



Bioactive apatite–wollastonite glass ceramics coating on metallic titanium for biomedical applications: effect of boron

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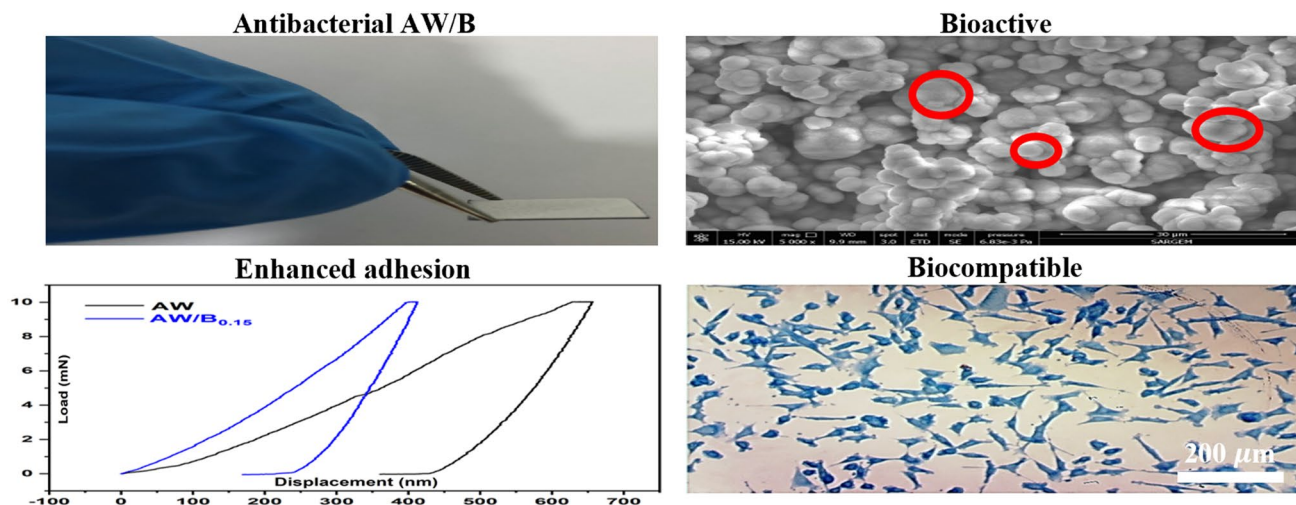
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Abstract

Metallic titanium (Ti) implant surfaces need improvement for bioproperties and antibacterial behavior. For this purpose, a new boron-doped bioactive apatite–wollastonite (AW) coating was successfully developed on the Ti plate surface. The effects of boron addition on the microstructure, mechanical properties, and bioproperties of the AW coating were investigated. With the addition of boron (B), the AW coating morphology became less porous and compact. In terms of bio properties, the rate of apatite formation increased with the addition of B, and the cell viability rate increased from approximately 66–81%. B addition increased the elastic modulus of the AW coating from about 24–46 GPa and increased its hardness about 2.5 times. In addition, while no antibacterial activity was observed in the AW coating, the addition of boron slightly introduced antibacterial properties. The novel AW/B composite coating obtained is promising for Ti implant surfaces.

Graphical abstract



Keywords Titanium implant · Boron · Apatite–wollastonite · Coating

Introduction

Titanium (Ti) and its alloys are the most suitable candidates for bone replacement implant materials due to their load-bearing potential, non-toxicity, and biocompatibility [1–3]. However, due to their bioinert surfaces, their bonding to the

surrounding living bone tissue is weak, which weakens their osseointegration feature. In addition, in terms of mechanical properties, the elastic modulus of Ti and its alloys is higher than that of bone, although low compared to other metallic materials [4]. This creates a ‘stress shielding effect’, leading to the problem of implant loosening [5]. In addition, Ti and its alloys do not show antibacterial properties [6].

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These problems can be eliminated with bioactive ceramic or glass–ceramic-based coatings [7, 8]. Calcium phosphate-containing materials such as hydroxyapatite (HA) and tricalcium phosphate are the most commonly used bioactive coatings due to their high biocompatibility and ability to form apatite as a result of ion exchange reactions in body fluid [9, 10]. Previous studies have also reported that apatite–wollastonite (AW) glass ceramic induces apatite formation after implantation [11]. In these studies, wollastonite (W) was produced as a compact piece and as a coating material [12]. In the studies of Lakshmi et al. and Ming et al., respectively, W and AW were produced in bulk (in pellet form), and characterization and biocompatibility studies were carried out [13–16]. On the other hand, Bao et al. and Liu et al., in their studies, coated W on the surface of Ti and its alloys and observed the characterization and apatite formation capabilities of the coatings [17, 18]. W (CaSiO_3), a calcium silicate bioactive ceramic, appears to be the desired material to enhance bone tissue regeneration.

