Dilatometric analysis of thermal debinding of injection moulded iron compacts

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The less than desired tolerance control of powder injection moulded compacts is a result of inconsistent dimensional changes in the compacts accumulated during moulding, debinding, and sintering. This study investigated the *in situ* length changes and their causes during thermal debinding on compacts which have been solvent debound. The dilatometric analysis showed that the specimen shrank in the early stage between 250 and 370°C, not because of sintering, but through the loss of N, C, and O in the carbonyl iron powder. At temperatures between 370 and 450°C, the specimen expanded owing to the carburisation of the iron powder. The length change was also influenced by the heating rate, debinding atmosphere, and the amount of the backbone binder. These dilatometric results are helpful in establishing the guidelines in designing binder compositions and debinding schedules. PM/0898

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INTRODUCTION

Powder injection moulding (PIM) has been accepted by the manufacturing industries as an attractive process in fabricating complex shaped parts.^{1,2} However, owing to the large amount of shrinkage which occurs during the process, the dimensional control is difficult and has become one of the most critical hindrances for the further growth of this technology. Thus, how to improve the tolerance of PIM parts has become an important subject in recent research and development.^{3,4}

The PIM process involves several processing steps: kneading, moulding, debinding, and sintering. The debinding is usually the slowest step and, to improve its efficiency, several faster processes have been developed.⁵⁻⁷ Among them, solvent debinding is one of the most widely adopted methods because it has a relatively short debinding cycle time and requires little investment in equipment.⁸ In the solvent debinding process, soluble binder components are removed first by solvent extraction. The remaining non-soluble binders are then decomposed in subsequent thermal debinding. The solvent debinding step creates interconnected pore channels which provide paths through which decomposed gas formed during the subsequent thermal debinding can escape to the ambient.⁹ With this process, some defects commonly seen in the straight thermal debinding, such as cracking, exfoliation, and distortion, are eliminated or alleviated.¹⁰⁻¹² Despite these advantages, the amount of tolerance control that can be achieved in the solvent then thermal debinding process is still not satisfac-

tory. Figure 1 shows that wide standard deviations can occur, and these are mainly attributed to sintering and thermal debinding; lesser deviations are caused by solvent debinding and moulding. Similar results have also been reported by Cardamone *et al.* on PIM tungsten heavy alloys.¹³ Part of the reasons is that a large amount of binder is contained in the compact, usually between 30 to 50 vol.-%. This allows about 12 to 20% linear shrinkage after debinding and sintering. If this shrinkage is anisotropic, distortion and poor dimensional control will then occur.

Lin and Hwang have shown by using a laser dilatometer that the dimensional changes during solvent debinding are mainly a result of the swelling of the binder when parts are immersed in the solvent. The amount of expansion is influenced by the binder amount, binder type, the debinding temperature, and the solvent type. When these parameters are not carefully selected, distortion and inconsistent dimensional changes may occur.¹⁴ This study continues to investigate the length change behaviour during the subsequent thermal debinding. With an understanding of the causes of these dimensional changes, the distortion and tolerance of PIM parts can then be improved by adjusting processing parameters, redesigning the part geometry, and optimising the material systems.

EXPERIMENTAL PROCEDURE

The spherical carbonyl iron powder, designated as CIP-S-1641, was used in this study. It had an average particle size of 4.6 µm (Fisher Subsieve Size) and contained small amounts of C, N, and O. The characteristics of the powder are listed in Table 1.

To prepare the feedstock, the iron powder was mixed with thermoplastic binders in a weight ratio of 93:7. The binder consisted of 40 wt-% low density polyethylene (LDPE), 55 wt-% paraffin wax (PW), and 5 wt-% stearic acid (SA). After being kneaded, the feedstock was granulated and then moulded into rectangular specimens of 2 × 10 × 100 mm. A two stage solvent thermal debinding process was then carried out. For solvent debinding, the compact was immersed in heptane at 45°C until 90% of the soluble binders, PW and SA, had been removed. During the subsequent thermal debinding, the solvent debound compacts were heated in a hydrogen atmosphere at a rate

Table 1 Characteristics of carbonyl powder used in this study

Iron powder	Characteristics
Designation	Carbonyl iron powder (CIP-S-1641)
Supplier	ISP Corp, Wayne, NJ, USA
Average particle size (Fisher)	4.6 µm
Shape	Spherical
Surface area (BET)	0.77 m ² g ⁻¹
Density (pycnometer)	7.542 g cm ⁻³
C, wt-%	0.712
S, wt-%	0.001
N, wt-%	0.738
O, wt-%	0.687

1 Standard deviation of length of two PIM compacts after being processed through moulding, solvent debinding, thermal debinding, and sintering

2 TGA curve of mixed binder (55 wt-% PW, 5 wt-% SA, and 40 wt-% LDPE) in hydrogen

of 5 K min⁻¹ to 650°C. The *in situ* dimensional changes of the specimens were measured by a thermal dilatometer (SETSYS TMA16/18, SETRAM Co., Caluire, France).

