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Publisher’s version / Version de l'éditeur:

Proceedings: World Powder Metallurgy Congress & Exhibition, PM2010: 10th - 14th October 2010, Fortezza da Basso Congress Centre, Florence, Italy, 4: PM lightweight & porous materials, powder injection moulding, PM biomaterials, pp.

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BENEFITS OF SUPERCRITICAL CO2 DEBINDING FOR TITANIUM POWDER INJECTION MOULDING?

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ABSTRACT

Supercritical CO_2 debinding has been described as a clean and environmentally friendly alternative to other debinding routes. The claims are that SC-CO_2 should prevent oxidation, lead to less defects and reduce the debinding time. This appears therefore as the process of choice for titanium MIM since this material is very sensitive to contamination by interstitial elements during the whole process which, in turn, affects the mechanical properties and integrity required for demanding sectors such as biomedical. In this paper, the potential benefits of using the SC-CO_2 technology for titanium MIM parts have been evaluated as a replacement for the conventional immersion in solvent process. The efficiency of the debinding processes (SC-CO_2 and hexane) as well as their effect on final properties of titanium MIM dental implants, and in particular on interstitials composition (C wt.%, O wt.% and N wt.%) and dimensional variations is presented and discussed, as a function of the processing debinding parameters.

INTRODUCTION

In the last few years, the interest in titanium component manufacturing has been growing significantly. With the capability to near net shape intricate parts with minimal material usage, the powder injection moulding (PIM) is seen as an excellent process for the fabrication of titanium components for medical, dental, consumer's goods applications. Recent publications reviewed the current status of titanium powder injection moulding process [1,2,3]. The key for successful application of titanium PIM remains to control the impurity levels, in particular the oxygen [4] and carbon content, while obtaining high density. These interstitial elements affect negatively the mechanical properties required for demanding sectors such as medical, dental and aerospace.

Part of PIM process is the need for debinding the fugitive binder before sintering of the powder into solid part. Many debinding processes differ from a unique thermal treatment by a primary debinding stage using solvent/water or catalytic debinding followed by thermal debinding coupled with the sintering cycle. Benefits and drawbacks of different debinding methods are described in [5]. For instance, solvents can be used to decrease processing time, but the use of solvent carries with it additional concerns about toxicity, workplace exposure, waste management, regulatory restrictions and slumping [5]. For Ti-PIM, most of the debinding options have been explored. But from the standpoint of minimizing contamination, first stage solvent debinding proves most successful [3].

Supercritical CO_2 (SC-CO_2) debinding is another process that has been adapted from other industrial extraction applications (food and perfume industries) and described as a clean and environmentally friendly alternative to other processes, with therefore less regulatory concerns. A supercritical fluid is formed by increasing the temperature and pressure of a substance higher than its critical point. Above this point, only one phase exists that exhibits physicochemical properties (density, viscosity, diffusivity,…) intermediate between those of liquid and a gas. These properties may vary significantly depending on the temperature and pressure and affect the solvating and extracting power of the supercritical fluid. At high pressure, its density could reach liquid-like density while having low viscosity like a gas. The SC-CO_2 debinding technology has been developed taking advantage of these benefits and also because carbon dioxide become supercritical at relatively low temperature and low pressure (T_c=31°C and P_c=7.37 MPa). Besides, supercritical CO_2 is able to dissolve non polar molecules such as paraffin wax, largely used as a primary binder in PIM feedstock, but is unable to dissolve polar molecules or high molecular weight polymers, such as polyolefines that could remain in place and maintain the shape of the debound part.

