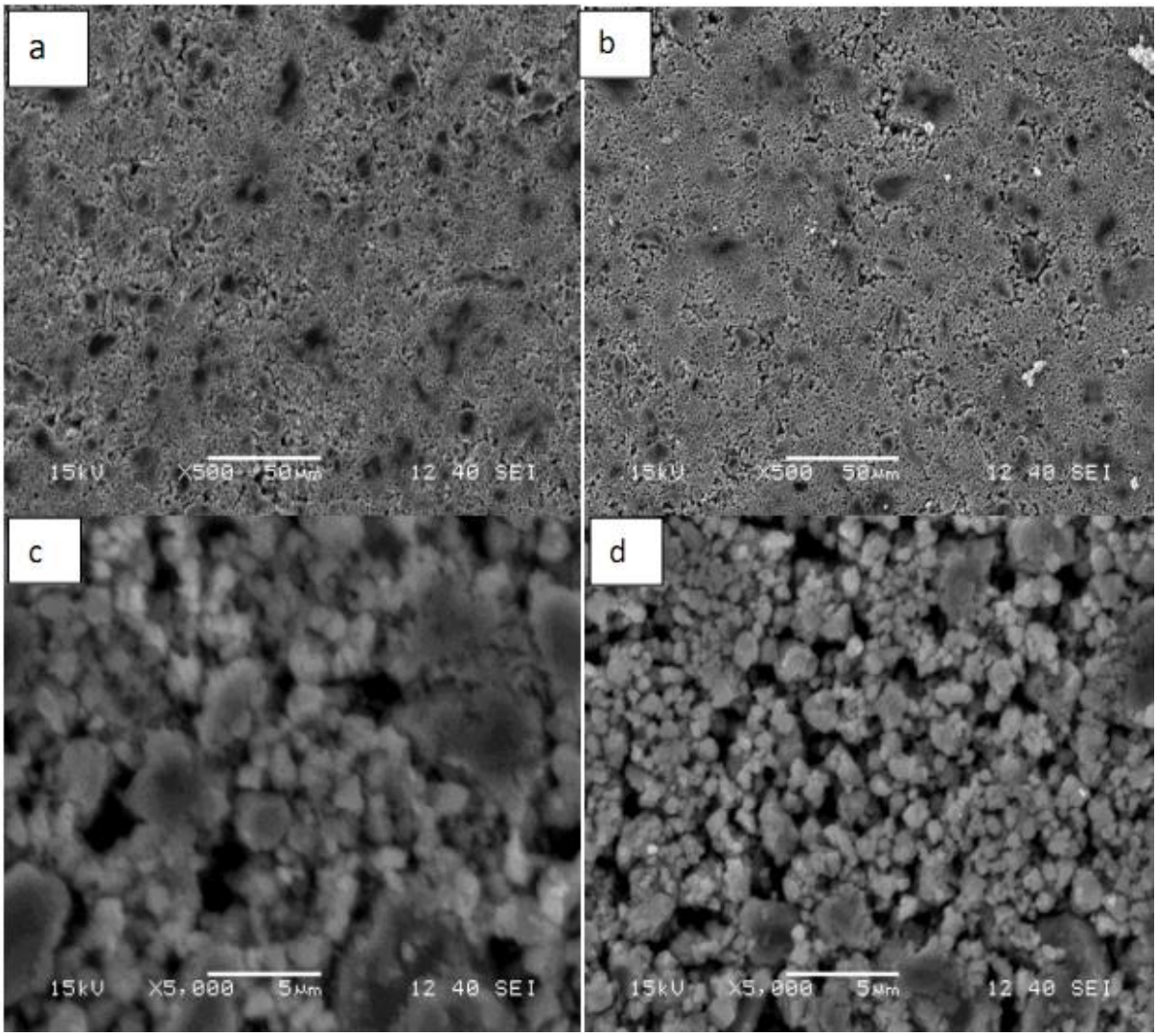

Figure 4.1 Scanning Electron Micrograph of Milled Titanium (a) x 500 and 50µm (b) x 500 and 50µm (c) x 5000 and 5µm (d) x 5000 and 5µm

Figure 4.1 shows the particle size of the titanium powder obtained after ball milling. It shows that the particle are in agglomerated form with average particle size around 0.5-1µm and this particles are then processed for preparation foam.

