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Effect of FeB additions on sintering characteristics of injection moulded 17-4PH stainless steel powder

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High density sintering of precipitation hardening stainless steel such as 17-4 PH involves a combination of relatively high temperature (>1350°C) and extended sintering time. In this study, the effect of addition of FeB on sintering characteristics of 17-4 PH stainless steel was investigated. Addition of boron is promoted to get highly dense sintered steels. The amount of boron plays a role in determining the sintered microstructure and properties. With the increased amount of FeB sintered density and tensile strength increase while sintering time and temperature decrease.

1. Introduction

The alloy 17-4 PH is a precipitation-hardenable martensitic stainless steel. Due to its high strength and good corrosion resistance 17-4 PH has widespread applications, especially in medical, automotive, military and aerospace instruments. Many 17-4 PH components can be manufactured cost-effectively by powder injection molding, a net-shape forming process with an advantage of shape complexity, material utilization and high final density. This alloy is, however, hard to be machined. Therefore, it has been attempted to apply a near net shape production technique such as metal PIM to this useful material [1–4].

The PIM process consists of four steps; (1) preparation of feedstock by mixing alloy powder with different binders such as base polymeric and wax binder; (2) injection of feedstock into a mold to make an oversized preform; (3) thermal or solvent debinding to remove the majority of the binder; and (4) sintering in a controlled atmosphere to density the metal powder. If it is necessary, secondary operations such as heat and surface treatments after sintering can be performed. 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 [5, 6].

Several investigations have used boron as a sintering additive to achieve sintered density in stainless steels at lover sintering temperatures. High density is imperative for improved corrosion resistance and mechanical properties in all PM parts. Residual pores in sintered stainless steel decrease mechanical properties and corrosion resistance [7]. Madan and German observed that additions of boron as FeB and Fe_2B to iron resulted in greater densification as compared to crystalline or amorphous boron [8]. Toennes and German showed that full density and a noticeable improvement in the mechanical properties were obtained by the addition of 200 ppm of boron to martensitic stainless steel [9]. Tandon and German investigated the addition of boron to 316 L powder as elemental boron, FeB, CrB_2 and NiB. Their study showed that the addition of 0.5 and 1 wt% elemental boron powder to 316L stainless steel powders increased theoretical density, mechanical properties and corrosion resistance [7]. Lal *et al.* investigated the effect of boron additions on melting, densification, and distortion of stainless steel. They observed that boron doped 316 L stainless steel powder had a considerably lower sintering temperature [10]. Kamada *et al.* investigated the addition of FeB to SUS630 stainless steel. The SUS630 stainless steel is same 17-4 PH stainless steel as chemical composition. Their study showed that addition of 0.20 wt% FeB powder to SUS630 stainless steel powders improved theoretical density and mechanical properties. As a consequence, a noticeable improvement in the mechanical properties is obtained [11]. An analogous effect on corrosion resistance can be expected, since porosity is the parameter mainly responsible for poor corrosion performance in comparison with the corresponding wrought material.

Earlier investigations on PM or PIM 17-4 PH focused on the effect of powder characteristics, sintering atmosphere, sintering temperature, sintering time, and heat treatment, and residual carbon content on microstructure, and corresponding mechanical and corrosion properties. Fox *et al.* [12], Zhang *et al.* [2], Sanderow *et al.* [13], Sung *et al.* [14] and Kubish *et al.*

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TABLE I Chemical composition of 17-4 PH stainless steel powder

Composition in weight percent (wt%)										
Fe	Cr	Ni	Cu	Mn	Nb	Si	Mo	C	P	S
Bal.	16.2	4.6	4.6	0.54	0.30	0.30	0.095	0.038	0.026	0.002

TABLE II Debinding schedule

Ramp (°C /min)	Temp. (°C)	Hold time (min)
0.633	190	120
0.4	290	90
1	390	150
0.86	520	150
2.75	950	60

[1] investigated the effect of different powder, gas and water atomized powder blends, sintering temperature, sintering atmosphere and heat treatment conditions on mechanical properties.