Bioactive ceramics or glass ceramics are used as fillers in many cases of significant bone loss, such as trauma, cancer, congenital abnormalities, or bone deficiency. They are also used as a coating material on metallic implant surfaces [16, 19]. However, the low fracture toughness of ceramic or glass–ceramic materials limits their use. Polymer (collagen, chitosan, etc.) or metallic ion (magnesium, silver, strontium, zinc, etc.) additives have been widely studied in recent years to improve the mechanical properties, cell behavior, and antibacterial characteristics of calcium-phosphorus-based biomaterials [20]. Boron (B), a remarkable trace element, especially in humans, is known to have numerous functions in the regulation of bone metabolism [12, 21]. In animal experiments, B supplementation has been reported to reduce the effects of vitamin D deficiency. Boron deprivation in animals leads to impaired growth and abnormal bone development. Another study showed that supplementing B as boric acid improved bone structure and strength in rats. It has also been found that daily supplementation of 1 mg/L of B in postmenopausal women significantly improves bone osteocalcin levels [22]. Therefore, researchers focused on synthesizing boron-doped HA as a candidate for biomedical applications and investigating its structural, mechanical, and biological properties. EO Tuncay et al., in their study, increased the proliferation and osteoblastic differentiation of MC3T3-E1 cells by adding B to the HA coating [23]. Aksoy et al., on the other hand, increased the adhesion strength of the coating by adding B to the HA coating and improved the corrosion resistance [24]. The number of studies in which B reinforcement was carried out on glass–ceramic-based materials is limited. Gorustovich et al. increased osseointegration and bone formation by producing 2 wt% B_2O_3 reinforced bioactive glass [25]. In the study of Deilmann et al., they increased the elastic modulus by adding B to the porous

bioactive glass [26]. The antibacterial effect of B has also been proven in some studies.

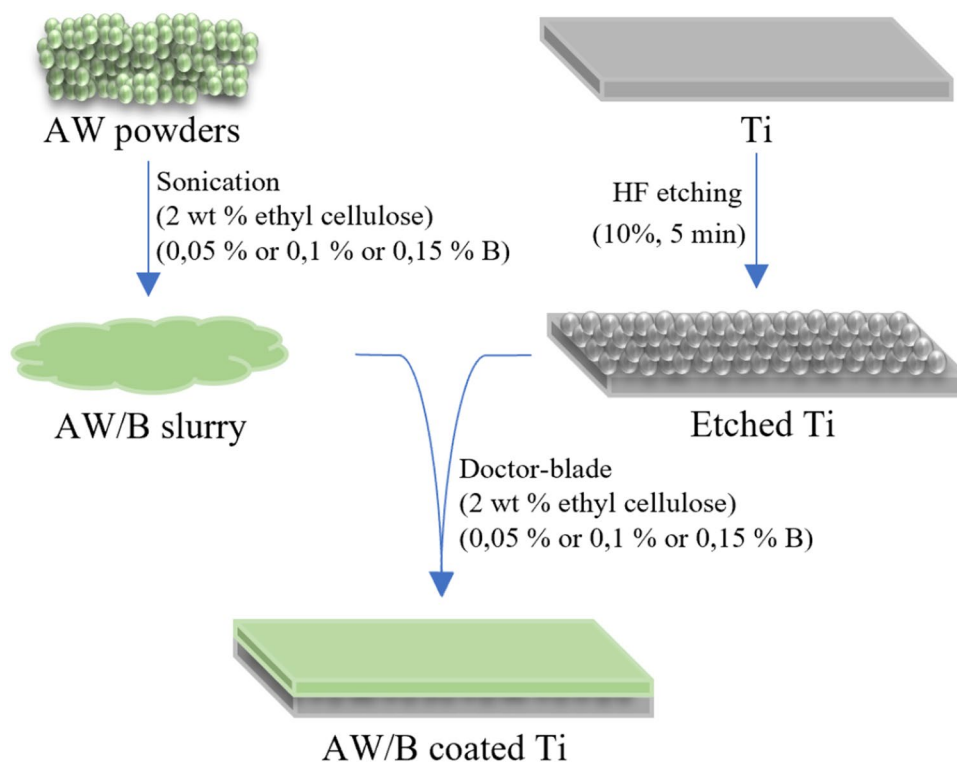
In this study, B-reinforced AW coating for implant applications that can be used instead of bone to improve the bioproperties of the Ti surface was investigated. Although bioglass studies containing B in bulk form are rare in the literature, no AW coating with B content has been found. In addition, in this study, there are comprehensive studies on microstructure, phase studies, mechanical properties, and cellular and antibacterial studies, unlike previous B-reinforced bioglass studies.

