Processing of Controlled Porosity Titanium-based Materials

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Abstract

Titanium and titanium-based alloys are used extensively in aerospace, biomedical and many other industrial applications based on their high strength, low density and excellent corrosion resistance. To extend the range of applications, designers and engineers are now seeking titanium-based materials with controlled porosity. Such alloys are currently being developed at the Fraunhofer USA Center for Manufacturing and Advanced Materials, Newark, DE. Traditional powder metallurgy processing routes have been combined with novel forming techniques to fabricate open-celled foams in CP grade titanium. The processing, microstructures and selected properties of these controlled-porosity materials are presented, along with a discussion of potential uses as biomaterials and other applications.

Introduction

Porous titanium components are of interest as filtration media for corrosive and high temperature fluids, lightweight structural aerospace components, catalytic supports and other applications requiring superior strength-to-weight ratios, resistance to chemical attack, high heat transfer efficiency or other characteristics. One particularly important application is as a bioimplant material, where titanium's unique combination of properties are unmatched by all but a few materials.

For orthopaedic implants, in addition to the requirement for biocompatibility, load-bearing capabilities, fatigue strength and corrosion resistance, the need for durable bone implant fixation is of paramount importance. A common approach for enhancing tissue-to-implant fixation is the use of surface-textured implants. Numerous fabrication approaches have been developed for producing porous surfaces on orthopaedic implants, including sintering of metal or ceramic powders or beads onto the outer surface of the implant device, plasma spraying, sintering of added chopped metal fibers, pressing/sintering of long metal fibers or metal felts, among others.

The functional requirements of such porous layers are to provide internal porosity for bone in-growth and fixation to the implants, and to demonstrate sufficient shear strength and mechanical integrity for long-term stability. Pilliar [1] has reviewed various techniques used for surface modification to create macroscopic surface features. Examples for machined macroscopic anchorage elements are millimeter-sized threads, vents, fins and surface grooves or serrations. Microscopic surface features are typical of sub-micron or micron dimensions, and are formed by: (i) removal of material from an implant surface by grit blasting, or chemical or ion etching, and (ii) the addition of material onto the implant surface through plasma spraying or sintering of particles onto the surface.

The thickness of porous surface coatings on solid metallic substrates ranges from 10-30 μm for plasma spraying and up to 1 mm or greater for sintered metal powder layers. Although porous

sintered layers of metal powders are among the most common surface modifications used in orthopaedic implants, they are far from being ideal. Aseptic loosening, especially 10 years or more after implantation, is a principal concern, particularly as younger patients with active lifestyles and increased life expectancy are undergoing joint replacement procedures. Thus, the metal foam technology detailed here may represent a more desirable surface modification to promote improved bone in-growth compared to existing techniques.

Powder metallurgical processing techniques have been used for nearly three decades for the development of surgical implants. The sintering of metal powders onto a metallic core implant material, produced by machining or casting a solid metal piece, creates a porous surface layer with uniform distribution of interconnected pores. Implants produced in this manner have surface areas five or more times greater than as-machined or as-cast metal implants [2]. As a result, higher rates of metal ion release due to corrosion of the implant by biochemical fluids are expected. Thus, the consideration of implant biocompatibility during material selection and implant preparation is crucial. The optimal pore size of the sintered surface layer for human use has not been well established, although it is generally believed that pore openings in the range of 100 to 500 μm are suitable [3]. A varied surface pore size can be achieved by using more than one particle layer. The resulting multi-layered particulate surface zones provide extensive interconnected porous networks.

Pilliar et al. [4] reported the importance of eliminating local contaminants in the surface zone in order to avoid tissue inflammatory responses, and to establish initial implant stability. Sintered porous surface structures have demonstrated more favorable conditions for mineralization and bone formulation than other surface designs that do not have three-dimensional pore interconnectivity. The work of Simmons et al. [5] on implants placed in rabbits demonstrated that the pullout force of sintered porous-surfaced implants was 5 to 10 times greater that that for plasma sprayed implants, which had no interconnected pores. Furthermore, the rate of implant fixation was also much enhanced in the case of porous-surfaced implants. There is also *in-vitro* evidence suggesting that sintered porous coatings on metallic surfaces promote osteoblast (i.e. bone forming cells) adhesion [6,7] as well as maturation and matrix mineralization [8,9]. This suggests that the long-term stability of the interface between bone and the porous surface may depend on the influence of the macroscopic/microscopic surface characteristics on cellular function and activities. Finally, bone in-growth into the sintered porous-surfaced region is believed to provide effective force transfer between implant and bone, and hence, implant stability. Such mechanical coupling can be beneficial or undesirable, depending on the implant stress relative to the normal physiological stress level and the occurrence of implant "stress shielding" [10]. This observation points to the importance of proper design of the porous implants for optimum load transfer and long-term implant fixation.

