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EFFECT OF ATMOSPHERE ON THE SINTERED TITANIUM ALLOY PRODUCED BY METAL INJECTION MOLDING (MIM) TECHNIQUE

RINGKASAN: *Titanium aloi implan telah dihasilkan bagi aplikasi kraniofasial melalui teknik "Metal Injection Molding" (MIM). MIM adalah satu kaedah yang cekap untuk menghasilkan komponen berbentuk kompleks pada kadar pengeluaran tinggi. Dalam atmosfera normal, implan akan bertindak balas dengan elemen pemanas grafit pada suhu yang tinggi untuk membentuk karbida titanium (TiC) yang juga disebabkan oleh tindak balas dengan sistem pengikat. Justeru itu, pengaruh atmosfera kepada implan yang melalui proses pensinteran pada suhu yang tinggi telah diselidiki, supaya dapat meningkatkan sifat-sifat gabungan titanium aloi implan yang disinter. Tindakbalas ini dapat dielakkan dengan cara memasukkan gas argon atau dijalankan dalam keadaan vakum ketika proses pembakaran. Implan yang mengandungi serbuk titanium aloi dan sistem pengikat berdasarkan stearin sawit dan polietilena, dicampur melalui mesin pencampuran z-blade. Sistem pengikat kemudian dikeluarkan melalui proses penyahikatan dan dibakar dalam argon dan keadaan vakum pada suhu 1250 °C selama 4 jam. Keputusan kajian menunjukkan bahawa implan yang di sinter di dalam gas argon pada suhu 1250 °C, mengalami peningkatan kepadatan 4.525 g/cm^3, serta kekerasan, 458 HV dibandingkan dengan implan disinter dalam keadaan vakum yang sedikit lebih rendah dengan kepadatan dan kekerasan 4.512 g/cm^3 dan 426 HV. Penumpatan tinggi implan dalam gas lengai; argon, telah dicapai kerana pergabungan zarah logam. Ini sebagai hasil pencegahan titanium aloi dari tindak balas dengan suasana normal, seterusnya memperbaiki penghabluran pertumbuhan bijian yang kecil berbanding implan dalam keadaan vakum. Pola XRD (X-ray Diffraction) juga menunjukkan bahawa dengan penambahan gas argon dalam proses pensinteran, pembentukan TiC dapat dikurangkan secara berkesan.*

ABSTRACT: Titanium alloy produced as an implant for craniofacial application was prepared through Metal Injection Molding (MIM) technique. The MIM is an efficient method for the high volume production of complex shaped components. In normal atmosphere, the implants will react with graphite heating element at high temperature to form titanium carbide (TiC) which was also due to its reactions with binder system. Therefore the influence of the atmosphere during sintering of implants at high temperature was investigated in order to improve the properties of sintered titanium alloy implant. This reaction can be avoided by introducing argon gases or in vacuum atmosphere during the sintering process. The implant which contained titanium alloy powder and binder system based on palm stearin (PS) and polyethylene (PE), are mixed using the z-blade mixer. The binder system was then removed through the debinding process and sintered in either argon or vacuum atmosphere at 1250 °C for 4 hours. The result showed that the implants sintered in argon at 1250 °C, experienced an increased in density of 4.525 g/cm^3, as well as hardness, 458 HV compared to the implants sintered in vacuum atmosphere; which is slightly lower with density of 4.512 g/cm^3 and hardness of 426 HV. The high densification of implant in argon was achieved due to the each individual particles powder which became more interconnected to each other. As opposed to the normal atmosphere which produced TiC, sintering in argon results in improved crystallinity of the grain growth which is smaller compared with the vacuum atmosphere. The XRD (X-ray Diffraction) pattern also reveals that addition of argon gas in the sintering process, effectively reduce the formation of TiC.

Keywords: implant, palm stearin, titanium alloy, argon and vacuum atmosphere

INTRODUCTION

Titanium alloy (Ti6Al4V) has been widely used in medical, craniofacial and dental implants, aircraft structural components, hand tools, and many various applications that require high density, strength and hardness. Metal Injection Molding (MIM) is an efficient method that has the capability in processing of complex and near-net shape components from metal powders (German *et al.*, 1997 and Ibrahim *et al.*, 2010). In the present work, titanium alloy which is produced as an implant for craniofacial application, was prepared through MIM process. Sintering is a thermal treatment for bonding the particles into a coherent, solid mass once the binder is extracted. Pores are eliminated as part of particle bonding during high temperature sintering (German *et al.*, 1997). This process is critical for determining the final quality of the parts because high sintered density is imperative for good mechanical properties such as hardness. Achieving full or near-full density has been the major objective for sintering processes (Mariappan *et al.*, 2009).