SC-CO_2 debinding has been mainly evaluated for ceramic powder injection moulding, but experiments with metallic and carbide powders and even with titanium aluminides powder could be found in the literature [6,7,8,9,10,11].For example , Chartier *et al*. [7] obtained with alumina powders better mechanical properties after 3 hours of SC-CO_2 treatment than after 18 hours of thermal pyrolysis. They reported that the major factors causing defects in the pyrolytic binder removal, such as liquid binder redistribution and the uncontrolled outward diffusion of degradation products, do not take place in the SC-CO_2 debinding approach. Shimizu *et al*. [10] claimed that the SC-CO_2 debinding process reduced the extraction time as well as the oxidation of titanium aluminides when compared to thermal debinding in inert gas. Rei *et al*. [11] observed with 316L feedstock processed by low pressure injection moulding that cracks occured with debinding in heptane while no crack was observed with SC-CO_2 debinding. Cracks were said to occur because of swelling and internal stresses in the parts due to heptane diffusion in the wax and slow wax extraction. Therefore, based on comparison with the thermal debinding route, literature generally claimed that SC-CO_2 should prevent oxidation, lead to less defects and reduce the debinding time. Therefore, this appears as the debinding process of choice for titanium PIM.

In this paper, the potential benefits of using the SC-CO_2 technology to remove the primary binder (paraffin wax) of titanium MIM parts have been evaluated as a replacement for the first stage solvent immersion process. The effect of processing parameters on the efficiency of the debinding processes (SC-CO_2 and organic solvent) as well as their effect on final properties of titanium MIM dental implants, and in particular on interstitials composition (C wt.%, O wt.% and N wt.%) and dimensional variations is presented and discussed.

EXPERIMENTAL DETAILS

Materials

CpTi–Grade 1 (-45 µm) spherical powder produced by plasma atomization (AP&C, Boisbriand, Canada) was used in this study. Interstitial element contents were 0.16wt.% of oxygen, 0.009wt.% of nitrogen and 0.005wt.% of carbon. The binder mixture used in this work was composed of polyolefines, paraffin wax (40 or 55 wt.%) and stearic acid (5wt.%). Three paraffin waxes were used: high density paraffin wax (PW_{HD} : 0.923g/cm^3 and $T_{melting}$~69°C), low density and low melting temperature paraffin wax ($PW1_{LD}$: 0.903g/cm^3 with $T_{melting}$~55°C) and low density and intermediate melting temperature ($PW2_{LD}$: 0.908g/cm^3 with $T_{melting}$~60°C).

MIM processing conditions

The different feedstocks were prepared at solid load of 66%vol. with a planetary mixer using HV-type blade at 150°C. The feedstocks were then extruded through a Buhler twin screw compounder to complete the mixing and produce small granules. Injection moulding of dental implant preforms was done on a Battenfeld Microsystem-50 machine with a melt temperature of 150°C and a mould temperature of 45°C. A typical production run was composed of 225 parts. The first 25 parts, during the stabilisation of the process, were rejected. The shape of the component is illustrated in Figure 1. As described in [12], more than 6 features are specified for the internal structure of the implant. The main specified features that were measured in this study are the 3.02 mm hexagonal hole as well as the 5.4 mm central hole.

Figure 1: Dental implant design characteristics, and as-moulded and sintered implant

Specimens with a step-wise geometry (Figure 2) were produced on an Arburg injection press with a melt temperature of 150°C and a mould temperature of 45°C. As seen in Figure 2, a 4mm diameter, through-the thickness, hole was located at the center of the thin section and the mould was filled through a gate located at the thick section end. With this geometry, the effect of the PW type and content was studied. The detailed composition will be presented in the next sections.

