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A Metallurgical Overview Of Ti – Based Alloy In Biomedical Applications

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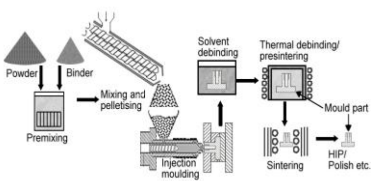
Graphical abstract



Powder metallurgy method

Abstract

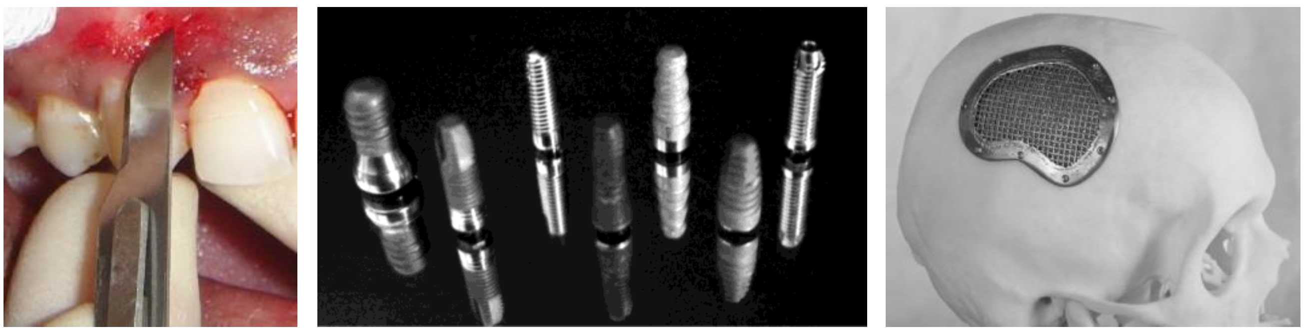
Titanium (Ti)-based alloys are prominently used in biomedical application. This review paper emphasizes on some of the important aspects of the Ti-alloys in terms of metallurgical aspects, manufacturing routes and biocompatibility. Two kinds of structure are reviewed namely dense and porous, both differs in terms of purpose and satisfies different needs. This advancement of materials and equipment helps to improve the quality of life for patients and alleviate their health problems. Metallic materials, mainly Ti-based alloys have been used commercially as bone implant owing to its promising mechanical properties, biocompatibility and bioactivity. The outmost important issue in manufacturing of this alloy is the impurity contents, specifically oxygen and carbon which contribute to decreasing in material performance of the alloy attributed from the formation of unwanted oxide compounds such as TiO_2 and TiC. Another issue is the mismatch value of the Young's modulus between the metallic implant and bone that result in stress shielding effect. The structure of Ti-based alloy is mainly comprised of α-phase, β-phase or a combination of both that result in variation of Young's modulus ranging from 45 -110 GPa. Compared to α-phase Ti alloy, the β-phase rich alloys may exhibit lower value of Young modulus through the right processing technique. Therefore, the development of β-phase Ti-alloys has been researched progressively in line with the need of low Young's modulus that suit for implant applications.

Keywords: Powder metallurgy (PM), vacuum arc melting (VAM), Ti CP, Ti-6Al-4V, impurity contents

1.0 INTRODUCTION

Biomedical materials can be divided into two main categories; dense and porous which both differ in terms of functions and applications. The application of dense parts can be found in devices (scalpel, scissors, throngs, etc.) and implants (fracture fixation, orthodontics screw, etc) as shown in Fig. 1 (a) and (b) respectively. For decades, dense metallic materials made of titanium, cobalt chromium and stainless steel have been used extensively as bone replacement in orthodontic, dental implants, knee and hip replacement and also as plates in facial reconstruction. Although they have demonstrated history of corrosion resistance and biocompatibility, their Young's modulus are considerably greater than that of the natural human bones [1]–[3].