2. Experimental procedures

The 17-4 PH stainless steel powders used in this study were produced by high-pressure gas atomization method, provided by Osprey Metals Ldt. with a tap density 4.25 g/cm^3 and a pycnometer density of 7.50 gc/m^3. The particle size distribution of this powder is $D_{10} = 3.25$ μm, $D_{50} = 10.65$ μm, $D_{90} = 28.42$ μm. The chemical composition of the powder is given in Table I. Fig. 1 shows a scanning electron micrograph of 17-4 PH stainless steel powder. The particle size distribution of FeB powder is $D_{10} = 4.91$ μm, $D_{50} = 11.18$ μm, $D_{90} = 26.88$ μm. The amount of additive was adjusted to give 0.25, 0.5, 0.75 and 1 wt% FeB in starting mixture. Mixing of various combinations of 17-4 PH and plus boron powder was carried out in a Turbula mixer, for eight hours.

The binder used consisted of 69 wt% paraffin wax, 20 wt% polypropylene, 10 wt% carnauba wax, and 1 wt% stearic acid. Feedstock was prepared at 175°C with binder melted first and then powder blend added incrementally. The powder loading in this mixture was 62.5 vol%. After cooling, the feedstock was pelletised by hand. These feedstocks were injected using a 12.5 MPa special injection molding machine and tensile specimen (MPIF 50) mould [15]. The melt temperature was 175°C, the mould was 35°C and cycle time was about 20 s. The green density of the molded specimens was 5.2 g/cm^3.

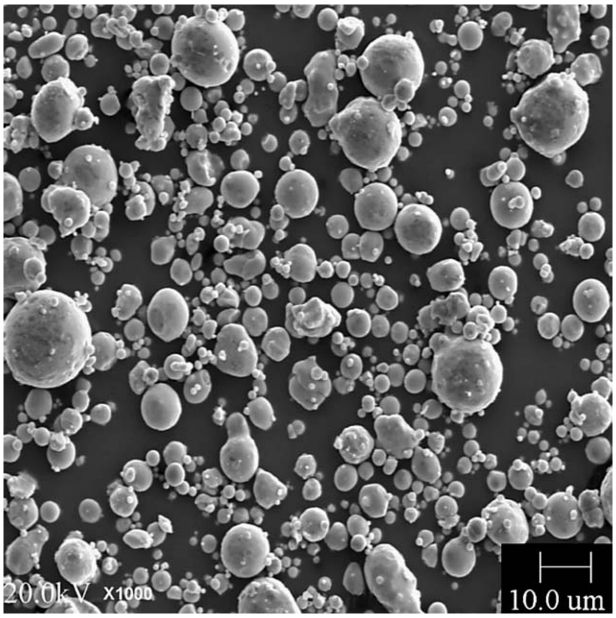


Figure 1 Scanning electron micrograph of 17-4 PH stainless steel powder.

The specimens molded using the multicomponent binder were all thermally debinding in a special furnace using a 100% H_2 to reduce part oxidation. All specimens were placed into boats containing fine alumina powder for wicking purposed and temperature/time relationship are as shown Table II. All specimens of the 17-4 PH and additive alloys required this additional temperature to impart sufficient green strength to survive removal from the alumina intact. No distortion or other visible reduction in part quality or surface finish was observed.

The effect of sintering additives on the solidus and liquid temperature of the alloy were determined by using differential thermal analysis (DTA) (Setaram/TGDTA92). The experiments were performed at a constant heating rate of 20°C/min under an argon atmosphere. 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 specimen were sintered with heating 1100°C at a rate 10°C/min and holding at 1100°C for 5 min, then heating to 1265, 1275 and 1285°C at a rate 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 of the sintered specimens were measured by means of the water-immersion method. The center of gauge section of sintered specimens was cut from tensile bars in each sintering specimens. After, these samples was mounted, ground, and polished using standard metallographic procedures. A Kalling's reagent, composed of 2 g $CuCl_2$, 40 mL HCl, 60 mL ethanol, and 40 mL H_2O, was used to etch the samples for optical metallography. The specimens were performed heat treatment. The heat treatment consisted of a solution treatment in argon for 1 h at 1050°C, followed by a water quench and aging treatment in argon for 4 h at 480°C with an air cool. Hardness and tensile testing were performed each specimens. Measurements were carried out at the grain center and average of three values were reported.

