Improvements in sintered density and dimensional stability of powder injection-molded 316L compacts by adjusting the alloying compositions

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Abstract

Powder injection molding is a process that provides advantages when making small parts with high density and complicated shapes. However, dimensional control of powder injection-molded stainless steel parts is difficult due to the presence of the liquid phase and the large amount of shrinkage that occurs during sintering. This study examines whether such a problem can be overcome through adjustments in the alloy composition and by making use of Thermo-Calc analysis. The results show that, with an increase in the molybdenum content up to the maximum limit according to existing specifications, a compact can be sintered to high densities without the presence of the liquid phase, while maintaining it in the dual-phase region of $\gamma + \delta$. In addition, dimensional control is improved. A slower heating rate is also found to be beneficial. These results are explained through dilatometric analysis and phase diagrams that are calculated using the Thermo-Calc program.

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1. Introduction

Powder injection molding (PIM) is a net-shape-forming technology that is particularly advantageous in fabricating small complex-shaped parts with high sintered densities. However, the ability to obtain close tolerances with this method is limited. The main reason is that the solid content in green compacts is low, usually between 50 and 70 vol.%. With the low solid content in molded parts and the high sintered densities required in finished products, large amounts of linear shrinkage, usually from 11% to 20%, occur after sintering. Furthermore, the PIM process includes many steps, including kneading, molding, debinding, and sintering. The dimensional precision can be influenced by processing parameters and material characteristics in each step, such as variability in raw powders

and feedstocks [1,2]. The molding process and part design can also cause non-uniform flow of the material in the mold cavity, causing variations in the green density and resulting in anisotropic shrinkages in the same part [3,4]. Serious defects and distortions may also occur during solvent debinding if the debinding temperature, binder types, and binder amounts selected are inadequate [5,6]. Further defects, such as exfoliation, blistering, and non-uniform shrinkage, can also occur during thermal debinding and sintering if the selected heating schedules, setter plates, or powders are inappropriate [7–10]. When all these factors have been considered and controlled well, the dimensional control achieved is still not comparable to that possible with many other manufacturing processes. Thus, even a tolerance of $\pm 0.3\%$, which is easy to attain with many competing manufacturing processes, is still a challenge for many PIM producers [3,11].

In the case of PIM 316L components, in order to obtain high sintered densities, high-temperature sintering and, sometimes, liquid-phase sintering are required to reach

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densities greater than 7.6 g/cm³ or 94.8%. The liquid provides a fast diffusion path and capillary forces, both of which contribute to rapid densification [12,13]. However, when too much liquid is present, anisotropic shrinkage or even slumping may occur, particularly in complicated parts with cantilevered sections. This is because the capillary force of the liquid can cause rapid particle rearrangement. In addition, the dissolution of small particles and the sharp corners of large particles can reduce the mechanical locking effect among powders. The effect of gravity and the differences in densities between the liquid and solid particles can sometimes also be significant enough to cause uneven liquid distribution [14–17]. These are all influenced by the amount of liquid. Thus, the uniformity of the temperature within the component and within the furnace, and the consistency of the alloy composition, must be carefully controlled. However, studies in these areas are still very limited. The purpose of the present study was therefore to investigate the effects of the sintering temperature and composition variations on the dimensional control of PIM 316L compacts and to propose methods for improvements.

2. Experimental

Water-atomized 316L stainless steel powders were used in this study. The characteristics of these powders are given in Table 1. To understand the effect of the composition on the dimensional stability of 316L compacts, fine Mo and Ni powders were added, but keeping within the specifications of the Metal Powder Industries Federation (MPIF) standard 35 [18]. The characteristics of the Mo and Ni powders are given in Table 2. The morphologies of all the powders are shown in Fig. 1.