There are some justifications for using argon atmosphere instead of a vacuum medium during sintering. Vacuum sintering is used to maintain a clean, reproducible and controlled nonreactive atmosphere. Sintering under vacuum cleans a surface from oxide contaminations. A low partial pressure of oxygen leads to oxide reduction for many metals (German, 1994). Graphite and ultra porous carbon materials which constitute the internal parts of some furnaces are considered to be incompatible with high vacuum demands (Frage *et al.*, 2004). Sintering by using inert gas is the heating process that runs in a nonreactive atmosphere where there is less chemical reactions among the substances. The inert gas can avoid ordinarily non-reactive substances from becoming reactive, based on its noble gas nature which is resistant to bonding with other elements. In this case, an argon atmosphere is used in graphite electric furnaces to prevent the graphite heating element from burning. A carbon residue can be disastrous to the mechanical and physical properties of materials such as titanium alloy. Thus sintering without a residue is important in controlling the final chemistry.

The purpose of this study is to optimize the density and hardness properties of titanium alloy implant under two different sintering atmospheres of argon and vacuum at high temperatures. In normal atmosphere, the implants will react with graphite heating element at high temperature and also the reaction with the vapor of the binder materials to form titanium carbide (TiC) which seems to present a problem of brittleness on the sintered implants. These reactions can be avoided by introducing argon gases during the sintering process and also conducted in vacuum condition in order to provide clean, non-reactive and controlled conditions.

MATERIALS AND METHODS

Titanium alloy (Ti6Al4V) spherical shape powder (TLS Technik Gmbh & Co. Spezialpulzer Kg) was used as a starting material with 25 µm of particle size and tap density of 2.50 g/cm^3, apparent density of 2.00 g/cm^3 and pycnometer density of 4.50 g/cm^3. In the beginning, the feedstock which contained titanium alloy powder and the binder system of palm stearin and polyethylene are mixed homogeneously at a ratio of 66/34 using z-blade mixer. The feedstock were then injected into a desired shape mould, using a vertical injection molding at the temperature of 180 to 200 °C with injection pressure of 6 to 9 bar. The debinding process is implemented through two steps i.e. solvent extraction to remove the PS binder and thermal pyrolysis for the remaining binders.

Table 1. Melting and evaporation temperature of each component binder system.

Binder Material	Melting temperature (°C)	Evaporation temperature (°C)
Polyethylene (PE)	125.9	488.0
Palm Stearin (PS)	54.2	436.5

Table 1 shows the melting and evaporation temperature of PE and PS which were measured using Simultaneous Thermal Analysis (STA). The melting and evaporation temperature is then used as an indicator for designing the cycle for removal of the binder system. During solvent extraction process, the implants were immersed in heptane at 60 °C for 6 hours. As for the thermal pyrolysis process, the implants were heated at 440 °C and soaked for an hour for removal of PS and partly of PE. Table 2 indicates the sintering process using High Temperature Control Atmosphere Furnace (HTCAF) from 30 °C until it reaches 770 °C for 1 hour of soaking time selected based on the α modification at the temperature below than 882 °C. The alpha (α) to beta (β) allotropic transformation cycle continues until 1250 °C with heating rate of 10 °C/min based on the high temperature β that is stable between 882 °C and its melting point of 1668 °C. The weight percentage of element was analyzed and measured using an XRD-D8 Advanced instrument (Bruker, Germany) with a Cu Kα radiation source at 40 KV and 40 mA. Implants were scanned at a speed of 0.04 °/sec, ranging from 2θ = 10° to 90°.

Table 2. Sintering condition of titanium alloy implants.

Sintering Condition	Sintering temperature (1250 °C)	
	Argon	Vacuum
Implant	A	B

RESULTS AND DISCUSSION

Carbon control is a pervasive problem and excess of this element needs to be eliminated in the final stage of debinding and early stage of sintering. An improper sintering atmosphere is a primary cause of carbon residue problems and furthermore, if the impurities are carried over to high temperature, they can react to form volatile species (German *et al.*, 1997). The sintered properties can be increased or decreased due to the removal of binder system during pre-sintering conditions. Because the final stage of debinding is via decomposition of the polymer binder, there is a concern for the relative burnout of the remaining backbone polymer. Thus, complete binder removal without a residue is important in controlling the final chemistry. At this stage, the binder burnout occurs from within the particle and it flows to the compact surface. The surface then dries by evaporation of near-surface pendular bonds.

