Powder injection molding 440C stainless steel

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Abstract In this work, the processing steps for producing 440C stainless steel parts by means of powder injection molding technique were investigated. The molded specimens were debinded by solvent debinding followed by thermal debinding methods and were sintered under vacuum atmosphere. Effective densification took place in the temperature range 1,230–1,240°C in the sintering. After heat treatment, specimens sintered at 1,240°C for 30 min had the tensile strength of 876.3 MPa, the hardness of 57.7 HRC. Pitting mainly occurred in injection molding 440C stainless steel specimens in NaCl solution. The content of carbon has serious effect on the shape retention. Some methods, such as preventing from oxidation, are presented to avoid the as-sintered specimens from deformation.

Keywords Metal injection molding · Debinding · Sintering · Corrosion resistance · Deformation

1 Introduction

The alloy 440C is a high carbon martensitic stainless steel with moderate corrosion resistance, good strength, and the ability to obtain and keep excellent hardness and wear resistance. Due to excellent properties, 440C stainless steel has widespread applications, such as Ball bearings and races, gage blocks, molds and dies, knives and measuring instruments [1, 2]. Powder injection molding (PIM) has become a widely exploited manufacturing technology for the production of near net shaped components [3]. PIM has features of low production cost, shape complexity, tight

tolerances, applicability to several materials and high final properties over conventional production technologies. The low solid content in powder injection molding 440C stainless steel parts usually causes large amount of shrinkage after sintering and thus poor dimensional processes. Rapid sintering densification of 440C stainless steel powders is possible by exceeding the solidus temperature in an approach termed supersolidus liquid phase sintering. This process is often limited by a narrow processing window for attaining densification without distortion [4]. It also has been reported that the processing of 440C stainless steels is difficult because of their tendency to form a continuous grain boundary carbide network during sintering and hence, are not generally used for PM applications [5]. All the above-mentioned make injection molding 440C steel difficult in both performance and deformation control.

However, metal injection molding 440C stainless steel is rarely reported. Few efforts have been devoted to understanding the whole process and sintering deformation. Nevertheless, the present work is set out to investigate the various processing parameters, including debinding, sintering temperature, and heat treatment conditions, on the performance and shape retention of 440C stainless steel and to ascertain whether some of the problems encountered during previous research could be successfully overcome.

2 Experimental

2.1 Materials and experimental procedures

Gas-atomized 440C stainless steel powders were used in this study. The characteristics of these are given in Table 1. The powders are largely round in shape as shown in Fig. 1. The multiple-component binder system used was composed of paraffin wax, pure peanut oil, and polyolefin.

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Table 1 The characteristics of the gas-atomized 440C stainless steel powder

	Characteristics
Type	Gas-atomized powder
Composition	17.6% Cr, 1.1% C, 0.65% Mo, 0.34% Mn, 0.18% Ni, 0.051% O, and balance; Fe
Average particle size	D90=20 μm
Shape	Spherical
Pycnometric density	7.74 g/cm^3
Supplier	Ospray

Feedstock was prepared with the powder loading (volume fraction) of 57%. The binder and 440C stainless steel were mixed at 160°C for 2 h to form a mixture, which was granulated in a single screw squeezing machine to acquire a homogeneous feedstock for injection. The green parts, with the shape shown in Fig. 2, were molded by an injection molding machine.

Debinding was performed in two stages of solvent debinding by methylene dichloride solvent followed by thermal debinding in a vacuum furnace under argon atmosphere, and then sintering was carried out in the same furnace under vacuum atmosphere. The as-sintered specimens were quenched at 1,050°C and then tempered at 150°C for 2 h. Specimens were immersed in 3.5% NaCl solution, which was maintained at 25°C for 240 min, in order to study erosion in the presence of chloride ions.

2.2 Measurement methods

Density of sintered samples was determined using a water replacement method (Archimedes method). The hardness and strength of the specimens were determined on the hardness tester and the tensile tester, respectively. Microstructures of sintered and heat-treated parts were evaluated with the optical

microscope (Netophot). Morphological analysis of eroded microstructure was carried out using a scanning electron microscope (SEM). The residual carbon and oxygen were determined by CS/44 and TC/436 analyzer, respectively.

3 Results and discussion

3.1 Debinding

For safe and rapid binder removal with minimum possibility of cracks and blister formation, solvent debinding followed by thermal debinding was used. Solvent debinding was performed by means of methylene dichloride as a solvent at 37°C for 6 h. After solvent debinding, the specimens had good strength, which was enough to be handled easily.

Figure 3 shows that the binder weight loss ratio versus time for the specimens. As it is shown after 6 h, the weight loss ratio is about 62%. Almost wax and oil can be removed. For the specimens with 3.12 mm thickness, after 1 h, 42% of binder had been removed. It is considered that after removing 40% of binder, there exists some interconnected capillary porosity inside of the specimen, which makes leaving of gaseous products in subsequent thermal debinding easy in a short time [6]. Hence, the solvent debinding rate can reach 2 mm/h through the use of this kind of binder.

