Sintering of a boron-doped injection moulded 17-4PH stanless steel

H. Ö. GÜLSOY*, S. SALMAN
Material Department, Technical Education Faculty, Marmara University, Göztepe, Istanbul, 81040, Turkey
E-mail: ogulsoy@marmara.edu.tr

S. ÖZBEK
Tubitak-MRC, Materials and Chemical Technologies Research Institute, Kocaeli, 41470, Turkey

F. FINDIK
Material Department, Technical Education Faculty, Sakarya University, Sakarya, 54187, Turkey

Powder injection molding (PIM) is an attractive process to produce complex, near-net shaped components. The process overcomes the shape limitation of traditional powder compaction, the cost of machining, the productivity limits of isostatic pressing and slip casting, and the defect and tolerance limitations of conventional casting. Over 50% of the injection molded and sintered components are made from stainless steel composition [1–3]. The alloy 17-4 PH stainless steel powders—a precipitation-hardening martensitic stainless steel, shaped and processed via injection molding can achieve high complexity of part geometrical with mechanical and corrosion properties, similar or superior to wrought material. Due to its high strength and good corrosion resistance 17-4 PH has widespread applications, especially in medical, automotive, military, and aerospace instruments [4–6].

Earlier investigations on PM or PIM 17-4 PH focused on the effect of powder characteristics, sintering atmosphere, sintering temperature, sintering time, heat treatment, residual carbon content on microstructure, corresponding microstructural characterization, mechanical and corrosion properties [4–6]. In several investigations boron as a sintering additive has been used to achieve higher sintered density in stainless steels at lower sintering temperatures [7–9]. As a consequence, a noticeable improvement in the mechanical properties is obtained. Boron can be added either in its elemental form (both amorphous and crystalline) or as a compound (for example, Fe_2B, BN, NiB, and CrB). A small particle size of the additive is desirable to obtain a uniform dispersion. Boron additions increase hardenability in steels, increase strength (via increase in sintered density), improve grain boundary cohesive strength, enhance corrosion resistance, and improve ductility [7, 9].

The aim of this study is to investigate the effect of added boron on the sintering behavior and final properties of powder injection molded 17-4 PH stainless steel. In this research, gas atomized 17-4 PH stainless steel powders (Fe-16.2Cr-4.6Ni-4.6Cu-0.54Mn-0.30Nb-0.30Si-0.095Mo-0.038C-0.026P-0.002S) provided by Osprey Metals Ltd. were used. It has particle size distribution of $D_{10} = 3.25\ \mu$m, $D_{50} = 10.65\ \mu$m, $D_{90} = 28.42\ \mu$m. The boron additive powder used was elemental boron (>99.5 pure) provided by SB Boron Corp. It has particle size distribution of $D_{10} = 0.20\,\mu$m, $D_{50} = 0.50\,\mu$m, $D_{90} = 3.64\,\mu$m. The amount of additive was adjusted to give 0.25 and 0.5 wt.% boron in starting mixture. Mixing of various combinations of 17-4 PH plus boron powder was carried out in a Turbula mixer. The powders were mixed with a wax-polypropylene-based binder system and injection molded to produce tensile test specimens (MPIF 50) [11]. Debinding was conducted in a thermal operation. Different thermal debinding steps were carried out in hydrogen atmosphere. The debinding details are given in Ref. [10]. The green density of the molded specimens was 5.2 g/cm^3. Sintering of all specimens was performed within a Vacuum Industries furnace due in part to the high temperatures necessary for the stainless steel and also the furnace size. The specimens were sintered by heating to 1100 °C at a rate of 10 °C/min and holding at 1100 °C for 5 min, then heating to 1220 °C, 1230 °C, 1240 °C, and 1250 °C at a rate of 5 °C/min and holding at each temperature for 10, 20, 30, and 45 min. The pure 17-4 PH stainless steel specimens were sintered at 1350 °C for 1 h. The densities were determined by Archimedes water immersion method. The samples were plane polished to expose the internal microstructure of the sintered material. Etching was performed with a Kalling's reagent, composed of 2 g $CuCl_2$, 40 mL HCl, 60 mL ethanol, and 40 mL H_2O, for optical metallography. The specimens were subjected to heat treatment. The heat treatment details are given in Ref. [10]. Hardness and tensile testing were performed with each specimen. All tensile tests were performed using Zwick 2010 and Losenhausen mechanical tester at constant crosshead speed of 1 mm/min (25 mm gauge length). The hardness tests were performed using an Instron-Wolpert Dia Testor 7551 at HRC scale. Measurements were carried out at the grain center and averages of five values were reported. Sintered and heat treated sample fracture surface, were analyzed under scanning electron microscope.