3. Results and discussion

Fig. 2 shows the DTA plot for the debinding samples of 17-4 PH with 0.25 wt% FeB additions. The 0.25 wt% FeB additive samples show endothermic peaks indicating liquid formation at 1236°C. There are similar results on different powders in literature. The behavior is Fig. 2 is similar to that presented on a similar boron treated austenitic stainless steel by Bolton *et al.* [16], Tandon

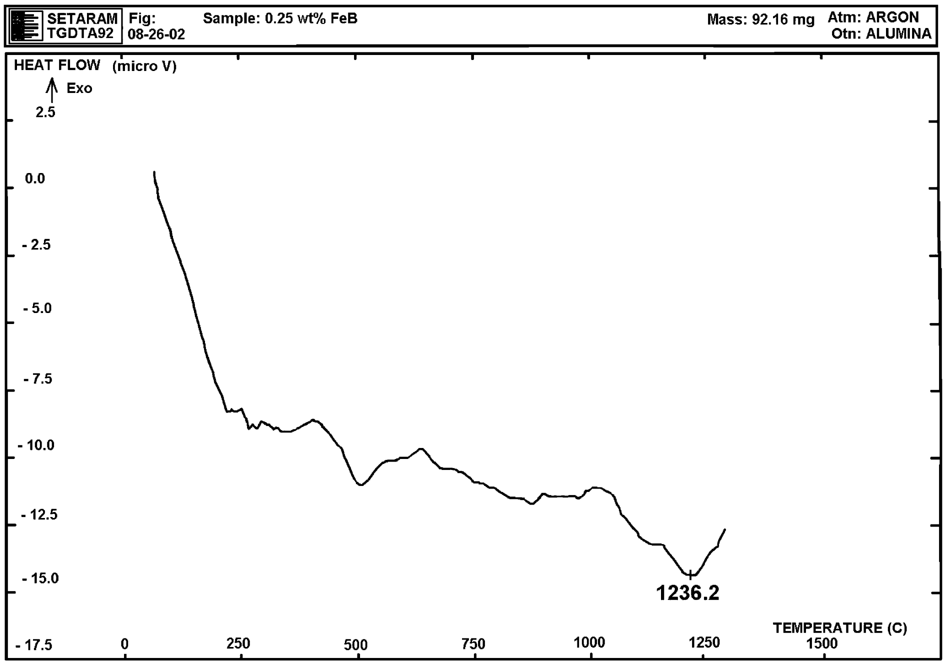


Figure 2 DTA curves showing melting characteristics for 17-4 PH stainless steel with 0.25 wt% FeB additions.

et al. [7], Bakan *et al.* [17], Lal *et al.* [10]. Tandon and German observed that addition of boron in the amount of 0.5 and 1 wt% to 316 L stainless steel powders having an average particle size of 79 μm showed liquid formation temperature at 1226°C. Lal *et al.* observed that addition of boron in the amount of 0.5 and 1 wt% to 316 L stainless steel powders having an average particle size of 53 μm showed liquid formation temperature at 1225 and 1212°C, respectively. Thermodynamics shows that boron forms a eutectic liquid with Fe at 1175°C. The increase in the eutectic temperature for 17-4 PH is attributed to the presence of substitutional elements like Cr.

