

Microstructures and mechanical properties of injection molded 17-4PH stainless steel powder with nickel boride additions

H. Ö. GÜLSOY*, S. SALMAN

Marmara University, Technical Education Faculty, Material Dep., Göztepe, Istanbul, 81040

E-mail: ogulsoy@marmara.edu.tr

This paper describes the sintering of an injection molded 17-4 PH stainless steel with additions of nickel boride (NiB), with the aim of producing high mechanical properties. Boron is evaluated as the best sintering enhancing element in terms of densifying the iron-based materials by formation the liquid phase. Sintered density and mechanical properties were increased with the increased amount of NiB while sintering time and temperature were decreased. Sintering to full density and highest mechanical properties were obtained with the addition of 1 wt% NiB at 1280°C for 45 min. The formation of borides caused the increase of mechanical properties. This material may therefore find a wider technological application, because of its improved mechanical properties.

© 2005 Springer Science + Business Media, Inc.

1. Introduction

Powder injection molding (PIM) is a powder metallurgy process currently used for the production of complicated and near-net-shape parts of high performance materials. This technique basically combines the advantages of the plastic injection molding with the versatility of the traditional powder metallurgy, producing highly complex part of small size, tight tolerance, and low production cost. 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 [1–4]. Mechanical properties of a well processed powder injection molded material and indistinguishable from cast and wrought material. The PIM process is composed of four sequential steps; mixing of the powder and organic binder, injection molding, debinding (binder removal), and sintering. If it is necessary, secondary operations such as heat and surface treatments after sintering can be performed [5, 7].

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 aircraft components. 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 [5–13].

High density is imperative for improved mechanical properties and corrosion resistance in all PM parts. Residual pores in sintered stainless steel decrease mechanical properties and corrosion resistance [7–9]. In several investigations boron as a sintering additive have been used to achieve higher sintered density in stainless steels at lower sintering temperatures [14–25]. Different boron additions can be selected for full density and higher performance, because of low melting temperature, excellent wetting characteristics and an extremely low solubility in the solid. Due to these attractive characteristics intensive research efforts have been dedicated to the study of several iron-based alloying systems [14, 25] including stainless steels. In several studies was observed that additions of boron as FeB, Fe₂B, NiB, CrB₂ to iron and stainless steels resulted in greater densification [14, 16–20]. Full density and a noticeable improvement in the mechanical properties were obtained by the addition of 200 ppm of boron to martensitic stainless steel [16]. The addition of 0.5 wt% and 1 wt% elemental boron powder to 316L stainless steel powders increased theoretical density, mechanical properties and corrosion resistance [14]. The boron additions effect on melting and densification characteristics, and distortion of PM stainless steel [17]. 0.20 wt% FeB powder to 17-4 PH stainless steel powders improved the final density to the theoretical values. As a consequence, a noticeable improvement in the mechanical properties is obtained [10, 25].

Earlier investigations on PM or PIM 17-4 PH focused on the effect of powder characteristics, sintering atmosphere, sintering temperature, sintering time,

* Author to whom all correspondence should be addressed.

heat treatment, residual carbon content on microstructure, corresponding microstructural characterization, mechanical and corrosion properties [4–9, 11–13]. Although they found poor corrosion performance in comparison with the corresponding wrought material because of the porosity left in the final product, mechanical properties were somewhat improved with increased sintering parameters.

This present work was aimed to investigate the effect of NiB additions on the sintering behavior and on the final properties of powder injection molded 17-4 PH stainless steel. Thermal analysis and metallographic techniques were employed to sintered tensile bars to investigate the sintering behaviors. Tensile, unnotched Charpy impact, hardness and corrosion properties of the sintered products were evaluated in heat-treated condition. Powder morphology, molded, debinded, sintered and heat treated sample fracture surface, and corrosion surface pits were analyzed under scanning electron microscope.

2. Experimental procedures

17-4 PH stainless steel powder used in this study was supplied by Osprey Metals Ltd., which was produced by high-pressure gas atomization method with a tap density of 4.2 g/cm^3 and a pycnometer density of 7.5 g/cm^3 . The particle size distribution of this powder was $D_{10} = 3 \mu\text{m}$, $D_{50} = 10 \mu\text{m}$, $D_{90} = 28 \mu\text{m}$. 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. NiB powder used in this study was supplied by F.W. WINTER Inc. & Co. The particle size distribution of NiB powder was $D_{10} = 4 \mu\text{m}$, $D_{50} = 11 \mu\text{m}$, $D_{90} = 26 \mu\text{m}$. The amount of additive was adjusted to give 0.25, 0.5, 0.75 and 1 wt% NiB in starting mixture and each mixture was blended 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 the 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 specially made injection-molding machine to produce tensile (MPIF 50) [26] and unnotched Charpy impact (MPIF 59) [27] test specimens. The melt temperature was 175°C , the mold temperature was kept at 35°C and cycle time was 20 s.

