Iğdır Üniversitesi Fen Bilimleri Enstitüsü Dergisi, 14(1), 412 - 421, 2024
Journal of the Institute of Science and Technology, 14(1), 412 - 421, 2024

ISSN: 2146-0574, eISSN: 2536-4618

Metalurji ve Malzeme Mühendisliği / *Metallurgical and Materials Engineering*

DOI: 10.21597/jist.1301838

Araştırma Makalesi / *Research Article*

Geliş tarihi / *Received*: 24.05.2023 **Kabul tarihi / *Accepted*: 16.10.2023**

To Cite: İçin, K., Sezer, R. & Sünbül, S. E. (2024). Enhancing the Structural and Mechanical Properties of Ti-Zr Alloy through Boron Doping. *Journal of the Institute of Science and Technology*, 14(1), 412 - 421.

Enhancing the Structural and Mechanical Properties of Ti-Zr Alloy through Boron Doping

Kürşat İÇİN[1*], Sefa Emre SÜNBÜL[2], Raşit SEZER[1]

Highlights:

- Boron promotes TiB intermetallic phase formation in Ti15Zr-B alloys.
- Increasing boron content enhances hardness in Ti-Zr-B alloys.
- Small amounts of boron improve tensile and yield strength, but excessive amounts decrease strength

Keywords:

- Ti-15Zr
- Boron Doping
- Vacuum Arc Melting
- Mechanical properties

ABSTRACT:

This study aims to improve the structural strength of the commonly used Ti-15Zr alloy in dental applications by investigating the effects of low boron additions. Ti-15Zr alloys containing 1-4% boron have been produced by vacuum arc melting. The phase ratios in the microstructure of the produced alloys vary according to the boron content. With increasing boron content, the ratio of TiB compound in the phase structure increases. The hardness of Ti-Zr-B alloys exhibited a notable increase in correlation with rising boron content. Measured hardness values of 36.31, 39.50, 44.14, and 53.40 displayed a clear upward trend with higher boron percentages. The tensile strength of the Ti-Zr-B alloys exhibits a trend of initially increasing with boron content, reaching its highest value of 888 MPa at 1% boron. The yield strength follows a similar with tensile strengh, with an initial rise from 449 MPa at 0% boron to a peak of 562 MPa at 1% boron content. Beyond this point, the yield strength slightly decreases to 469 MPa at 2% boron but sharply drops to 186 MPa at 4% boron content. As boron content increases in the Ti-Zr-B alloys, the percentage elongation, indicating the material's plastic deformation capacity before fracture, consistently decreases from 17.03% at 0% boron to 0.70% at 4% boron content.

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INTRODUCTION

Continuous research has been conducted on implantation since its first modern production in 1960. As a result of the constantly evolving implant technology, individuals can achieve a healthy life with a success rate of 96-98% through simple surgical interventions. Over the past fifty years, the biocompatibility and osseointegration (compatibility with living bone tissue) durations of dental implant materials such as Ti alloys and CoCr alloys have become current research topics. The presence of the Cr^{4+} ion resulting from the dissolution of the Cr element in CoCr alloys has placed chromium in the list of toxic elements today due to the various diseases it causes in human health. Cr^{4+} ion has been reported to be toxic and carcinogenic (lung cancer) even if ingested with food (Achmad et al., 2017; Gev et al., 2019; Jiang et al., 2019).

Among the many dental implant materials developed to date, Ti-based alloys have become one of the most popular dental implant materials in terms of both biocompatibility and osseointegration duration, thanks to their superior biocompatibility and shorter osseointegration periods (Ferlic et al., 2020). In the research conducted to date, pure commercial titanium (cpTi) has been found to be suitable for use as an implant material due to its high specific density, corrosion resistance, biocompatibility, and low cost (Kaczmarek et al., 2016). However, the inadequate mechanical properties such as hardness, wear resistance, and strength, in addition to the mentioned characteristics, limit the use of titanium metal (Zhu et al., 2003). In implant applications, the most significant feature that comes to mind is biocompatibility rather than mechanical, chemical, or physical properties (Demirci et al., 2015). However, the alloy to be used as an implant must not cause toxicological or allergic reactions in human health. In this regard, the most suitable titanium alloy, Ti-6Al-4V alloy, is the most commonly used dental implant material in the implant industry due to its better physical and mechanical properties compared to pure titanium. However, research has raised concerns that the release of Al and V ions during the use of the Ti-6Al-4V alloy may cause health problems in the long term (Ho et al., 2008; Ho et al., 2009). In line with these concerns, a study reported that these ions could lead to neurological problems such as Alzheimer's disease and various deformations in tissues (Correa et al., 2014). Based on the findings obtained from these studies, new-generation dental implant materials, known as β-phase alloys, have emerged by using elements with higher biocompatibility such as Nb, Zr, and Mo instead of Al and V, which can cause various diseases in the body (Medvedev et al., 2016). Recently, research has been conducted on binary alloy systems such as Ti-Zr, Ti-Mo, Ti-Hf, and Ti-Ta as alternative materials for dental implants and prostheses. Commercialization of Ti-based alloys using high-melting elements such as Ta (Melting point, 2996 °C), Hf (Melting point, 2225 °C), and Mo (Melting point, 2615 °C) has not been possible due to technical challenges and limited biological compatibility.