The following heating cycle was used for thermal debinding. From room temperature to 200°C, the temperature increased with heating rate of 3°C/min held at that temperature for 1 h. And from 200°C to 385°C, paraffin wax and oil were removed from the specimen in a low-heating rate of 2°C/min to prevent formation of defects and held at that temperature for

Fig. 1 SEM photograph of the gas-atomized 440C stainless steel powder **Fig. 2** MIM tensile sample

Fig. 3 Rate of weight decreasing of the sample with time in solvent of methylene dichloride at 37°C

1 h. Next, from 385°C to 425°C, the component of macromolecule began to degrade. The macromolecule was removed with rate of 2°C/min and remained at 425°C for 1 h. The following is from 425°C to 600°C with the rate of 3°C/min and remained at 600°C for 30 min to make sure that the binder was removed completely. Then the temperature increased with 5°C/min to 950°C to finish presintering.

Figure 4 shows scanning electron micrograph of a debinded specimen cross section. As can be seen, nearly all the binder has been removed from the specimen and sintering neck has formed to keep the shape.

3.2 Sintering

To understand how sintering temperatures and the phases present during sintering influence the sintered densities,

Fig. 4 Scanning electron micrograph of a debinded specimen at 950°C

Fig. 5 Effect of sintering temperature on final density

440C stainless steel specimens were sintered under vacuum from 1,200°C to 1,260°C for 30 min. Figure 5 shows that the sintered density increased from 6.89 to 7.56 g/cm³ when sintering temperature increase from 1,200°C to 1,260°C. Effective densification took place in the temperature range of 1,230–1,260°C. Densification rates at temperatures below approximately 1,220°C were consistent with solid state diffusion and were extremely low, but only liquid phases began to appear; the densification rate accelerated rapidly. These results are very possibly related to the presence of the liquid phase at high temperatures. There is an optimal maximum sintering temperature that relates to the volume fraction of liquid. This is in turn on the alloy composition. For 440C stainless steel, every little increase in temperature increases a large amount of liquid. Around the optimum temperature is a narrow range of acceptable sintering temperatures that is about 10 K wide [7]. If a small quantity of liquid forms, then there is poor densification because the specimen has too much solid–solid contact. However, temperatures in excess of the optimal range results in grain growth, slumping, nonuniform densification, pore coalescence, and swelling.

Figure 6 showed the microstructure of specimens sintered at different temperatures. At sintering temperature of 1,210°C (Fig. 6a), there were still a number of spheroidal pores visible throughout the sample, indicating that sintering had not gone to completion. When temperature was increased to 1,230°C (Fig. 6b), there was a reduction in the size of the pores and moderate increase in grain size. At 1,260°C (Fig. 6c), there was a marked difference in the microstructure. An abrupt increase in grain size was observed with the morphology of the carbide changing to a largely continuous grain boundary network.

Fig. 6 Microstructure of specimens sintered at different temperatures. **a** 1,210°C. **b** 1,230°C. **c** 1,260°C

3.3 Heat treatment

Figure 7 shows the average tensile strength and hardness of sintered parts under different sintering temperatures after heat treatment. From 1,200°C to 1,240°C, the performance increased with the increase of sintering temperature because

Fig. 7 Effect of sintering temperature on tensile strength and hardness after heat treatment

hardenability of stainless steel was determined by sintering density. As the sintering density increased, the heat conductivity of this material was improved, therefore, the surface hardness increased after heat treatment. However, too high temperature was not beneficial for mechanic performance of 440C stainless steel. In spite of this, the high density can be obtained, there will be grain growth, and large quantity of carbides can be accumulated in the grain boundary, which will deteriorate the mechanical performance of 440C stainless steel. The highest tensile strength and hardness of heat-treated specimens sintered at 1,240°C were about 876.3 MPa and 57.7 HRC.

Figure 8 shows that the heat-treated specimens were composed of martensite, retained austenite, and carbides. However, the carbide had become spherical and finely dispersed throughout the grain boundary and the matrix. It will form a continuous grain boundary network when sintered at high temperatures. Continuous grain boundary carbide net-

Fig. 8 Microstructure of specimens sintered at 1,230°C after heat treatment

Fig. 9 Backscattered electron image of stainless samples sintered at different temperatures. **a** 1,210°C. **b** 1,240°C

work is difficult to vanish even after heat treatment; this would have a very deleterious effect on the toughness of material.

3.4 Corrosion resistance

The SEM micrographs in Fig. 9 clearly reveal the large difference in the degree of corrosion between specimens sintered at 1,210°C and at 1,240°C. Pitting was mainly exit in injection molding 440 C stainless steel specimens in NaCl solution. When sintering temperature was higher, the corrosion in the specimens was slighter. The phenomenon depends on the material (with the pore features). The density increased with the increase of sintering temperature. It is obvious that there are fewer pores which are small and spherical due to shrinkage and high sintering temperature. Compared to lower temperature sintering, it was effective to prevent from corrosion by NaCl for less area contacting with the solution.

Precipitation of carbide is one of the reasons for deterioration of 440C stainless steel corrosion resistance after tempering. It was related to lacking of chromium (Cr) if there was precipitation of carbide. Figure 10 illustrates that carbide was to separate out from retained austenite matrix after tempering at 150°C, the areas lacking of Cr were corroded priority, therefore, pitting was formed.