To prepare the feedstock, the 316L powder was kneaded with a multi-component binder using a sigma-shaped kneader. The binder consisted of polyethylene, paraffin wax, and stearic acid. The solid content of the feedstock was 61 vol.%, or 93 wt.%. After kneading, the feedstock was molded into rectangular flat specimens of 2 × 10 × 100 mm using a 40-ton molding machine (270C/400,

Table 2

The characteristics of Mo and Ni powders used in this study

	Mo	Ni
Designation	OMP 901	Ni-123
Particle size (laser scattering method)	$D_{10} = 1.23 \mu\text{m}$ $D_{50} = 2.67 \mu\text{m}$ $D_{90} = 5.88 \mu\text{m}$	$D_{10} = 2.35 \mu\text{m}$ $D_{50} = 3.69 \mu\text{m}$ $D_{90} = 6.88 \mu\text{m}$
Shape	Irregular	Spiky
Pycnometer density	10.18 g/cm ³	8.89 g/cm ³
Chemistry		
C (wt.%)	0.001	0.079
S (wt.%)	0.004	0.002
N (wt.%)	0.727	0.208
O (wt.%)	0.005	0.001
Supplier	H.C. Starck	INCO

Arburg, Lossburg, Germany). To remove the binder, the compact was immersed in heptane at 45 °C until about 80% of the soluble binders (paraffin wax and stearic acid) were removed. During the subsequent thermal debinding, the solvent-debound compacts were heated at 5 °C/min to 800 °C and then held for 1 h in hydrogen to remove the remaining wax and stearic acid and the non-soluble polyethylene. Debound compacts were then heated at a rate of 10 °C/min to the set temperatures between 1300 and 1390 °C. The atmosphere employed was either dry hydrogen or vacuum, which was backfilled with argon and was kept at 1 Torr.

To evaluate the dimensional control of specimens produced using different sintering processes or different material compositions, only the 100 mm sample dimension was measured. This is because the differences in this dimension are large enough when a conventional micrometer having an accuracy of 0.01 mm is used. Although only the length was measured, the findings thus obtained should be general and can still provide the required information on the dimensional control of complicated parts. The reported data on densities and dimensions are averages of a minimum of eight specimens.

To understand the effects of sintering parameters and the changes in Mo and Ni content on the dimensional control of PIM 316L compacts, a thermal dilatometer (SET-SYS, TMA16/18, SETARAM, Caluire, France) with an accuracy of better than 0.1 μm was employed to monitor the in situ dimensional changes during heating and sintering. The specimen used was thermally debound and the heating conditions of the dilatometer runs were the same as those employed for the sintering runs. To alleviate the “hot pressing” effect from the pushrod at high temperatures, an alumina plate was placed between the pushrod and the 5 × 5 × 5 mm specimen. The counterweight on the pushrod was also adjusted so that only a 10 g force was applied on the specimen, which is equivalent to a pressure of 0.003920 MPa, less than the 8 MPa bending strength of the specimen. No indentations were observed in any of the specimens. The sintering and dilatometry results are discussed based on the phase diagrams of 316L stainless steels, which were calculated using Thermo-Calc software and a

Table 1

The characteristics of the water-atomized 316L powder used in this study

	Characteristics
Type	Water-atomized powder
Designation	PF-20F
Composition	16.55% Cr, 12.56% Ni, 2.09% Mo, 0.78% Mn, 0.027% C, 0.04% N, 0.81% Si, 0.015% P; balance: Fe
Average particle size (laser scattering method)	$D_{10} = 5.75 \mu\text{m}$ $D_{50} = 13.67 \mu\text{m}$ $D_{90} = 27.42 \mu\text{m}$
Shape	Irregular
Pycnometer density	7.93 g/cm ³
Supplier	ATMIX

Fig. 1. Morphologies of (a) 316L stainless steel, (b) Mo, and (c) Ni powders.

TCFE2 database (Thermo-Calc Software, Stockholm, Sweden) based on the composition listed in Table 1.

To examine whether there was any body-centered cubic structure present in the sintered compact that influenced the corrosion resistance, a Feritscope (MP30, Fisher Co., Sindel Fingen, Germany) was used to measure the mag-

netic response of the compact. The corrosion resistance was measured following MPIF standard 62, in which specimens were immersed in 2% sulfuric acid for 30 days, followed by drying at 110 °C for 45 min before the weight loss was measured [19]. The FeCl_3 solution test was also employed. The specimens were immersed for 2 days in a solution at 55 °C, which was prepared by dissolving 100 g of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ in 900 ml of distilled water. After being dried at 100 °C for 45 min, the specimens were measured to determine the weight loss.

