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Effects of Porosity and Boron Reinforcement in AISI 316L Stainless Steel for Biomedical Applications

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Abstract: AISI 316L stainless steel (SS) is one of the most widely used biomaterials in the manufacture of implants and biomaterials. It has advantages over equivalent biomaterials such as low cost, good mechanical properties and biocompatibility. The pores found in porous biomaterials provide mechanical interlock, ensuring strong attachment of the implant to the tissue. In this study, 20%, 30% and 40% by volume of polyvinyl alcohol (PVA) and Boron powder were added into 316L powder to obtain porous SS implant. To investigate the effect of porosity and boron effect on the stainless-steel implant material, the samples produced in PVA and Boron added groups, were sintered at 1180 ^{o}C under an argon atmosphere. With the evaporation of PVA in the structure, porous and boron added samples were obtained in two groups. Finally, the samples were subjected to Brinell hardness and compression tests and analyzed by SEM, EDS and XRD. As a result of the hardness tests, the highest values were measured as 37.006, 31.32, 25.28 HB. 39.5, 34.5, 26.2 MPa strengths were measured for 20%, 30% and 40% porous samples respectively.

Keywords: AISI 316L stainless steel, boron, powder metallurgy, space holder, mechanical properties

Biyomedikal Uygulamalarda AISI 316L Paslanmaz Çelik için Gözeneklilik ve Bor Takviyesinin Etkileri

Öz: AISI 316L paslanmaz çelik (SS), implant ve biyomalzeme üretiminde en yaygın kullanılan metalik biyomalzemelerden biridir. Muadil biyomateryallerle kıyaslandığında düşük maliyet, iyi mekanik özellik ve biyouyumluluk gibi avantajları mevcuttur. Gözenekli biyomalzemelerde bulunan gözenekler mekanik bir kenetlenme sağlayarak implantın dokuya güçlü bir şekilde tutunmasını sağlar. Bu çalışmada gözenekli SS implant elde etmek için 316L alaşım tozu içerisine hacimce %20, %30 ve %40 oranında polivinil alkol (PVA) ve Bor ilave edildi. Paslanmaz çelik implant malzemesi üzerinde gözeneklilik ve bor etkisinin araştırılması amacıyla PVA ve Bor katkılı gruplarda üretilen numuneler, 1180 ^{o}C' de argon atmosferi altında sinterlenmiştir. Yapıdaki PVA' nın buharlaştırılmasıyla iki grup halinde gözenekli ve bor katkılı numuneler elde edildi. Son olarak numuneler Brinell sertlik ve basma testlerine tabi tutularak SEM, EDS ve XRD analizleri yapıldı. Sertlik testleri sonucunda en yüksek değerler 37.006, 31.32, 25.28 HB olarak ölçülmüştür. Basma dayanımı ise %20, %30 ve %40 gözenekli numuneler için sırasıyla 39.5, 34.5, 26.2 MPa olarak ölçülmüştür.

Anahtar kelimeler: AISI 316L paslanmaz çelik, bor, toz metalurjisi, boşluk tutucu yöntem, mekanik özellikler

1. INTRODUCTION

Bioimplants play an important role in improving the quality of human life. Historically, there are documents indicating that the Egyptians and Romans developed various implantation practices for dental applications as early as four thousand years ago [1]. However, the systematization of these practices into the science of implantology did not begin until the late 18th century [2]. The development of implants with superior mechanical and physical properties is closely related to the development of implant science [3]. In 1969, the science of biomaterials made a breakthrough in the scientific world and has attracted great interest in recent years [4]. From this point of view, the correct choice of biomaterial is crucial in terms of implant production, mechanical properties, cost and long-term use [5], [6].

Metallic biomaterials account for more than 70% of existing biomaterials and medical devices [7], [8]. Metallic biomaterials as researchers prefer implant materials due to their superior mechanical properties in long-term implantation applications [9], [10]. Commonly used metallic biomaterials include Ti6Al4V, Co-Cr alloys and 316L stainless steel [11]. Due to its low cost, ideal corrosion resistance and ease of use, 316L stainless steel has

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attracted considerable attention in implant fabrication [12], [13]. Implants made of these materials are less expensive than titanium and cobalt-based implants [14], [15].

There is a lot of research on the eutectic reaction between austenitic stainless-steel matrix and boron. In general, it has become possible to produce almost completely dense materials with very low levels of boron addition (0.2-0.8 wt%) [16-19]. However, although it is necessary to go to high densities to improve mechanical properties in powder metallurgy applications, the pores formed in the structure of sintered stainless-steel cause a decrease in the mechanical property values [20]. Many studies have reported that the addition of boron to metal powder reduces the amount of porosity after sintering. While the liquid phase formed because of the eutectic reaction between iron and boron improves sintering, complex borides such as FeB, Ni_2B, CrB and Fe_2B formed in the material improve mechanical properties [21].