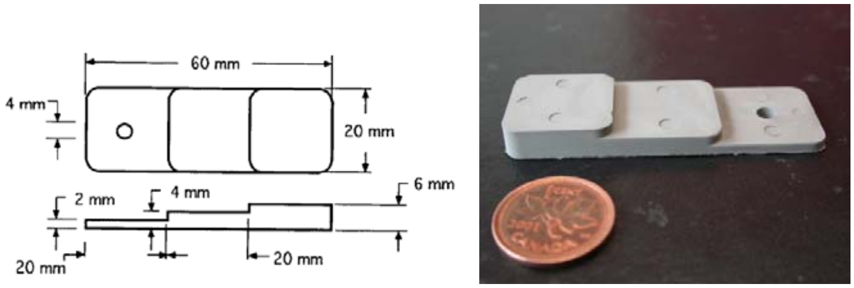

Figure 2: Multistep part characteristics

Implants as well as the 2 mm, 4 mm and 6 mm sections of the multiple step parts were then first step debound through solvent immersion (hexane or heptane) or supercritical carbon dioxide. Detailed experimental conditions are described in next sections. After first step debinding, the remaining polyolefines were eliminated during thermal debinding and pre-sintering performed in repurified argon up to 900°C. Parts were finally sintered in a cold wall vacuum furnace with tungsten heating elements. The sintering was conducted at 1280°C during 8 hours with a vacuum of ~10^{-5} mbar.

Supercritical CO_2 debinding

In this study, a 7 litre SC-CO_2 debinding system from Applied Separations, Inc. (Allentown, PA) was used. This system could be used in 'static' (batch) mode or in 'dynamic' mode with continuous flow of CO_2 and recycling of CO_2 in the condenser, with pressures up to 69 MPa (10,000 psi) and temperatures up to 150°C. Static mode was used in this study with pressures and temperatures varying from 15 to 60 MPa and 45°C to 80°C, and with different extraction times. To prevent precipitation of the waxes on the parts when depressurizing the vessel, the dynamic mode was used during the last 30 minutes of the debinding experiment to extract the solubilised wax from the vessel and precipitate it in the separator. The CO_2 flow used during this last flush corresponds to flushing 10 times the vessel.

Characterization

The efficiency of the binder removal by the SC-CO_2 process as a function of extracting pressure and temperature as well as type and content of paraffin wax used was studied by measuring the weights of 2 mm, 4 mm and 6 mm square parts before and after debinding.

Comparisons between the solvent and SC-CO_2 debinding processes were done on the dental implant by measuring first the variations of weight on about 20 parts. In addition, the dimensional variations on 5 specimens after each step of the process (as-moulded, as-debound, after pre-sintering and after sintering) were measured using a coordinates measurement machine (CMM), which has an accuracy of less than 3 µm. Chemical analyses were performed on titanium implant after pre-sintering using LECO analysers.

RESULTS

Effect of temperature and pressure on binder removal using SC-CO_2 debinding process

Figure 3 shows the effects of vessel pressure on the yield of first stage binder removal (wax removal) as a function of the part thickness for an extracting temperature of ~80°C. At this temperature, higher than the melting point of the high density paraffin wax (PW_{HD}), the yield of binder removal increases significantly by increasing the pressure from 15 MPa up to 25-30 MPa. At pressures above 30 MPa, the binder removal yield is not increasing anymore. In addition, the removal yield is inversely proportional to the thickness of the part. Above 30 MPa, between 40-45 wt.% binder removal is observed for the 2 mm thick part, corresponding to the total content of paraffin wax (40 wt%) and stearic acid (5 wt%). On the other hand, 87.5 wt% and 67.5 wt% of paraffin wax removal are observed for 4 mm and 6 mm thicknesses respectively at 30 MPa. At higher pressures, the binder removal yield slightly reduces.