Materials and method

Ti foil (Alfa Aesar) of 0.25-mm thickness was cut in dimensions of 10 mm \times 10 mm as the substrate material. Before coating, Ti foils were cleaned in acetone and kept in HF acid solution of 10% by volume for 5 min to ensure the adhesion of the coating to the substrate. It was then rinsed and dried in an oven. AW powders, the primary material of each coating, were produced following the path in our previous study [27]. In summary, the raw materials of CaO , SiO_2 , P_2O_5 , MgO , Al_2O_3 , and CaF_2 were weighed in appropriate proportions and mixed in an alumina crucible. After waiting 1 h at 1400 °C, the molten mixture was poured into the water and frit. After drying, AW powders were produced by grinding in the mill. The ethanol solution containing a certain amount of AW powder was sonicated until its viscosity increased and it became sludgy. To prevent cracking in the subsequent heat treatment and to increase the adhesion of the coating, 2% (wt) ethyl cellulose was added to the solution medium. Then the sludge was poured on the pre-treated Ti substrate, and the samples were dried in the oven at room temperature. As a final treatment, heat treatment was carried out at 800 °C (AW) to increase the adhesion strength of the coating. Three different B-added coatings were obtained by adding 5% (AW/ $\text{B}_{0.05}$), 10% (AW/ $\text{B}_{0.1}$), and 15% (AW/ $\text{B}_{0.15}$) B_2O_3 powder to the ethanol solution containing AW powder. For B-containing coatings, the production route in the AW coating described above was followed, as shown in the flowchart in Fig. 1.

The phase contents and characterization studies of each produced coating were examined by XRD analysis (RIGAKU D/MAX 2200), FTIR analysis (Perkin Elmer), and Raman spectra (Kaiser Raman RXN1). Microstructure examinations of the coatings before and after soaking in simulated body fluid (SBF) were performed with FESEM (Quanta 450 FEG). SBF was prepared according to Kokuba's recipe, samples were incubated at 37 °C at 7.4 pH for 7 days, and the SBF was renewed daily. The chemical content, especially the change in the Ca/P ratio, after holding in SBF was interpreted by EDS analysis.

Fig. 1 Flowchart of the preparation of AW/B-coated Ti substrate



In addition, the behavior of each coating sample against NIH-3T3 mouse embryonic fibroblast cells was examined. Before cell tests, each sample was UV sterilized for 15 min. The sterilized samples were first washed with sterile phosphate buffered saline (PBS). Then two separate 24-well sterile plates were placed in the wells for cytotoxicity and cell adhesion experiments. Three of each coating sample were used for cytotoxicity and cell adhesion assay. 30,000 cells per well (in 300 μL DMEM) were seeded on the samples placed in the wells. The volume was completed to 600 μL by adding 300 μL of Dulbecco's modified Eagle medium (DMEM). Then the cultures were incubated at 37 $^{\circ}\text{C}$ in a humidified atmosphere of 5% CO_2 in air for 48 h. For the adhesion test, cells were fixed with 4% paraformaldehyde and washed three times for 5 min with PBS. The samples were stained with 0.1% Giemsa, kept in the dark for 15 min, washed with PBS and viewed under a light microscope. For the cytotoxicity, at the end of the incubation period, the DMEM medium in the wells was pipetted, and 300 μL of fresh DMEM was added. 30 μL of MTT (4,5-dimethylthiazol-2-yl-2,5 diphenyltetrazolium bromide; thiazolyl blue) dye was added on it and incubated for 4 h. After 4 h of incubation, sodium dodecyl sulfate (SDS) solution was added to the wells to dissolve the formazone crystals and incubated for 12 h in an oven. Then 200 μL of each sample was transferred to a clean 96-well plate and read in a spectrophotometer at 570 nm. As a result of the study, the absorbance values obtained from the spectrophotometric measurements of

the samples were evaluated, and the results were given as % cell proliferation. The images of cell adhesion experiments carried out together with cytotoxicity experiments at the end of 48 h were evaluated with light microscopy. A decrease in the number of viable cells leads to a decrease in metabolic activity in the sample. Such a reduction is directly related to the amount of blue-violet formazan formed, as monitored by the optical density (OD) at 570 nm. The following equation is used to calculate the decrease in viability compared to the negative control:

$$\text{Viab.}\% = 100 \times \frac{\text{OD}_{570\text{e}}}{\text{OD}_{570\text{nc}}} \quad (1)$$

$\text{OD}_{570\text{e}}$ is the average value of the measured optical density of 100% extracts of the test sample and $\text{OD}_{570\text{nc}}$ is the average value of the measured optical density of the negative control. A lower Viab.% value means higher cytotoxicity. The rate of cytotoxicity is graded based on cell viability; non-cytotoxic > 90% cell viability, slightly cytotoxic = 60–90% cell viability, moderately cytotoxic = 30–59% cell viability, and severely cytotoxic = < 30% cell viability [28].