For the thermal properties of the binders employed, a Du Pont 9900 TGA analyser (Du Pont, Wilmington, DE, USA) was used to characterise the thermogravimetric (TGA) curve of the kneaded binder and the solvent debound compact under hydrogen. The melting point of the mixed feedstock was measured by using a Du Pont 910 differential scanning calorimeter (DSC). To understand the powder property changes through the process, specimens were pulled out of the furnace at different stages of debinding and were measured for changes in density and chemistry. The true density was measured by a pycnometer (Ultrapycnometer 100, Quantachrome, Syosset, NY, USA). The C, N, and O contents of the specimens were measured with a Leco CS-244 carbon analyser and Leco TC-136 oxygen/nitrogen analyser (LECO Co., St Joseph, Michigan, USA). The phase changes were examined by X-ray diffraction using a Philips PW1729 diffractometer (Philips Co., Eindhoven, Holland).

RESULTS

Thermal analysis

The thermal characteristics of binder components usually provide good references for designing a proper debinding temperature profile. Figure 2 shows the TGA curve of the

3 TGA curve of solvent debound compact that contains about 10 wt-% residual binders, PW, and SA

mixed binder in a hydrogen atmosphere. It exhibited a two stage decomposition behaviour. The first stage was caused by the decomposition of PW and SA, and it was completed at about 280°C. As the temperature increased to 370°C, the insoluble backbone binder (LDPE) began to decompose, and the reaction stopped at about 440°C.

Figure 3 shows the TGA curve of the solvent debound compact in a hydrogen atmosphere. Two stages were noticed. In stage 1, between 150 and 250°C, the amount of weight loss was approximately 0.4 wt-%. It was caused by the decomposition of the residual soluble binder, PW and SA. In stage 2, the curve exhibited a continuous decline from 270 to 430°C. Since the LDPE decomposition does not occur until 370°C, as shown in Fig. 2, this weight loss must have been caused by the weight change of the carbonyl iron powder. To confirm this, straight iron powders were heated to 370°C and then cooled to room temperature. The total weight loss was 1.03 wt-% and was mainly owing to the loss of light elements, N, O, and C, as shown in Table 2. Similar results on the loss of impurities have also been reported.^{15,16}

Dimensional changes

Since a dilatometer was used as the main tool in analysing the dimensional change of the compacts during debinding, the load employed on the push rod, 10 g, could not cause a significant amount of shrinkage of the specimen. Figure 4 compares the length changes of both as moulded and as solvent debound compacts during heating in the dilatometer. The as moulded compact expanded first owing to the large amount of PW in the compact. It then shrank significantly at about 100°C. This was because the melting points of the PW, SA, and LDPE were 43.3, 58.8, and 98.2°C, respectively, as was demonstrated by the DSC test shown in Fig. 5. In contrast, the solvent debound compact did not expand or shrink, as it was heated to 160°C. This indicated that the solvent debound compact had enough strength, even above the melting point of LDPE, to sustain

Table 2 Changes of N, O, and C in iron powder after being heated to 370°C in hydrogen

	N, wt-%	O, wt-%	C, wt-%	Total, wt-%
As received	0.738	0.687	0.712	...
Heated to 37°C in hydrogen	0.009	0.501	0.604	...
Change	-0.729	-0.186	-0.108	1.023

4 Thermal mechanical curve of as moulded and solvent debound compacts

5 DSC curve of PIM compact

6 Dilatometer curve of solvent debound compact during thermal debinding in hydrogen

the force exerted by the push rod in the thermal dilatometer during thermal debinding.

Figure 6 shows the *in situ* length change of a solvent debound specimen that was heated under hydrogen in the thermal dilatometer. The specimen started to shrink at 250°C and reached 0.8% at 370°C. It then expanded between 370 and 450°C. The shrinkage that occurred between 250 and 370°C could have been caused by the capillary force exerted by the molten binder, the sintering

7 Dilatometer curve of specimens containing 0, 6.5, 7.0, and 8.0 wt-% binder

8 Four point bending strength of pure iron compacts after being sintered at various temperatures

of iron powders, and/or the loss of the light elements in the iron powder. To verify the effects of capillary force resulting from the molten binder, the dilatometer curves of compacts with 6.5, 7.0, and 8.0 wt-% binder were compared, as shown in Fig. 7. It was noticed that, below 370°C, the dimensional changes in these compacts were similar. The pure iron compacts also exhibit the same trend. Since the amount of binder had a minimal effect, it seems unlikely that the main cause of the shrinkage was the capillary force from the liquid LDPE.