3. Results

3.1. Effect of sintering temperature

To understand how sintering temperatures and the phases present during sintering influence the sintered densities and standard deviations (SDs) in length, 316L stainless steel specimens were sintered under vacuum at 1360, 1370, 1380, and 1390 °C for 1 h. The heating rate selected was 10 °C/min. Fig. 2 shows that the sintered density increased from 7.60 to 7.89 g/cm³ when the sintering temperature increased from 1360 to 1390 °C. However, the SD of the 100 mm length also increased from 0.05% to 0.15%. These results are very possibly related to the presence of the liquid phase at high temperatures. To support this hypothesis, the Thermo-Calc program was used to calculate the phases present between 1200 and 1500 °C. Fig. 3 indicates that δ phase and liquid phase start to form at 1357 and 1384 °C, respectively. To confirm this, specimens that had been thermally debound were placed in a dilatometer, heated to 1390 °C, and then held at that temperature for 1 h. Fig. 4 shows that the shrinkage rate reached a maximum at about 1275 °C and then decreased. The curve inflected slightly between 1350 and 1360 °C. This is most likely attributable to the formation of the δ phase. The shrinkage rate then increased again between 1380 and 1390 °C due to the formation of the liquid phase. Based on these results, it is suggested that the deterioration of

Fig. 2. Sintered densities and SDs of the length dimension of 316L compacts sintered at different temperatures.

Fig. 3. Predicted amounts of phases for 316L compacts sintered at different temperatures.

Fig. 4. Shrinkage rate of 316L compact heated at 10 °C/min to 1390 °C and then sintered for 1 h.

the SDs of the lengths of compacts that were sintered at 1390 °C was caused by the formation of liquid. Considering that the temperature in the furnace was not ideally uniform and that temperature overshooting could have occurred at the end of the heating, the liquid phase might also have occurred in compacts sintered at 1380 °C, thus leading to the poor SD in sample length shown in Fig. 2.

3.2. Effect of alloying additives

The above results suggest that the liquid phase should be avoided if dimensional precision is to be attained in sintered PIM 316L compacts. This, however, reduces the sintered density. In an attempt to overcome this dilemma, the amounts of Mo and Ni in the compact were increased from 2.09 and 12.56 wt.% to 3 and 14 wt.%, respectively, the maximum amounts allowed in the specifications of the MPIF standard [14]. These two elements were selected

because Mo is a typical α or δ phase stabilizer, while Ni is a γ phase stabilizer. The phases present after Mo was added were calculated using the Thermo-Calc program, and the results are shown in Fig. 5(a). Since Mo is a body-centered cubic phase stabilizer, the δ phase region was broadened as compared to Fig. 3, and its formation temperature decreased from 1357 to 1308 °C. The melting point also decreased from 1384 to 1376 °C. When Ni was added, the δ phase disappeared, as shown in Fig. 5(b), and the melting point of the liquid phase decreased slightly from the 1384 °C of the as-received powder, as shown in Fig. 3, to about 1382 °C.

The sintering behaviors of the 316L specimens with Mo and Ni additions were then examined using the thermal dilatometer. The specimens were heated at 10 °C/min to 1390 °C and then held at that temperature for 1 h. Similar

a

b

Fig. 5. The effects of adding (a) 0.91 wt.% Mo and (b) 1.44 wt.% Ni on the amounts of phases of 316L compacts at high temperatures.

to the as-received powder, the shrinkage rate of the 316L + Mo specimens increased first as the temperature increased, reached a maximum at about 1080 °C, and then decreased, as shown in Fig. 6. The decreasing trend stopped at about 1310 °C, when δ phase formed. The shrinkage rate then increased again above 1375 °C, when the liquid phase formed. For the 316L + Ni compacts, only one inflection was observed in the curve above 1300 °C, at about 1380 °C, also shown in Fig. 6. This suggests that no δ phase formed during heating. Comparing Figs. 6 and 4, it is noticeable that the increase in the shrinkage rate of the 316L + Ni specimen after the liquid formed is higher than those of the 316L and 316L + Mo specimens. This indicates that more liquid phase was present at 1390 °C in the 316L + Ni specimen than in the as-received powder and 316L + Mo specimen.