In recent years, the research and development of biomedical materials have been focusing on porous structure made from titanium and its intermetallic[4]. Ti-alloy is well known exhibits excellent biocompatibility and corrosion resistance, having the Young's modulus about half of cobalt chromium and stainless steel alloys (100–110 GPa in contrast to 200–220 GPa) [5], making it the most preferable bone substitution in reducing stress shielding resulting from mismatch of Young's moduli. As stated by Lefebvre et al., the selection of the material structure is based on its end- application. Although dense materials offer excellent mechanical properties, it does not allow the access to the internal surface of the object. Dense materials are mainly used in structural member such as in load bearing application. On the other hand, porous structures are generally associated with the access to the interior of the material and usually utilized in functional applications in which the load bearing capability is not the main objective [4]. Fig.1 (c) is an example of porous implant structure fabricated through electron beam melting process. This paper highlights some important aspects of commercially used implant, Ti-6Al-4V with currently improved alloy, taking into account the fundamental aspects of metallurgy, manufacturing route and biocompatibility factors.



(a) (b) (c)

Figure 1(a) Scalpel used in gum treatment [6] (b) dense dental implant [7] and (c) porous skull implant [8].

2.0 TITANIUM ALLOY

The usage of titanium as implants was discovered in 1952 by Professor Per-Ingvar Branemark M.D [9]. Most widespread titanium base implant biomaterials are extra low interstitial Ti-6Al-4V (ELI) and commercially pure Ti (Ti CP)[10]. However, given that the pure Ti tensile strength is not adequate, particularly for joint replacement and since vanadium (V) and aluminium (Al) in Ti-6Al-4V ELI have been detected to give negative effect to the human body, the search towards promising implant is still progressively carried out. Owing to toxicity level of V element for long term implantation, current research are looking for potential element substitution such as niobium (Nb) and iron (Fe), producing Ti-6Al-7Nb or Ti-5Al- 2.5Fe [11]. It seems to be a rising demand on Ti-6Al-7Nb which largely comes from the dentistry field [12]. Later, V and Al-free Ti alloys such as Ti-15Sn-4Nb-2Ta-0.2Pd and Ti-15Zr-4Nb-2Ta-0.2Pd have been developed [13].

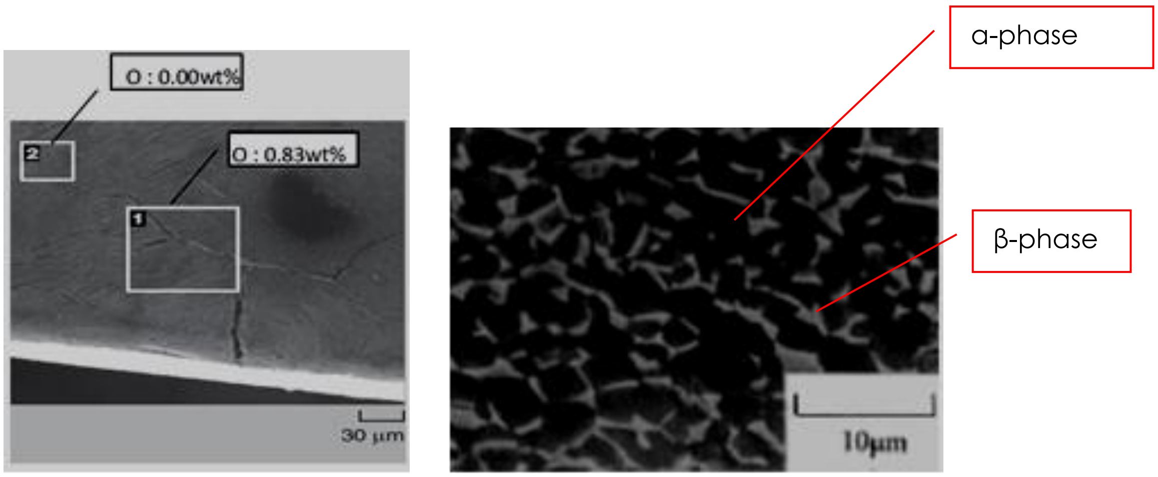
In many cases, the formation of α + β type is common as reported in many studies related to Ti-alloys production. Mechanical biocompatibility with bone was put into consideration and not only the biocompatibility of the alloying elements. Thus, the improvement of Ti alloys that demonstrate comparable Young's moduli to that of cortical bone is being carried out broadly. Furthermore, since it is well recognized that the Young's moduli of β- type Ti alloys are considerably lower than those of the α- and (α + β)-type Ti alloys, the development of low-modulus β-type Ti alloys is now the current main area of research [12]. β-type alloys, such as Ti-12Mo-6Zr-2Fe, Ti-13Nb-13Zr, Ti-29Nb-13Ta-4.6Zr (TNTZ), Ti-35Nb-7Zr-5Ta , Ti-15Mo-5Zr-3Al, and Ti-15Mo have been developed [2], [5], [14], [15].