Powder metallurgy is one of the main fabrication methods used to produce porous structures due to its ability to combine different components and low cost [22], [23]. The low cost, precise fabrication, and ability to adjust pore size and quantity have made powder metallurgy and space-holder methods favored by researchers in recent times [24], [25].

In this study, 316L scaffold structures with 20%, 30% and 40% porosity were fabricated using the PVA space holder and powder metallurgy method due to its superior bonding and layering properties. On the other hand, to investigate the effect of boron on 316L stainless steel, 20%, 30% and 40% boron added 316L metallic structures were fabricated and their morphological, structural and mechanical properties were investigated.

2. MATERIALS AND METHODS

2.1. Production of Porous SS Structures

316L (45 μm, Goodfellow) powders were used as matrix material, PVA (100-150 μm, Sigma Aldrich) particles as a space holder and boron (100 μm, Merck) as reinforcing material at 20, 30 and 40% by volume. In the structures prepared in two groups, porous and boron added, PVA and boron were added to the matrix material at 20%, 30% and 40% by volume. The polymeric binder PEG400 was used to ensure the binding of the materials in the mixture. The prepared powders were mixed in a ball mixer at a speed of 210 rpm for 1 hour. The resulting blends were then subjected to cold pressing at a pressure of 350 MPa. The images of the green reinforced samples are shown in Figure 1. The pressed PVA and boron added samples were sintered under argon gas in a controlled atmosphere furnace at 1180 °C for 3 hours. The parameters at the stage of structural production of the samples obtained are given in table 1.

Table 1. Classification of the structural properties of the samples obtained.

Group no:	Notation	316L(SS) (%vol.)	Boron (B) (%vol.)	PVA (%vol.)	Stearic acid (% wt.)	Pressure (kN)
1	80SS/20B	80	20	-	1	4
2	70SS/30B	70	30	-	1	4
3	60SS/40B	60	40	-	1	4
4	80SS/20PVA	80	-	20	1	3
5	70SS/30PVA	70	-	30	1	3
6	60SS/40PVA	60	-	40	1	3

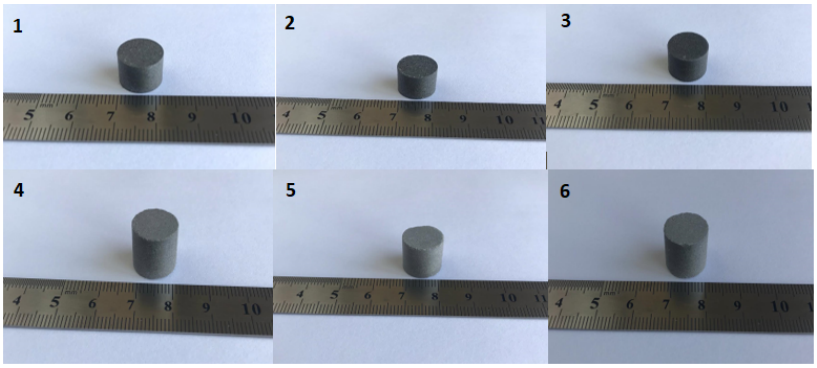

Figure 1. Images of sample groups with green compact

For structural characterization of the sintered samples, X-ray diffraction (XRD, Rigaku miniflex600) patterns were taken at a scanning rate of 2 degrees/min and a range of 10-80 degrees. Scanning electron microscopy (Hitachi SU3500) and energy dispersive X-ray spectroscopy (EDS, Oxford) coupled to SEM were used for morphological and elemental analysis. Tensile testing (100 kN, Shimatsu) was used for compressive strength.

3.RESULT AND DISCUSSION

3.1. Morphological and Structural Characterizations

Structures based on 316L stainless steel with 20%, 30%, 40% by volume PVA space holder and boron added were prepared in two groups. The porosity density of the porous samples is calculated with the Archimedes principle and given in Table 2. Examination of the table shows that the sintering process removes almost all of the PVA from the structure of the porous specimens. SEM-EDS images of the boron doped samples are shown in Figures 2, 3 and 4. The images show that the metallurgy bonding is not fully realized in the sample structures. The literature indicates that adding boron increases the structure's density and enhances sintering [20], [26-28]. In the present study, although better bonding in the microstructure was expected with increasing boron addition, the desired result was not achieved. This is thought to be due to the insufficient sintering temperature applied.