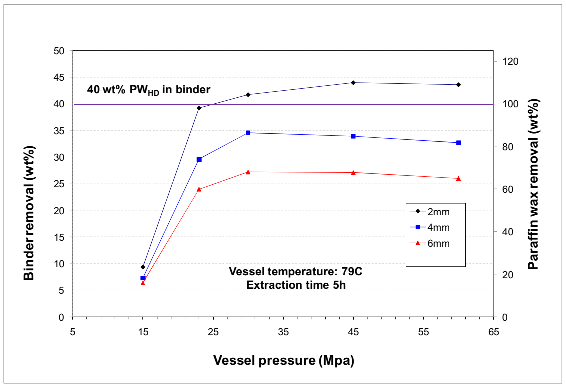

Figure 3: Binder removal vs. extracting pressure

Figure 4 shows the temperature effect on paraffin wax extraction at 30 MPa. Below 69°C, when the PW_{HD} is solid, there is a significant increase of the binder removal yield with the temperature. On the other hand, above the PW_{HD} melting temperature (69°C), the yield is only slightly increasing. Figure 5 shows the kinetic of binder removal at 30 MPa and 65°C and 79°C. At these sufficiently high temperatures and pressure, the extraction changes rapidly from a solubility-controlled to a diffusion-controlled process.

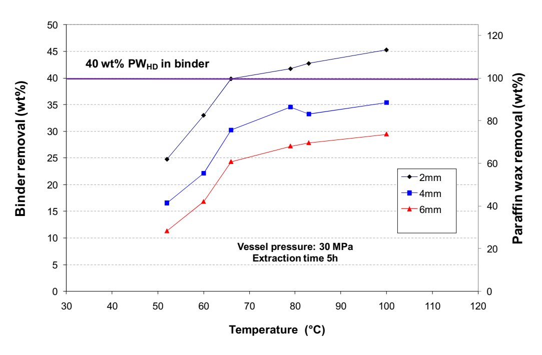

Figure 4: Binder removal vs extraction temperature

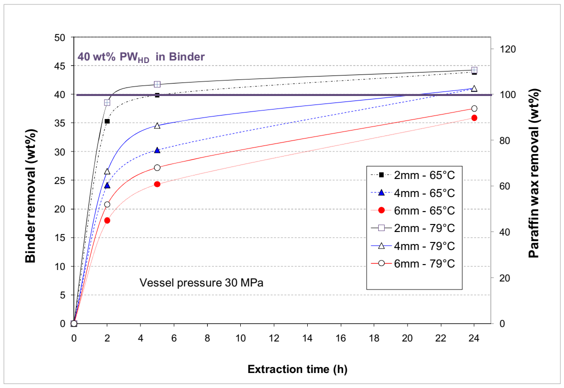

Figure 5: Kinetics of SC-CO_2 debinding

Basically, liquid solvent debinding is controlled by the following mechanisms: solubilisation of organic binder molecules, diffusion and migration of the dissolved species out of the moulded part. During debinding, the solvent/binder interface progresses from the surface inwardly creating a tortuous network of channels through the opened porosity [13,15]. When the binder is in the liquid state (above the melting temperature), a third mechanism is acting using capillary forces leading to the migration of the binder toward the free open porosity. Similar mechanisms are expected for supercritical fluid debinding [6]. For paraffin waxes, it seems that the largest contribution to the increased binder removal is the increase in solubility. Indeed, when the pressure increases, the density of SC-CO_2 increases which increase its solvating power. In addition, when sufficient pressure is used, temperature is the dominant factor for both obtaining high paraffin solubility and also higher diffusion rate through the porous network. Similar results were also obtained, using similar binder formulation, by Wu [14] with 2 µm Al_2O_3 powder and Kim [15] with 1.25 µm WC-Co powders.

Effect of type and content of paraffin wax on binder removal efficiency

Figure 6 shows the effect of the paraffin wax density on the extraction rate obtained at 79°C and 30 MPa. Higher rates are observed when the wax density is reduced. This could be mainly explained by the higher diffusion rates of low density paraffin waxes (PW_{LD}). Indeed, lower molecular weight of PW_{LD} leads to lower viscosities of solubilised species which then migrate faster outward the parts. The solubility of these paraffin waxes is also higher at low temperature leading to higher debinding rates at lower temperature as shown in Figure 7. In this case, the higher solubility, even at lower temperature, combined to the higher diffusion rates of solubilised species lead to a complete extraction of the wax at 60°C after 5h of debinding even for the thickest section (6 mm). At higher temperature, slightly higher binder removal is still obtained with extraction of both the paraffin wax (55wt%) and stearic acid (5 wt%).