The main reason for the use and commercialization of TiZr alloys as implant materials is the unlimited solubility of the two elements in each other, according to the Ti-Zr binary phase diagram. This allows for solid solution strengthening of these alloys. Therefore, the low mechanical properties of Ti can be improved through solid solution strengthening by adding Zr to its structure. The presence of a single β(Ti,Zr) phase at high temperatures and an α(Ti,Zr) phase at low temperatures distinguishes this alloy from others. Due to this characteristic, there is no specific critical ratio for the alloy formed by adding Zr to the Ti structure. Different studies have investigated the effects of adding zirconium to the alloy on its overall mechanical and antibacterial properties to determine the suitable Zr ratio.

In a study by Kobayashi et al., Ti-Zr binary systems with different ratios were examined in terms of mechanical properties, and the highest hardness was found in the composition of 50% Ti-50% Zr, while the highest tensile strength was obtained in the composition of 75% Ti-25% Zr (Kobayashi et al., 1995). According to the study conducted by Ho et al. on Ti-Zr binary systems, Ti-10Zr, T-20Zr, Ti-30Zr, and T-40Zr alloys were produced by arc melting, and their structural properties, mechanical properties, and wear resistance were investigated. The investigations showed that hardness and flexural strength increased with increasing Zr content. The hardness of pure Ti was 186 $Hv_{0.1}$, while it was determined as 266 HV0.1 for Ti-10Zr and 350 $Hv_{0.1}$ for Ti-40Zr. Flexural strengths also exhibited similar trends with an increase in Zr content. However, flexural and elastic moduli were higher than that of pure Ti but decreased with increasing Zr content, and the highest flexural modulus was achieved in Ti-10Zr. The high elastic modulus of Ti-10Zr indicates good workability. Similarly, its wear resistance was better compared to other alloys (Ho et al., 2008). These properties of the Ti-10Zr alloy demonstrate the desirable characteristics expected from an ideal implant material.

In a different study, Ti-15Zr alloy was compared with Ti-grade4 in terms of microstructure and mechanical properties. It was found that Ti-15Zr alloy had a smaller grain size and higher tensile strength compared to Ti-grade4. Additionally, the fatigue limit of Ti-15Zr alloy was 30% higher. Based on this study, Ti-15Zr alloy was suggested as a promising candidate for dental implant materials (Correa et al., 2014). The addition of boron to titanium and zirconium alloys has been investigated in many studies, where boride precipitates such as Ti-B (Zhu et al., 2003; Tamirisakandala et al., 2005; Louzguina-Luzgina et al., 2009;) and Zr-B (Chui, 2018; Xia et al., 2015) have been formed. In these studies, it has been found that the addition of boron in small amounts enhances the mechanical properties. Due to the much smaller atomic radius of boron (85 pm) compared to titanium (140 pm) and zirconium (155 pm), it can enter the interstitial sites within the HCP crystal structure (approximately 26% void fraction) and improve the mechanical properties (Correa et al., 2018; Pan et al., 2019). According to the the Ti-B phase diagram, it can be observed that Ti-B alloys containing trace amounts of boron form α-Ti and TiB (intermetallic) phases at low temperatures (T<884°C), while β-Ti and TiB phases form at high temperatures (884<T<1540). A similar situation is observed in the Zr-B binary phase diagram, where the addition of boron in low proportions (up to 4 wt.%) will result in the formation of intermetallic phases (TiB and ZrB_2) along with (α-Ti, Zr). Furthermore, it has been found in the conducted studies that the addition of boron in different proportions alters the morphology of the phases formed in the microstructure of titanium and zirconium alloys.

In the scope of the research, it is proposed to address these disadvantages of titanium by improving its mechanical properties, enhancing biocompatibility, and shortening the osseointegration period through the addition of 15% by weight of Zr and varying amounts of the B element (0-4%) to Ti metal. Despite the investigation of the effects of boron on the properties of metal materials such as Ti and Zr in many publications based on binary (Ti-B/Zr-B) alloys and the improvement of dental properties, the contribution of the B element in the Ti-15Zr alloy, which has superior dental implant properties, has not been investigated. Therefore, below, the reasons for selecting the Ti-Zr alloy in line with the research's objectives and subsequently why boron is chosen to be added to the binary system and how it affects the properties are explained. To investigate the structural and mechanical effects of low percentages (1, 2, and 4%) of boron addition on the Ti-15Zr alloy, commonly used in dental applications, and explore the potential for creating a structurally stronger alloy for dental applications. To achieve this objective, Ti-15Zr-xB alloys were produced using the vacuum arc melting method, which enables high-temperature processing. The mechanical properties and structural characteristics of the produced alloys were thoroughly examined, taking into account the specific requirements of dental applications.