Antibacterial activities on *Escherichia coli* (*E.coli*, ATCC 8739) and *Staphylococcus aureus* (*S. aureus*) ATCC 29213 bacteria were performed by plate counting method for the produced AW coating and AW/B_{0.15} sample (the sample with the highest cell viability). *S. aureus* has a high affinity for skin and bones, is the organism associated with postoperative

orthopedic infection that causes bone matrix resorption and stimulation of osteonecrosis [29]. *Escherichia coli* is one of the first causes of Gram-negative orthopedic implant infections. Gram-negative bacilli cause approximately 6–23% of all orthopedic implant infections, and *Escherichia coli* is the most frequently isolated microorganism in these cases [30]. Therefore, these two bacterial types were preferred in this study. The surfaces of the composite films were sterilized with UV light (Osram Puritec HNS S 9W G23) for 30 min. 100 μL of bacterial culture (1×10^6 CFU/mL) activated 24 h in advance was transferred to the films and covered with a polyethylene film. The films were then incubated at 90% relative humidity and 37.5 °C for 24 h. The films were washed with 20 mL of 1% peptone (Merck) water and inoculated by the spread coating method on nutrient agar (Merck). After 24 h of incubation at 37.5 °C, colonies in the medium were counted using the colony counter. Uncoated 0.25-mm thick Ti foil was used as negative control. Percent antibacterial activity was calculated according to Eq. 2.

$$A = [(B - S)/B] \times 100 \quad (2)$$

where A is the antibacterial effect (%), B is the average number of bacteria colonies on the control (without AW/B_{0.15}), and S is the average number of bacteria colonies in the test sample (AW/B_{0.15}).

For the AW/B_{0.15} sample, which gave the best bioproperty results, the hardness and elastic modulus examinations were carried out with the nanoindentation test Berkovich recessed tip. In addition, the mechanical properties of the AW sample were also investigated for comparison.

Results and discussion

XRD patterns of AW and boron-doped AW coatings are given in Fig. 2a. For each coating, it can be said that the surface of the Ti substrate is completely covered since the peak of Ti is not visible (Figure S1). The maximum peak of AW appeared at approximately $2\theta = 30^\circ$ for all coating samples. The existence of the AW phase has been proven, consistent with the studies in the literature [17, 31]. The XRD patterns of the boron-doped coatings were similar to those of the AW coating, no significant change was observed. A similar situation was reported in another study in which boron was added to HA [23]. In the study of Tunçay et al., there was no significant change in XRD peaks with the addition of boron to HA. The presence of boron in the coatings has been proven by FESEM, EDS, FTIR, and RAMAN analyses.

Figure 3 shows the surface morphology images of each coating before and after soaking in SBF. FESEM images were taken at the same magnification (5000 \times). No cracks were detected on the coated sample surfaces, and

a homogeneous morphology was observed (Fig. 3a1–d1). Here, it can be thought that slow heating and slow cooling steps (10 °C/min) are effective in the heat treatment applied after coating. The coating thicknesses were measured similarly because the coatings were carried out with the same method, and therefore the cross-sectional FESEM image of the AW/B_{0.10} coating is presented in the supplementary (Figure S3). It has been observed that the average coating thickness of 55.58 μm is in the appropriate range for implant material coatings used in the biomaterial field [32]. The AW-coated sample surface consisted of particles in the 1–8.5 μm . With the addition of boron to AW, this particle form disappeared, and the particles were fused to give an irregular morphology. Boron supplementation to AW improved the surface morphology by providing increased adhesion between particles. ME Aksoy et al. reported that boron addition provides better interconnection between grains and pores in their study of boron-doped HA coating [24]. As boron was added to AW, the interparticle pores decreased, and a more rigid morphology was formed. A similar effect was reported in the studies of A. E. Pazarçeviren et al. examining the addition of boron to HA [33]. After the coated samples were kept in SBF for 7 days, 3–6.5- μm spherical apatite particles (indicated by red circles) were formed on their surfaces (Fig. 3a2–d2). Especially in boron-added coatings, the diameter of apatite spherical particles increased compared to AW coating, and the surface was covered entirely with spherical particles. It has also been reported in the literature that boron accelerates apatite precipitation in SBF [34]. The ability of the apatite particles to form showed that the coatings had excellent mineralization ability and good bioactivity.

The EDS results obtained from the coating surfaces before and after holding in SBF are given in Table S1. Ca, Si, P, Mg, Al, and O elements due to the presence of AW were detected in all samples. In addition to these elements, there is element B in boron-added coatings. A sharp decrease was observed in the Si concentration of wollastonite due to the formation of an apatite layer in the coatings kept in SBF. In addition, the Ca/P ratio (between 1.59–1.95) after soaking in SBF approached the stoichiometric ratio of apatite (range 1.67) compared to pre-incubation in SBF (between 5.53–5.95) [35]. In some studies in the literature, the apatite formation ability of wollastonite-based coatings has been confirmed. For the mechanism of apatite formation on the W coating, it was suggested that after immersion in SBF, the calcium ions were initially exchanged with H⁺, and silanol (Si–OH) formed on the layer surface, and an increase in the pH value at the coating–SBF interface. As a result, a negatively charged surface with a functional group (Si–O) is formed on the surface. Due to the negatively charged surface, the Ca²⁺ ions in the SBF solution are attracted to the interface between the coating and the solution. Thus, the ionic activity of apatite at the interface increases as apatite

