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Sintering of 17-4 PH feedstock for metal injection molding

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Abstract

The sintering behavior of 17-4PH feedstock for metal injection molding was investigated in the temperature range of 650-1050 °C. Effects of sintering conditions, such as sintering temperature and sintering atmosphere, were examined. Results showed that when sintered in the hydrogen/nitrogen atmosphere, the 17-4 PH feedstock was oxidized over the temperature range of investigation. The degree of oxidation increased with the sintering temperature. The main oxidation product was Cr_2O_3 as revealed by X-ray diffraction and composition analysis. The oxidation can be avoided by sintering in vacuum or argon atmosphere.

Keywords: Sintering; Powder technology; 17-4PH; Metal injection molding

1. Introduction

17-4 PH stainless steel is widely used in medical, chemical, automotive, military, aerospace and nuclear industries for various applications that require high strength and good corrosion resistance [1, 2]. The high hardness of the alloy resulting from precipitation hardening, however, makes machining the alloy a challenging task. To overcome the manufacturing difficulties, metal injection molding (MIM) has been considered an alternative for the fabrication of 17-4 PH stainless steel parts [3-5]. As a near-net shape process, MIM combines the shaping advantages of plastic injection molding with the capability of powder metallurgy for processing metal powders. Previous work has shown that MIM can be advantageously applied to the fabrication of 17-4 PH stainless steel parts [6-10].

Sintering is critical for determining the final quality of the parts produced by MIM. Because high sintered density is imperative for good mechanical properties and corrosion resistance, achieving full or near-full density has been a major objective of sintering [11-14]. Therefore, most research on 17-4PH steel sintering to date has focused on the sintering behavior of the molded parts at the high sintering temperatures of 1300-1350°C. Very little attention has been paid to what happens at low temperature. To fully understand the sintering properties of the 17-4 PH steel, the present work examines the sintering behavior of injection molded 17-4 PH feedstock at temperatures below the normal sintering temperature.

2. Experimental procedures

The 17-4 PH feedstock for MIM was provided by Advanced Metalworking Practices Inc. and contained approximately 6 wt.% of binder. The metallic powder in the feedstock was manufactured by a high-pressure gas atomization process and the particles were spherical with an average diameter of 8 μm . The feedstock was compacted in a half-inch diameter die at 190°C. The compacted samples were thermally debound in hydrogen/nitrogen atmosphere with the N_2/H_2 (volume ratio 1:1). The debinding profile was determined by the results of thermogravimetric analysis (TGA) for the feedstock. Then, the samples were sintered at temperatures of 650 – 1050 °C for 3 hrs. At the beginning of the debinding/sintering cycle, the furnace was purged with nitrogen for 30 minutes, followed by continuous flow of protection gas during the entire cycle. The weight change during sintering was determined by measuring the sample weight before and after sintering. The microstructure of the samples was characterized using a Hitachi S-3500 scanning electron microscope (SEM) with an energy dispersive spectrometer (EDS) attachment. The samples were subjected to X-ray diffraction analysis using a Rigaku XRD diffractometer with Cu K_α radiation.

3. Results and discussions

3.1 Effect of sintering temperature

After sintering at 650 °C and 750 °C for 3 hours, there was no apparent bonding between the particles in the samples, suggesting that these temperatures were too low to active densification. Microstructure examination was conducted on samples sintered at higher temperatures only. The optical micrographs of the samples sintered at 850 °C, 950 °C and 1050 °C were shown in Figure 1. As shown in the figure, with the increase of

sintering temperature, the particle boundaries became thicker and darker, indicating that a high sintering temperature resulted in intense reactions on particle boundaries during sintering.

During sintering, the amount of weight gain increased with the sintering temperature up to 1050°C. The weight gain was 1.3% after sintering at 650°C, and increased to 3.1%, 4.7%, 5.4%, and 5.6% corresponding to a sintering temperature of 750°C, 850°C, 950°C and 1050°C, respectively. It was expected that during the heating process, the residual binder would continue to decompose and hence led to a decrease in weight. The weight gain during sintering with increase in temperature implied that some reactions besides the decomposition of the residual binder had occurred during sintering.

Figure 1. Optical micrographs for the samples sintered in the N_2/H_2 atmosphere at: a) 850°C, b) 950°C, and c) 1050°C

3.2 Effect of sintering atmosphere

To understand whether the reactions are related to the sintering atmosphere, the debound specimens were also sintered at 1050 °C in vacuum and argon atmosphere. The SEM micrographs of the samples sintered in at 1050 °C in different atmospheres are shown in Figure 2. After sintering in the vacuum or argon, the particles in the samples became interconnected, signifying that the densification was beyond the necking and entered the intermediate stage (Figure 2a and 2b). In contrast, the sample sintered in the N_2/H_2 atmosphere showed clear contours of the original spherical particles (Figure 2c), suggesting no inter-particle growth. In addition, the particle boundaries were filled with grayish substances. After sintered in the argon atmosphere and vacuum, the weight of the samples decreased 0.4% and 0.6%, respectively, due to the

Figure 2 SEM micrographs for the samples sintered at 1050 °C in different atmosphere

a) vacuum, b) argon, and c) N₂/H₂ atmosphere

removal of the residual binder. The results confirmed that the weight gain for the samples sintered in the N₂/H₂ atmosphere was indeed a result of the interactions of the steel particles with the sintering atmosphere.