Table 2. Porosity and density of the resultant samples.

Notation	Mass before sintering (g)	Mass after sintering (g)	Density before sintering (g/cm^3)	Density after sintering (g/cm^3)	Porosity %
80SS/20PVA	3.5	2.86	3.09	2.53	19%
70SS/30PVA	3.4	2.4	3	2.12	30%
60SS/40PVA	3.6	2.2	3.18	1.94	39%

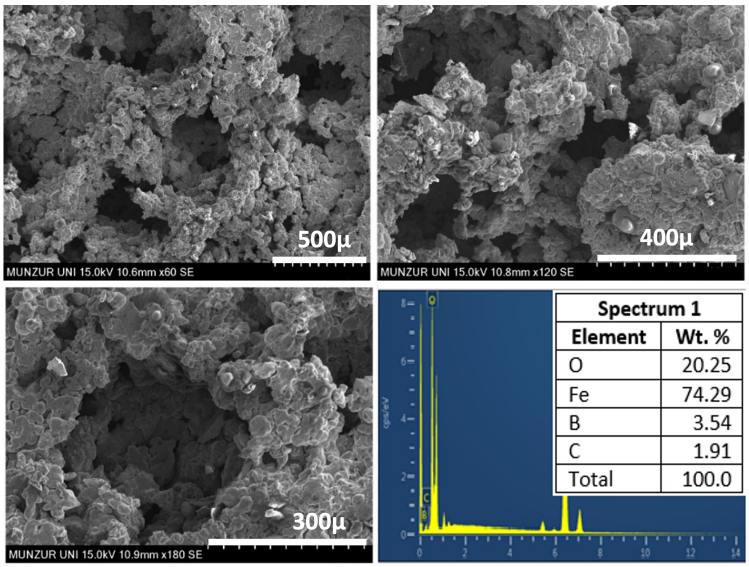

Figure 2. SEM images and EDS spectrum of 80SS/20B sample

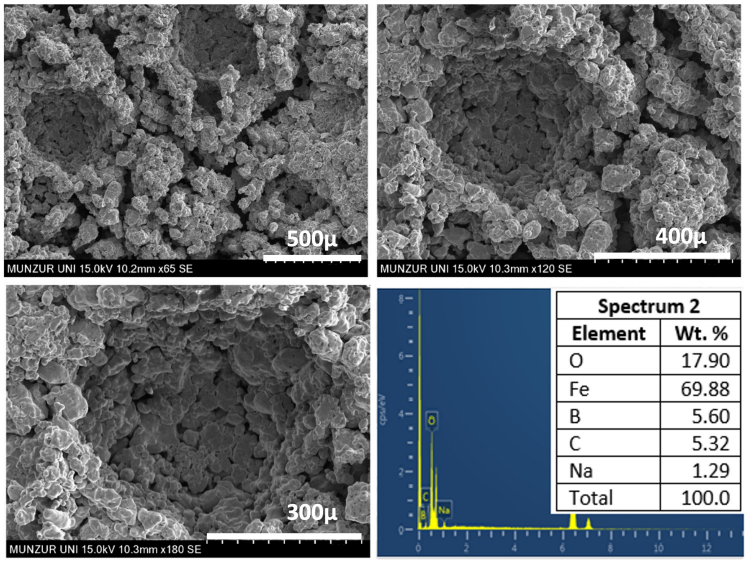

Figure 3. SEM images and EDS spectrum of 70SS/30B sample

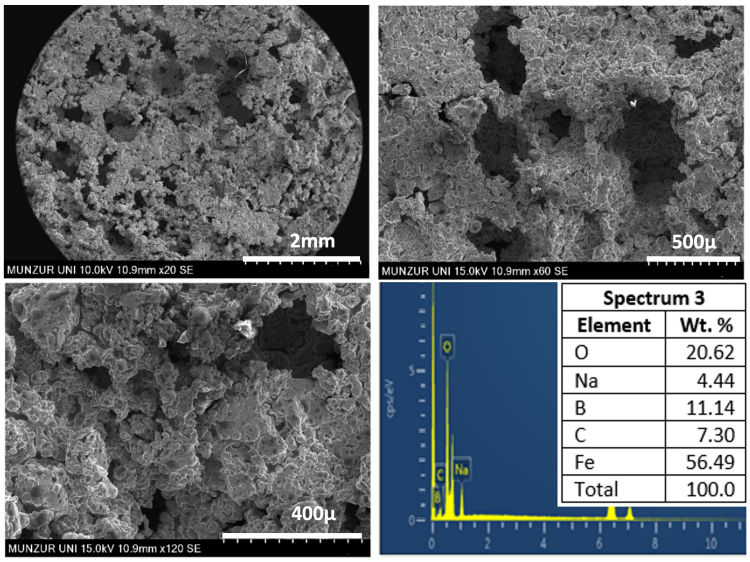

Figure 4. SEM images and EDS spectrum of 60SS/40B sample

Figures 5, 6 and 7 show SEM-EDS images of the porous structures of the other sample group produced with the PVA space holder. The figures show that there is better metallurgical bonding in all sample groups compared to the boron samples. This shows that the amount of intergranular constriction decreases as the porosity increases. This situation again indicates that the sintering temperature is insufficient. The presence of the C peak in the EDS spectra of the boron added samples can be attributed to the carbon in the matrix material. On the other hand, the high C peaks seen in the EDS spectra of the porous structures indicate that PVA, a C-based synthetic polymer [29], does not completely evaporate from the structure during sintering but remains in the pores. In addition, when the EDS spectra of both groups of samples are analysed, O peaks are detected in the structures. This situation can be evaluated separately for both groups of samples. In the porous samples, O peaks were formed because the structure was oxidised during sintering. On the other hand, the formation of B_2O_3 structures in the structure after 450 °C in boron added samples [30] is another reason for the formation of O peaks.

