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Micro powder injection molding process using TiH_2 powder

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In this work, TiH_2 feedstock using wax-based binder system was developed for micro powder injection molding. A powder loading for the TiH_2 feedstock was determined to be 68 vol.% and viscosity of the feedstock showed pseudo-plastic flow behavior. An amount of residual carbon after debinding was sensitive to heating rate and gas species, and influenced largely the surface quality of final product after sintering. The TiC layer was formed on the surface of the sintered parts due to the reaction between Ti and the residual carbon. Through an additional wicking process following the thermal debinding, which extracts the residual binder through capillary action, the sound sintered Ti part was obtained without any TiC surface layer.

Key words: Powder injection molding, Feedstock, TiH_2 powder, Debindng atmosphere, Sintering.

Introduction

Titanium and its alloys are materials of great interest because of their unique properties, including high specific strength, low density and lightweight, excellent corrosion resistance, and biocompatibility [1, 2]. Nevertheless, the application of titanium and titanium alloy is limited due to its inferior machining capability and high production cost [3]. To overcome the limitation, there has been increasing interest in developing lower cost methods of processing titanium and one particularly attractive approach is powder injection molding (PIM) [4]. Nowadays, the interests in Ti application areas such as microsystem, medical technology and biotechnology are moving towards miniaturization of devices. This component miniaturization displays the huge potential for new application fields and owing to the requirements, much attention has been paid to micro component manufacture. Recently, micro PIM technology has been developed in order to manufacture the components with sub-millimeter dimensions [5, 6]. In comparison to conventional PIM, there are some requirements for micro PIM and one of them is a use of very fine powders to achieve high precision dimension and low surface roughness. In this study, to obtain micro titanium part from TiH_2 powder, TiH_2 feedstock by wax-based binder system was developed for micro PIM. Debinding and sintering process using the feedstock was investigated and optimized by an analysis of microstructure in the sintered parts.

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Experiment

TiH_2 powders with average particle size of 350 nm was used as a starting material. The binder consisted of low-density polyethylene (LDPE), paraffin wax, stearic acid. The mixing of powder and binder was conducted on a double-screw mixer (C.W. brabender Instruments Inc., Plasti-Corder) at 100 °C and powder loading of 68 vol.% was determined from a curve on torque and an amount of powder. The TiH_2 feedstock was injection-molded at 90 °C with the optimized injection speed determined by "In-mold Rheology" method. Fig. 1 shows the debinding and sintering schedules. A thermal debinding of the molded parts was performed at various heating rate up to 600 °C in H_2 and Ar atmosphere, respectively. Also, for debinding by wicking process, the injection-molded TiH_2 parts were embedded in fine zirconia powder of 30 nm. Sintering of the debound TiH_2 parts was carried out in vacuum atmosphere of 5×10^{-5} torr

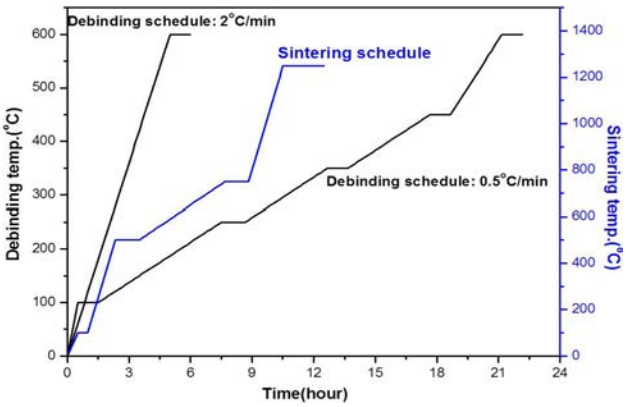

Fig. 1. Debinding and sintering schedules of TiH_2 feedstock.

according to the schedule shown in Fig. 1. The microstructure was observed with an optical microscope and a scanning electron microscopy (SEM, model FEI QUANTA 200F). The residual carbon contents of the debound parts were measured using CS analyzer (ELTRA CS-800).