MATERIALS AND METHODS

In order to prepare the relevant alloys, high-purity titanium (Ti), zirconium (Zr), and boron (B) metals were obtained in rod and ingot forms from domestic and international companies. Using the respective pure elements, the primary alloy of the project, Ti15Zr binary alloy, was first prepared, followed by the preparation of Ti15Zr-xB ternary alloys. For the prepared binary alloy, the metals were melted and alloyed in a vacuum arc melting device. Each alloy was melted five times, alternating between upright and inverted positions. After the five melting cycles, Ti15Zr, Ti15Zr-1B, Ti15Zr-2B, and Ti15Zr-4B alloys were prepared in six different compositions. The elemental ratios for these alloys are given in Table 1.

Table 1. Chemical composition of Ti15Zr-xB ternary alloys

	Ti (g)	Zr (g)	B (g)	Ti (wt.%)	Zr (wt.%)	B (wt.%)
Ti15Zr	9.60	1.69	0.00	85.03	14.97	0.00
Ti15Zr-1B	9.49	1.69	0.12	83.98	14.96	1.06
Ti15Zr-2B	9.37	1.69	0.23	83.03	14.97	2.00
Ti15Zr-4B	9.15	1.69	0.45	81.03	14.97	4.00

The alloying processes of the prepared elements were carried out using a vacuum arc melting device operated with a non-consumable electrode (tungsten). The external appearance of the vacuum arc melting device, along with the supporting equipment and control mechanism, as well as a technical drawing, are presented in Figure 1. It was determined that the metallic elements in ingot form did not undergo any contamination resulting from the crucible during the melting process. The copper crucible used for melting was water-cooled and showed no signs of deterioration, deformation, or adhesion during the melting process. Furthermore, thanks to the PLC software, the temperature of the water cooling the copper crucible can be continuously monitored from the control screen of the arc melting device.

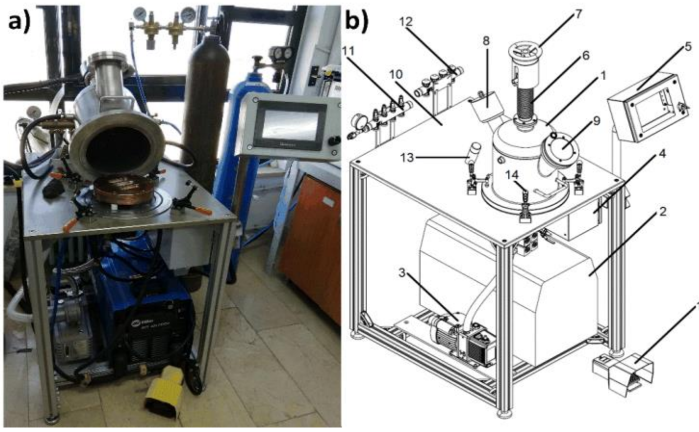

Figure 1. Vacuum arc melting experimental setup a) Photograph image, b) schematic picture (1: Sleeve, 2: Power unit, 3: Vacuum pump, 4: Control panel, 5: Control unit, 6: Bellows, 7: Electrode movement wheel, 8: Lighting window, 9: Observation window, 10: Tray, 11: Water inlet control circuit, 12: Water outlet control circuit, 13: Supporting apparatus, 14: Stabilizing hinge, 15: Arc control pedal)

The effect of boron on the phase formations of the alloys produced by the arc melting method was determined by x-ray diffractometry technique (XRD). In addition, hardness and tensile tests were applied to determine the effects of boron Ti-15Zr alloy on hardness, yield, tensile stress and elongation. Before proceeding to these analyses, 4 different alloys produced by arc melting were divided into pieces by wire erosion method. The oxide layer formed on the surface due to the cooling liquid used during wire erosion cutting was removed by grinding. XRD analyzes were performed with a PANalytical brand Xpert Powder[3] model device at room temperature using Cu Kα radiation (λ = 1.5406 Å)at a scanning speed of

0.013 degrees/minute between 20-80º. After X-ray analysis, Rockwell hardness analysis was applied to all alloys using 150 kgf. Hardness measurements were repeated from 5 different points on the surface of each sample and the hardness value was determined according to the average of the measurements. Innovatest mark Nemesis 9000 series universal hardness measurement system was used to measure the hardness values.In order to apply tensile tests to the produced alloys, the samples were cut with wire erosion in the dimensions of 1.51x2.6x10 mm (thickness, width, length) and their surfaces were ground. Tensile tests were performed with an Instron 3382 model tensile tester at a deformation rate of $5x10^{-4}$ mm/s. Three samples were prepared for the tensile tests and the average yield, tensile strength and elongation were determined.