The samples molded using the binder were all thermally debinded in an atmosphere controlled furnace under high purity H_2 to reduce oxidation with the following schedule: Hold at 150°C for 12 h, at 280°C for 12 h, 390°C for 12 h, 520°C for 6 h and at 950°C 1 h with heating rates $1^\circ\text{C}/\text{min}$. After applying this debinding no

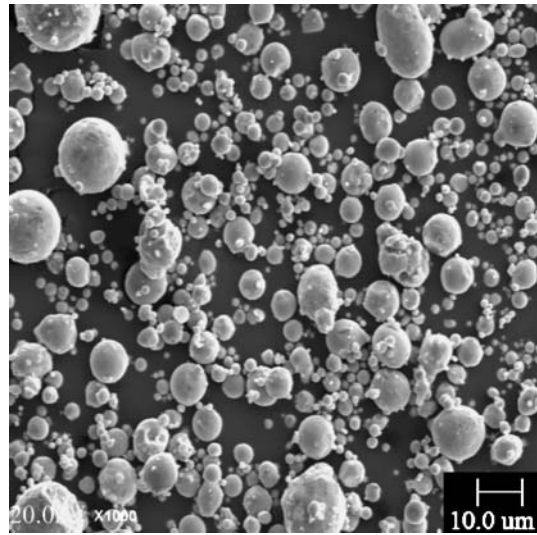


Figure 1 Scanning electron micrograph of 17-4 PH stainless steel powder.

distortion or other visible reduction in part quality or surface finish was observed.

The effect of sintering additives on the solidus and liquidus temperature of the alloy was determined by using differential thermal analysis (DTA), Setaram/TGDTA92. The experiments were performed at a constant heating rate of $20^\circ\text{C}/\text{min}$ under an argon atmosphere. Sintering of all samples was performed within a vacuum/atmosphere-controlled high temperature furnace of Vacuum Industries. The sintering cycle applied to the samples was as follows; samples were heated to 1100°C at a rate of $10^\circ\text{C}/\text{min}$ and held at 1100°C for 5 min., then the samples were heated to various sintering temperatures of 1200, 1220, 1240, 1260 and 1280°C at a rate $5^\circ\text{C}/\text{min}$ and they were held at each temperature for 10, 20, 30 and 45 min. 17-4 PH stainless steel samples without boron addition were sintered at 1350°C for 1 h. The densities of the sintered samples were measured by means of the Archimedes water-immersion method. For metallographic examination, samples were cut from the center of the each sintered tensile test bars. 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. 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 and microhardness tests were performed using a Shimadzu Microhardness Tester. The samples, from which the highest tensile strength was obtained, were subjected to heat treatment. The heat treatment was performed applying a solution treatment in argon for 1 h at 1050°C , followed by a water quenching and aging treatment carried out in argon for 4 h at 480°C than cooled in air. X-ray diffractometry (XRD) was used to characterize the sample with NiB added and heat treated samples. Finally, immersion tests were performed at highest ultimate tensile strength samples and for comparison base alloy, 17-4 PH. During immersion tests the samples were periodically removed from the liquid, dried and weighed. The samples were polished to an 800-grid