X-ray diffraction patterns for the feedstock, the debound sample and the sample sintered at 1050 °C in N₂/H₂ are shown as Figure 3. The patterns for the feedstock and the debound samples were essentially the same, only elemental Fe, Cr, Ni and Cu peaks detected. After sintering in the N₂/H₂ atmosphere, a new phase, Cr₂O₃, appeared in the pattern with strong intensity, affirming that significant amount of Cr₂O₃ had formed during sintering in the N₂/H₂ atmosphere.

Figure 4 shows the EDS line scanning spectra across particles for the samples sintered at 1050 °C. When sintered in vacuum or argon, only Fe, Cr, Ni and Cu were detected in the samples. The elements distributed evenly along the line, without apparent difference between the interior and the boundary of the particles (Figure 4a and 4b). However, the sample sintered in the N₂/H₂ atmosphere contained oxygen in addition to Fe, Cr, Ni and Cu. Furthermore, the distribution of elements varied significantly from the interior of the particles to the boundary. Oxygen and Cr enriched at the particle boundary with a sharp decrease of Fe concentration (as shown in Figure 4c), revealing that the particle boundary was occupied predominantly by chromium oxide. These results are consistent with the XRD pattern for the sample sintered in the N₂/H₂ atmosphere. It can be concluded that the weight gain in the samples sintered in the N₂/H₂ atmosphere was due to the formation of Cr₂O₃ on the surface of the particle. Higher sintering temperature improved the formation kinetics, and hence increased the total amount of the Cr₂O₃ formed in the samples. The formation

Figure 3. X-ray diffraction patterns for the samples at different stages

(▼ - Cr_2O_3 ▲ - Fe, Cr, Ni, ► - Cu ■ - Fe, Cr, * - Cr-O)

Figure 4 EDS spectra for samples sintered at 1050 °C in: a) vacuum, b) argon, c) N_2/H_2

of Cr_2O_3 on the particle surface provides a barrier to atomic diffusion between particles and therefore inhibits the densification process. To achieve a high final sintering density, oxidation during sintering should be completely avoided. Argon atmosphere or vacuum sintering is a preferred choice.

3.3 Factors effecting oxidization

Samples made from pure 17-4 PH powders were sintered at 1050°C in the N_2/H_2 atmosphere as well. The average weight gain was lower than those made from MIM feedstock. Considering the fact that no oxidation occurred for the MIM feedstock samples when sintering in vacuum or argon atmosphere, the increased oxidization of the feedstock could not be attributed to any chemical reaction between the binder and the metal. It is believed that the increased oxidization was caused by the difference in the exposed surface areas resulted from the binder addition. When compacted, the metal particles without the binder directly contact with neighboring particles. Local plastic deformation further improves the contact areas between the particles, hence reduces the “free” exposed surface areas in the compact. In contrast, the metal particles in the compact made of the MIM feedstock are separated by the organic binder. After debinding, the metal particles come into contact with each other, mostly in point contact, leaving essentially all the surfaces of the particles exposed to the environment. Since the oxidization occurs at the surface where oxygen comes into contact with the metallic atoms, such an increase of exposed surface areas will lead to increased oxidization.

It should be pointed out that no weight gains or oxide formation was observed when pure iron was sintered in the N_2/H_2 atmosphere under similar conditions. Also, there was no iron oxide identified in the sintered 17-4 PH samples in which Cr_2O_3 existed. This was due to the different affinities of Fe and Cr with oxygen, as reflected by the free energy of the formation and reduction of the corresponding oxides. According to reference [15], Cr will be oxidized before iron because the free energy to form chromium oxide is much lower than that to form iron oxide. Furthermore, the positive free energy to reduce Cr_2O_3 by hydrogen in the entire temperature range of sintering (up to 1050 °C) indicates that Cr_2O_3 , once formed, can not be reduced by hydrogen. However, the free energy to reduce Fe_2O_3 turns to negative at above 570°C, proposing that the iron oxide can be reduced when the temperature is over 570°C. Therefore, no iron oxide was detected by the XRD after sintering in hydrogen contented atmosphere.

Summary

The sintering behavior of 17-4 PH injection molding feedstock in the temperature range of 650-1050 °C has been investigated. The findings can be summarized as follows:

- Sintering of the 17-4 PH feedstock in the N_2/H_2 atmosphere resulted in the oxidization of chromium to form Cr_2O_3 , leading to weight gains in the sintered samples, most likely due to the existence of residual oxygen in the atmosphere after purging with nitrogen.
- The oxidization progressed with increasing in sintering temperature, as exemplified by the increased weight gains at higher temperatures, mainly due to the increased reaction kinetics.
- The oxidization hinders the densification of the compact and is undesirable.
- To avoid the oxidation of 17-4 PH stainless steel during sintering, vacuum or inert atmosphere should be used.

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