The pure 17-4 PH stainless steel specimens were sintered at 1350 °C for 1 h; a maximum sintered density

*Author to whom all correspondence should be addressed.

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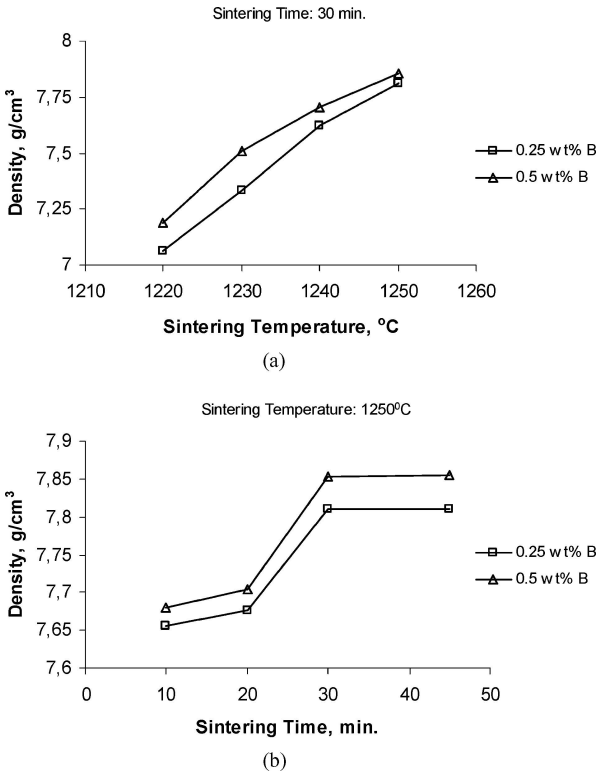

Figure 1 Effect of boron addition, sintering temperature, and sintering time on the sintered density (a) sintering temperature, (b) sintering time.

of only 7.4 g/cm^3 was achieved. The effect of boron additives, sintering time and temperature on the sintered density is shown in Fig. 1. The pure 17-4 PH stainless steel specimens were sintered at 1250 °C for 45 min; a maximum sintered density of only 6.9 g/cm^3 was achieved. At higher boron levels such as 0.5 wt% sintered density increases. Near full density, 7.85 g/cm^3, was obtained with a boron addition of 0.5 wt% at 1250 °C for 45 min.

Fig. 1a shows that, all samples attained a maximum sintered density of 7.06–7.19 g/cm^3 after sintering for 30 min at a sintering temperature of 1220 °C. When samples were sintered at 1250 °C, sintered density increases. Liquid phase occurred at 1175– 1220 °C. The liquid phase attack particle contact and pore regions with capillary forces. When samples added with 0.5 wt% boron were sintered at a temperature of 1250 °C, a maximum sintered density of 7.85 g/cm^3 was achieved. Clearly, sintering density increased with the sintering temperature such as 1200–1250 °C and boron addition. Amount of liquid phase increased with sintering temperature and boron addition.

The results of the effect of sintering time on boron addition 17-4 PH stainless steel are shown in Fig. 1b. From Fig. 1b it can be seen that at a sintering temperature of 1250 °C, the samples containing 0.5 wt% boron attained a maximum sintered density of 7.85 g/cm^3 after sintering for 30 min; however, higher sintering time improved sintered density noticeably. The sintering time higher than 45 min resulted in slumping at some samples that are not considered in here. The sample containing 0.5 wt% boron shows minimum sintered density of 7.68 g/cm^3 after sintering for 10 min. The sintering time and boron addition increases sintered density.