3.0 METALLURGICAL ASPECTS

The greatest hindrance in producing Ti alloy is how the material can be easily contaminated and causing the formation of compounds such as TiO_2 and TiC which resulting embrittlement of the final structure. Fig. 2 shows clearly the backscattered SEM images of the Ti-6V-4Al, different grey-scale regions can be seen indicating formation of oxide and carbide compounds. The crack can be seen clearly across the secondary phases containing higher contents of oxygen and carbon. Thus, these impurity levels need to be kept as low as possible. In the case of commercially used implant such as Ti-6Al-4V, the maximum oxygen content allowable is 0.13 weight% [16]. There is a need for a secure, contamination free method of processing, since Ti is highly reactive towards the atmospheric air and its surrounding, particularly at high temperature. Embrittlement is the loss of ductility which is usually followed with reduction in stress intensity threshold for crack propagation.

At temperatures above 883°C pure Ti is body-centred cubic (β-phase) and hexagonal close-packed (a-phase) at lower temperatures. Addition of nearly all other elements stabilizes either one phase or the other, a-Stabilizers consist of Al, O, N, and C while β-stabilizers are of two types:1. β-isomorphous (Mo, V, Nb and Ta) which may possess low elastic moduli if appropriately processed and 2. β-eutectoid (Fe, W, Cr, Si, Ni, Co, Mn and H) [17][18]. Elements Zr and Sn have no significant effect on either phase stabilization [5]. Fig. 2 (b) is a SEM image of Ti-Nb consisting a and β phase.

Fig. 3 shows a hybrid equilibrium phase diagram for Ti-Nb, as an example of a β-stabilized Ti-alloy. Also shown in the figure is the martensite transformation curve (M_s) of Moffat and Larbalestier [19].



(a) (b)

Figure 2 (a) Ti-6Al-4V microstructure examinations of alloys after electrochemical hydrogenation revealing hydrogen-induced cracking and pitting in the fully lamellar microstructure [20].(b) SEM micrograph of Ti-14%Nb alloy, the light regions are the β-phase meanwhile the dark regions are the a-phase [3]

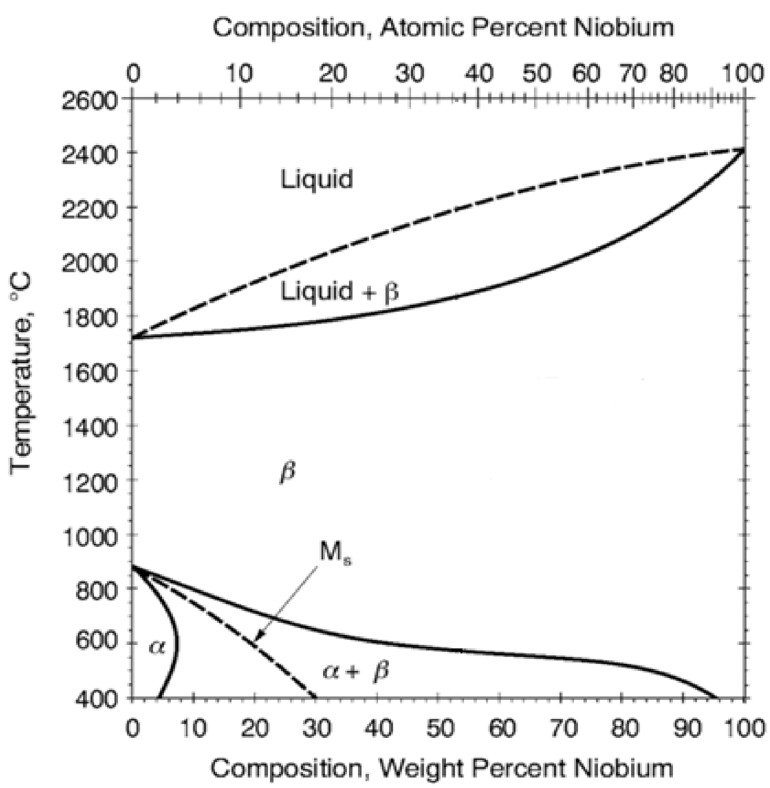


Figure 3 A hybrid equilibrium phase diagram for Ti-Nb [19]