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 | |

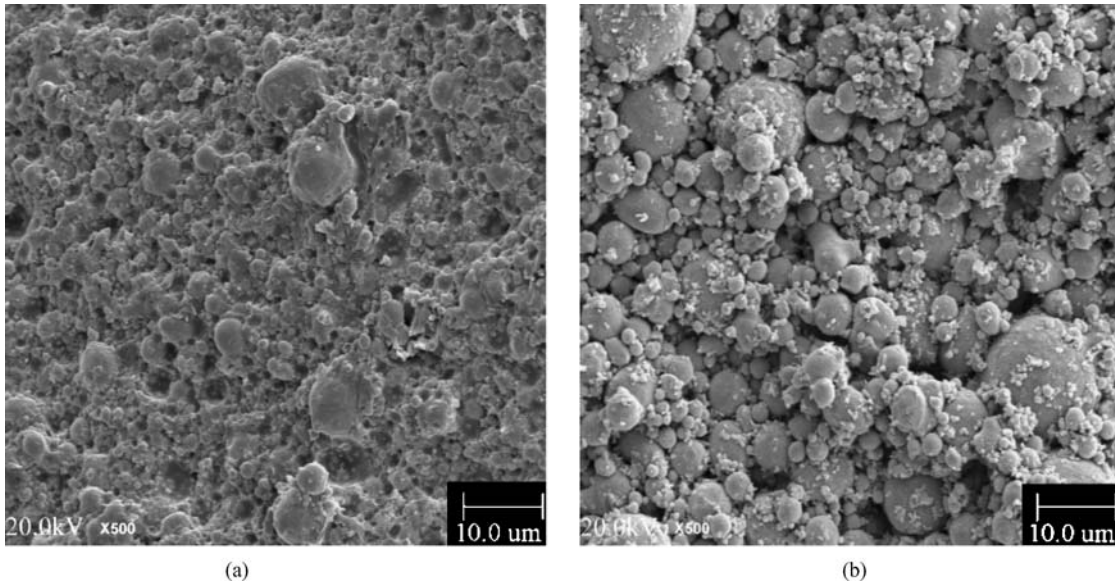


Figure 2 SEM micrographs of: (a) green and (b) brown parts with 1% NiB addition.

finish to adjust the sample weight to 2.3 g and exposed area was measured. The corrosion tests were performed in a water solution containing 53% sodium chloride at 22°C for 336 h. At least five specimens were tested under the same conditions to guarantee the reliability of the results.

3. Results and discussion

Figure 2a is a typical fracture surface of a green part shows that a good homogeneity was achieved for 17-4 PH stainless steel with 1% NiB addition. The measured green density was approximately 5.2 g/cm³ (65.90 % theoretical). Brown parts presented very good homogeneity, as shown in Fig. 2b; and NiB particles also can be seen in this micrograph. The measured brown density was approxi-

mately 6.3 g/cm³ (79.84 % theoretical). These images show excellent homogeneity in both green and brown microstructure.

Figure 3 shows the DTA plot for determining the debinding behavior of 17-4 PH and 17-4 PH with 0.25 wt% NiB additions. 17-4 PH with 0.25 NiB plot shows endothermic peak indicating liquid formation at 1219.6°C (plot A). It has already been shown by other studies [14, 17, 19, 25] that the solidus temperature decreases in various stainless steel powder products containing different boron. However, as shown in Fig. 3 17-4 PH alloy plot (plot B) does not exhibit any peaks at higher temperatures. Similar results were presented on boron treated austenitic stainless steel by different studies [14, 16–19]. Thermodynamic data show 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

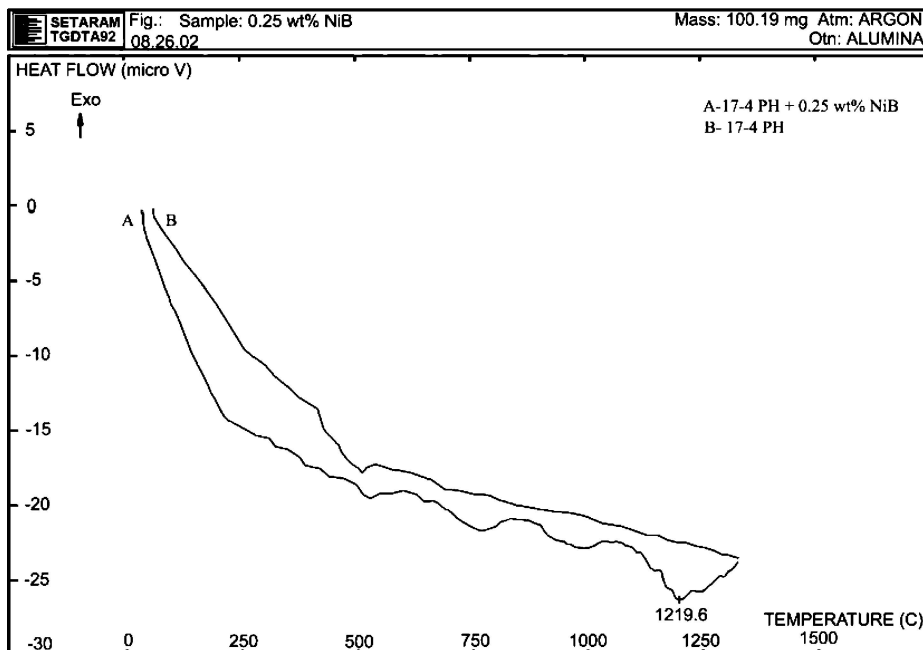


Figure 3 DTA curves showing melting characteristics for 17-4 PH and 17-4 PH with 0.25 wt% NiB additions.

like Cr. There is not any important study regarding the 17-4 PH with boron or different borides on the literature. But, similar other studies [14, 19, 25] were compared to present this study showed that there are close similarities between the present results and other previous results.