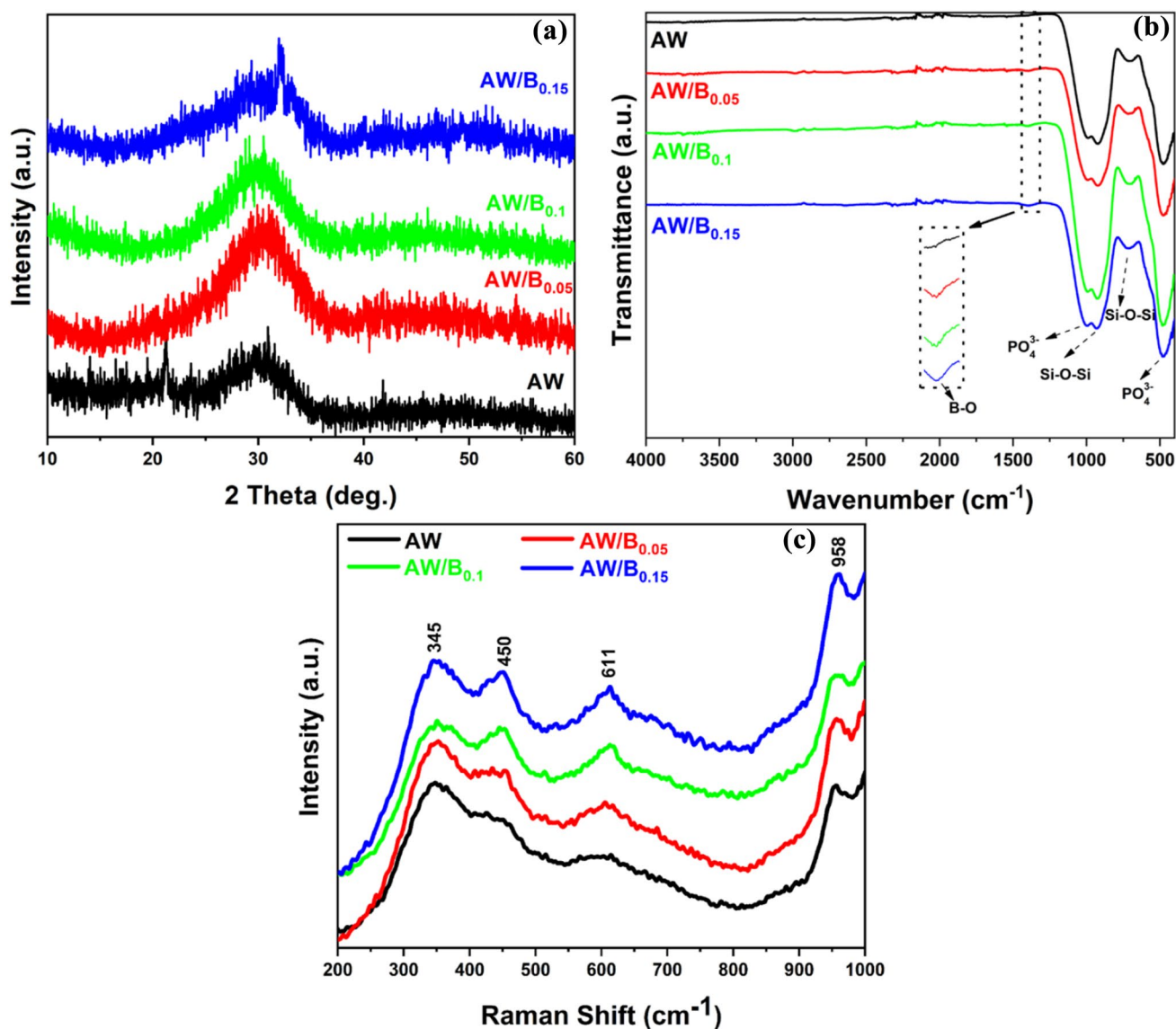


Fig. 2 **a** XRD spectra, **b** FTIR spectra, and **c** RAMAN spectra of AW, AW/B_{0.05}, AW/B_{0.1}, and AW/B_{0.15} coatings

precipitates on the coating surface [18, 31, 36–38]. The critical point here is apatite formation on the negatively charged functional group surface (Si–O). According to the literature, W partially dissolves in SBF and promotes apatite formation [39].

FTIR spectra of the coatings are shown in Fig. 2b. Characteristic absorption bands due to the presence of apatite and W were observed for each coating. Bands at about 550 cm⁻¹ (ν_4 ; PO₄³⁻; asymmetrical O–P–O bending) and 1030 cm⁻¹ (ν_3 ; PO₄³⁻) are associated with phosphate groups. Absorption bands caused by Si–O–Si asymmetric stretching vibration and Si–O–Si symmetric stretching vibration are observed in the range of 900 cm⁻¹ and 750 cm⁻¹, respectively [40]. Significant peaks in the FTIR spectrum prove the presence of AW and are compatible with XRD analysis. In addition,

the calcium carbonate peak reported in the FTIR analysis of W or HA-based coatings in the literature was not observed in this study. It is thought that due to the heat treatment after coating, calcium participates in forming W, and CO₂ gas is removed. In addition, around 1450 cm⁻¹, the adsorption band attributed to B–O stretching vibration for boron-doped coatings appeared [41].