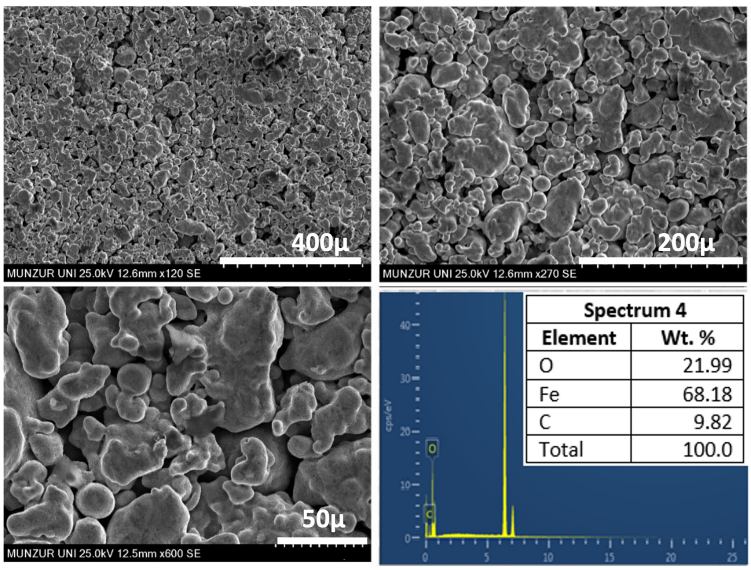

Figure 5. SEM images and EDS spectrum of 80SS/20PVA sample

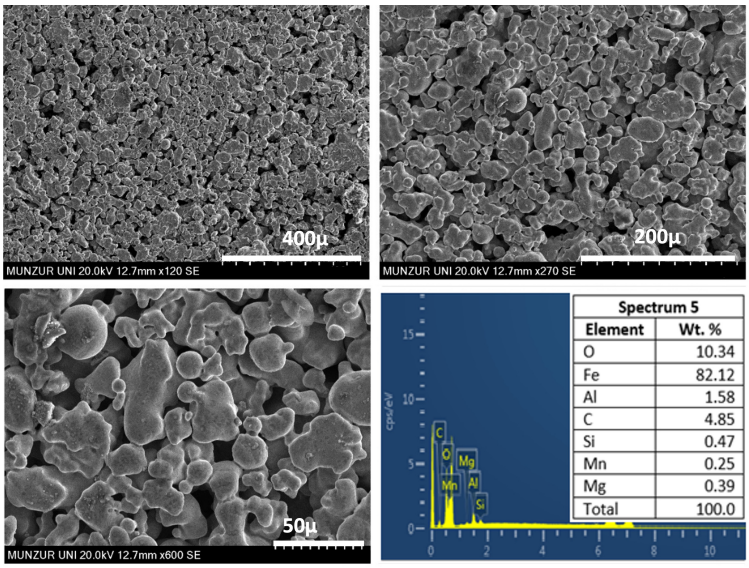

Figure 6. SEM images and EDS spectrum of 70SS/30PVA sample

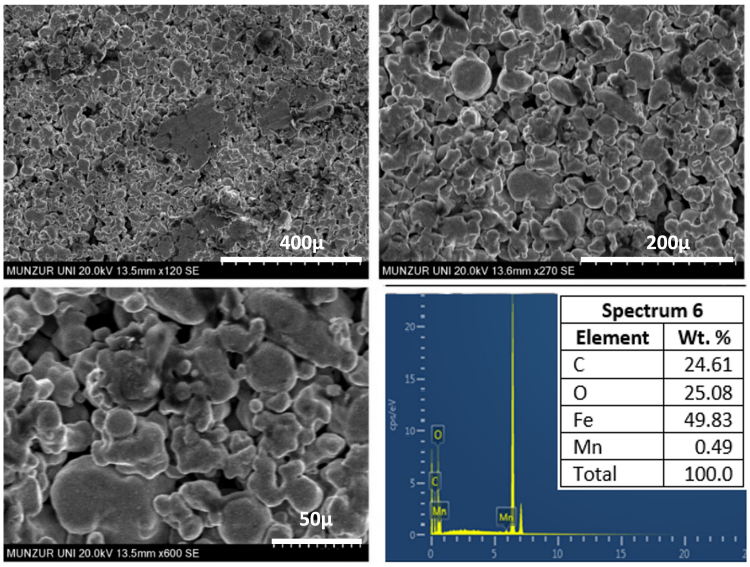

Figure 7. SEM images and EDS spectrum of 60SS/40PVA sample

X-ray diffraction patterns were used to determine the elemental analysis of the structures obtained. XRD spectra of samples added with 20% by volume boron and PVA are shown in Figure 8. As can be seen from the figure, characteristic peaks belonging to B_2O_3 formed by heat treatment were observed [29-31]. The sharpness of the austenite peaks in the spectrum can be related to the characteristic of the austenitic stainless steel 316L. Literature shows that heat treatment at 800-900 degrees leads to a single-phase austenitic phase, whereas at temperatures of 1100 degrees and above, an austenite-ferrite phase composition is obtained [32]. In this context, the presence of a small amount of ferrite phase in the XRD spectra obtained is indicative of austenite to ferrite transformation. On the other hand, the sharp peaks of stainless steel can be explained by the presence of crystallinity of the structure.

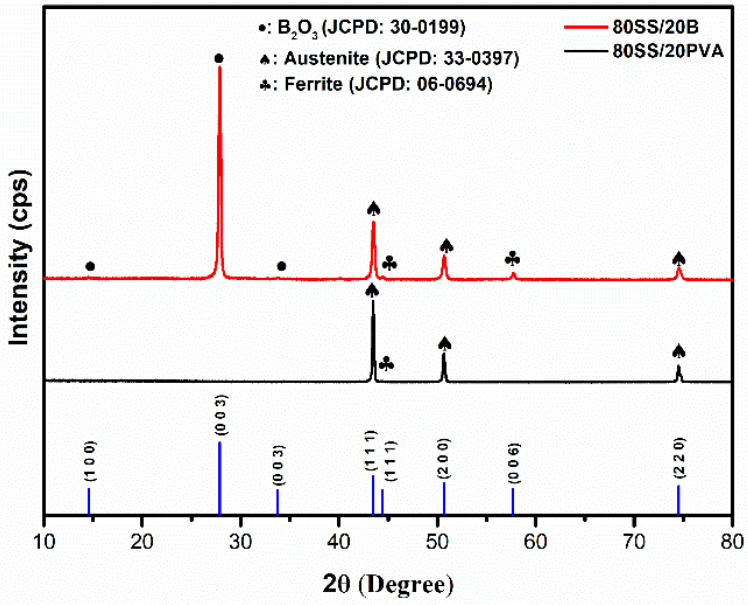

Figure 8. XRD analysis result of 80SS/20B and 80SS/20PVA samples

3.2. Mechanical Measurements