A number of metallic systems have been processed with sintered porous surfaces for orthopaedic applications. The most commonly accepted materials are Co-Cr-Mo, Ti-6Al-4V and commercially pure (i.e. CP grade) Ti. The sintering temperatures are 1300°C for Co-based alloys and 1250°C for Ti-based alloys. Non-oxidizing environments (Ar atmosphere for Co-Cr-Mo alloys and high vacuum for Ti alloys) are needed. Co-Cr-Mo alloys have a long history of applications and excellent wear resistance. The formation of continuous carbide-containing zones during sintering, however, can make implants susceptible to particle debonding and, hence, wear due to third-body particles, as well as crack propagation in the solid core material. The fatigue strengths of Co-Cr-Mo cast or forged porous-coated implants range from 400 to 650 MPa [11].

Both vacuum sintering and pressure sintering have been used for fabricating Ti and Ti alloy implants. Because of the reactive nature of these materials, the furnace atmospheres need to be sufficiently non-oxidizing, and hydrogen embrittlement must be prevented. High vacuum sintering ($<10^{-3}$ Torr) is required for Ti-6Al-4V powders and fibers. Appropriate selection of sintering time

and temperature is essential for ensuring the formation of sufficiently large sintered neck regions between adjoining particles, while maintaining the desired open-pored structure. It has been reported that sintered neck diameters of 0.4 times the particle diameter give suitable combination of strength and porosity [1].

Ti-6Al-4V is used extensively for orthopaedic devices because of its excellent *in vivo* corrosion resistance due to the passive surface oxide layer formed in oxidizing environments, and high fatigue strength. Titanium is also reported to promote more efficient tissue and bone in-growth than Co-based alloys. Sintering Ti alloys at 1250°C may modify the fine-grained, equiaxed structure to a lamellar structure, resulting in a drop in fatigue strength of about 15%. However, a much more severe drop in fatigue strength is associated with stress concentrations that result at the particle-substrate sintered neck region [12]. Reductions in fatigue strength occur for textured Ti alloys surface produced by grit blasting, plasma spray coating, and ion-etching, due to the similar development of stress concentrators. Thus, it has been recommended that proper design of Ti-6Al-4V implants is required to ensure that stresses are maintained below the fatigue endurance limit of 200 MPa and that porous surface regions be avoided at implant surfaces subjected to high tensile stress.

In summary, there are a number of technological barriers and challenges in the fabrication of metallic implants with sintered surfaces, including the following:

- The selection of powders of uniform size is essential for achieving a continuous open-pore surface structure. Smaller pore sizes can be accomplished with finer particles, but at higher costs and at greater processing risk due to the enhanced reactivity of the finer powder.
- The diameter of sintered neck region between adjoining particles may control the strength of the surface-pored layer. Fracture at the neck region gives rise to loose metal particles and third-body wear.
- Typical sintered metal powder surfaces cannot be fabricated with high porosity levels (>60 volume %), anticipated to be required to achieve fixation affecting shear strength and integrity.

Reticulated Open Cell Metal Foams as Porous Coatings

In view of some of the limitations inherent to metallic implants with sintered porous surfaces, it is desirable to explore the technological advantages of metal foam materials for porous-surfaced implants. Metal foam materials can be categorized as one form of *cellular materials*. A cellular solid is one made up of an interconnected network of solid struts or plates which form the edges and faces of cells. *Honeycombs* are typical 2-D cellular materials while *foams* are commonly referred to as 3-D cellular solids. For foams, distinctions are made between *open* and *closed* cell materials, which are inherently different.

Almost all solids can be foamed. Techniques now exist for making three-dimensional cellular solids out of polymers, metals, ceramics and glasses. Different techniques are used for foaming different types of solids. Polymers can be foamed by introducing gas bubbles into the liquid monomer or hot polymer. Metallic foams can be made by either liquid or solid state processing. Glass foams are made by methods paralleling those for polymers. Carbon foams are made by graphitizing polymeric foams in a carefully controlled environment. Ceramic foams are made by infiltrating a polymer foam with a slip, then burning out the polymer, leaving a "mold" with internal channels formed by the polymer foam. Or, foams can be made by chemical vapor deposition onto a substrate of reticulated carbon or polymer foam. Microcellular silica foams, with cell sizes less than 100 nm and densities as low as 4 kg/m^3, have been made by the sol-gel polymerization of alkoxy silanes [13].