Results and discussion

TiH_2 powder was produced by horizontal ball milling of hydrogenated titanium. The jar for ball milling was filled with pure Ar gas to avoid oxygen contamination. After milling for 10 hrs, size of the milled TiH_2 powder was measured with $d_{10} = 178$ nm, $d_{50} = 344$ nm and $d_{90} = 39.5$ μm by particle size analyzer and average particle size was 300 nm in BET(Quantachrome) measurement. The particle size distribution curve and SEM morphology of the powder are shown in Fig. 2. The 300 nm sized TiH_2 powders were agglomerated to a coarse particle. Fig. 3 (a) shows the variation of mixing torque with TiH_2 powder loading (volumetric ratio of solid TiH_2 powder to the total volume of powder and binder). The torque increases with increase of the powder loading. The torque is increased rapidly due to the addition of the powder and reaches a steady state with mixing time. The steady-state torque means a homogeneous mixing of the TiH_2 powder and binder and in this study, the solid loading of 68 vol.% was selected for TiH_2 feedstock as higher content of powder particles in feedstock is preferred to limit shrinkage during debinding and sintering. The FE-SEM morphology of the feedstock is shown in Fig 3 (b). The fine particles are dispersed homogeneously and surrounded well by the binder. Fig. 3 (c) shows viscosity variation of the TiH_2 feedstock with shear rate at 90 °C and 100 °C. In PIM, the rheological properties of feedstock are important in injection molding step as it concerns the flow of the feedstock into cavity during injection molding. The viscosity of TiH_2 feedstock decreases with increasing shear rate, indicating pseudo-plastic flow behavior called generally non-Newtonian flow. Pseudo-plastic flow behavior eases mold filling, minimizes jetting and helps to retain the shape of the molded part [7]. Also, the viscosity decreases below 2000 pa·s over shear rate of 100 s^{-1}. Fig. 4 shows SEM morphologies of the injection-molded and the sintered parts, respectively. Both of the molded (Fig. 4 (a)) and the sintered (Fig. 4 (b)) parts keeps its sound micro features filled completely into sharp edges without any crack or distortion. These results mean that the TiH_2 feedstock is suitable for powder injection molding process.

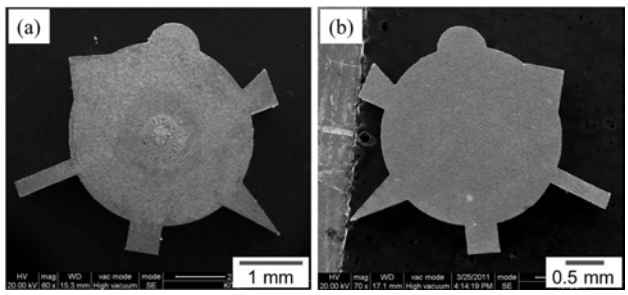

Fig. 4. SEM micrographs of (a) a molded part and (b) a part sintered at 1250 °C in vacuum after debinding up to 600 °C at heating rate of 2 °C/min under H_2 atmosphere.

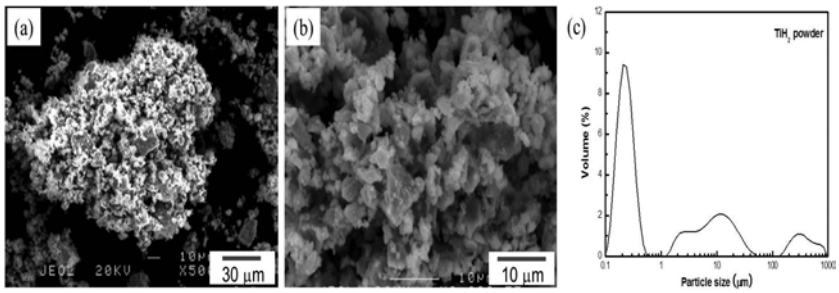

Fig. 2. SEM morphologies of the agglomerated TiH_2 powder and powder size distribution.

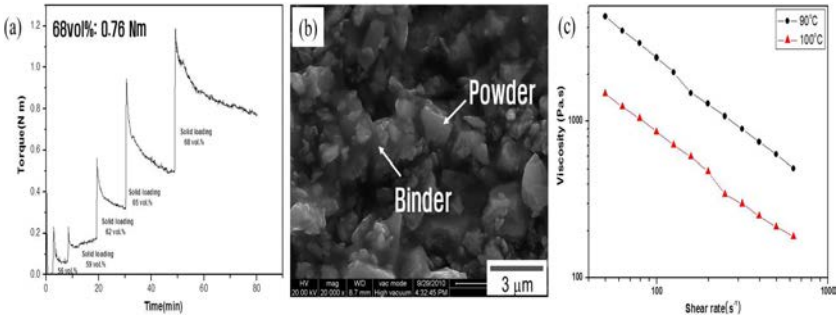

Fig. 3. (a) Characteristics of TiH_2 feedstock and SEM morphology. (a) Mixing behavior with powder loading, (b) SEM morphology, (c) viscosity-shear rate curve of feedstock with powder loading of 68 vol.%.

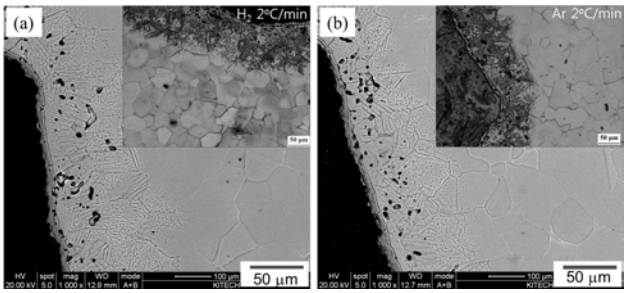

Fig. 5. OM and SEM microstructure of the parts sintered at 1250 °C in vacuum after debinding (a) at heating rate of 2 °C/min under H_2 atmosphere and (b) at heating rate of 2 °C/min under Ar atmoshphere, respectively.