The pure 17-4 PH stainless steel specimens were sintered at 1350°C for 1 h; a maximum sintered density of only 7.4 g/cm^3 was achieved. The effect of FeB additives on the sintered density is shown in Fig. 3. The pure 17-4 PH stainless steel specimens were sintered at 1285°C for 45 min; a maximum sintered density of only 6.9 g/cm^3 was achieved. FeB additions less than 0.25 wt% to the 17-4 PH stainless steel did not have a significant effect on densification because the value fraction of eutectic liquid was too small to induce densification. At high FeB levels, sintered density increases. Near full density is attainable with a FeB addition of 1 wt%. Maximum sintered density is 7.891 g/cm^3 at 1 wt% FeB addition.

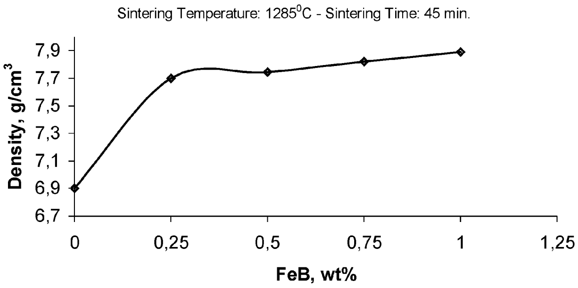


Figure 3 Effect of FeB additive on the sintered density.

Boron activates the sintering process of the iron powders by the formation of the liquid phase, produced by the eutectic reaction, $Fe_2B + Fe \rightarrow$ liquid, which occurs at 1161–1175°C. The liquid phase has a very low solubility in iron and remains as an almost continuous network between solid grains, favoring the classical phenomenon of the liquid phase sintering. If the amount of boron and the sintering temperature are correctly chosen, near full density may be obtained. A number of investigations showed that boron tends to segregate to grain boundaries and surfaces. This means that a certain content of boron is necessary to form a layer at the particle contact areas or the grain boundaries that provides a path of high diffusivity and therefore allows rapid densification. With increasing boron content, the number of the pores is reduced; the pore shape is smoothed from irregular to spherical. This indicated that a layer of high diffusivity is formed at the grain boundaries resulting in fast densification and in pore-grain boundary separation as soon as the reduced number and size of pores can no longer pin the grain boundaries [18, 19].

The effect of sintering temperature and sintering time on the sintered density of FeB addition 17-4 PH stainless steel is shown in Figs 4 and 5, respectively. Fig. 4 shows that at a sintering temperature of 1265°C, the samples containing 1 wt% FeB attained a maximum sintered density of 7.495 g/cm^3 after sintering for 45 min. The 1 wt% FeB addition samples could also be sintered at temperature of 1285°C for a maximum sintered density of 7.891 g/cm^3. The samples containing 0.5 wt% FeB attained a maximum sintered density of 7.743 g/cm^3 after sintering for 1285°C and 45 min. The sintering temperature and FeB addition increases with sintering density.

The effect of sintering time on FeB addition 17-4 PH stainless steel is shown in Fig. 5. From Fig. 5 it can be seen that at sintering temperature of 1285°C, the samples containing 1 wt% FeB attained a maximum sintered density of 7.891 g/cm^3 after sintering for

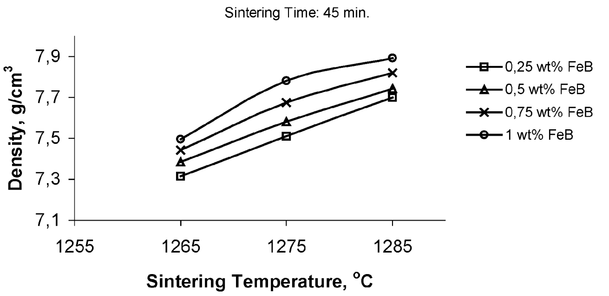


Figure 4 Effect of sintering temperature on the sintered density.