Porous cellular metals (i.e. metal foams) can be produced by various processes, including metal casting, powder metallurgy, electro-deposition, and chemical or physical vapor deposition [14-16]. Metal foams can be fabricated with either open-cell or closed-cell microstructures. The selection of an appropriate fabrication process is based on the desired characteristics of the cellular metal foam, such as volume fraction of porosity, average pore size and pore size distribution, component geometry, and functional requirements.

Cellular materials are found in everyday uses for their lightweight, high specific stiffness, and other properties. Their applications range from lightweight construction and packaging, to thermal insulation, vibration damping, and chemical filtration. Metallic cellular materials, namely metal foams, in particular are becoming a new class of engineering materials. These properties should make metal foam an attractive material for orthopaedic implants. The medical use of these foams has not been fully explored.

Fabrication of metal foams using P/M processing routes

The microstructure and cell morphology of the metal foams can be modeled after the reticulated open cell polymer foams that are commercially available in a broad range of pore cell sizes. The total porosity of the foam structures can be varied from 50 to as high as 95 volume %. The pore sizes can be varied over the range 200 to 500 μm consistent with bone in-growth requirements.

To prepare open celled Ti implants by powder infiltration of polymer scaffolds, sections of reticulated polymer foam are cut, replicating the net shape of the desired porous component. A solvent/binder solution is prepared using about 2-5 weight % PVA or PEG in alcohol. Aqueous solutions can also be used if compatible with the selected metal powder, but the use of volatile solvents reduces the drying time between powder coating operations. The polymer scaffold is immersed in the solvent polymer solution to fully wet the structure, then removed. At the point during the drying process when the majority of the liquid has evaporated yet remains "tacky", the polymer scaffold is coated by applying metal powder in a fine flowing stream or by covering the substrate with a powder bed. The coated scaffold is then removed from the powder bed and lightly agitated to free any powder not bonded to the polymer scaffold ligaments. Upon complete drying, the process is repeated until a sufficiently thick layer of metal powder is developed. Once the desired pore structure has been fabricated, the coated scaffold is thermal debindered and sintered to final density using standard P/M processing conditions. Figure 1 shows the technique of coating reticulated polymer foams with powdered metal/ binder systems being developed at Fraunhofer USA. Figures 2 and 3 show the porous microstructure of the sintered Ti materials fabricated using this process.