RESULTS AND DISCUSSION

Solidification of Ti-Zr alloys prepared through arc melting method was followed by phase identification using X-ray diffraction (XRD) analysis. The XRD patterns of the obtained alloys are presented in Figure 2. In the boron-free Ti15Zr alloy, diffraction peaks corresponding to the Ti-Zr binary alloy phase were observed. Titanium and zirconium metals have similar chemical and physical properties, allowing them to dissolve in each other in any proportion (as per Hume-Rothery rules). Therefore, Ti-Zr alloys form a single phase regardless of the alloy composition. By introducing boron (B) in different amounts to the Ti15Zr alloy, the formation of the TiB intermetallic phase was observed. No peaks corresponding to other intermetallic phases such as TiB_2 and ZrB were detected (Kuroda, et al. 1998). This is because under the given conditions, TiB is the most stable phase among the possible boride phases. The presence of TiB intermetallic phase in the Ti15Zr-B alloys can be attributed to the reaction between boron and the alloying elements during solidification. Boron atoms substitute for titanium or zirconium atoms in the crystal lattice, leading to the formation of TiB. The intensity and position of the TiB peaks varied with the boron content, indicating a change in the volume fraction and lattice parameters of the TiB phase. The formation of TiB intermetallic phase can have significant effects on the properties of Ti-Zr alloys. TiB is known for its high hardness, excellent wear resistance, and thermal stability. The presence of TiB can improve the mechanical properties of Ti-Zr alloys, such as hardness, strength, and wear resistance. Furthermore, TiB has a beneficial effect on the microstructure of the alloys, refining the grain size and promoting a more homogeneous distribution of phases. The XRD analysis provides valuable information about the phase composition and crystallographic characteristics of the Ti-Zr-B alloys. It confirms the formation of a single Ti-Zr phase in the boron-free alloy and the subsequent formation of TiB intermetallic phase with the addition of boron. The presence of TiB phase opens up possibilities for tailoring the mechanical and structural properties of Ti-Zr alloys for various applications, including aerospace, biomedical, and automotive industries. In conclusion, the XRD analysis of the Ti-Zr-B alloys revealed the formation of the Ti-Zr phase in the boron-free alloy and the formation of TiB intermetallic phase with the addition of boron (Grandin et al., 2012). The findings highlight the potential for improving the properties of Ti-Zr alloys by controlling the boron content and the resulting phase composition. Further investigations can focus on characterizing the mechanical, thermal, and corrosion properties of these alloys to assess their suitability for specific applications (Uluisik, et al., 2018).