A more detailed examination of the chemical characterization composition of the coatings was carried out by Raman analysis. For each coating, Raman bands at 345 cm⁻¹ and 958 cm⁻¹ are associated with the W phase, while 611 cm⁻¹ Raman bands correspond to the phosphate group [42]. A band appeared at 450 cm⁻¹ in boron-added coatings. This band is attributed to O–B–O bending (Fig. 2c) [23]. According to the results and analyses obtained, and in the light of

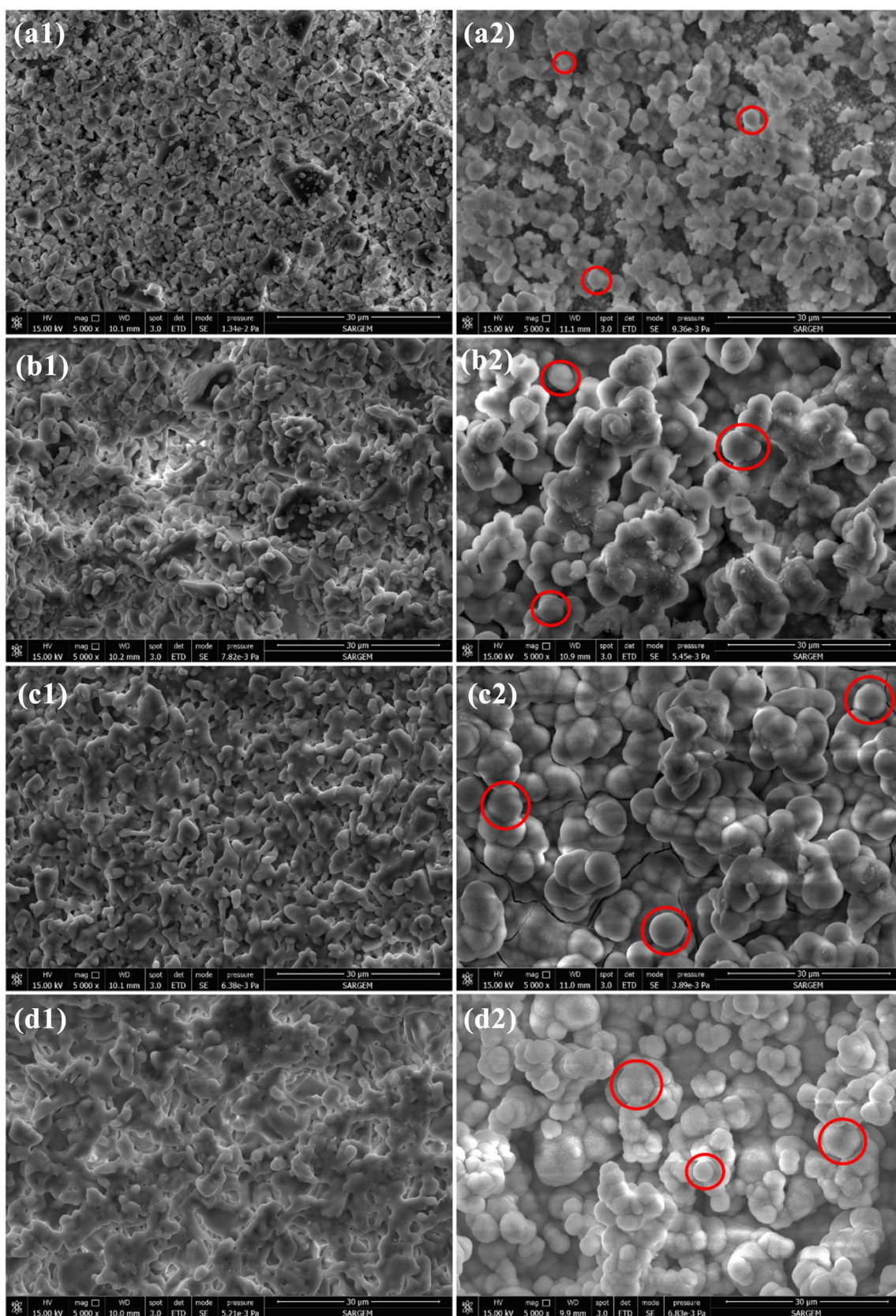


Fig. 3 FESEM images of AW (a1), AW/B_{0.05} (b1), AW/B_{0.1} (c1), AW/B_{0.15} (d1) before soaking in SBF and FESEM images of AW (a2), AW/B_{0.05} (b2), AW/B_{0.1} (c2), AW/B_{0.15} (d2) after soaking in SBF for 7 days