4.0 MANUFACTURING ROUTES

The development of microstructure strongly depends on the manufacturing route employed. Titanium is a highly sensitive material; hence, great precaution should be taken into consideration in selecting its processing route. In addition, the treatments after manufacturing process will also influence the microstructure and mechanical properties. The most common route for processing of titanium is the conventional method (which includes casting and machining process) and powder metallurgy (PM).

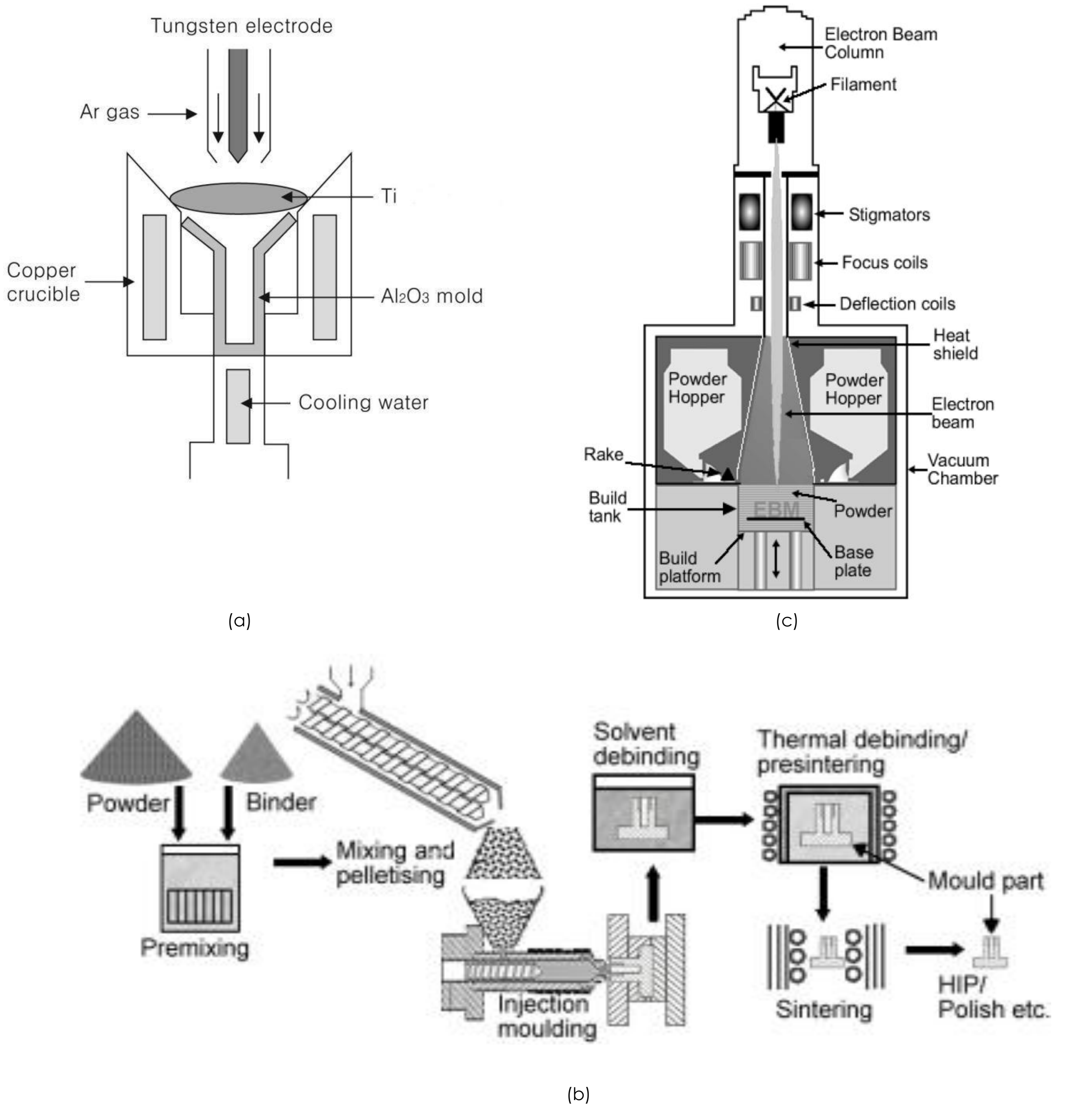


Figure 4 (a) Schematic diagram of drop casting procedure of titanium with a plasma arc melting furnace[21] (b)Metal injection moulding flow diagram[23] (c)Schematic diagram of electron beam melting system[23].

4.1 Conventional Casting and Machining

In conventional method, ingots are melted into moulds and then machined into desired shapes and size. In this method, the molten metal and the hot casting are at risk to atmospheric contamination, since Ti is very reactive with oxygen and other atmospheric gases, the melting and casting procedure involve high temperature fusion [10]. Hence, casting under vacuum or protective neutral atmospheres is a must for Ti. An example of a conventional but controlled process is the vacuum arc melting (VAM) method. Usually in avoiding contamination and ensuring homogeneity, the ingots will be melted for up to 4 times in the vacuum chamber of the vacuum arc melter. Another casting problem is the preservation of good flow over rigorous changes of dimensions or direction within the mould. After the casting process the metal will require a machining process. Problems with regards to the cutting tool, machining time and effect from the machining heat (which may alter the microstructure) will usually arise due to the low machinability of titanium and its alloy. Figure 3 (a) is an example of casting process : drop casting procedure of titanium with a plasma arc melting furnace[21].

4.2 Powder Metallurgy (PM)

Powder metallurgy (PM) is an unconventional processing method which is usually performed through techniques such as Hot Isostatic Pressing (HIP) and Metal Injection Moulding (MIM) particularly for small and intricate components. The fundamentals of PM includes; composition (powdered metals with or without binder), mixing, compacting, sintering and post treatment. This method is employed mainly to produce