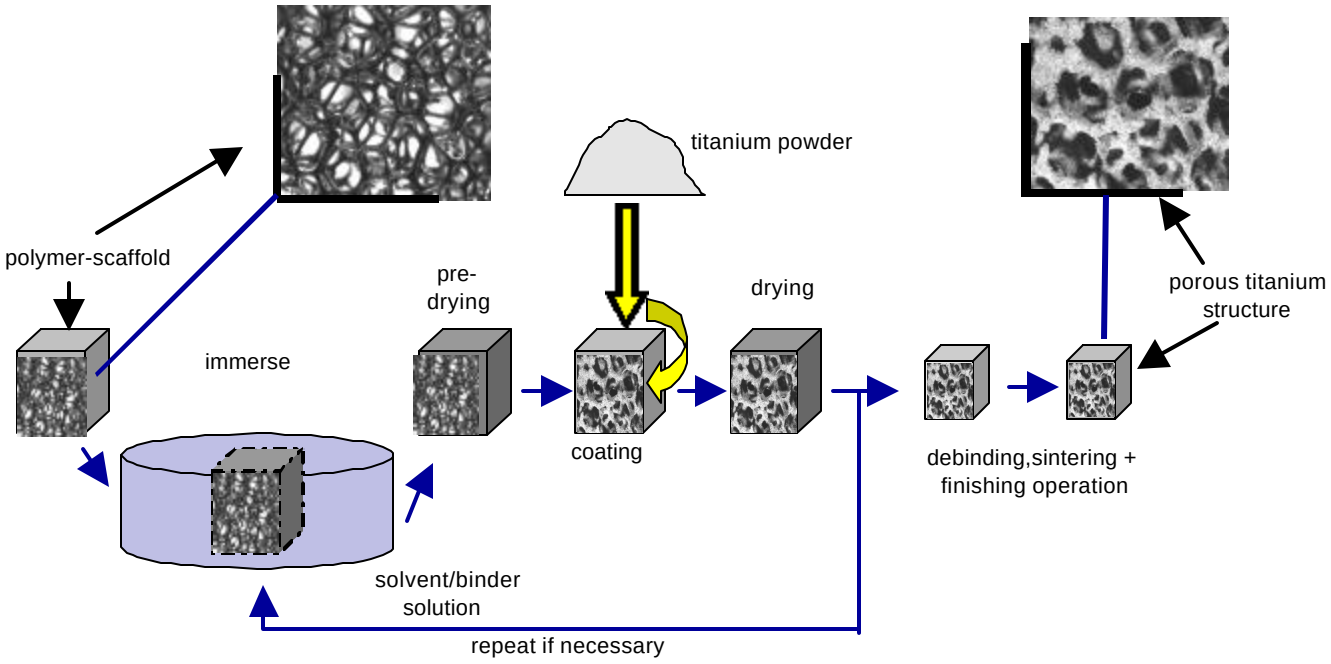

Figure 1: Schematic representation of P/M process to produce porous Ti scaffolds.

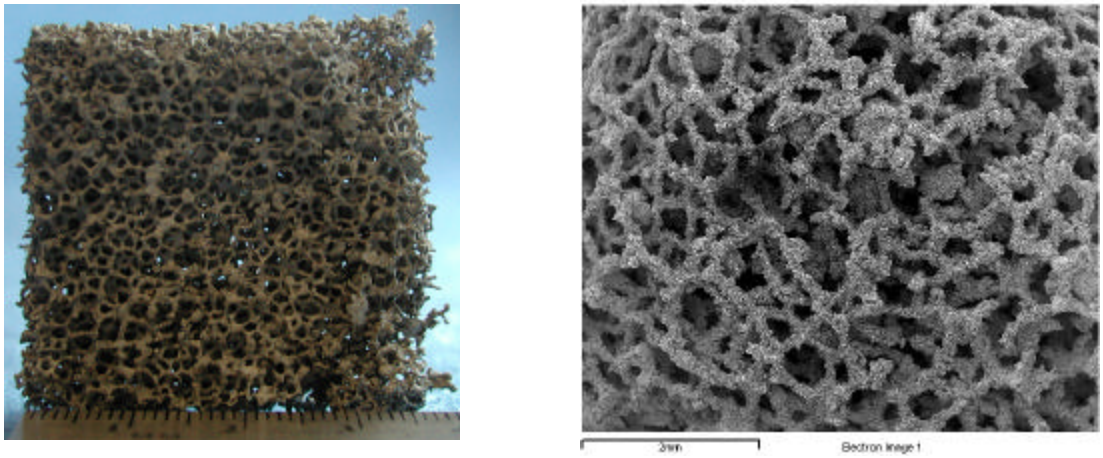

Figure 2 and 3: Optical (left) and SEM (right) images of sintered Ti scaffolds.

Potential Advantages of Reticulated Open Cell Metal Foams

The objective of current research at Fraunhofer is to develop a porous metal foam having an improved reticulated microstructure that more closely simulates the structure of natural bone, thus providing greater strength and long-term reliability, as well as the "material bed" with adequate interconnected porosity necessary for tissue in-growth. More specifically, the metal foam surface layer/core metal combination will eliminate or minimize most of the technical problems encountered in implants with sintered porous-surfaced layers, as stated earlier. This structural similarity should enhance the functional compatibility between the synthetic cast open cell foam implant surface and natural bone. Other applications for this type of structure including aerospace components, filters for high temperature and corrosive environments, thermal management and catalytic supports are being investigated.

Conclusions

A process for fabricating porous Ti alloys and other P/M materials has been demonstrated using reticulated polymer foams as the scaffold or template onto which the powdered metal or ceramic material is deposited. After the "green" structure is built, standard powder processing procedures are used to debind and sinter the structure to final density. By varying the pore structure of the polymer scaffold in terms of pore size and distribution, sintered P/M microstructures can be closely controlled for bulk density and final pore characteristics. In taking advantage of the wide range of compositions and structures, components can be fabricated to meet the demands of rigorous application areas such as the aerospace, medical and industrial markets.

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