The second possible cause for the shrinkage was that light sintering of the iron powder occurred. Since densification of particles is always accompanied by neck growth, the strength of the compact must also increase. However, Fig. 8 shows that the strength of the compact did not increase until 450°C. Thus, the most likely cause of the 0.8% shrinkage between 25 and 370°C is the loss of impurities in the iron powder. Table 3 lists the true density

Table 3 Comparison of weight, density, and volume of carbonyl iron powder after being treated to 370°C in hydrogen

	Weight, g	Density, g cm ⁻³	Volume, cm ³
As received	100	7.54	13.26
Heated to 37°C in hydrogen	98.97	7.66	12.92
Change	-1.03%	1.59%	-2.56%

9 Dilatometer curve of specimen made from hydrogen reduced carbonyl iron powder

measured by pycnometer and the weight loss of the iron powder after being heated to 370°C in hydrogen. Although the iron powder lost 1.03% in weight owing to the loss of N, O, and C, its density increased by 1.59%. Based on these data, the calculated volume change and the linear shrinkage of the powder alone were 2.56 and 0.84%, respectively. This linear shrinkage value agreed with that observed in Fig. 7.

To further identify the effects of the light elements, a specimen was made from a powder that had been reduced in hydrogen at 370°C for 5 min. The dilatometer curve of this specimen, shown in Fig. 9, shows that there was little shrinkage between 250 and 370°C compared with that shown in Fig. 6. This confirms that the loss of N, C, and O in the powder is the main cause of the shrinkage of the specimen in the early debinding stage.

Figure 6 shows that after about 0.8% shrinkage, the PIM specimens expanded between 370 and 450°C. It is tempting to assume that the expansion is caused by the pressure of the decomposed gas formed during debinding; further examination of the data showed that this was not so. The TGA curve in Fig. 2 does show that the decomposition of LDPE started at 370°C and stopped at about 440°C. As the decomposed gas formed, pressure could build up inside the compact and cause separation between particles or even break up the lightly sintered interparticle necks. However, when vacuum or nitrogen was employed, no expansion between 370 and 440°C was observed, as shown in Fig. 10. This suggests that the gas pressure of the decomposed gas did not cause the expansion.

When the carbon content in the iron compacts was monitored throughout the debinding process, it was found that the carbon content changed significantly. Figure 11 shows that the carbon content in the as solvent debound compact was about 3.5 wt-% owing to the presence of LDPE, residual PW, and SA, as well as the intrinsic carbon in the iron powder. As the thermal debinding temperature increased to 370°C, the carbon content started to decrease and reached about 2.5 wt-% at 450°C. At 550°C, the carbon content decreased to 0.1 wt-%. It is possible that these amounts include the dissolved carbon and the carbon soot on the iron powder surface, since iron is a catalyst for polymer decomposition.¹⁷ To measure the intrinsic carbon content of the iron powder throughout the process, the compact was immersed in toluene at 95°C to dissolve the LDPE and the residual PW and SA. Figure 11 shows that, before thermal debinding, the carbon in the iron powder was about 0.8 wt-%, similar to that of the as received iron powder, as is given in Table 1. As the temperature increased to 370°C, the carbon content started to increase, reaching

10 Dilatometer curve of specimens debound under vacuum, hydrogen, and nitrogen

11 Carbon content of iron compact after being debound at various temperatures

2.5 wt-% at 450°C, and then decreased. This indicated that carburisation occurred. X-ray diffraction analysis further shows that the iron compacts pulled out of the furnace after reaching 370, 450, and 600°C, respectively, formed Fe₃C at 450°C, as shown in Fig. 12. Thus, it is demonstrated that the expansion of the specimens between 370 and 450°C was most likely caused by the carburisation of the iron powder.

Effect of atmosphere

Figure 10 shows that the temperature where the compacts began to shrink varied according to atmosphere, with the lowest temperature in hydrogen and the highest in nitrogen. This result supports previous studies indicating that the impurities of carbonyl iron powder can be removed at a lower temperature in hydrogen than in nitrogen.^{18,19} Moreover, the specimens in nitrogen and in vacuum did not expand throughout the debinding process. This again suggests that the expansion that occurred in hydrogen atmosphere was possibly caused by carburisation from the decomposed hydrocarbon gas.