Although samples prepared from as-received 17-4 PH stainless steel powder were sintered at 1350°C for 1 h, a maximum sintered density of only 7.4 g/cm³ was achieved. A set of sintering experiment was conducted at 1280°C for 45 min to study the effect of NiB addition on the final sintered density and the results are shown in Fig. 4. As expected, 17-4 PH stainless steel samples without NiB addition were produced a maximum sintered density of only 6.9 g/cm³. Less than 0.25 wt% NiB additions to 17-4 PH stainless steel did not seemed to have a significant effect on densification, because the fraction of eutectic liquid formed at this temperature was too small to induce densification. At higher NiB levels, sintered density increases. Near full density, 7.89 g/cm³, was obtained with a NiB addition of 1 wt%.

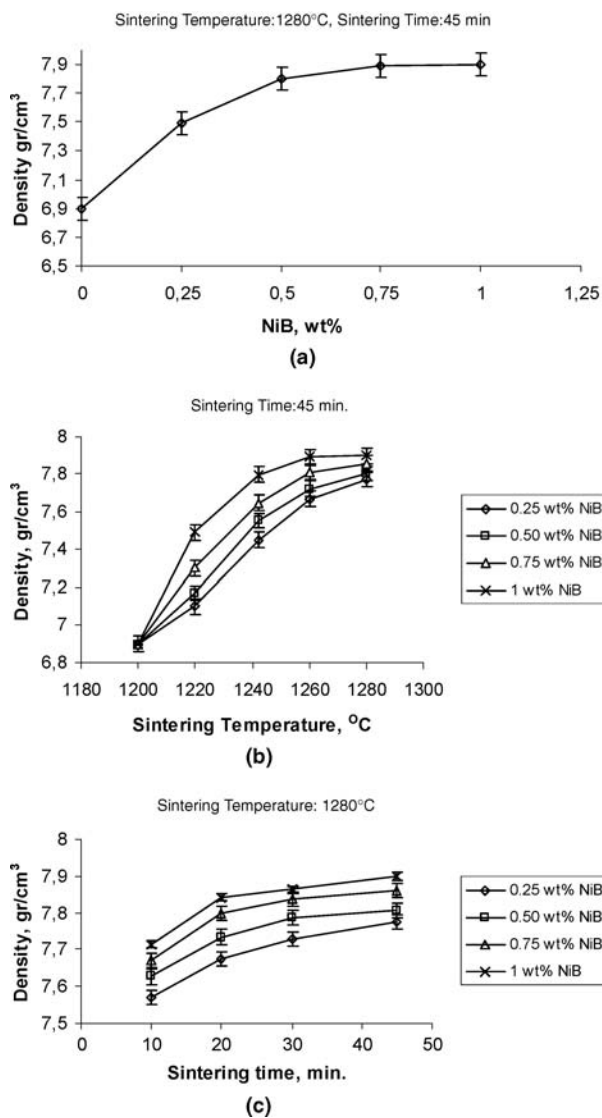


Figure 4 Effect of NiB addition, sintering time and temperature on the sintered density: (a) NiB addition, (b) sintering temperature, (c) sintering time.

Boron activates the sintering process of the iron powders by the formation of the liquid phase, produced by the eutectic reaction, $\text{Fe}_2\text{B} + \text{Fe} \rightarrow \text{liquid}$, 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 [14–19]. 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 [14, 16, 17, 21].

The effect of sintering temperature and sintering time on the sintered density of NiB addition 17-4 PH stainless steel is shown in Fig. 4. Fig. 4a shows that at a sintering temperature of 1240°C, the samples containing 1 wt% NiB attained a maximum sintered density of 7.80 g/cm³ after sintering for 45 min. When samples added with 1 wt% NiB sintered at temperature of 1280°C, a maximum sintered density of 7.89 g/cm³ was achieved. The samples containing 0.5 wt% NiB attained a maximum sintered density of 7.80 g/cm³ after sintering for 1280°C and 45 min. Clearly, sintering density was increased with the sintering temperature and NiB addition.

The results of the effect of sintering time on NiB addition 17-4 PH stainless steel are shown in Fig. 4b. From Fig. 4b it can be seen that at sintering temperature of 1280°C, the samples containing 1 wt% NiB attained a maximum sintered density of 7.89 g/cm³ after sintering for 45 min, however, higher sintering time improved noticeably sintered density. The sintering time higher than 45 min. resulted in slumping at some samples that are not considered in here. The sample containing 1 wt% NiB shows minimum sintered density of 7.71 g/cm³ after sintering for 10 min. The sintering time and NiB addition increases sintered density.