4.2 Scanning Electron Microscope (SEM)

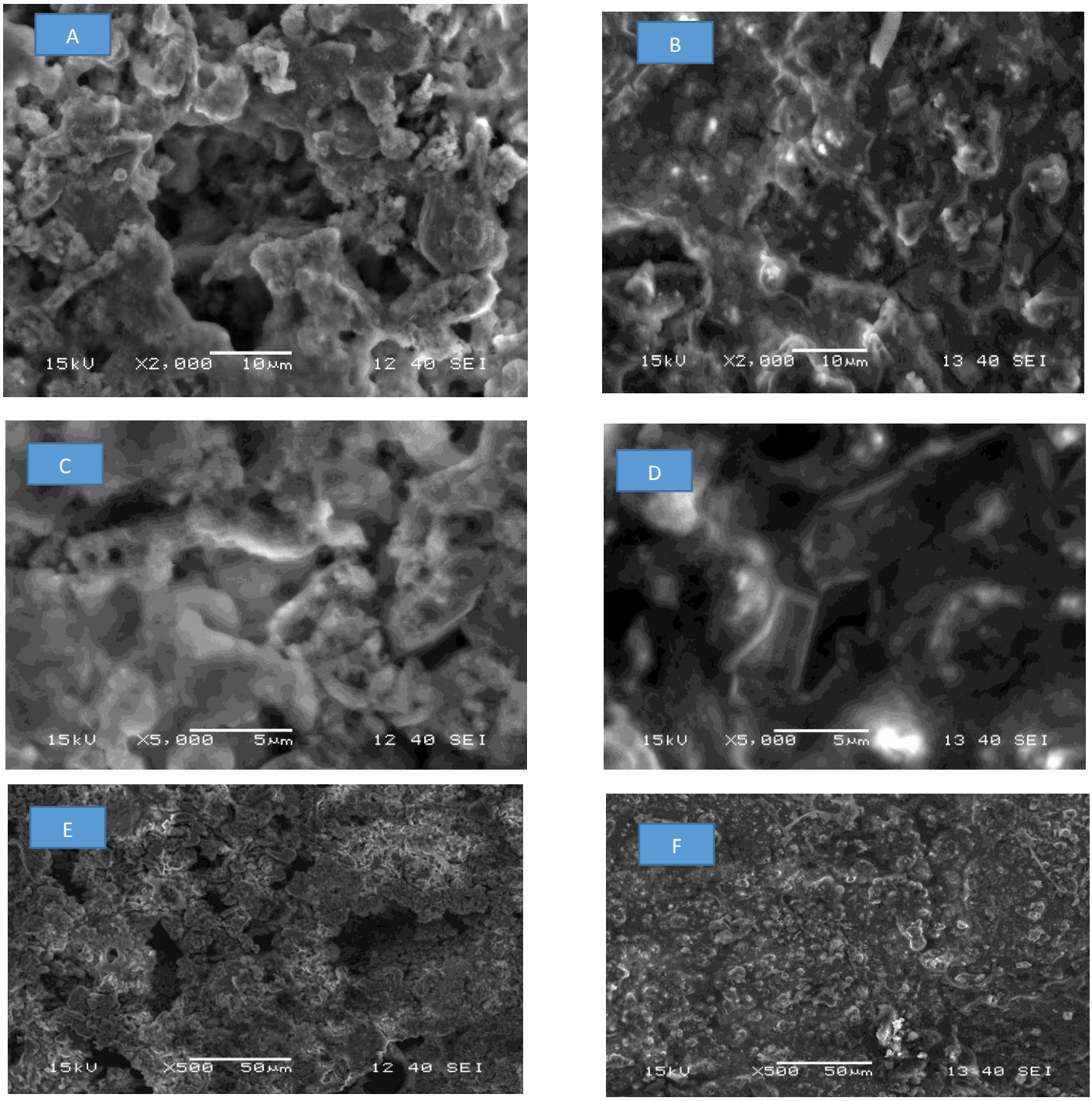

Figure 4.2 SEM of (A) 50% porosity x 2000 and 5µm (B) 60% porosity x 2000 and 5µm (C) 50% porosity x 5000 and 5µm (D) 60% porosity x 5000 and 5µm (E) 50% porosity x 500 and 50µm (F) 50% porosity x 500 and 50µm

SEM images of Titanium foams with 50% and 60% porosities are shown in Figure 4.2 (a, c and d) and (b, d and e) respectively. These figures confirm that near complete densification of the titanium matrix is achieved. The elongated and oval shaped pores in titanium foam thus formed can mimic the structure of bone which accounts for its mechanical anisotropic properties. Moreover at higher magnification the interconnectivity of the pores are also visible which is very important for cell growth. The pore size and porosity get varies by varying the size of NaCl and the ratio of Ti:NaCl in Ti–NaCl mixture.