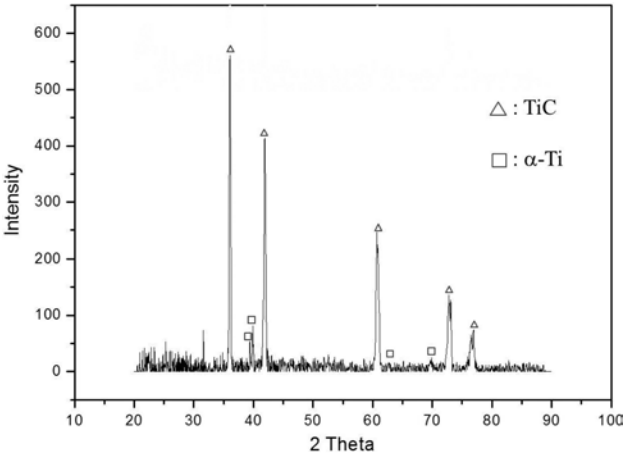

Fig. 6. XRD pattern on surface of sintered part.

Table 1. Residual carbon contents in the parts debound in different heating rates and atmospheres.

Debinding condition		Residual carbon
2 °C/min	H_2 Atmosphere	0.5%
	Ar atmosphere	0.33%
0.5 °C/min	H_2 atmosphere	0.09%
	Ar atmosphere	0.3%

Fig. 5 shows etched microstructures of parts sintered after debinding at heating rate of 2 °C/min under H_2 and Ar atmosphere, respectively. The surface of the sintered α-Ti parts is covered by thin layer of another kind regardless of debinding condition. The surface phase was analyzed with XRD (Fig. 6) and proved as TiC. To investigate the reason of formation, an amount of residual carbon was analyzed in debound parts under hydrogen and argon atmosphere, respectively, and the results are listed in Table 1. The residual carbons of 0.57 wt.% and 0.33 wt.% were detected in the parts debound in H_2 and Ar atmosphere, respectively, inferring that the formation of TiC phase results from reaction of the residual carbon and fine Ti powder of 300 nm during sintering. On the other hand, it is generally known that an amount of residual carbon after debinding is larger in Ar atmosphere than in H_2.

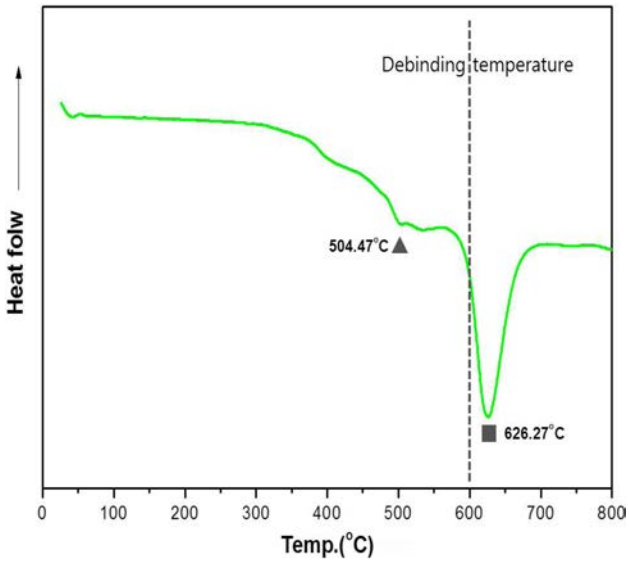

Fig. 7. DTA curve of TiH_2 powder in Ar atmosphere.

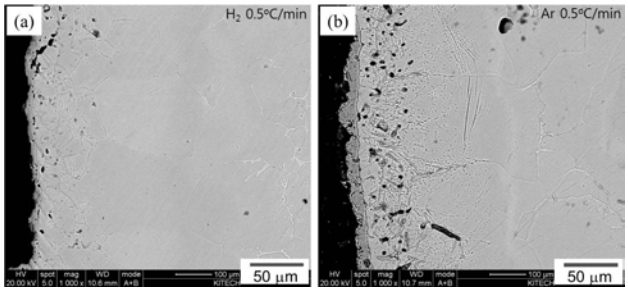

Fig. 8. SEM microstructure of the parts sintered at 1250 °C in vacuum after debinding at heating rate of 0.5 °C/min under (a) H_2 atmosphere and (b) Ar atmoshphere.