Figure 5 shows the microstructures of the samples with and without NiB. Fig. 5(a) and (b) shows a microstructure of additive free sample that was sintered at 1350°C for 1 h. This microstructure exhibits δ -ferrite, sintered particles and pores inside particles, similar findings were also reported in literature [4–9, 12, 13]. Fig. 5c and d show the microstructures of the 0.5 wt% and 1 wt% NiB added stainless steel samples. Samples with 0.5 wt% and 1 wt% NiB addition, sufficient amount of eutectic liquid formed to provide nearly full densification. 1 wt% NiB added alloy exhibits that the grains were well surrounded with eutectic phase. It can be seen in these figures that the amount of liquid phase formed in Fig. 5c is less than the Fig. 5d. It is well known that in liquid phase sintering process rearrangement

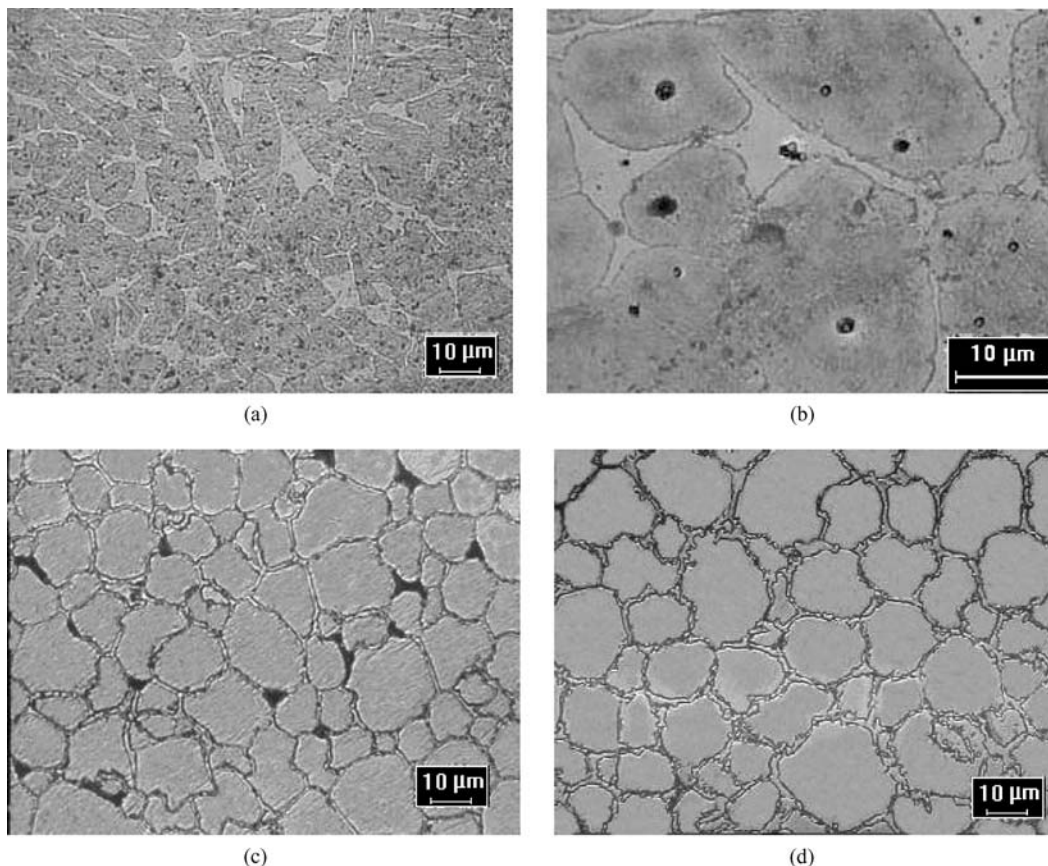


Figure 5 Microstructures of the samples with and without NiB a and b 1350°C for 60 min. non-NiB, (c) 1280°C for 45 min. 0.5 wt% NiB, (d) 1280°C for 45 min. 1 wt% NiB.

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, as 17-4 PH stainless steel powder in this study. Small particles have higher capillary stress, by which the particles are pulled together, resulting in rapid shrinkage.

Figure 6 shows the XRD patterns for heat-treated samples containing 1 wt% NiB at 1280°C for 45 min. This result proves the presence of retained austenite (γ), martensite (α), $\text{Fe}_{11}\text{Cr}_{0.9}\text{B}_{0.9}$, $\text{B}_{0.44}\text{C}_{1.41}\text{Cr}_3$ and Cr_2B . Martensite and different boride phases increase ultimate tensile strength and hardness values.