4.3 XRD Test

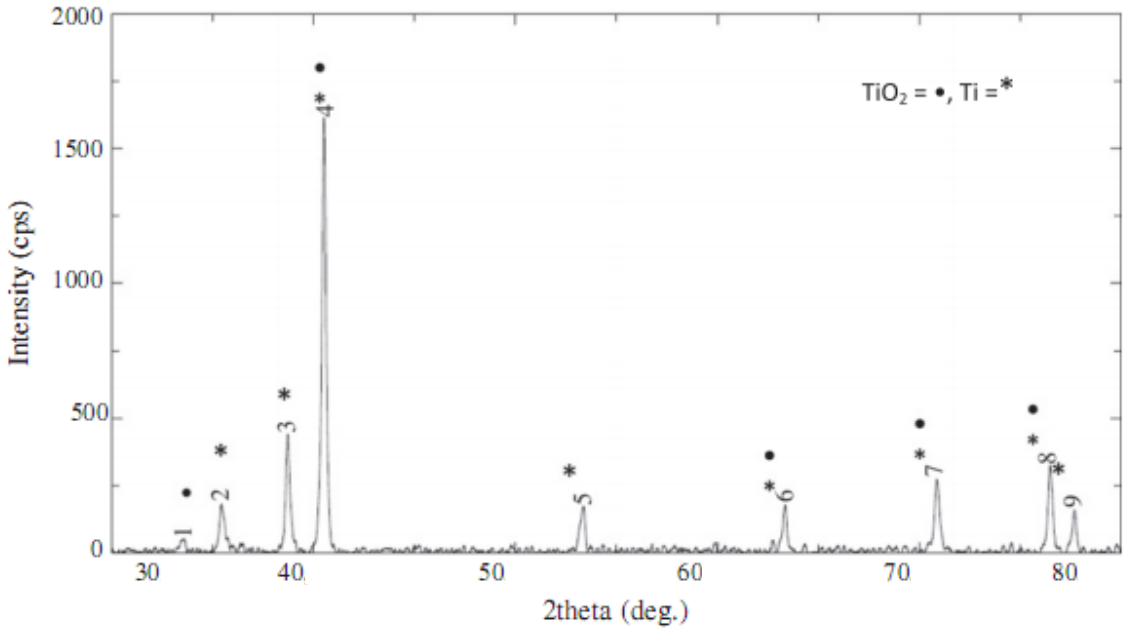

Figure 4.3 XRD of Ti-NaCl foam

Figure 4.3 shows the XRD profile of the titanium foam. The XRD analysis shows the presence of Titanium and Titanium dioxide phase in the foam. The titanium characteristic peaks are marked in the figure as per the JCPDS reference 44-1294 for titanium and 73-1765 for titanium dioxide. Traces of sodium (Na) and chlorine (Cl) were not found in the foam. This confirms that NaCl is completely separated out from Ti-foam by high temperature water treatment for a period of 24 hours.

4.4 Hardness Test

Table 4.1: Micro hardness value for sintered Titanium foam for 150 mins

Load Applied (in gm)	MICROHARDNESS(HV)
300	108.9
300	127.8
300	169.7
300	220.0
300	234.3

The microhardness of Ti-foam were observed to vary in the range from 108.9–234.3 HV. The overall average microhardness value of the titanium foam was found to be 172.14 HV which is less than the commercially used titanium metal.

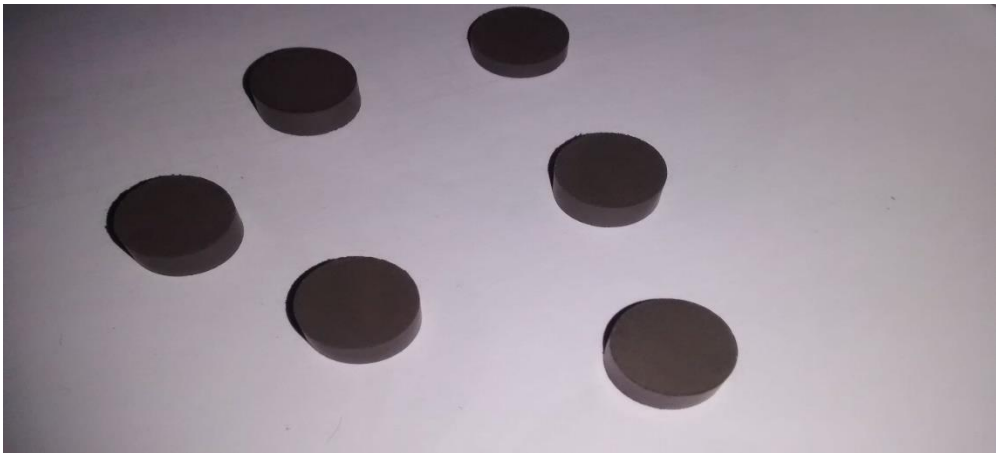

Figure 4.4 50 % and 60% Ti-NaCl foam

CHAPTER 5

Conclusion

Conclusion

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- Ti foam with Porosity 50% and 60% is obtained
- From XRD it is concluded that foam contains mainly titanium and titanium dioxide
- No clue of sodium (Na) and chlorine (Cl) were found.
- NaCl is completely separated out from Ti-foam by high temperature water.
- Ti does not react with NaCl to form titanium chloride.
- The pores are vast.
- Average hardness of Ti-foam is 172.14 HV

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