simple shapes with good dimensional stability, to form shapes with material of extremely high melting temperatures and to produce parts not feasible by other way. Formation of near-net-shape could be achieved before the sintering process gives an added advantage to the PM process, as powders follows the shape of its container, producing net final shape products and abolishing the machining processes [22]. Compared to the conventional method, PM offers energy saving, efficient process and no scrap materials. Figure 3 (b) is an example of PM : metal injection moulding[23].

4.3 Additive Layer Manufacturing (ALM)

A new manufacturing method has been developed with the advancement of technology. Focusing on effectiveness and net shape, additive layer manufacturing (ALM) is also able to produce a functionally graded implant. Derived from the advancements in 3D printing technology, ALM may utilize laser in selectively sintering a bed of powdered metals. Additive fabrication is performed directly from a 3D CAD file in which a geometrical model of part is stored, allowing the manufacturing of complex and intricate shape and able to create non-homogenized parts. This manufacturing method will allow highly customized load bearing capabilities of an implant and mimicking the original parts of the human body. There are already cases where ALM was employed in manufacturing implants for facial reconstruction purpose [24]. Figure 3 (c) is an example of ALM : electron beam melting process [23].

5.0 BIOCOMPATIBILITY

In defining biocompatibility, generally in 1987, "*Biocompatibility refers to the ability of a material to perform with an appropriate host response in a specific situation*" [25]. In regards to the metallic elements employed in the manufacturing of Ti alloy, the metal ions being released to the human body is a big issue which should be taken into consideration. Although the implants in use are usually coated to eliminate ion release, with long term implantation and corrosion that occurs in the human body, there is a large possibility of elemental ions being released into the human body. Nickel allergy for example, will lead to the inflammation of the human body. There are also other elements such as Aluminium which may cause cancer and Vanadium which cause irritation which if possible should be avoided [26], [27]. Ni, Co and Cr are famous for triggering allergic reaction in the human body [27].