The Brinell hardness test was applied to the obtained porous and boron added samples and the values obtained are shown in Figure 9. Analyzing the plots, we see that the best hardness value is obtained in 80SS/20PVA sample with 37.006 HB. In the boron added samples, the hardness results were quite low due to the inadequacy of the metallurgical bond. On the other hand, the compression test was carried out on the porous samples and force-extension values were obtained. The stress-strain curves of these force-strain values are shown in Figure 10. Analysis of the graph shows that the compressive strength values of the 20%, 30% and 40% porous specimens were 39.5, 34.5 and 26.2 MPa respectively. According to reports, sintering conditions above the eutectic temperature (above 1200 ^{0}C), the liquid phase sintering mechanism occurs and the formation of complex borides in the structure because of the eutectic reaction between the stainless-steel matrix and boron improves sintering [32], [33]. In this study, as the sintering temperature was below 1200 ^{0}C, the liquid phase sintering mechanism was not formed and full metallurgical bonding could not be achieved. For this reason, the compression test could only be applied to porous specimens. On the other hand, a study in the literature investigated the effect of porosity on the compressive strength of stainless steel [34]. In the study, specimens with 40%, 46% and 50% porosity were prepared and measured to be 32, 25 and 20 MPa respectively. The decrease in compressive strength with increasing porosity supports our study. Although the closest value to cancellous bone with a compressive strength value between 2-12 MPa [33] was obtained in the 60SS/40PVA specimen, inadequate metallurgical bonding is not a desirable situation.