The mechanical properties of the samples that were processed under different conditions are shown in Table II. Graphs of comparison of mechanical properties results were shown in Fig. 7. The effect of NiB additions on the ultimate tensile strength, elongation, hardness and impact energy of 17-4 PH stainless steel with 1 wt% NiB addition in sintering temperature at 1280°C are shown in Fig. 6. Ultimate tensile strength, elongation, hardness and impact energy increases with NiB additions. The low mechanical properties in low sintered density are due to incomplete densification. At 1280°C and high sintered density, enough liquid phase exists to provide full densification and consequently the mechanical properties were increased. In Fig. 5d, it can be seen that sample containing 1 wt% NiB has very high

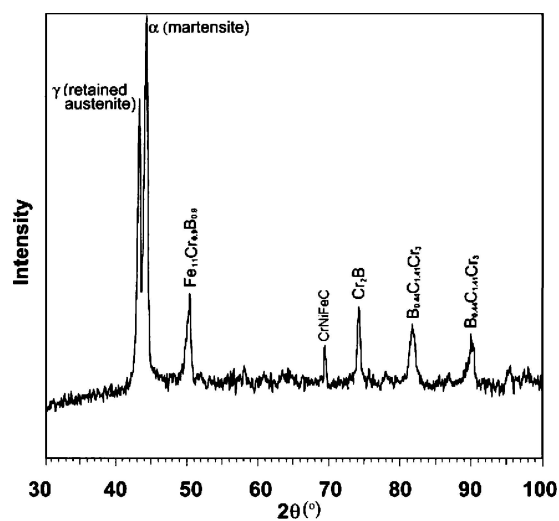


Figure 6 X-ray diffraction pattern of heat-treated samples containing 1 wt% NiB at 1280°C for 45 min.

eutectic contents deposited at grain boundaries. The boride phase in the eutectic network has a brittle nature and affected the mechanical properties of the samples. The maximum ultimate tensile strength of 1183 MPa, elongation of 7.3, hardness of 35.5 HRC and impact energy of 25 J was reached with samples added 1 wt% NiB sintered at 1280°C for 45 min and 7,89 gr/cm³.

The heat treated and non-heat treated samples produced in this study were both capable of increasing the mechanical properties, as compared to 17-4 PH stainless steel without NiB addition. The maximum ultimate tensile strength of 976 MPa was reached with

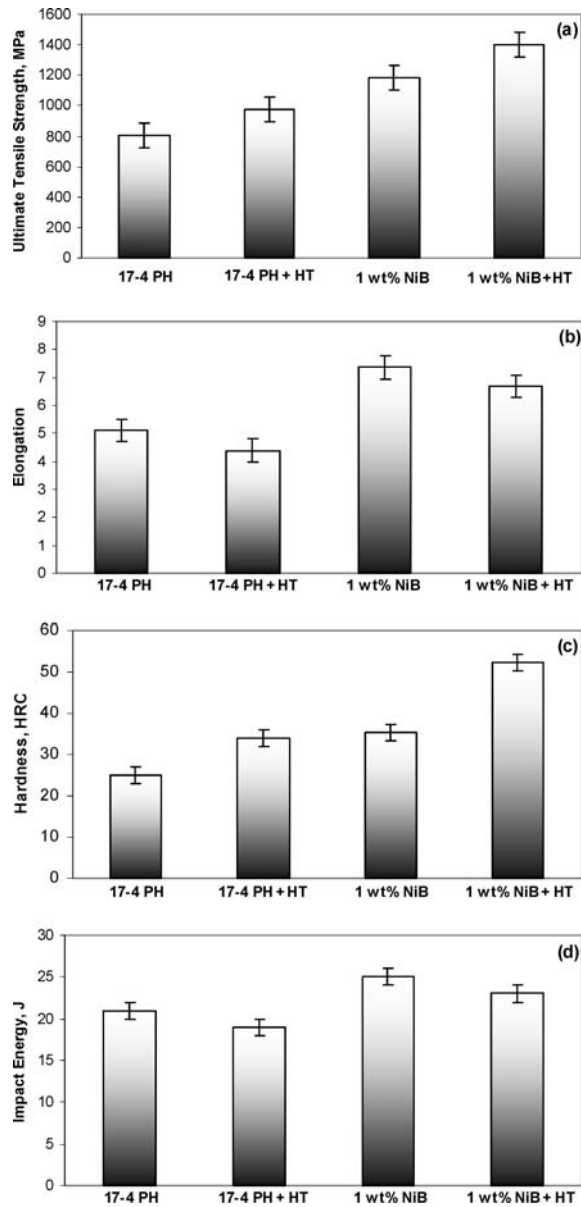


Figure 7 Comparison of mechanical properties with and without NiB addition: (a) Ultimate tensile strength, (b) elongation, (c) hardness, (d) impact energy (HT: Heat treatment).