Effect of backbone binder content

Figure 13 shows the effect of the backbone binder content on the dimensional change of solvent debound compacts

12 X-ray diffraction pattern of debound compacts after heating to 370, 450, and 600°C in hydrogen

13 Dilatometer curve of compacts which consist of 20, 30, and 40 wt-% LDPE in binder system

during thermal debinding. As the amount of the LDPE decreased, the amount of expansion decreased. Since the carburising hydrocarbon gas was supplied by the backbone binder, it is reasonable to assume a positive correlation between the amounts of backbone binder and amount of expansion.

Effect of heating rate

In thermal debinding, the heating rate is always regarded as one of the important processing parameters. Faster heating rates shorten the debinding time and save on cost,

14 Dilatometer curve of specimens thermally debound at different heating rates

but they may easily cause defects such as cracking, slumping, and warping. Four heating rates, 1, 5, 10, and 20 K min⁻¹, were evaluated. After debinding, none of the specimens showed cracks or blisters, indicating that the pore channels created during solvent debinding were open enough for the decomposed gas to escape to the ambient. Figure 14 shows that as the heating rate decreased, the set points of the temperature at which shrinkage and expansion began decreased. One possible reason for this is that more time was allowed for the weight loss reaction and carburisation to occur before reaching the set temperature. Moreover, when the heating rate of 1 K min⁻¹ was employed, the amount of expansion occurring at about 300°C was only 0.15%, much less than the amount of expansion occurring at higher heating rates.

DISCUSSION

The above results show that processing parameters (heating rate and debinding atmosphere) and material characteristics (iron powder impurities and binder content) both affect the dimensional changes of PIM compacts during debinding. These variables could cause both expansion and shrinkage during debinding. Since dimensional stability is better achieved without abrupt shrinkage or expansion, a smooth and consistent shrinkage throughout the debinding will be favoured. The above results suggest that lower quantities of backbone binder, slower heating rates, and vacuum or inert gases should be used for the thermal debinding of solvent debound compacts. Moreover, a smaller amount of the total shrinkage is also favoured for consistent final dimensions. This means that iron powders with lower amounts of N, O, and C should be used so that the 0.8% shrinkage that occurred between 250 and 370°C can be decreased.

From the thermal mechanical behaviour of compacts, as shown in Fig. 4, the advantages of removing some binder components before the thermal debinding should also be noted. After soluble binder components, such as PW and SA, have been removed, the compact will have a greater strength to withstand distortion and slumping during the subsequent thermal debinding. Figure 4 also suggests that the solvent debinding must be performed below 100°C, which is the softening point of a green compact. This limit does not cause any problems in solvent debinding, since most solvent debinding can be performed effectively at temperatures lower than 60°C. In comparison, both straight thermal debinding and vacuum debinding, which depolymerise the binder through pyrolysis, will be limited by this 100°C ceiling. This will increase the debinding time significantly.

Another factor influencing the dimension of the compacts during debinding is the carburisation effect. This phenomenon occurs when a hydrogen atmosphere is used. In general, hydrogen is regarded as a strong reducing atmosphere. It can remove the oxygen and carbon in the powder, and it also helps remove lubricants and binders.²⁰ However, during the backbone binder removal, the hydrogen can react with carbon and form carburising molecules such as methane.²¹ If the concentration of the methane is over the equilibrium constant, which is very likely considering the large amount of decomposed gas inside the small pore channels in the compact, carburisation of the iron powder may then occur. If such carburisation is not uniform, as in the parts with various cross-sectional thicknesses, distortion could then happen owing to the uneven amount of expansion of the part. To alleviate this problem, inert gases or vacuum, slower heating rates, and parts with uniform thickness should be considered during the engineering stage. The amount of expansion can also be decreased by using lower amounts of LDPE, such as 20 wt-%, as shown in Fig. 13. However, with an insufficient amount of the backbone binder, the length changes during solvent debinding can become inconsistent, as was demonstrated by Lin and Hwang.¹⁴ Thus, a compromise must be reached when all PIM processes are considered.

CONCLUSION

The *in situ* dimensional changes of solvent debound compacts during thermal debinding were monitored using a thermal dilatometer. The specimens shrank first between 250 and 370°C and then expanded between 370 and 450°C. The loss of light elements, N, O, and C, of the carbonyl iron powder was found to be the cause of the shrinkage, and the carburisation of the iron powder was responsible for the expansion.

To avoid abrupt shrinkage and expansion of the compact during debinding, both of which are harmful for dimensional controls, slower heating rates, smaller amounts of backbone binders, and inert gases or vacuum should be employed in thermal debinding.

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