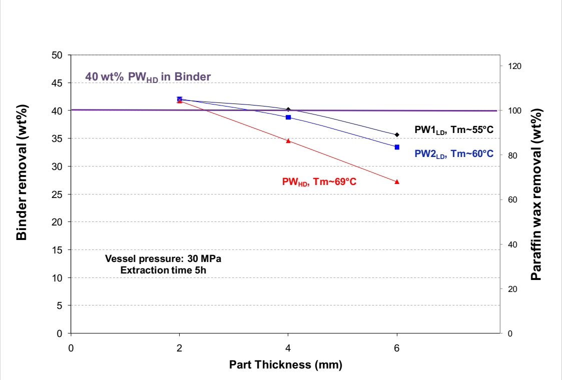

Figure 6: Effect of type of Paraffin waxes

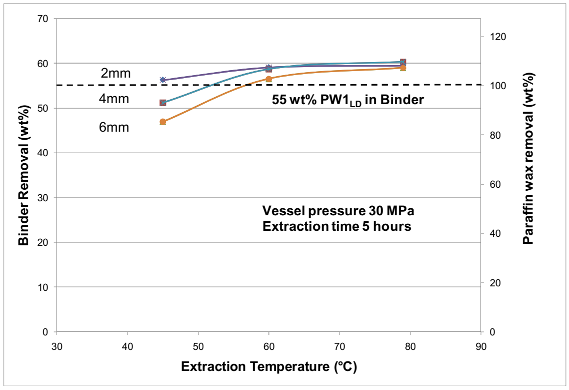

Figure 7: Binder removal vs. temperature for 55 wt%

Efficiency of binder removal in SC-CO_2 *vs n-alkane solvent for the dental implant*

In most publications, justifications for using SC-CO_2 are the higher diffusivity of SC-CO_2 in solid organic materials than organic solvents as well as the much lower viscosities and the absence of surface tension of SC-CO_2. The higher extraction rates are mainly explained by the ability of the SC fluid to penetrate into small pores within the matrix inaccessible to liquids. For instance, Hirata [16] found that additives could be extracted at 90% recoveries from PE and PP films using SC-CO_2 at 25.4 MPa and 35°C within 2h, compared with 24h Soxhlet extraction.

However, in the case of the debinding of PIM parts, SC-CO_2 paraffin wax extraction is not performing as fast as in organic solvent. Indeed, the binder removal is shown to be significantly faster with hexane or heptane than with SC-CO_2 (see Figure 8). It should be noted that at 45°C, even though the paraffin wax is in solid state, all the paraffin wax is removed in 5h in hexane and only ~30% is extracted with SC-CO_2. At 65°C, almost all the paraffin wax is removed using SC-CO_2, while both the paraffin wax and stearic acid are removed in heptane. At ~80°C, lower molecular weight chains of the polymeric backbone seems to be also extracted after immersion 5h in heptane, while only the paraffin wax seems to be removed in SC-CO_2.

The faster debinding rate in organic solvent vs. SC-CO_2 as compared to the extraction rate of additives in polymeric compounds might be explained by the high amount of paraffin wax, that represents ~14% in volume of the part. Removal of the paraffin wax, starting from the part surface, creates a network with relatively large pore channels due to large particle size and low surface area of titanium powders. Therefore the higher diffusivity of SC-CO_2 in solid organic materials as compared to organic solvent is not so determinative in the debinding of PIM parts because the large pore network gives an efficient access to the debinding fluid. It is then more the higher solubility of paraffin waxes in hexane and heptane, even at low temperature below their melting point, and the higher diffusion of solubilised species, that could explain this higher debinding rate.