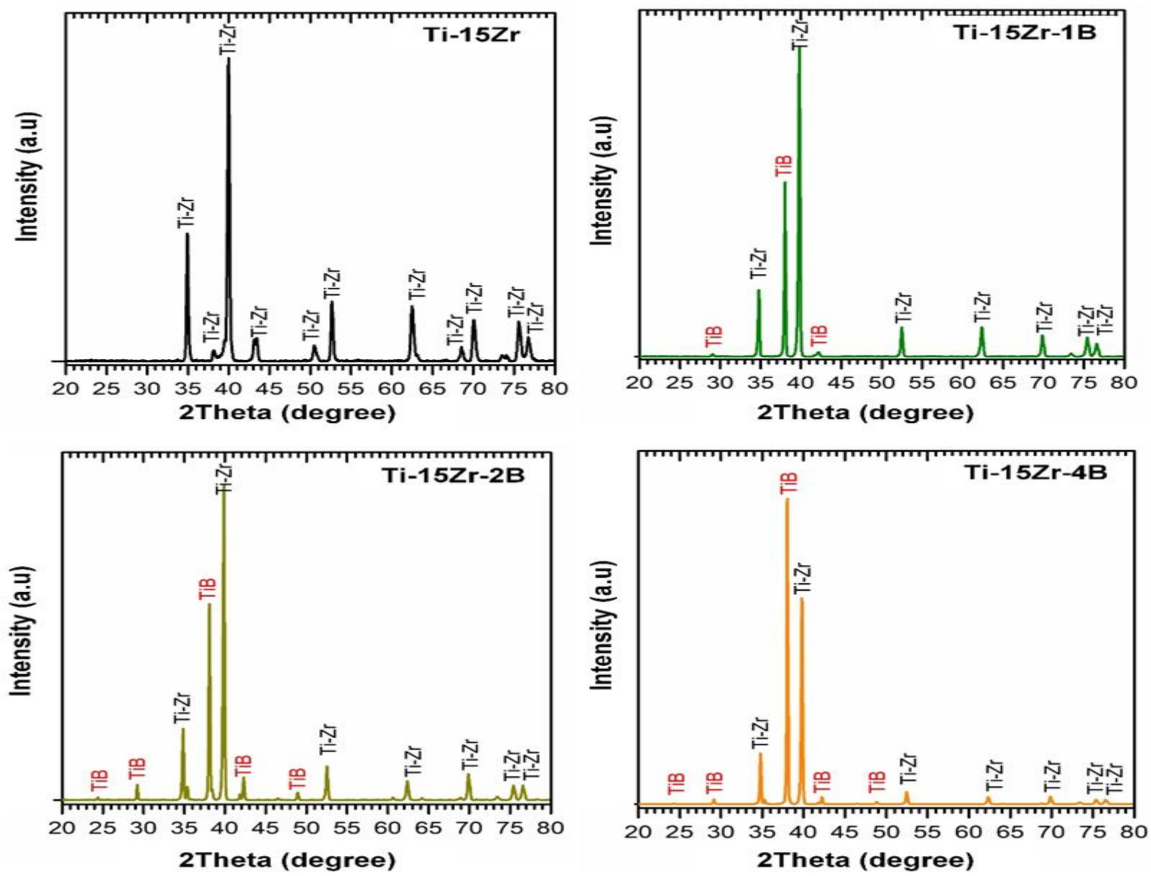

Figure 2. XRD plots of the Ti-15Zr-xB (x=0, 1, 2 and 4) alloys

The hardness of Ti-Zr-B alloys can be influenced by the formation of the TiB intermetallic compound. In order to evaluate the hardness variations with respect to the TiB phase content, the hardness values at different boron (B) percentages were measured as 36.31, 39.50, 44.14 and 53.40, respectively. The hardness of the alloys show a clear trend of increasing hardness with an increase in the boron content. This can be attributed to the presence of the TiB intermetallic phase, which is known for its high hardness. As the boron content increases, the volume fraction of TiB phase in the alloy also increases, leading to a greater contribution of the hard TiB phase to the overall hardness of the material. The observed increase in hardness can be explained by the strengthening mechanisms associated with the TiB phase. The presence of a second phase, such as TiB, can hinder the movement of dislocations, thereby impeding plastic deformation and increasing the material's resistance to indentation. Additionally, the high hardness of the TiB phase itself contributes to the overall hardness of the alloy. The relationship between boron content and hardness can be understood by considering the atomic size and crystal structure of the TiB phase. Boron has a smaller atomic radius compared to titanium and zirconium, which allows it to occupy interstitial sites within the crystal lattice of the alloy. This leads to the formation of the TiB phase, which has a different crystal structure and distinct mechanical properties compared to the Ti-Zr matrix. The presence of the TiB phase contributes to the strengthening of the alloy, resulting in higher hardness values. The observed increase in hardness with increasing boron content suggests that the TiB phase plays a significant role in determining the mechanical properties of Ti-Zr-B alloys. By controlling the boron content, it is possible to tailor the hardness and mechanical properties of the alloys to meet specific application requirements (Sopchenski et al., 2018; Pereira, et al., 2011). Higher boron contents result in a higher volume fraction of TiB phase and, consequently, increased hardness. It is important to note that hardness is just one aspect of the overall mechanical behavior of materials. Other mechanical properties, such as tensile strength, ductility, and fracture toughness, should also be considered for a comprehensive assessment of the alloy's performance. Further studies can focus on investigating these properties to gain a more comprehensive understanding of the relationship between boron content, TiB phase formation, and mechanical behavior in Ti-Zr-B alloys. In conclusion, the hardness values of the Ti-Zr-B alloys increase with increasing boron content due to the formation of the TiB intermetallic phase. The presence of the TiB phase, known for its high hardness, contributes to the overall hardness of the alloy. This relationship between boron content and hardness provides opportunities for tailoring the mechanical properties of Ti-Zr-B alloys for specific applications that require enhanced hardness and wear resistance (Xue, et al., 2013).