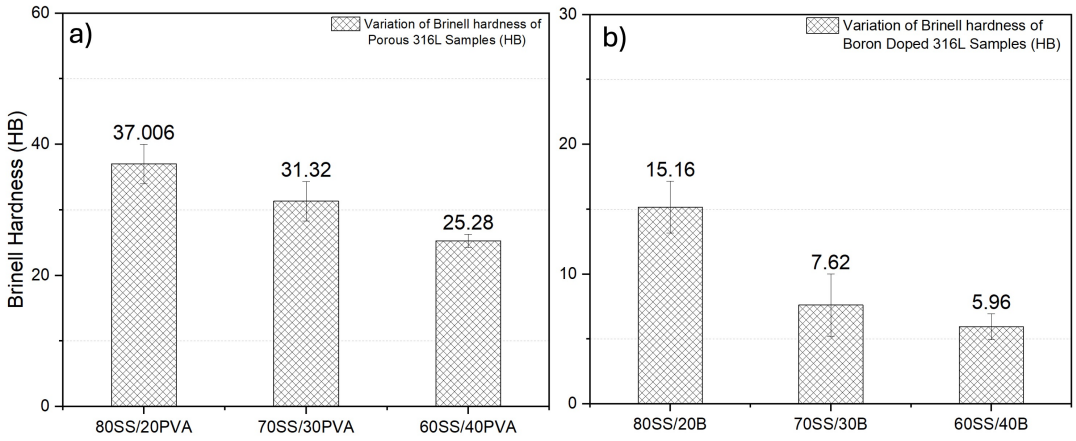

Figure 9. Brinell hardness data for (a) porous and (b) boron added samples

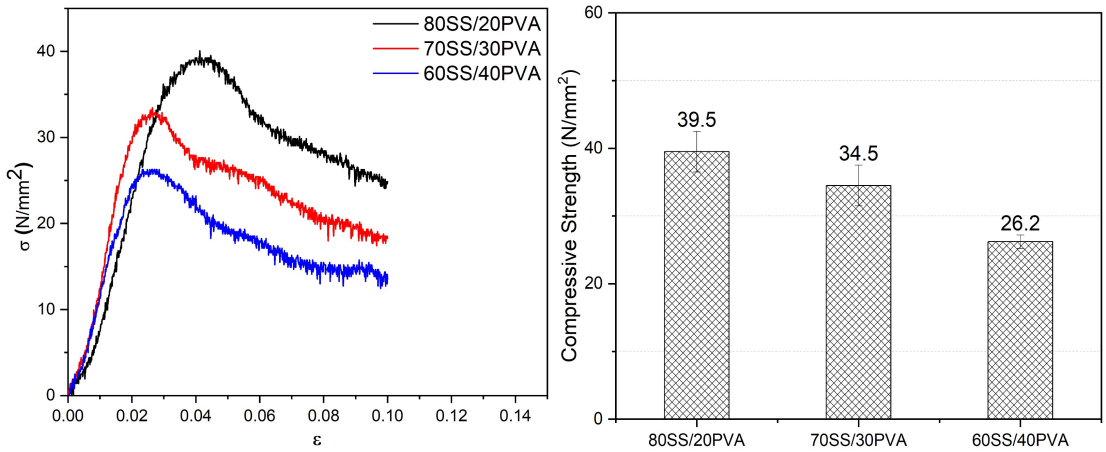

Figure 10. (a) stress-strain curve and (b) compressive strength values of porous samples