heat-treated 17-4 PH without NiB addition. The maximum ultimate tensile strength of 1402 MPa, elongation of 6.7, hardness of 52.3 HRC and impact energy of 23 J was reached with heat-treated samples containing 1 wt% NiB. Mechanical properties increase with heat-treated samples containing 1 wt% NiB. Elongation and impact energy decreases with heat-treated samples containing 1 wt% NiB. The maximum elongation and impact energy of 5.1 and 21 J were reached with heat-treated 17-4 PH stainless steel without NiB addition. The maximum elongation of 6.7 and impact energy of 23 J was reached with heat-treated samples containing 1 wt% NiB addition (sintering temperature 1280°C and sintering time 45 min). The results of hardness measurements exhibited an increasing trend similar to that of tensile strength. The maximum hardness of 34 HRC was reached with heat-treated 17-4 PH stainless steel without NiB addition. The maximum hardness of 52.3 HRC was reached with 1 wt% NiB addition. The microhardness values of matrix grain of base alloy and NiB added system were 341-355 HV0.02, respectively. The microhardness of matrix grain was not much influenced by NiB addition. The microhardness of eutectic network was 1418 HV0.02 with 1 wt% NiB addition and heat treatment. Results of microhardness testing were Table II. HRC values show that the eutectic network greatly affects the hardness of resultant matrix.

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. 8a. It can be seen that sample exhibit dimpled rupture and porosities. δ -ferrite, which occurred during the sintering, decreases the amount of porosity and exhibits ductile fracture as founded by others [6, 12, 13]. The morphologies of surface of 1 wt% NiB added samples are shown in Fig. 8b and this sample exhibited a brittle fracture. It is also well known that the brittle nature of intermetallics. In this case the brittle fracture occurred through the eutectic network. $(\text{Fe, Cr})_2\text{B}$ phase formed around the grain boundaries. The eutectic network improved sintered density and mechanical properties and decreased porosity.

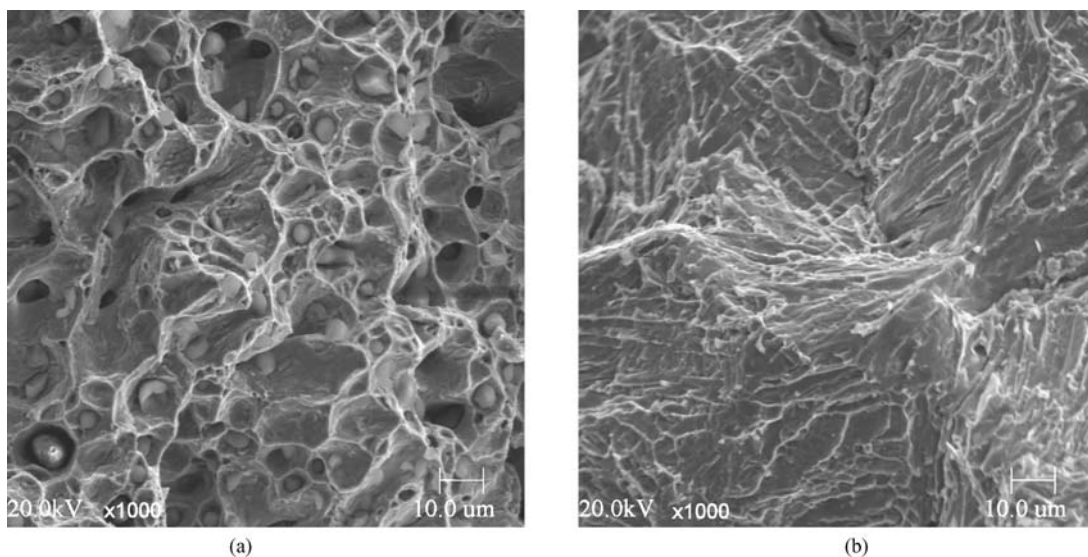


Figure 8 Fractographs of samples with and without NiB addition with heat treatment: (a) 1350°C for 60 min. non-NiB, (b) 1280°C for 45 min. 1 wt% NiB.

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

| Sample | Process condition | Sintered density (gr/cm ³) | Ultimate tensile strength (MPa) | Elongation (%) | Hardness HRC | Microhardness HV0.02 | | Impact energy (J) |
|---------------------|------------------------|--|---------------------------------|----------------|--------------|----------------------|----------|-------------------|
| | | | | | | Matrix | Eutectic | |
| 17-4 PH | 1350°C, 60 min. | 7.4 | 802 | 5.1 | 25 | 273 | n.d. | 21 |
| 17-4 PH | 1350°C, 60 min. and HT | 7.4 | 976 | 4.4 | 34 | 341 | n.d. | 19 |
| 17-4 PH + 1 wt% NiB | 1280°C, 45 min. | 7.89 | 1183 | 7.3 | 35.5 | 284 | 1412 | 25 |
| 17-4 PH + 1 wt% NiB | 1280°C, 45 min. and HT | 7.89 | 1402 | 6.7 | 52.3 | 355 | 1418 | 23 |

4. Conclusions

The addition of NiB for developing the high strength 17-4 PH stainless steel was investigated. 1 wt% NiB addition decreased traditional sintering time and sintering temperature. Sintering to full density is only possible with the addition of 1 wt% NiB at 1280°C for 45 min. 1 wt% NiB addition increased sintered density, ultimate tensile strength, elongation, impact energy and hardness. Ultimate tensile strength of 1402 MPa, elongation of 4.8, impact energy of 23 J and hardness of 52.3 HRC were achieved with the heat treated product containing 1 wt% NiB.