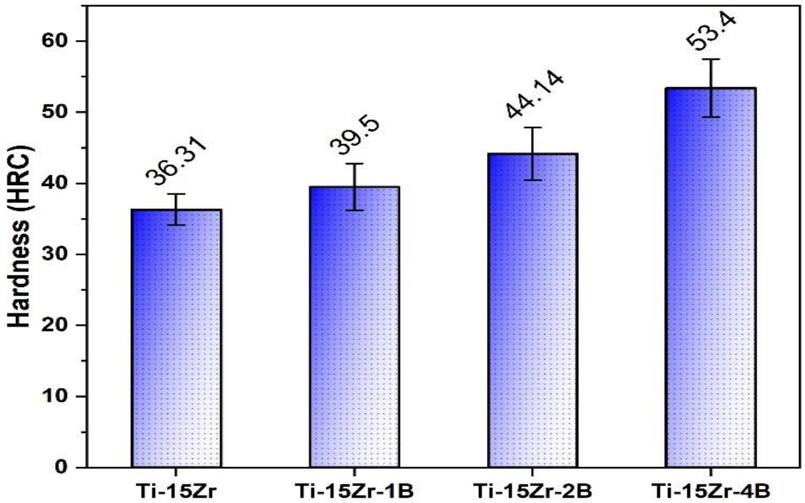

Figure 3. Effect of B addition to Ti-15Zr alloy on hardness

From the tensile test results, several observations can be made regarding the tensile properties of the Ti-Zr-B alloys as the boron content varies. The tensile strength, which represents the maximum stress the material can withstand before failure, shows a slight increase from 772 MPa to 888 MPa as the boron content increases from 0% to 2%. However, there is a significant drop to 231 MPa at 4% boron content. This indicates that the addition of a small amount of boron can enhance the tensile strength, but an excessive increase in boron content can lead to a decrease in strength. The yield strength, which signifies the stress at which plastic deformation begins, exhibits a similar trend as the tensile strength. It increases from 449 MPa to 562 MPa with the addition of 1% boron and then slightly decreases to 469 MPa at 2% boron content. However, the yield strength drops significantly to 186 MPa at 4% boron content. Elongation refers to the ability of a material to deform plastically before fracture. The data shows that the elongation decreases with increasing boron content. At 0% boron, the alloy exhibits an elongation of 17.03%, which decreases to 7.51% and 8.54% at 1% and 2% boron content, respectively. The lowest elongation value of 0.70% is observed at 4% boron content. The observed trends in the tensile properties can be explained by the influence of boron on the microstructure and mechanical behavior of the Ti-Zr-B alloys. The addition of boron can alter the grain structure, precipitate phases, and influence the deformation mechanisms within the alloy.

In the case of low boron content (1-2%), the presence of the TiB intermetallic phase, known for its high hardness, can contribute to the enhancement of strength and yield strength. The intermetallic phase acts as a strengthening agent, impeding dislocation motion and leading to an increase in the strength of the material (Zhang, et al. 2018). However, at higher boron content (4%), the formation of excessive boride phases may result in decreased strength and ductility due to their brittle nature. The decrease in elongation with increasing boron content can be attributed to the formation of brittle phases or the suppression of ductile deformation mechanisms. The presence of intermetallic phases, such as

TiB, can hinder plastic deformation and reduce the material's ability to elongate before fracture. It is important to note that the tensile properties are influenced not only by the boron content but also by other factors such as alloy composition, processing conditions, and microstructure. Further investigations can focus on optimizing the boron content and alloy composition to achieve a balance between strength and ductility for specific application requirements. Medvedev et al. (Medvedev, et al. 2016) found the mechanical properties of Ti15Zr alloy produced by selective laser melting (SLM) method to be yield strength of 784±34 MPa, the ultimate strength of 987±35 MPa and elongation of 6.0±0.7%. When this study is compared with our study, almost similar mechanical properties were found without any optimizing process, such as homogenization, heat treatment etc. Xia et al. found the yield strength (σ0.2), the ultimate strength (σb) and the elongation-to-failure (εf) values for Ti-25Zr-1B as-cast alloy to be 754.67 MPa, 924.80 MPa and 3.69%, respectively (Xia, et al. 2018).

In summary, the tensile test data shows that the addition of a small amount of boron (1-2%) can enhance the tensile strength and yield strength of Ti-Zr-B alloys, while excessive boron content (4%) leads to a decrease in strength. However, the elongation is negatively affected by increasing boron content, resulting in reduced ductility. The observed trends highlight the complex relationship between boron content, microstructure, and mechanical properties in Ti-Zr-B alloys.