Nevertheless, in this work, the content of residual carbon was rather lower in Ar atmosphere. It comes evidently from dehydrogenation reaction of TiH_2 powder during debinding. That is, during debinding in Ar atmosphere, TiH_2 is decomposed to hydrogen and Ti (see Fig. 7) and hydrogen formed in the inside of the sample makes easy removal of binder through the formation of hydrocarbon, whereas dehydrogenation reaction does not occur during debinding in H_2 atmosphere. It has been reported that the lower heating rate is effective for low residual carbon [8]. Thus, to investigate the effects of heating rate, the debinding was again conducted at relatively slower heating rate of 0.5 °C/min in H_2 and Ar atmosphere, respectively and the results are listed in Table 1. As can be seen in Table 1, the content of residual carbon was rapidly reduced after debinding at heating rate of 0.5 °C/min in H_2 atmosphere, while the content at 0.5 °C/min in Ar atmosphere was almost similar to that at 2 °C/min in Ar. Also, as seen in Fig. 8 (a), in the sample debound at heating rate of 0.5 °C/min in H_2 atmosphere, the thinner TiC layer after sintering was formed than in sample at heating rate of 2 °C/min. The thicknesses in both samples debound in Ar atmosphere are similar to

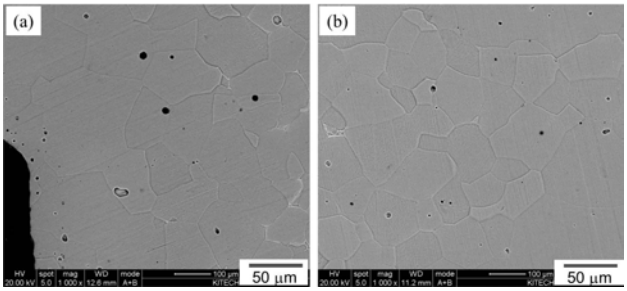

Fig. 9. SEM microstructures (a) near surface and (b) in center of a part sintered using wicking at 1250 °C in vacuum atmosphere after debinding at heating rate of 0.5°C/min under H_2 atmoshphere.

regardless of heating rate. These results clearly indicate that decrease of heating rate in H_2 atmosphere and dehydrogenation reaction of TiH_2 in Ar are very effective in removal of binder. Also, considering the rapid decrease of residual carbon with heating rate in H_2 atmosphere, it is suggested that the removal of binder depends predominantly on the kind of flowing gas for debinding.

On the other hand, it is generally accepted that carbon content remains in the range of 0.3 wt.% to 0.5 wt.% after debinding and the residual carbon is removed during sintering. In our previous works using 4 μm-316 L stainless steel feedstock, any carbon product on surface was not observed after sintering in vacuum though debound part had residual carbon above 0.3 wt.%. However, in this work using 300 nm-TiH_2 feedstock, the residual carbon in the debound part resulted in the formation of TiC phase layer on surface during sintering, despite of its negligible quantity (0.09%). It seems that this can be explained from particle size and reactivity of Ti points of view. As debinding temperature increases, the binder has a low viscosity and is pushed to the part surface by expansion of the internal decomposed gas, leaving a nearly binder-free region at the center of the part. At the final stage, all residual binder is trapped at contact points between particles near surface. The trapped binder forms a film on the surface of powders surrounding the pore, showing capillary action. The magnitude of capillary force becomes much higher with decrease of the size of particles. Thus, during sintering, the removal of the residual binder is more difficult in the part consisting of 300 nm Ti powders than in that of a few μm powders. In addition, since the nm-sized Ti powders have very high reactivity, those react easily the residual carbon at high sintering temperature, resulting in TiC phase layer near surface.

To enhance the removal of residual carbon near surface, the wicking process, which extracts the binder through capillary action, was introduced during sintering. Fig. 9 shows the microstructures of the sintered part experiencing wicking process during sintering in vacuum after debound at heating rate of 0.5 °C/min in H_2 atmosphere. Any TiC phase was not observed on surface and in center of the sintered part, as seen in Fig.9 (a) and (b). These results indicate strongly that wicking process is very useful of removal of small amount of residual binder existing near surface.

Conclusions

In this study, TiH_2 feedstock, having a wax-based binder system, was developed for micro powder injection molding and subsequent processing steps were optimized. Based on the results, the following conclusions were made:

1. A solid loading of 68 vol.% for the TiH_2 feedstock was determined to limit shrinkage during debinding and sintering. Rheological tests show that TiH_2 feedstock exhibits pseudo-plastic flow behavior.
2. The lower heating rate in H_2 atmosphere and dehydrogenation reaction of TiH_2 in Ar are very effective in removal of binder. Also, considering the rapid decrease of residual carbon with heating rate in H_2 atmosphere, it is suggested that the removal of binder depends predominantly on the kind of flowing gas for debinding.
3. The sound sintered Ti part without any TiC surface layer was obtained through an additional wicking process, which extracts the binder through capillary action, following the thermal debinding.

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