Acknowledgements

This work is support by TUBITAK-MRC (The Scientific and Technical Research Council of Turkey, Marmara Research Centre). The powders were provided by Osprey Metals Ltd. and F.W.WINTER Inc.&Co.

References

1. R. M. GERMAN, in "Powder Injection Molding" (Metal Powder Industries Federation, Princeton, NJ, 1990) p. 110.
2. R. M. GERMAN and A. BOSE, in "Injection Molding of Metals and Ceramics" (Metal Powder Industries Federation, Princeton, NJ, 1997) p. 11.
3. M. T. MARTNY, D. A. ISSITT, B. HAWORTH and P. J. JAMES, *Powder Metall.* **31** (1998) 106.
4. H. SUNG, T.K. HA, S. AHN and Y. W. CHANG, *J. Mater. Process. Technol.* **130** (2002) 321.
5. Y. WU, R. M. GERMAN, D. BLAINE, B. MARX and C. SCHLAEFER, *J. Mater. Sci.* **37** (2002) 3573.
6. Y. WU, D. BALAINE, B. MARX, C. SCHLAEFER and R. M. GERMAN, *Metall. Mater. Trans.* **33A** (2002) 2185.
7. R. M. GERMAN and D. KUBISH, *Int. J. Powder Metall.* **29** (1993) 47.
8. H. ZHANG and R. M. GERMAN, in "Proceedings of The 1992 Powder Injection Molding Symposium", San Francisco, June 1992, edited by P.H. Booker, J. Gaspervich and R.M. German (Metal Powder Industries Federation, Princeton, NJ, 1992) p. 219.

9. Y. S. KWON, Y. WU, P. SURI and R. M. GERMAN, *Metall. Mater. Trans.* **35A** (2004) 257.
10. K. KAMADA, M. NAKAMURA and H. HORIE, in "Proceedings of 2000 Powder Metallurgy World Congress", Kyoto, Japan, October (2000) p. 1021.
11. H. I. SANDEROW, J. D. RUHKAMP and H. A. RODRIGUES, in "Modern Developments in Powder Metallurgy", (Metal Powder Industries Federation, Princeton, NJ, 1992) Vol. 16, p. 167.
12. T. BABA, H. MIURA, T. HONDA and Y. TOKUYAMA, *Adv. Powder Metall. Part. Mater.* **6** (1995) 271.
13. J. J. VALENCIA, T. J. MCCABE and H. DONG, *ibid.* **6** (1995) 205.
14. R. TANDON and R. M. GERMAN, *Int. J. Powder Metall.* **34** (1998) 40.
15. D. S. MADAN and R. M. GERMAN, *Adv. Powder Metall. Part. Mater.* **1** (1989) 147.
16. C. TOENNES, P. ERNST, G. MEYER and R. M. GERMAN, *ibid.* **2** (1992) 371.
17. A. LAL, R. IACocca and R. M. GERMAN, *Metall. Mater. Trans.* **30A** (1999) 2201.
18. J. D. BOLTON and B. S. BECKER, in "Proceedings of 2000 Powder Metallurgy World Congress," Kyoto, Japan (2000) p. 984.
19. I. H. BAKAN, D. HEANEY and R. M. GERMAN, *Powder Metall.* **44** (2001) 235.
20. A. MOLINARI, G. STARAFFELLINI, T. PIECZONKA and J. KAZIOR, *Int. J. Powder Metall.* **34** (1998) 21.
21. M. SARASOLA, T. GOMEZ-ACEBO and F. CASTRO, *Acta Mater.* **52** (2004) 4615.
22. A. SELECKA, A. SALAK and H. DANNINGER, *J. Mater. Process. Technol.* **141** (2003) 379.
23. J. LIU, A. CARDAMONE, T. POTTER, R. M. GERMAN and F. J. SEMEL, *Powder Metall.* **43** (2003) 57.
24. R. M. GERMAN, K. S. HWANG and D. S. MADAN, *Powder Metall. Int.* **19** (1987) 15.
25. H. O. GULSOY, S. SALMAN and S. OZBEK, *J Mater Sci.* **39** (2004) 4835.
26. MPIF Standard 50, "Materials Standards for Metal Injected Molded Parts" (Princeton, NJ, MPIF, 2000).
27. MPIF Standard 59, "Materials Standards for Metal Injected Molded Parts" (Princeton, NJ, MPIF, 2001).

Received 18 October 2004
and accepted 7 February 2005