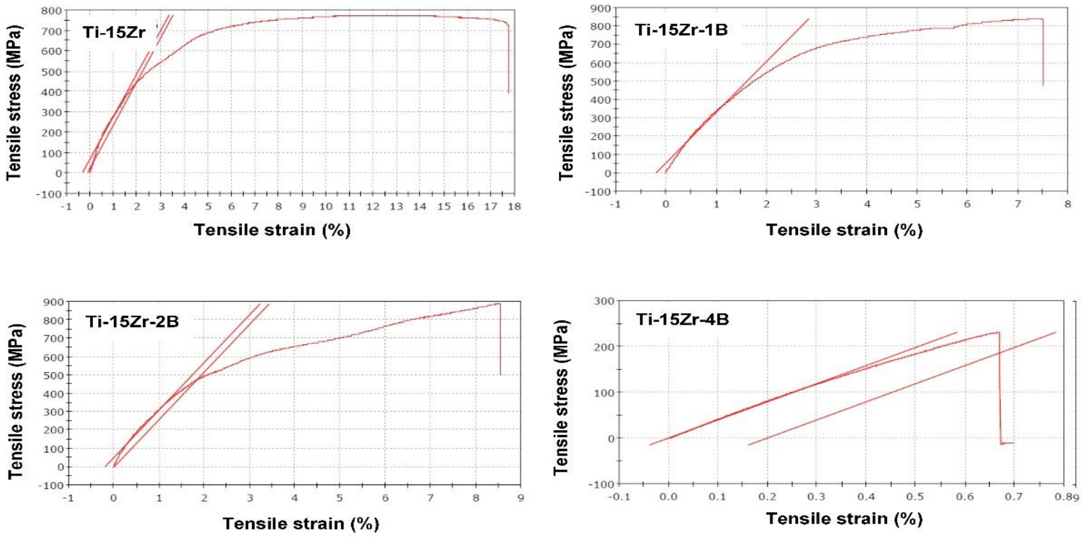

Figure 4. Variation of stress-strain curves according to boron ratio in Ti-15Zr alloy

CONCLUSION

The Ti15Zr-xB (x=0, 1, 2, and 4) alloys produced through vacuum arc melting method have shown promising results in terms of their structural and mechanical properties. The changes in the structural and mechanical properties of the alloys produced are briefly summarized below.

• The addition of boron resulted in the formation of the TiB intermetallic phase in the Ti15Zr-B alloys. No peaks corresponding to other intermetallic phases such as TiB2 and ZrB were detected.

• The hardness of Ti-Zr-B alloys increases significantly as the boron content increases. The measured hardness values of 36.31, 39.50, 44.14, and 53.40 demonstrate a clear trend of increasing hardness with higher boron percentages.

• Tensile strength and yield strength generally increase with the addition of a small amount of boron (1-2%), indicating that boron can enhance the strength of the alloys. However, excessive boron content (4%) leads to a significant decrease in strength.

• Elongation decreases as the boron content increases, indicating a decrease in ductility. Higher boron content restricts plastic deformation, resulting in reduced elongation before fracture..

ACKNOWLEDGEMENTS

This study was supported by Karadeniz Technical University University Scientific Research Projects Coordination Unit with Project number of FBA-2020-8810.

Conflict of Interest

Authors approve that to the best of their knowledge, there is not any conflict of interest or common interest with an institution/organization or a person that may affect the review process of the paper.

Author's Contributions

The authors declare that they have contributed equally to the article.

REFERENCES

Achmad, R., B. Budiawan and E. Auerkari (2017). "Effects of Chromium on Human Body." Annual *Research & Review in Biology* 13(2): 1-8.

Chui, P. F. (2018). "Effect of boron content on microstructure and mechanical properties of Ti50Zr50 alloys." *Vacuum* 154: 25-31.

Correa, D. R. N., P. A. B. Kuroda, M. L. Lourenco, M. A. R. Buzalaf, M. E. Mendoza, B. S. Archanjo, C. A. Achete, L. A. Rocha and C. R. Grandini (2018). "Microstructure and selected mechanical properties of aged Ti-15Zr-based alloys for biomedical applications." *Materials Science & Engineering C-Materials for Biological Applications* 91: 762-771.

Correa, D. R. N., F. B. Vicente, T. A. G. Donato, V. E. Arana-Chavez, M. A. R. Buzalaf and C. R. Grandini (2014). "The effect of the solute on the structure, selected mechanical properties, and biocompatibility of Ti-Zr system alloys for dental applications." *Materials Science & Engineering C-Materials for Biological Applications* 34: 354-359.

Demirci, S., M. S. Kaya, A. Dogan, S. Kalay, N. O. Altin, A. Yarat, S. H. Akyuz and F. Sahin (2015). "Antibacterial and cytotoxic properties of boron-containing dental composite." *Turkish Journal of Biology* 39(3): 417-426.

Ge, H., Z. Li, L. Jiang, Q. Li, C. Geng, X. Yao, X. Shi, Y. Liu and J. Cao (2019). "Cr (VI) induces crosstalk between apoptosis and autophagy through endoplasmic reticulum stress in A549 cells." *Chemico-Biological Interactions* 298: 35-42.

Grandin, H. M., S. Berner and M. Dard (2012). "A Review of Titanium Zirconium (TiZr) Alloys for Use in Endosseous Dental Implants." *Materials* 5(8): 1348-1360.