Rapid evaporative debinding is aided by a high temperature and agitated atmosphere that is constantly being replenished with inert argon gas. Argon molecule diffuse within the particles, flow with the vapor binder and leaves only the particles. There will be no chemical reaction or contamination caused by the binder, as it was removed or prevented by the argon molecules. It also helps to reduce the size of pores among the particles left by the binder evaporation and improved the densification of Ti6Al4V compact. Vacuum state is able to remove air or vapor binder on the compact surface. However it has limitations if the binder is trapped among the particles when the temperature is raised thus affecting the particle interconnection and produced more pores in the samples.

It is stated that almost 80 % of the binder is removed by solvent extraction and the remaining 20 % forms a gaseous product during thermal pyrolysis, as the binder evaporates and leaves the pores among the particles. Implant A showed an improved density due to the use of inert gas which does not undergo chemical reactions and do not react with any substances, thus avoiding unwanted chemical reactions which can reduce the quality of the implant. These undesirable chemical reactions are often oxidation and hydrolysis reactions with oxygen and moisture in air. PS melted completely during solvent extraction and is totally removed after heated at 436.5 °C due to its evaporation temperature.

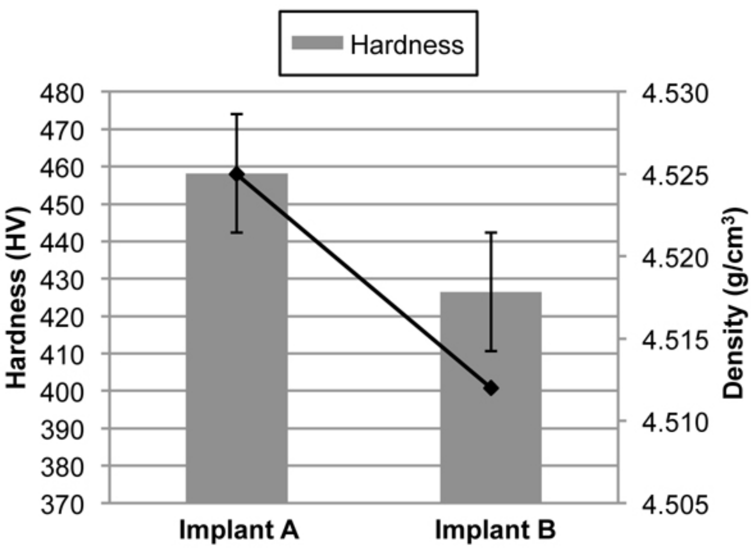
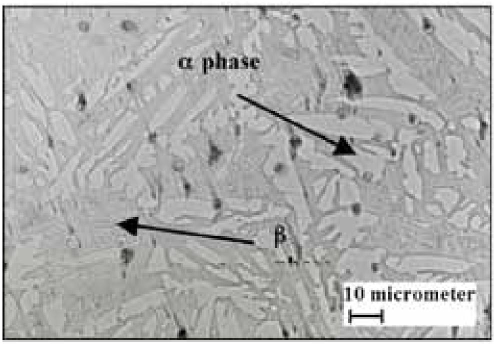


Figure 1. *Hardness and density properties of titanium alloy sintered implants.*

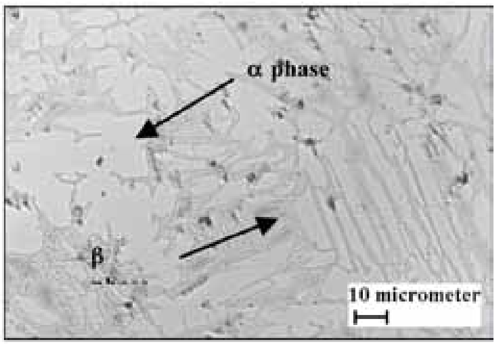
Table 3. Hardness and density properties of titanium alloy sintered implants.

Physical and Mechanical Properties	Implant A	Implant B
Density (g/cm^3)	4.525	4.512
Hardness (HV)	458	427

Pure metallic components were obtained after sintering with 15 to 20 % shrinkage. During sintering, the debound part is heated, thus allowing densification of the powder into a dense solid with elimination of pores. The density of the sintered part was measured using a Shimadzu SGM-330H-A Specific Gravity Meter. In Figure 1, Implant A experienced an increased in density of 4.525 g/cm^3 compared to Implant B; sintered in vacuum condition which was slightly lower in density of 4.512 g/cm^3 showing a difference of 0.013 g/cm^3. During sintering process, pores were observed on the sintered part of both implants during binder removal, and this situation allows the particle to pack densely and fulfil the voids left by the binder. Uniform packing of the particles reflected the shrinkage of the implants based on constant removal of binder system among the Ti6Al4V particle. The hardness test which was carried out on a Zwick Roell ZHV10 tester shows that Implant A reached a hardness value of 458 HV, whilst Implant B was 426 HV. This shows that due to the high particle packing of Implant A, the hardness reached 458 HV.