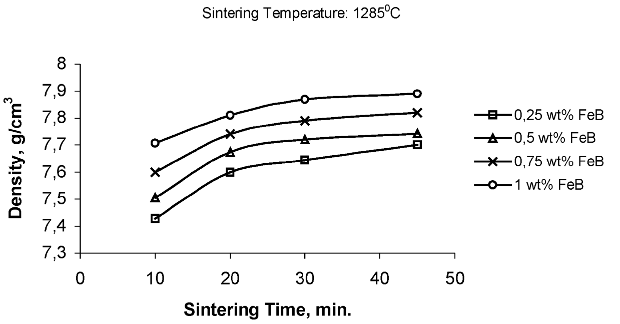
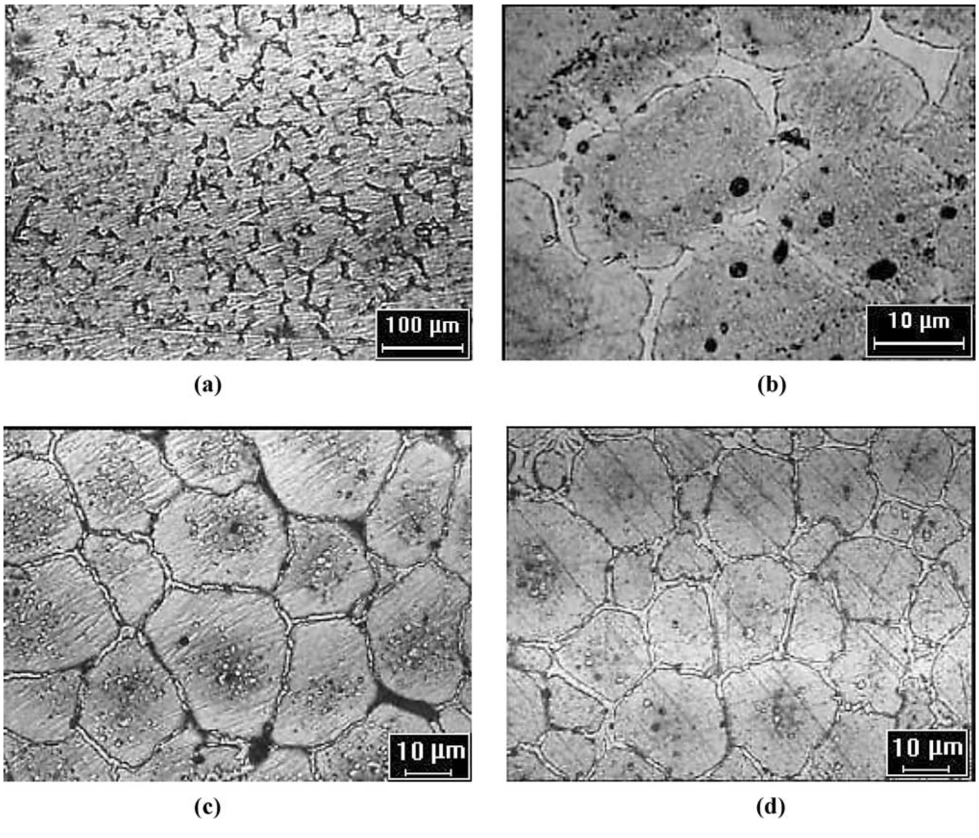


Figure 5 Effect of sintering time on the sintered density.

45 min. The sample containing 1 wt% FeB shows minimum sintered density 7.708 g/cm^3 after sintering for 10 min. The sintering time and FeB addition increases sintered density.