Ho, W. F., W. K. Chen, S. C. Wu and H. C. Hsu (2008). "Structure, mechanical properties, and grindability of dental Ti-Zr alloys." *Journal of Materials Science-Materials in Medicine* 19(10): 3179-3186.

Ho, W. F., C. H. Cheng, C. H. Pan, S. C. Wu and H. C. Hsu (2009). "Structure, mechanical properties and grindability of dental Ti-10Zr-X alloys." *Materials Science & Engineering CBiomimetic and Supramolecular Systems* 29(1): 36-43.

Jiang, F., W. Zhu, C. Zhao, Y. Li, P. Wei, T. Wan, H. Ye, S. Pan and F. Ren (2019). "A strong, wear- and corrosion-resistant, and antibacterial Co–30 at.% Cr–5 at.% Ag ternary alloy for medical implants." *Materials & Design* 184: 108190.

Kaczmarek, M., M. U. Jurczyk, A. Miklaszewski, A. Paszel-Jaworska, A. Romaniuk, N. Lipinska, J. Zurawski, P. Urbaniak and K. Jurczyk (2016). "In vitro biocompatibility of titanium after plasma surface alloying with boron." *Materials Science & Engineering C-Materials for Biological Application*s 69: 1240-1247.

Kobayashi, E., S. Matsumoto, H. Doi, T. Yoneyama and H. Hamanaka (1995). "Mechanical- Properties of the Binary Titanium-Zirconium Alloys and Their Potential for Biomedical Materials." *Journal of Biomedical Materials Research* 29(8): 943-950.

Louzguina-Luzgina, L. V., D. V. Louzguine-Luzgin and A. Inoue (2009). "Effect of B addition to hypereutectic Ti-based alloys." *Journal of Alloys and Compounds* 474(1-2): 131-133.

Medvedev, A. E., A. Molotnikov, R. Lapovok, R. Zeller, S. Berner, P. Habersetzer and F. Dalla Torre (2016). "Microstructure and mechanical properties of Ti-15Zr alloy used as dental implant material." *Journal of the Mechanical Behavior of Biomedical Materials* 62: 384-398.

Pan, Y. F., C. Zhang, J. X. Zhang, L. Huang, X. Y. Yang, Y. Dui and F. H. Luo (2019)."Thermodynamic Modeling of the B-Ti-Zr System Over the Whole Composition and Temperature Ranges." *Journal of Phase Equilibria and Diffusion* 40(3): 364-374.

Pereira, C., E. Eskelson, V. Cavalli, P. Liporoni, A. Jorge and M. d. Rego (2011). "Streptococcus mutans Biofilm Adhesion on Composite Resin Surfaces After Different Finishing and Polishing Techniques." 36(3): 311-317.

Sopchenski, L., S. Cogo, M. F. Dias-Ntipanyj, S. Elifio-Espósito, K. C. Popat and P. Soares (2018). "Bioactive and antibacterial boron doped TiO2 coating obtained by PEO." *Applied Surface Science* 458: 49-58.

Tamirisakandala, S., R. B. Bhat, J. S. Tiley and D. B. Miracle (2005). "Grain refinement of cast titanium alloys via trace boron addition." *Scripta Materialia* 53(12): 1421-1426.

Uluisik, I., H. C. Karakaya and A. Koc (2018). "The importance of boron in biological systems." *Journal of Trace Elements in Medicine and Biology* 45: 156-162.

Xia, C. Q., X. J. Jiang, X. Y. Wang, Y. K. Zhou, Z. H. Feng, C. L. Tan, M. Z. Ma and R. P. Liu (2015). "Structure and mechanical properties of as-cast (ZrTi)(100-x)B-x alloys." *Journal of Alloys and Compounds* 637: 90-97.

Xia, C., Zhang, X., Liu, S., Chen, B., Tan, C., Zhang, X., Ma, M. and Liu. R. (2018). "Thermo-mechanical processing, microstructure and mechanical properties of TiZrB alloy." *Materials Science and Engineering: A* 712: 350-357.

Xue, X., Y. Wang and H. Yang (2013). "Preparation and characterization of boron-doped titania nano-materials with antibacterial activity." *Applied Surface Science* 264: 94-99.

Zhang, C. J., F. T. Kong, S. L. Xiao, E. T. Zhao, L. J. Xu and Y. Y. Chen (2012). "Evolution of microstructure and tensile properties of in situ titanium matrix composites with volume fraction of (TiB plus TiC) reinforcements." *Materials Science and Engineering a-Structural Materials Properties Microstructure and Processing* 548: 152-160.

Zhu, J., A. Kamiya, T. Yamada, W. Shi and K. Naganuma (2003). "Influence of boron addition on microstructure and mechanical properties of dental cast titanium alloys." *Materials Science and Engineering A-Structural Materials Properties Microstructure and Processing* 339(1-2): 53- 62.