(a)



(b)

Figure 2. *Microstructure of titanium alloy sintered implants (a) implant A, and (b) implant B.*

Figure 2 reveals the optical microstructure of the sintered implants. Titanium exists in two allotropic modifications; β having a body-centered cubic structure with high temperature that is stable between 882 °C and its melting point of 1668 °C, and α which has a closely packed hexagonal structure modification of titanium that exists at temperatures below 882 °C. Various elements forming solid solution with titanium are classified on the basis of their effect on the solubility of α and β phases. Elements stabilizing α phase are known as α stabilizers (Aluminium (Al), Gallium (Ga), Oxygen (O), Nitrogen (N), Carbon (C)), and elements stabilizing β phase are known as β stabilizers (Vanadium (V), Molybdenum (Mo), Niobium (Nb), Iron (Fe), Chromium (Cr), Nickel (Ni), etc.). Ti6Al4V belongs to a class of α+β alloys as these alloys contain larger amounts of beta stabilizers (4 to 6%). A central point in the evolution of microstructure in titanium alloys is the α→β transformation temperature, generally referred to as the β transus temperature, since it separates the single-phase β field from the two-phase α+β filled (Joshi, 2006).

Titanium alloys, when heat-treated above the β transus temperature, β will result in β transformation to various equilibrium or nonequilibrium phases, depending upon the cooling rate and alloying content (Joshi, 2006). Observations over a range of magnifications (100 – 500 magnification) reveal that the orientation of the microstructure for both implants is slightly different as it shows the transformed β (dark) microstructure with prior β boundaries. A thin continuous α (light) phase is present at the grain boundaries for Implant A and primary α phase for Implant B, where the grains of the α phase were well distributed in the matrix of the β phase. The large α grains were predominantly non-uniform in size and shape. Lamellar microstructures, originating from cooling out of the β phase field, and equiaxed microstructures, as a result of a recrystallization process, can either individually have a fine or coarse distribution or can both be present in a bimodal microstructure (Leyens *et al.*, 2003). Implant A reveals the improved crystallinity of grain growth where the α phase is becoming smaller in size with fine distributions compared to the Implant B.

Table 4. Weight percentage of elements in Ti6Al4V sintered implants.

Elements (wt.%)	Implant A	Implant B
Titanium Carbide (TiC)	66.77	70.47

The high densification of implants in argon was achieved due to the particles which became interconnected signifying that the densification was achieved due to the non-reactive properties of inert gases that prevent undesirable chemical reactions from taking place and improved the properties (Ye, *et al.*, 2008) compared to vacuum atmosphere which only prevents the chemical reaction on the surface of the sintered implants. Figure 3 shows the XRD pattern of Ti6Al4V sintered implants which reveals TiC peaks. Table 4 shows that implants in vacuum atmosphere exhibit dominant peaks of TiC until 70.47 wt.% compared to argon atmosphere with 66.77 wt.% of TiC. It is clear that the formation of TiC can be reduced through the addition of argon gas in sintering atmosphere.

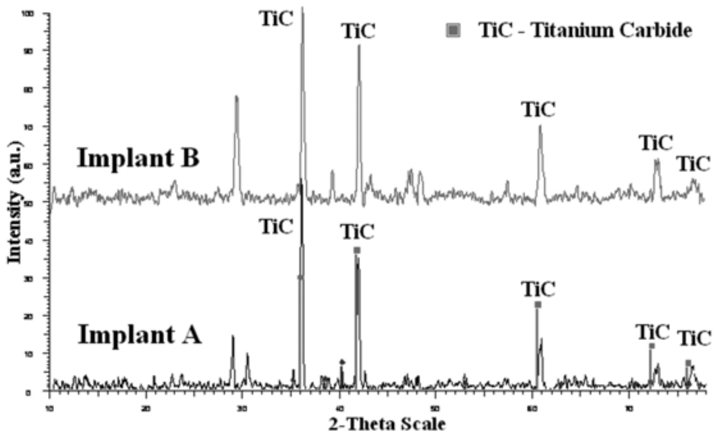


Figure 3. *XRD pattern of titanium alloy sintered implants.*

CONCLUSION

The use of argon gas in the sintering atmosphere appears to prevent reaction from the graphite heating element on the implant structure during sintering at high temperature. This prevention has improved the densification and hardness properties, compared to implants in vacuum atmosphere. The mechanical properties of Implant A have achieved the minimum requirement for sintered MIM parts as compared with the Standard Metal Powder Industries Federation (MPIF) 35 for titanium alloy. The improved cystallinity structure of titanium alloy sintered in argon was shown clearly on the micrograph. This study has proven that the formation of TiC can be reduced effectively through argon atmospheres.

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