Fig. 7 shows the sintered densities of 316L compacts with and without the composition modifications. The specimens were heated in dry hydrogen at 10 °C/min to 1200, 1300, 1350, 1370, and 1390 °C. The specimens were then held at that temperature for 1 h. The results show that higher sintered densities can be reached for 316L + Mo specimens above 1300 °C. For the as-received 316L specimen, the density increased significantly above 1350 °C. The 316L + Ni reached high densities only when the sintering temperature was increased to 1390 °C, at which point the densities of all specimens were almost the same because the liquid phase formed.

Fig. 6. Shrinkage rates of 316L + Mo and 316L + Ni compacts heated at 10 °C/min to 1390 °C and then sintered for 1 h.

Fig. 7. Sintered densities of 316L, 316L + Mo, and 316L + Ni compacts sintered at different temperatures.

Fig. 8 illustrates the effects of Mo and Ni additions on the SD of the length of PIM 316L specimens sintered at 1370 °C. The dimensional control was improved when Mo was added to the 316L powders, 0.061% for the as-received powder versus 0.039% for the Mo-added powder, despite the fact that Mo-added specimens had a larger amount of shrinkage. The addition of Ni was also effective, with the SD decreasing to 0.045%. This, however, is not a fair comparison because the density of the 316L + Ni specimen was lower and the amount of shrinkage was smaller compared to the specimens made from the as-received 316L powder.

Although these results demonstrate the advantages of adding Mo, it must be kept in mind that such an addition

Fig. 8. Effect of Mo and Ni additions on the SD in length of injection-molded 316L compacts.

Table 3

The effect of Mo and Ni additions on the weight loss (g/m²/day) of PIM 316L compacts

	As-received 316L	316L + Mo	316L + Ni
H ₂ SO ₄ (MPIF 62)	3.68×10^{-4}	3.41×10^{-4}	3.49×10^{-4}
FeCl ₃ solution	0.83	0.82	0.71

cannot be allowed to impair the corrosion resistance of the 316L specimen. Examinations were thus carried out using the sulfuric acid test (MPIF standard 62) and the FeCl₃ solution test. Table 3 shows that Mo addition did not cause any increase in weight loss in either of the tests. This suggested that there was no δ phase present in the sintered compact. To confirm this, a Feritscope was also employed to check if there was any ferrite phase present. The results again showed that no ferrite phase was present.

3.3. Effect of heating rate

The above results show that the sintered density and dimensional stability can be influenced significantly by the sintering temperature. This suggests that the stability of the set isothermal sintering temperature, temperature overshooting at the end of the heating, temperature uniformity within the compact, and temperature uniformity within the furnace could all be critical factors. These factors in turn could be influenced by the heating rate. To

examine such an effect, three different heating rates, 5, 10, and 20 °C/min, were used to heat to 1380 °C compacts that were prepared from the as-received powder. In order to have a fair comparison, the sintering times were adjusted so that the three groups of specimens could reach the same sintered density. The SD in length of the 316L compacts was measured after molding, solvent debinding, and sintering. Fig. 9 shows that the final SD increased from 0.06% to 0.09% as the heating rate increased from 5 to 20 °C/min. Since the SDs were quite small after molding, solvent debinding, and thermal debinding, the differences must have been caused by the heating rates. These results agree with the findings for sintered iron compacts [20].

4. Discussion

The results obtained indicate that three phases, namely δ , γ , and liquid phases, were involved in the sintering of the 316L compacts. The formation temperatures of the δ and liquid phases in each of the specimens examined were measured using the dilatometer, and the results are summarized in Table 4. In all cases, the temperatures that were measured and those that were calculated using the Thermo-Calc program are very close. This shows that the Thermo-Calc calculations can be used reliably in explaining the sintering behavior and density results of the 316L compacts investigated in this study.