Figure 5 is a summarization of elements usually used in the production of implants and medical instruments and their level of harmfulness to the human body, which is adapted from Kuroda et al [28]. Polarization of the metals is associated with its biocompatibility. Elements were grouped into several classes namely toxic, capsule response and vital. The elements classified as vital should be given a fair chance of further research and development.

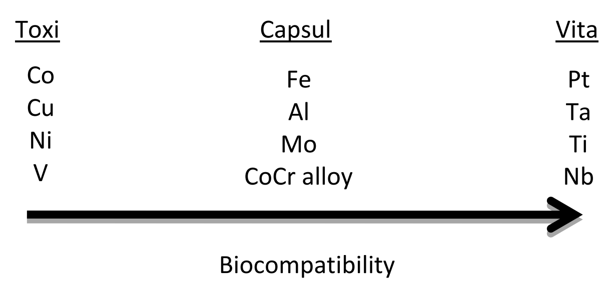


Figure 5 Biocompatibility of metals used for implant materials [28].

In terms of mechanical biocompatibility, there was a study by Niinomi Mitsuo on bone reabsorption after implantation. Niinomi Mitsuo reviews experimental tibial fractures in rabbits 24 weeks after the implantation of intramedullary rods made of low-modulus TNTZ (Young's modulus about 60 GPa), SUS 316L stainless steel (Young's modulus about 160 GPa) and Ti-6Al-4V ELI (Young's modulus about 110 GPa). As shown in figure 6, the posterior tibial bone had become very thin with the implantation of the intramedullary rod made of SUS 316L stainless steel but this phenomenon does not occur to the tibial bone implanted with the two titanium alloys, TNZT and Ti-6Al-4V [12]. This differences in bone structure after implantation is highly associated with the Young's modulus of the respective metals. Since the stiffer implanted material support most of the physical stresses from the original bone this situation will trigger the prosess of reabsorption, leading to the drop of bone density. This problem leads to debris–induced infections or contact loosening and ultimately, implant failure. This experiment by Niinomi Mitsuo highlights the adverse effect of mismatch in Young's modulus between bone and implant material.

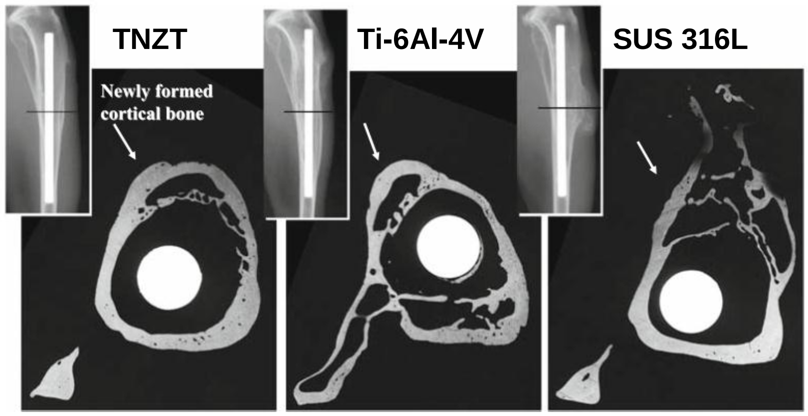


Figure 6 Contact microradiograph of cross section of rabbit's tibia after 24 weeks of metal implantation by Mitsuo Niinomi [12]

6.0 CONCLUSIONS

The fabrication of β phase Ti seems to be a promising route now in producing a mechanically biocompatible implant and bioactive implants. To avoid the allergy reaction in a human body, the elements which induce this problem should be avoided. Hence the authors would like to propose Ti-Nb alloy as a material of study in creating a mechanically and biologically compatible implant. Further research and development is required in order to obtain the best implant which can be considered for lifelong, permanent implantation without any adverse effect to the human body and with the ability to allow active tissue generation.

Based on this review Ti-Nb may be the answer in producing low Young's modulus alloy with material that is non toxic to the human body. In future works, processing conditions will be studied, in producing greater fraction of β-phase formation.

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