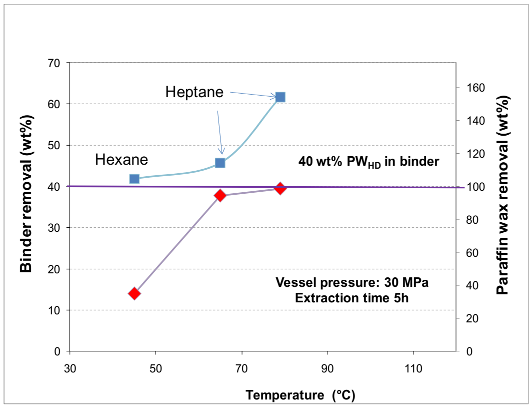

Figure 8: Comparison of binder removal in SC-CO_2 vs. liquid solvent

Dimensional variations and/or defects/cracks

The dimensions of the 3.3 mm hexagonal hole and of the 5.4 mm central hole were monitored on 5 specimens after each step of the process (moulding, first stage debinding, second-stage debinding/pre-sintering and sintering) using a coordinates measurement machine (CMM). Only variation of these dimensions between moulding and SC-CO_2/Solvent debinding are shown here in Figure 9. Similar trends were observed after the second-stage debinding/presintering step, except the SC debound parts at 45°C that collapsed due to the low amount of paraffin wax removed during the first stage debinding. Even though large standard deviations were obtained, significant shrinkage of the depth hole was observed for the solvent debound implant at 65 and ~80°C, while only small dimensional variations were noticed for SC-CO_2 parts. Such differences were not observed for the hexagonal hole.

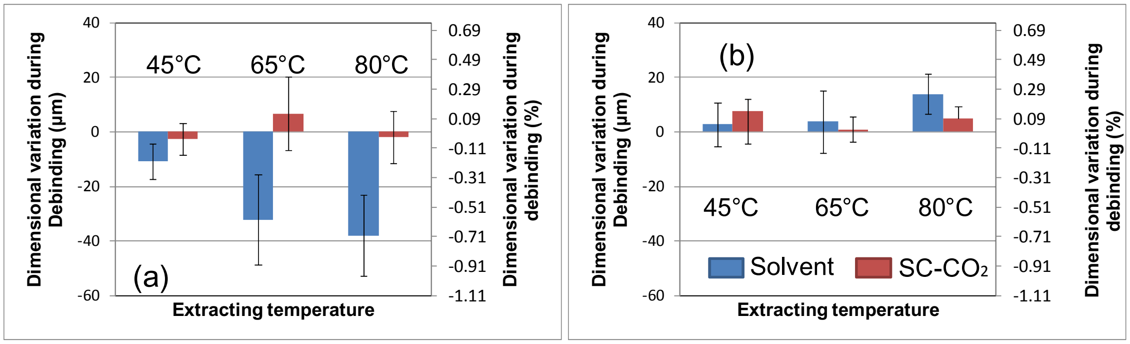

Figure 9: Dimensional variations after SC-CO_2 and solvent debinding for the (a) central hole and (b) hexagonal hole features

Observation of the bottom of the central hole of the pre-sintered implant indicates the occurrence of some cracks and surface pits for the 65 and 80°C organic solvent debound parts while nice surfaces were obtained for the 65°C SC-CO_2 debound parts (see Figure 10). Better surface finish was obtained with the solvent debound parts at 45°C; minor cracks were however still visible at the bottom of the central hole. Some distortion of the roundness of the top of the implant was also seen in the 65 and 80°C solvent debound parts. Even though the debinding rate was high in those conditions, it is clear that lower temperatures should be chosen while performing solvent debinding. One explanation should be the excessive swelling of the other constituents of the binder in solvent at these temperatures leading to cracks. Regarding SC-CO_2, even though it could also dissolve in some polymers such as amorphous polymers (i.e. PMMA), plasticizing them and leading to swelling, the phenomenon seems to be less important in case of semi-crystalline polyolefines since less distortion and cracking were observed for parts debound with SC-CO_2.