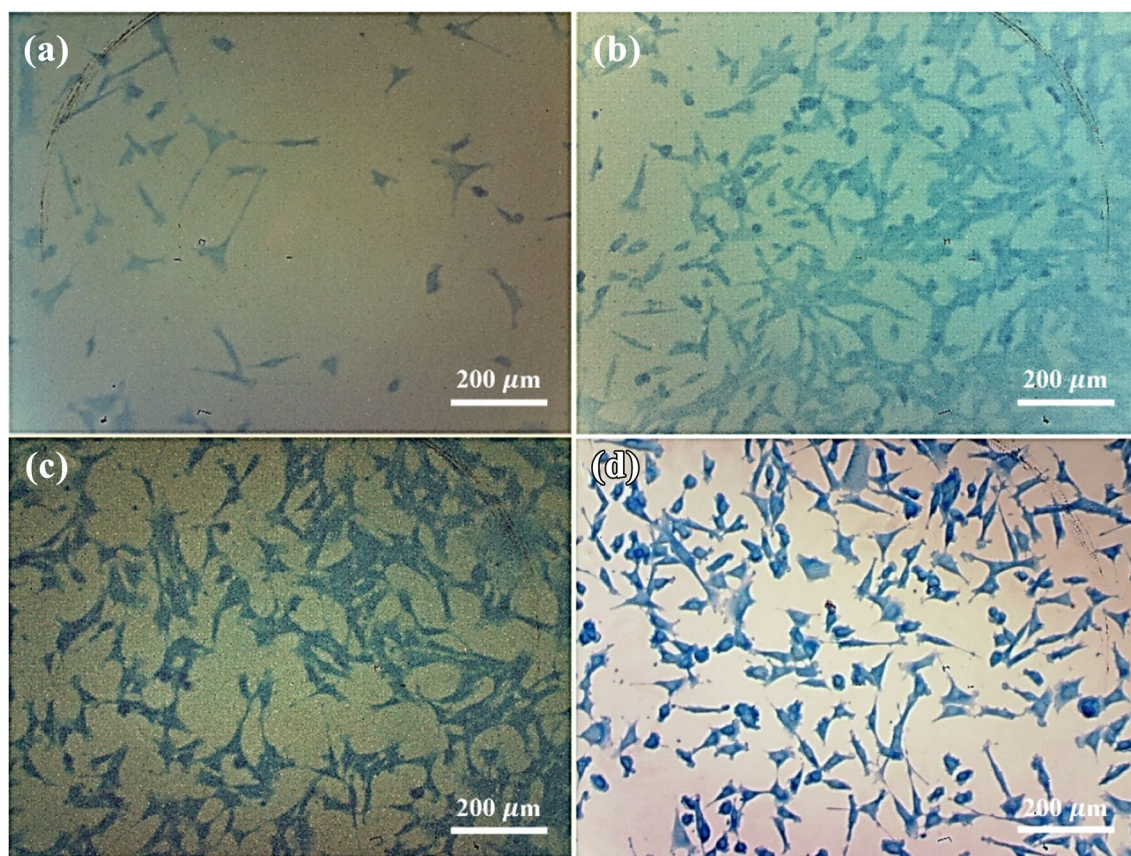


Fig. 4 Optical micrographs of the attached 3T3 fibroblast cells on the **a** AW, **b** AW/B_{0.05}, **c** AW/B_{0.1}, and **d** AW/B_{0.15} coatings

Table 2 Antibacterial activity (%) of AW, AW/B_{0.05}, AW/B_{0.1}, and AW/B_{0.15} coatings

Samples	Antibacterial activity (%)	
	<i>E. coli</i>	<i>S. aureus</i>
AW	0	0
AW/B _{0.15}	7.8	4.5
N. kontrol	0	0

microbial membranes. Such interactions can cause membrane functional activity changes, including membrane-associated enzymes. The mode of action of boric acid has been summarized as inhibition of membrane proteins and inhibition of enzymes and coenzymes within the cell. Inhibition of membrane proteins, including enzymes responsible for active transport, and interference with membrane structures can inhibit nutrient transport and uptake and slow down the metabolic processes of microorganisms [44].

As a result of the antibacterial analysis, sample AW/B_{0.15} exhibited antibacterial activity in wound healing against two possible sources of infection, such as *S. aureus* and *E. coli* (Table 2). It was revealed that AW-coated and blank films used as control did not show any activity,

while AW/B_{0.15}-coated films showed a certain amount of bactericidal effect. The highest activity was determined in the coating containing AW/B_{0.15}, with 7.8% for *E. coli* and 4.5% for *S. aureus*. This can be attributed to the thinner cell wall of *E. coli* than *S. aureus*. In Table 2, it was seen that antibacterial activity increased depending on the increase in boron concentration. In parallel with this study, Wang et al. determined that the antibacterial activity of boron-doped TiO₂ nanoparticles increased depending on the boron concentration [45]. There are limited studies on the antibacterial activities of boron-added coating materials. In a study investigating the antibacterial activity of boron-doped TiO₂ coatings, it was observed that the coating produced on *S. aureus* exhibited a killing rate of about 6%, similar to our study [46]. Another study evaluating the antibacterial activity of textile materials coated with nanoboron particles reported that the produced coated surfaces limited the growth of *E. coli* and *S. aureus* bacteria [47]. The antimicrobial results in this study clarified that the AW/B_{0.15} coating has some bactericidal effect against *E. coli* and *S. aureus*. These results are promising for biomaterials to be developed with boron. We continue and work to produce coatings with antimicrobial activity to

appropriately improve the boron dose and explain the tubing's interactions with different metal combinations.