The results in Fig. 2 demonstrate that the presence of the liquid phase at high temperatures enhances densification. However, it impairs the dimensional stability. The main reason is that the amount of the liquid phase changes significantly even with a slight variation in the temperature. This is illustrated by the steep liquid line shown in Fig. 3, which indicates that the amount of the liquid phase changes by 2.4%/K. This strong relationship between the temperature and the amount of the liquid phase can be further explained through the analysis of the phase diagram. As shown in Fig. 10, the typical 316L phase diagram demonstrates that the slope of the solidus of the (liquid + γ) and (liquid + γ + δ) region is quite flat. This implies that a small variation in temperature can cause a significant change in the amount of the liquid phase and thus large variations in densities and dimensions. This flat solidus is very similar to that of M2 high-speed steel compacts, which require a very narrow sintering window when precise dimensions are required [12,21]. This suggests that the temperature distribution in the furnace and within the 316L compacts must be very uniform if consistent dimensions

Fig. 9. Effect of heating rate on the SD in length of injection-molded 316L compacts.

Table 4

Comparison of the formation temperatures (°C) of δ and liquid phases measured using the dilatometer and those predicted using the Thermo-Calc software

	As-received 316L		316L + Mo		316L + Ni	
	Predicted (Fig. 3)	Measured (Fig. 4)	Predicted (Fig. 5(a))	Measured (Fig. 6)	Predicted (Fig. 5(b))	Measured (Fig. 6)
δ phase	1357	1350–1360	1308	1300–1310	–	–
Liquid phase	1384	1380–1390	1376	1370–1380	1382	1375–1385

Fig. 10. Effect of the Ni content on the type of phases present in 316L compacts at different temperatures.

are to be obtained. This challenge in the temperature uniformity will be even more difficult to achieve when high heating rates are used.

It is also evident by comparing Figs. 3, 5 and 10 that the liquid formation temperature decreases slightly as the Ni content increases. Furthermore, a decrease in the Ni content or an increase in the amount of Mo will shift the system from the liquid + γ region to the liquid + δ + γ region or shift the γ region to the δ + γ region in the regular sintering temperature range between 1350 and 1390 °C. These calculations indicate that the phases present and the amount of each phase could be influenced significantly by the composition of the powder. This implies that the composition of the 316L powders within the same lot and from lot to lot must be consistent in order to meet stringent requirements for dimensional control.

Due to the sensitivity of the effect of sintering temperature on the amount of liquid phase and the final dimensions of the compact, an intuitive approach to improving the dimensional stability of 316L compacts would thus be to lower the sintering temperature and to sinter compacts in the solid state throughout the sintering cycle. This, however, decreases the final sintered density. One method with which to obtain both high density and dimensional stability that is demonstrated in this study is to incorporate more Mo into the alloy up to the maximum limit of 3%, as per the specifications of powder metal 316L compacts. The calculations using the Thermo-Calc software, as shown in Fig. 5(a), indicate that the δ and liquid phases start to form at 1308 and 1376 °C, respectively. Thus, sintering will proceed in the dual-phase (δ + γ) region between these two temperatures. When such a temperature is selected, the densification will be enhanced because the diffusion rate in the δ phase is much faster than that in the γ phase. Moreover, the presence of the δ phase could impede the grain growth of the nearby γ phase. As a result, a flat region in the shrinkage rate curve, as shown in Fig. 6,

was observed between 1310 and 1375 °C, and the compact sintered at 1370 °C reached a high final density of 7.7 g/cm³, as shown in Fig. 7. Another factor that helps the dimensional control is that the slope of the curve shown in Fig. 7 at 1370 °C is smaller than those for the other two materials. This flatter slope of the density curve usually helps the density uniformity and thus the dimensional precision [22].

5. Conclusions

We have discussed the effects of alloy compositions, sintering temperatures, and heating rates on the sintered density and dimensional stability of injection-molded 316L stainless steel compacts. The results show that high densities can be obtained using liquid-phase sintering above 1380 °C but at the cost of dimensional precision, particularly when high heating rates are employed. Through analyses of the phase diagrams calculated using the Thermo-Calc program and of the dilatometry curves, it is shown that the amount of the liquid phase is sensitive to the alloy composition and the sintering temperature. Thus, obtaining dimensional control is difficult. To overcome this problem, Mo can be incorporated into the powder to its maximum limit according to specifications so that the sintering proceeds in the dual-phase (δ + γ) region. With a higher diffusion rate in the δ phase and impeded grain growth, high densities of 7.7 g/cm³ can be attained after 1 h of sintering at 1370 °C in hydrogen. In addition, the dimensional control is improved, since the formation of liquid phase is prevented.

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