3.5 Effect of carbon content on shape retention

Sintering action was heavily influenced by content and distribution of carbon. The carbon has been found to decrease the liquid temperature and to enhance the sintering kinetics. In the same sintering temperature, the quantity of liquid was influenced by the content of carbon. More carbon means more liquid in the sintering. Furthermore, the dissolved carbon changes the surface tension and viscosity of the steel melt

Fig. 10 Energy spectrum analysis of corrosion in the sample microstructure

Table 2 Carbon and oxygen content of 440C stainless steel in the process and its sintering deformation

	Condition	Content of carbon (%)	Content of oxygen (%)	Situation of deformation
Powder	Sealed	1.1	0.073	
Debinding specimens	Laid in the air	1.07	0.33	–
	Deoxidation in H ₂	1.05	0.092	
	Sealed in the vacuum	1.07	0.086	
	Use in the binding specimens laid in the air	0.86	0.0043	Serious deformation
Sintering specimens	Use the debinding specimens deoxidized in H ₂	1.04	0.0069	No deformation
	Use the debinding specimens sealed in the vacuum	1.06	0.0052	No deformation

significantly. All these affect the instability of stainless steel melt. J. Liu et al. [8] found that a liquid film provides a viscous resistance to grain movement and contributes to the rigidity of the structure during SLPS; the microstructural softening parameter ζ was influenced by quantity of liquid. Therefore, variety of content of carbon will decrease dimensional tolerances; the variety may even lead to sintering deformation by influencing the quantity and viscosity of liquid.

Table 2 showed carbon and oxygen content of 440C stainless steel in each process. The content of carbon of specimens debinding in H₂ atmosphere is slightly lower than that of powder. It was found that the content of carbon and oxygen was both reduced after sintering. It indicated that there was a reaction between C and O in the sintering. Cr₂O₃, which will retard the forming of sintering neck, was produced by reaction of O, and Cr. H. Ohtsubo [9] and Yunxin Wu et al. [10] found that densification of stainless steel was started approximately at 900°C. Meanwhile, between 900°C and 1,100°C, the densification became faster. If the specimens were laid in the air for several days, the content of oxygen increased to 0.33% and deformation happened in sintering. Oxidation-reduction reaction consumed the content of carbon and makes the carbon distribution nonuniform. Therefore, nonuniform distribution of liquid formed in the sintering lead to sintering deformation for nonuniform shrinkage. The sintering deformation can be avoided by deoxidation in H₂ if the product was already oxidation.

4 Conclusions

From the results of the present investigation, the following conclusions can be made. The debinding of injection-molded specimens with wax/oil-based binder using a solvent and thermal debinding method can result in a defect-free specimen. For vacuum sintering of injection molded 440C stainless steel, effective densification took place in the temperature range 1,230–1,240°C. Sintering at too high a temperature will result in a rapid grain growth, slumping, nonuniform densification, pore coalescence, and swelling.

After heat treatment, the microstructure of injection molding 440C stainless steel consisted of martensite, residual austenite, carbide, and specimens sintered at 1,240°C for 30 min have the tensile strength of 876.3 MPa, the hardness of 57.7 HRC. Pitting was mainly exit in injection molding 440C stainless steel specimens in NaCl solution.

The content of carbon has heavily effect ion on the shape retention. Some methods, such as preventing from oxidation, are presented to avoid the as-sintered specimens from deformation.

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References

1. John Sedriks A (1979) Corrosion of stainless steels. Wiley, New York
2. Li MQ, Ji SC (1997) Research of High-carbon stainless steel as pump and valve material I: effect of heat-treatment on material's micro-structure and performance. Journal of Lanzhou University (Natural Sciences) 33(4):53–59
3. Michaeli W, Opfermann K, Kamps T (2007) Int J Adv Manuf Tech 33:206–211
4. German RM (1990) Supersolids liquid phase sintering part I: process review. IJPM 26(1):23–34
5. Newel MA, Davies HA, Messer PF, Greensmith DJ (2005) Metal injection moulding of scissors using hardenable stainless steel powders. Powder Metal 48(3):227–230
6. Li Y, Jiang F, Zhao L, Huang B (2003) Critical thickness in binder removal process for injection molded compacts. Mater Sci Eng A362(1–2):292–299
7. Wohlfromml H (2002) Powder injection molding stainless steel—produce process, performance, application. Powder Metallurgy 12(4):7–15
8. Liu J, Lal A, German RM (1999) Densification and shape retention in supersolidus liquid phase sintering[J]. Acta Mater 47(18):4615–4626
9. Ohtsubo H, Maruta K, Nishimura K, Makiishi Y (1992) Deformation behavior of metal injection molded compacts during sintering [A], Powder injection molding symposium-[C], Princeton: Powder Industries Federation, pp 409–417
10. Wu YX, Blaine D, Marx B, Schlaefel C, German RM (2002) Sintering densification and microstructure evolution of injection molding grade 17-4PH stainless steel powder. Metallurgical and materials transactions A 33A(July):2185–2194