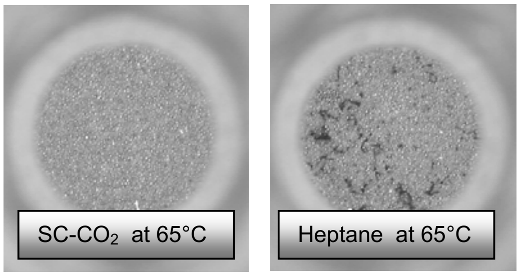

Figure 10 : Defects observed on the bottom of the central hole of the pre-sintered implant debound at 65°C

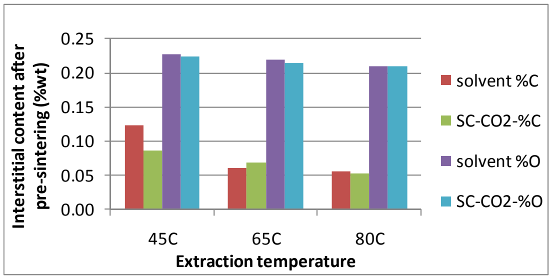

Figure 11: Carbon and oxygene analysis of pre-sintered parts debound either with solvent or SC-CO_2

Chemical analyses

It is well established that the mechanical properties of dense titanium and titanium alloys are sensitive to the presence of interstitial elements such as oxygen, nitrogen, carbon and hydrogen. Shimizu *et al.* [10] claimed that the SC-CO_2 debinding process enable to reduce the oxidation of titanium aluminides when compared to thermal debinding in inert gas. In this study, the effect of the two different solvents and SC-CO_2 debinding processes on the contamination of the titanium dental implant was evaluated. Figure 11 shows the oxygen and carbon content measured on organic solvent and SC-CO_2 debound parts after thermal second stage debinding and pre-sintering treatments. Similar contamination was observed with both debinding processes. Such results are explained by the binder formulation leaving very few residuals even without first stage debinding. In addition, since the first stage debinding is done well below 200°C, the oxidation of titanium should be minimal as shown in Baril *et al.*[4].

CONCLUSIONS

In this paper, the potential benefits of using the SC-CO_2 technology to remove the primary binder (paraffin wax) of titanium MIM parts was evaluated as a replacement for the first stage debinding with immersion in hexane or heptane. When using high density paraffin wax, lower debinding rate was observed with the supercritical route mainly because of the lower solubility of this high molecular weight wax and the lower diffusivity of the solubilized species. However, when performed at sufficiently high pressure and temperature close to the melting point of the wax (65°C and 30 MPa), similar debinding rate to the organic solvent immersion process done at 45°C was observed. If required, in particular when thick parts are processed, higher debinding rate could be obtained by using lower density paraffin waxes and by increasing the amount of paraffin waxes in the binder. On the other hand, when performed at 65°C or ~80°C, SC-CO_2 debinding lead to less dimensional variation and distortion than with solvent debinding. In this case, higher swelling should explain the higher distortion, defects and cracks clearly seen on debound parts. However, when opening the pore space when the paraffin wax is still solid at 45°C, the organic solvent immersion process lead to less distortion even though minor cracks were still visible.

In this study, the benefits of SC-CO_2 were not clearly demonstrated. Indeed, slower debinding rates were observed with SC-CO_2, when compared to organic solvent debinding. The relatively large particle size of titanium powders (-45μm) used in this study could be the root cause of this behaviour. In addition, similar interstitial contents were measured indicating that the solvent immersion and SC-CO_2 debinding routes lead to the same contamination on titanium parts. However, slightly better performances regarding part distortion and surface finish were observed with the SC-CO_2 process. More work should be performed to validate these benefits with larger parts.

ACKNOWLEDGEMENTS

The authors would like to acknowledge Oumou Coulibaly, Shirley Mercier, Pierre Pringault and Daniel Simard that performed the technical work presented in this paper.

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