Fig. 6 shows the microstructures of the samples with and without FeB. The additive free samples exhibit the porosity characteristic of medium density sintered steel as shown Fig. 6a. Fig. 6b shows microstructure of additive free samples is sintered at 1350°C, 1 h. This microstructure exhibits δ-ferrite, sintered particles and pores in the particles [3, 4]. Fig. 6c and d show the microstructures of the 0.5 and 1 wt% FeB addition stainless steel samples. With 0.5 and 1 wt% FeB addition, enough eutectic liquid exists to provide nearly full densification. 1 wt% alloy exhibits enough eutectic phase at the grain boundaries. The most remarkable liquid phase sintering process is rearrangement owing to capillary forces exerted by a wetting liquid. Rearrangement is often composed of two stages. Primary rearrangement involves the individual particles. The random packing of mixed powders and the uneven distribution of the liquid produce unbalanced capillary forces between contacts and cause sintering densification. A spherical shape and the smaller particle size are beneficial to rearrangement. Small particles have higher capillary stress, by which the particles are pulled together, resulting in rapid shrinkage. Secondary rearrangement occurs inside particles, involving particle disintegration into fragments and subsequent repacking of those fragments. Liquid forms at the particle contacts and penetrates grain boundaries within particles. Liquid forms on the grain boundaries soften the particles to allow densification in response to the capillary forces at the particle contacts.

The mechanical properties of the samples that were processed under different conditions are shown in Table III. Graphs of the strength and hardness results were shown in Figs 7 and 8. Both the heat treatment and



(a) (b)

(c) (d)

Figure 6 Microstructures of the samples with and without boron: (a) 1265°C for 45 min non-boron, (b) 1350°C for 60 min non-boron, (c) 1285°C for 45 min 0.5 wt% FeB and (d) 1285°C for 45 min 1 wt% FeB.

TABLE III Mechanical properties of various sintered 17-4 PH stainless steel samples as function of sintering additives (HT: Heat Treatment)

Sample	Process condition	Density (g/cm^3)	Ultimate tensile strength (MPa)	Hardness (HRC)
Pure 17-4 PH	1350°C, 60 min	7.4	976 (HT)	34 (HT)
17-4 PH + 0.25 wt% FeB	1285°C, 45 min	7.7	988	28.7
17-4 PH + 0.5 wt% FeB	1285°C, 45 min	7.743	1022	30.9
17-4 PH + 0.75 wt% FeB	1285°C, 45 min	7.82	1044	32.8
17-4 PH + 1 wt% FeB	1285°C, 45 min	7.891	1070 (1318 HT)	34 (50,2 HT)

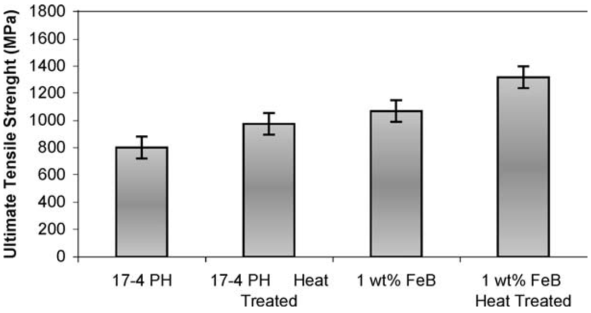


Figure 7 Comparison of tensile strength with and without FeB addition (HT: Heat Treatment).