Fig. 2 shows the microstructure of the samples with and without boron. Fig. 2a shows microstructure of additive free samples sintered at 1350 °C, 1 h. This microstructure exhibits δ-ferrite, sintered particles, and

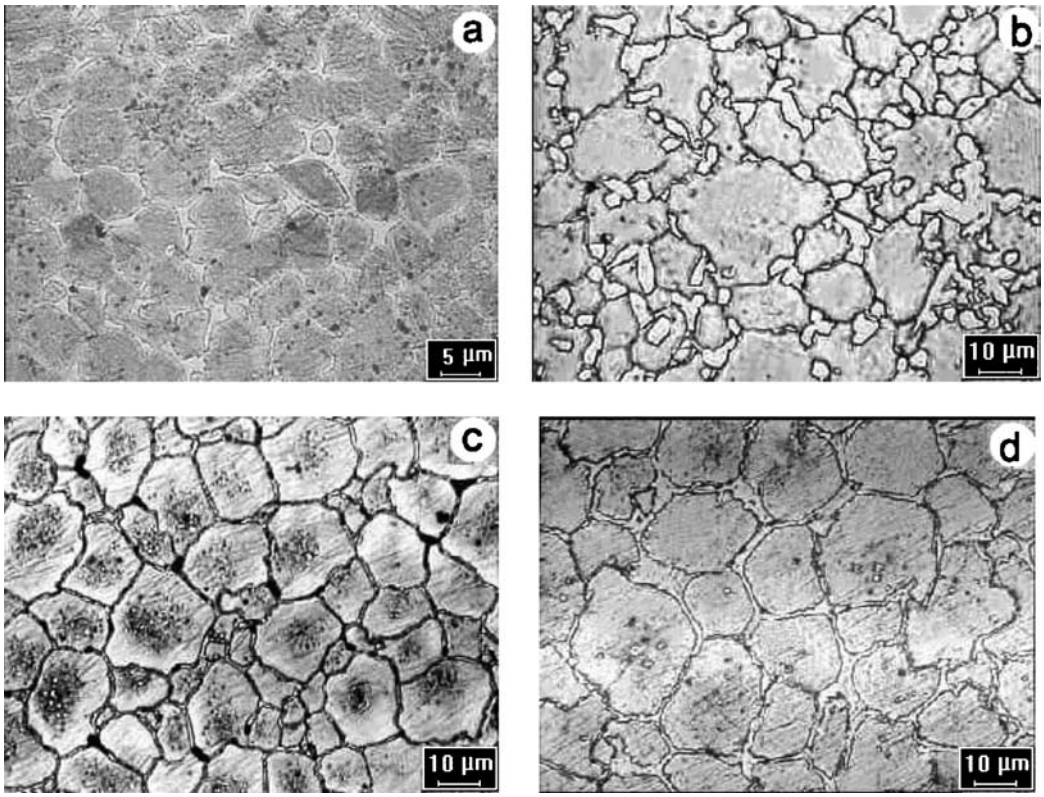

Figure 2 Microstructures of the samples with and without boron (a) 1350 °C for 60 min non-boron (b) 1250 °C for 10 min 0.5 wt% B (c) 1220 °C for 30 min 0.5 wt% B (d) 1250 °C for 30 min 0.5 wt% B.

TABLE I Ultimate tensile strength and hardness of various sintered 17-4 PH stainless steel samples as function of boron additives (HT: Heat Treatment)

Sample	Process condition	Ultimate tensile strength (MPa)	Hardness (HRC)
17-4 PH	1350 °C, 60 min	802	25
17-4 PH	1350 °C, 60 min and HT	976	34
17-4 PH + 0.5 wt% B	1250 °C, 30 min	1283	37.5
17-4 PH + 0.5 wt% B	1250 °C, 30 min, and HT	1520	55.1

pores in the particles [5, 6]. Fig. 2b–d shows the microstructures of the 0.5 wt% boron addition stainless steel samples. With 0.5 wt% boron addition, enough eutectic liquid exists to provide nearly full densification. The 0.5 wt% alloy exhibits enough eutectic phases at the grain boundaries. The liquid phase contained different borides not wetting particle contact areas at 1250 °C for 10 min 0.5 wt% boron. Liquid phase occurred at 1220 °C for 30 min 0.5 wt% boron but not enough. Liquid phase was wetting particle contact area at 1250 °C for 30 min 0.5 wt% boron and enhanced microstructure. The most remarkable liquid phase sintering process is rearrangement owing to capillary forces exerted by a wetting liquid. Liquid forms at the particle contacts and penetrates grain boundaries within particles. Liquid forms on the grain boundaries softening the particles to allow densification in response to the capillary forces at the particle contacts.

The heat treated and non–heat treated samples produced in this study were both capable of increasing hardness, as compared with 17-4 PH stainless steel without boron addition. The results of hardness measurements exhibited an increasing trend. The highest hardness was obtained with the highest sintered density attained. The maximum hardness of 34 HRC was reached with heat-treated 17-4 PH stainless steel without boron addition. The maximum hardness of 55.1 HRC was reached with 0.5 wt% boron addition and heat treatment. Eutectic liquid phase containing different borides in particle contact areas and martensite that was formed by heat treatment showed increased hardness.