4.CONCLUSIONS

PVA and boron added 20%, 30% and 40% by volume samples were prepared and two groups of samples, 20%, 30% and 40% porous and boron added, were obtained by evaporation of PVA into the structures of PVA added samples during sintering. The morpho-structural and mechanical properties of 20%, 30% and 40% volume boron added and porous specimens were investigated and the effect of different pore and boron adding ratios on these properties of 316L stainless steel was studied. As a tube furnace with a capacity of 1200 °C was used in the studies, the sintering process was carried out at 1180 °C. Due to the insufficient sintering temperature and the inability to reach higher temperatures, the morpho-structural characterization results show that complete metallurgical bonding could not be achieved in boron added samples. On the other hand, it is observed that intergranular bonds are formed in porous samples. The decrease in intergranular bonding with increasing porosity again reveals the inadequacy of the heat treatment temperature. As a result of XRD analysis, B_2O_3 peaks were clearly formed in the structure due to heat treatment in boron added samples. In the Brinell hardness test results, the best values were obtained in porous samples due to the formation of intergranular bonds in the structure. In the compression test applied to porous samples, the highest strength was obtained as 39.5 MPa in 80SS/20PVA sample, while the lowest strength was measured as 26.2 MPa in 60SS/40PVA sample.

References

[1] Manivasagam G, Dhinasekaran D, Rajamanickam A. “Biomedical Implants: Corrosion and its Prevention - A Review,” *Recent Patents Corros. Sci.*, 2010; vol. 2, no. 1, pp. 40–54.

[2] Luthringer BJC, Feyerabend F, Willumeit-Römer R. “Magnesium-based implants: a mini-review,” *Magnes. Res.*, 2014; vol. 27, no. 4, pp. 142–54.

[3] Ali S *et al.* “Biocompatibility and corrosion resistance of metallic biomaterials,” *Corros. Rev.*, 2020; vol. 38, no. 5, pp. 381–402.

[4] Geetha M, Singh AK, Asokamani R, Gogia AK. “Ti based biomaterials, the ultimate choice for orthopaedic implants - A review,” *Prog. Mater. Sci.*, 2009; vol. 54, no. 3, pp. 397–425.

[5] Kang CW, Fang FZ. “State of the art of bioimplants manufacturing: part II,” *Adv. Manuf. 2018 62*, vol. 6, no. 2, pp. 137–154.

[6] Al-Amin M *et al.* “Investigation of Coatings, Corrosion and Wear Characteristics of Machined Biomaterials through Hydroxyapatite Mixed-EDM Process: A Review,” *Mater. 2021, Vol. 14, Page 3597*, vol. 14, no. 13, p. 3597.

[7] Mahapatro A. “Metals for biomedical applications and devices,” *J. Biomater. Tissue Eng.*, 2012; vol. 2, no. 4, pp. 259–268.

[8] Okazaki Y. “Selection of metals for biomedical devices,” *Met. Biomed.,* 2019; *Devices*, pp. 31–94.

[9] Patnaik L, Maity SR, Kumar S. “Status of nickel free stainless steel in biomedical field: A review of last 10 years and what else can be done,” *Mater. Today Proc.*, 2019; vol. 26, pp. 638–643.

[10] Gabilondo M, Cearsolo X, Arrue M, Castro F. “Influence of Build Orientation, Chamber Temperature and Infill Pattern on Mechanical Properties of 316L Parts Manufactured by Bound Metal Deposition,” *Mater. 2022, Vol. 15, Page 1183*, vol. 15, no. 3, p. 1183.

[11] Motallebzadeh A, Peighambardoust NS, Sheikh S, Murakami H, Guo S, Canadinc D. “Microstructural, mechanical and electrochemical characterization of TiZrTaHfNb and Ti1.5ZrTa0.5Hf0.5Nb0.5 refractory high-entropy alloys for biomedical applications,” *Intermetallics*, 2019; vol. 113, p. 106572.

[12] Essa K, Jamshidi P, Zou J, Attallah MM, Hassanin H. “Porosity control in 316L stainless steel using cold and hot isostatic pressing,” *Mater. Des.*, 2018; vol. 138, pp. 21–29.

[13] Ali S *et al.* “The Influence of Nitrogen Absorption on Microstructure, Properties and Cytotoxicity Assessment of 316L Stainless Steel Alloy Reinforced with Boron and Niobium,” *Process. 2019, Vol. 7, Page 506*, vol. 7, no. 8, p. 506.

[14] Hamidi MFA *et al.* “A review of biocompatible metal injection moulding process parameters for biomedical applications,” *Mater. Sci. Eng. C. Mater. Biol. Appl.*, 2017; vol. 78, pp. 1263–1276.

[15] Talha M., Behera CK, Sinha OP. “A review on nickel-free nitrogen containing austenitic stainless steels for biomedical applications,” *Mater. Sci. Eng. C*, 2013; vol. 33, no. 7, pp. 3563–3575.