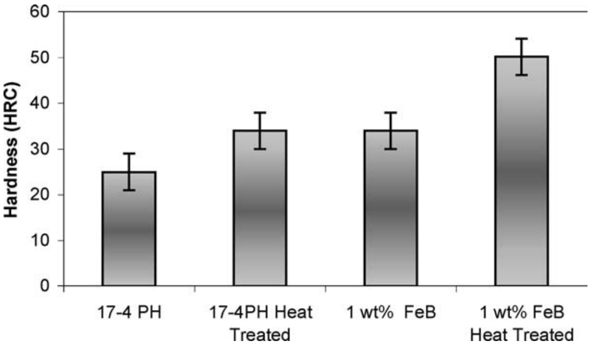
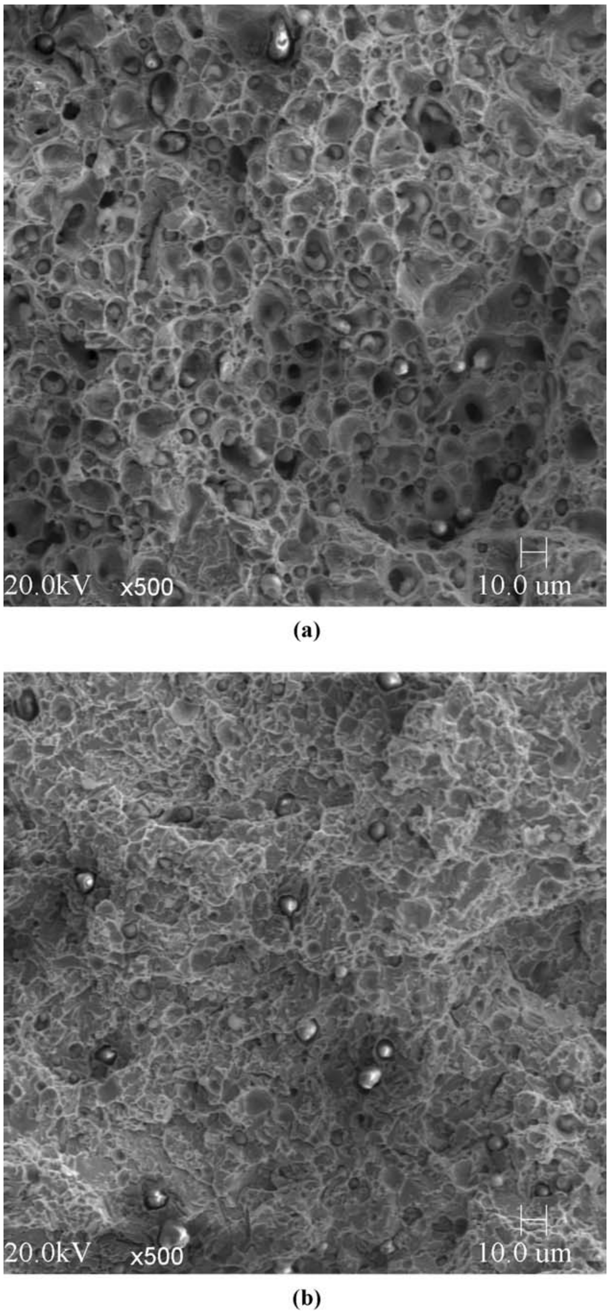


Figure 8 Comparison of hardness with and without FeB addition (HT: Heat Treatment).

no heat treatment are capable of increasing the ultimate tensile strength, as compared with pure 17-4 PH stainless steel. 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 1318 MPa was reached with 1 wt% FeB addition heat treated samples. Ultimate tensile strength increases with the additions of FeB. The hardness measurements 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 50.2 HRC was reached with 1-wt% FeB addition heat treated samples. Hardness increases with the addition of FeB.



(a)

(b)

Figure 9 Fractographs of samples with and without FeB addition with heat treatment: (a) 1350°C for 60 min non-FeB and (b) 1285°C for 45 min 1 wt% FeB.

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. 9a. It can be seen that sample exhibit dimpled rupture and pore. δ-ferrite, which occurred during the sintering, decreases the amount of porosity. Elongation is increased with the decreasing amount of porosity. Morphologies of fracture surface exhibit ductile fracture with the increasing amount of δ-ferrite. The morphologies of surface of 1 wt% FeB addition samples are shown in Fig. 9b. It can be seen that sample exhibits brittle fracture. Here brittle fracture occurs through the eutectic network. The eutectic network improved sintered density, decreased porosity and increased tensile strength.

4. Conclusions

The addition of FeB for developing the high strength 17-4 PH stainless steel was investigated. 1 wt% FeB addition decreased traditional sintering time and sintering temperature. Sintering to full density is only possible with the addition of 1 wt% FeB at 1285°C for 45 min 1 wt% FeB addition increased sintered density, tensile strength and hardness. Tensile strength is 1318 MPa and hardness is 50.2 HRC with 1 wt% FeB and heat treatment. Comparison of traditional 17-4 PH and FeB addition 17-4 PH parts according to tensile strength and hardness, tensile strength and hardness were increased 35%, 47%, respectively.

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