The mechanical properties of the samples that were processed under different conditions are shown in Table I. The maximum ultimate tensile strength of 976 MPa was reached with pure 17-4 PH with heat treatment samples. The maximum ultimate tensile strength of 1520 MPa was reached with 0.5 wt% boron addition heat treated samples. Ultimate tensile strength increases with the additions of boron. The hardness measurement results exhibited a trend similar to that seen with the tensile strength. The increase in hardness is a result of the higher sintered density. The maximum hardness of 34 HRC was reached with pure 17-4 PH with heat treated samples. The maximum hardness of 55.1 HRC was reached with 0.5 wt% boron addition heat treated samples.

The morphologies of fracture surface of the additive free 17-4 PH stainless steel after sintering at 1350 °C for 60 min is shown in Fig. 3a. It can be seen that samples exhibit dimpled rupture and porosities δ-ferrite, which occurred during the sintering. The morphologies of surface of 0.5 wt% boron added samples are

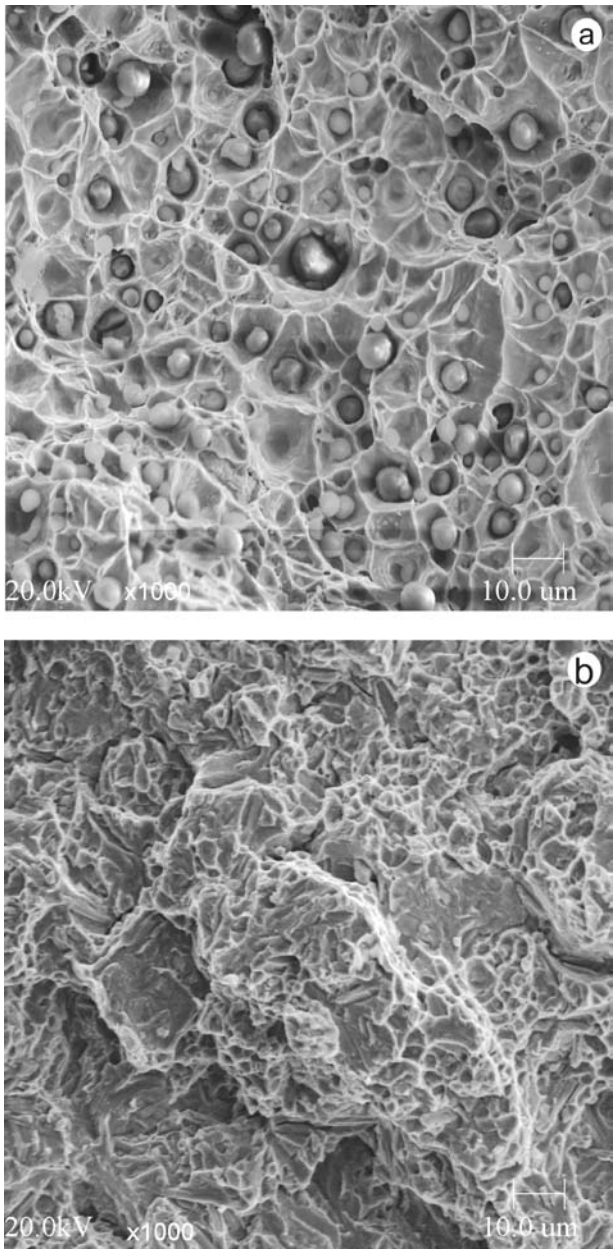

Figure 3 Fractographs of samples with and without boron addition with heat treatment (a) 1350 °C for 60 min non-boron (b) 1250 °C for 30 min 0.5 wt% boron.

shown in Fig. 3b and this sample also exhibited a brittle fracture. In this case the brittle fracture occurred through the eutectic network. The eutectic network improved sintered density and mechanical properties and decreased porosity.

In conclusion, our experiment results show that the addition of boron for developing the high strength 17-4 PH stainless steel resulted in improved properties.

Boron additions decreased traditional sintering time and sintering temperature. Sintering to full density is only possible with the addition of 0.5 wt% boron at 1250 °C for 30 min. The 0.5 wt% boron addition increased sintered density, ultimate tensile strength, and hardness.

Acknowledgements

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