[16] Molinari A, Kazior J, Marchetti F, Canteri R, Cristofolini I, Tiziani A. “Sintering Mechanisms of Boron Alloyed AISI 316L Stainless Steel,” vol. 37, no. 2, pp. 115–122, Jan. 2013.

[17] Molinari A, Kazior J, Straffelini G. “Investigation of liquid-phase sintering by image analysis,” *Mater. Charact.*, 1995; vol. 34, no. 4, pp. 271–276.

[18] Menapace C, Molinari A, Kazior J, Pieczonka T. “Surface self-densification in boron alloyed austenitic stainless steel and its effect on corrosion and impact resistance,” vol. 50, no. 4, pp. 326–335, Dec. 2013.

[19] Uzunsoy D. “Investigation of dry sliding wear properties of boron doped powder metallurgy 316L stainless steel,” *Mater. Des.*, 2010; vol. 31, no. 8, pp. 3896–3900.

[20] Gülsoy HÖ, “Production of injection moulded 316L stainless steels reinforced with TiC(N) particles,” vol. 24, no. 12, pp. 1484–1491, Dec. 2013.

[21] Ali S, Rani AMA, Altaf K, Baig Z. “Investigation of Boron addition and compaction pressure on the compactibility, densification and microhardness of 316L Stainless Steel,” *IOP Conf. Ser. Mater. Sci. Eng.*, 2018; vol. 344, no. 1.

[22] Choy MT, Tang CY, Chen , Wong CT, Tsui P. “In vitro and in vivo performance of bioactive Ti6Al4V/TiC/HA implants fabricated by a rapid microwave sintering technique,” *Mater. Sci. Eng. C*, 2014; vol. 42, pp. 746–756.

[23] Aslan N, Aksakal B. “Effect of graphene reinforcement on hybrid bioceramic coating deposited on the produced porous Ti64 alloys,” *J. Porous Mater.*, 2021; vol. 28, no. 4, pp. 1301–1313.

[24] Aslan N, Aksakal B, Findik F. “Fabrication of porous-Ti6Al4V alloy by using hot pressing technique and Mg space holder for hard-tissue biomedical applications,” *J. Mater. Sci. Mater. Med.*, 2021; vol. 32, no. 7, pp. 1–11.

[25] Topuz M, Dikici B, Gavgalı M. “Challenges in the Production of Titanium–based Scaffolds Bio–functionalized with Hydroxyapatite by Powder Metallurgy Technique,” *Avrupa Bilim ve Teknol. Derg.*, 2021; vol. 28, no. 28, pp. 46–51.

[26] Sulima I, Jaworska L, Karwan-Baczewska J. “Effect of boron sinteraid on the microstructure and properties of austenitic stainless Steel TiB2 composites,” *Arch. Metall. Mater.*, 2015; vol. 60, no. 4, pp. 2619–2624.

[27] Lozada L, Castro F. “Controlled densification of boron-containing stainless steels,” 2011.

[28] Skałoń M, Kazior J. “Enhanced sintering of austenitic stainless steel powder aisi 316L through boron containig master alloy addition,” *Arch. Metall. Mater.*, 2012; vol. 57, no. 3, pp. 789–797.

[29] Tran BH, Tieu K, Wan S, Zhu H, Cui S, Wang L. "Understanding the tribological impacts of alkali element on lubrication of binary borate melt," *RSC Adv.*, 2018; vol. 8, no. 51, pp. 28847–28860.

[30] Balci S, Sezgi NA, Eren E. "Boron Oxide Production Kinetics Using Boric Acid as Raw Material," *Ind. Eng. Chem. Res.*, 2012; vol. 51, no. 34, pp. 11091–11096.

[31] Spadaro F, Rossi A, Lainé E, Hartley J, Spencer ND. "Mechanical and tribological properties of boron oxide and zinc borate glasses," *Phys. Chem. Glas. Eur. J. Glas. Sci. Technol. Part B*, 2016; vol. 57, no. 6, pp. 233–244.

[32] Serafini FL *et al.* "Microstructure and mechanical behavior of 316L liquid phase sintered stainless steel with boron addition," *Mater. Charact.*, 2019; vol. 152, pp. 253–264.

[33] Peruzzo M, Serafini FL, Ordoñez MF, Souza RM, Farias MCM. "Reciprocating sliding wear of the sintered 316L stainless steel with boron additions," *Wear*, 2019; vol. 422–423, pp. 108–118.

[34] Dewidar MM, Khalil KA, Lim JK. "Processing and mechanical properties of porous 316L stainless steel for biomedical applications," *Trans. Nonferrous Met. Soc. China*, 2007; vol. 17, no. 3, pp. 468–473.