One of the most critical problems of intraosseous Ti implants is that they have a high elastic modulus compared to bone. The compatibility of the elastic modulus with the bone is important to minimize the undesirable complication of stress-protective osteolysis caused by the unbalanced stress distribution between the bone and the implant. In the literature, mechanical properties compatible with bone have been achieved in HA-based coatings. Data on the mechanical properties of AW and AW/B_{0.15} coatings are given in Fig. 5. The elastic modulus and hardness of the AW and AW/B_{0.15} coatings were measured as 24.6 GPa, 46.3 GPa, and 1692 MPa, 4304 MPa, respectively. Considering the load–penetration depth curves of the coatings, the penetration depths of AW and AW/B_{0.15} coatings under 10 mN load are approximately 6×10^2 nm and 3.5×10^2 nm, respectively (Fig. 5). As the hardness increases, the depth of penetration decreases [48]. The AW/B_{0.15} coating has a higher resistance to indentation than the AW coating. Addition of B to AW increased hardness and E. The elastic modulus of both coatings is compatible with that of cortical bone (10–30 GPa). The effect of B addition on mechanical properties can be explained by microstructure images (Fig. 3). With the addition of B to AW, better bonding between the particles in the coating morphology and decreased porosity affected the improvement of mechanical properties. In addition, it can be thought that the grain size reducing the effect of B may contribute to the advancement of mechanical properties. In the literature, as a result of the addition of B to HA with similar effects, the hardness and adhesion strength of the

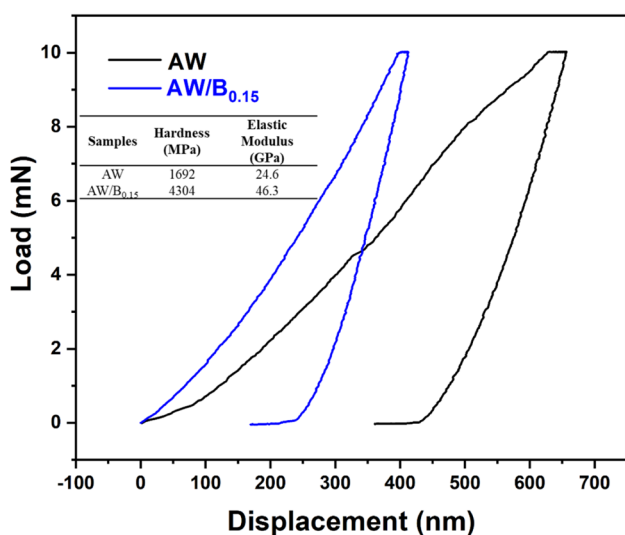


Fig. 5 Load–penetration depth curves for indents AW and AW/B_{0.15} coatings

coating increased, while the deformation and delamination of the coating decreased.

Conclusion

AW and boron-doped AW coatings were successfully applied to the Ti plate surface without deformation, delamination, or cracking. The effects of boron addition to AW on microstructure, mechanical properties, cell behavior, and antibacterial properties were investigated. The main findings can be summarized as follows:

- As boron was added to AW, the morphology of the coating changed from a particulate and porous appearance to a more compact and homogeneous structure. This change in morphology contributed to the increase in mechanical properties. The hardness and elastic modulus of the AW/B_{0.15} coating were measured at 4304 MPa and 46.3 GPa, respectively, while the values of the AW coating were 1692 MPa and 24.6 GPa. Compatibility of elastic modulus values with those of cortical bone will reduce the problem of implant loosening.
- Spherical apatite particles were formed on each coated sample surface after immersion in SBF. It was observed that the addition of boron accelerated the formation of apatite. It has been proven that these produced coatings have bioactive properties.
- 3T3 fibroblast cell viability values on the surface of the coatings increased from 66.76% to 81.99% as B was added to AW. Good cell adhesion was observed in the formed biocomposite coatings.
- While no antibacterial activity was observed in the AW coating, the coating gained antibacterial properties with the addition of B.
- As a result, the B-doped AW coating is recommended for Ti implant surfaces in terms of apatite formation ability, mechanical properties, cell behavior, and antibacterial properties.

Supplementary Information The online version contains supplementary material available at <https://doi.org/10.1007/s00775-023-02032-y>.

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Data availability Data will be made available on request.

Declarations

Conflict of interest The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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