A Review Study on Boron (B) Element and its Derivatives

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This theoretical review study included Boron (B) as the element, its deposits in Turkey and the world, existence forms, historical background, types, chemical structures, mechanical properties, production methods, and applications mentioned. In addition, detailed explanations were given of Boron carbide (B_4C), Boron nitride (BN), and Boron fibers (BF). As a result, the quality (purity) of B element and its derivatives (B_4C, BN, and BF) regardless of their derivatives the most important production parameters affecting smooth and homogeneous surface morphology and particle size depend on the B/C ratio, applied temperature, pressure, time, catalyst type and concentration used. Above 2000°C temperature, 8 GPa pressure, Ar gas environment, C solid substrate surface, and CVD production method create the most suitable conditions to have its high mechanical properties. Moreover, the applications of the Boron (B) element and its derivatives (B_4C, BN, and BF) are widely used in fields such as textile, health, defense, space, aviation, electronics, agriculture, sports, nuclear, and metallurgy. In the future experimental studies about Boron (B) should be done depending on the B/C ratio, the applied temperature, applied pressure, applied time, the type of catalyst used, its concentration, and various production methods. Comparative analyses should be done by applying various characterizations and tests such as XRD, SEM, FT-IR, TGA, DSC, hardness, and tensile strength, and appropriate applications should be determined specifically.

Keywords: Boron (B) element and its derivatives (B_4C, BN, BF); Chemical structures; Production methods; Mechanical properties; Applications

Introduction

The purpose of this mini-review study was to Boron (B) as the element, its deposits in Turkey and the world, existence forms, historical background, types, chemical structures, mechanical properties, production methods, and applications.

Boron (B) element and its derivatives in Turkey and the world

Boron is an element in group III B (13) in the periodic table, solid at room temperature, and abundant in borates and boro silicates on Earth [1,2]. The element boron is symbolized by the letter B and was discovered in 1808 by the French chemist Gay Lussac and the English chemist Humphrey Davey [1].

Thanks to the γ-B106 pure boron (B) structure, which has a complex and aggregated structure, it was proved in Sand's 1957 study on pure boron [3]. Its atomic number is 5, its relative atomic mass number is 10,811, its melting temperature is 2349 K, and its boiling temperature is 4200 K. It has properties between metals and nonmetals [2,4]. It can be found in both black monoclinic crystal lattice structures and yellow or green amorphous crystal lattice structures. The amorphous type has a specific density of 2.37 g/cm^3 and the crystal type has a specific density of 2.34 g/cm^3. It is in powder form and has flammable and explosive properties when in contact with air. It has a violent reaction with lead fluorite and silver fluoride [2]. Borates were used in Chinese ceramics around 300 BC. It was also used as a smelting mine in gold metallurgy in Babylonian civilization.

Moreover, it was used in mummification, gold metallurgy, and health in the Egyptian civilization. It was brought to Mecca and Medina from China by Arab traders in the 8th century AD [1,5,6]. Marco Polo brought borax to Europe for use in pottery applications [1,6]. Boron mining in Turkey started between 1861 and 1865 by a French company thanks to calcium borate [1,5,6]. Later, mining operation rights were transferred to the state, namely Etibank [1]. Turkey has 72% of the world's reserves but can produce and sell 35% of it. Boron (B) reserve in the world based on B_2O_3 content is known as 1.176 billion tons. It is known that between

803 million and 851 million tons of reserves (72.2%) of this figure are in Turkey. [1,2,6]. Turkey is the country with the richest boron deposits in the world [1,2,4,7]. World boron (B) reserves are available in Turkey (72.2%), the USA, Russia, China, Mexico, Argentina, Chile, Serbia, Kazakhstan, Bolivia, Peru, Iran, Germany, and other countries. They are available in Bigadiç, Emet, Kestelek, and Kırka in Turkey. Boron (B) element is available as mineral derivatives (Borates) such as colemanite ($Ca_2B_6O_{11}5(H_2O)$), borax-tincal ($Na_2B_4O_710(H_2O)$), and ulexite ($NaCaB_5O_98(H_2O)$) minerals [1,2,5,6,8,9]. The main boron minerals (Borates) in Turkey are tincal (Na Borate) and colemanite (Ca Borate). Clay minerals are found in the ore bed as quartz, volcanic tuff, calcite, gypsum, biotite, chlorite, and limonite [1,2].

Production methods and mechanical properties of the most common derivatives of Boron (B) mine

Concentration in colemanite ores is accomplished by fractionation, washing, and classification. (with grain sizes of 6 mm). Two different stages are applied in tincal ores. First, the weathering is sieved after brushing the ore, and grading is done using the cyclone. (with grain sizes of -6 mm + 0.1 mm). Secondly, the impact of environmental impact is minimized. The tincal ore is smelted and sent directly into the solution to produce B salts, after which the solid waste is stored in a suitable area. Colemanite, Borax, and Ulexite types differ from each other according to their chemical contents, ratios (%), hardness (Mohs) values, and specific densities [1,2]. Colemanite contains 50.80% B_2O_3 and 21.92% H_2O. It has a relative molecular weight of 411.11 g/mol and is white. It has a monoclinic crystal lattice structure. Its hardness is between

4 Mohs and 5 Mohs. Its density is between 2.42 g/cm³ and 2.43 g/cm³. Borax - Tinkal contains 36.51% B_2O_3 and 47.24% H_2O. It has a relative molecular weight of 381.37 g/mol and is colorless [1,2]. It has a monoclinic crystal lattice structure. Its hardness is between 2 Mohs and 5 Mohs. Its density is between 1.711 g/cm³ and 1.715 g/cm³. Ulexite contains 42.95% B_2O_3 and 35.57% H_2O. It has a triclinic crystal lattice structure. Its hardness is 2.5 Mohs. Its density is between 1.955 g/cm³ and 1.961 g/cm³ [1,2].

Chemical, amorphous, or crystal lattice structures at the atomic level of the most common derivatives Boron (B) mine

The actively explored boron clusters, Bn, normally refer to those with n varying from 3 to 100 atoms. A crucial first step in theoretically studying boron clusters is to identify their global energy minima. Yet, as n increases, each boron cluster would have an exponentially growing number of possible isomers due to a rich variety of B–B bonds [3]. Despite significant efforts by computational chemists to investigate large boron nanoparticles and two-dimensional sheets, boron clusters remain the only species that can't be evaluated experimentally. Clusters exhibit unique size-dependent properties that differ from molecules and solids. The characterization of the structure and properties of clusters has been the focus of the attention of many scientific researchers [10]. The structures of the main components that contribute to the photoelectron spectra of Bn - (n = 3–24) are presented in Figure 1 [10].
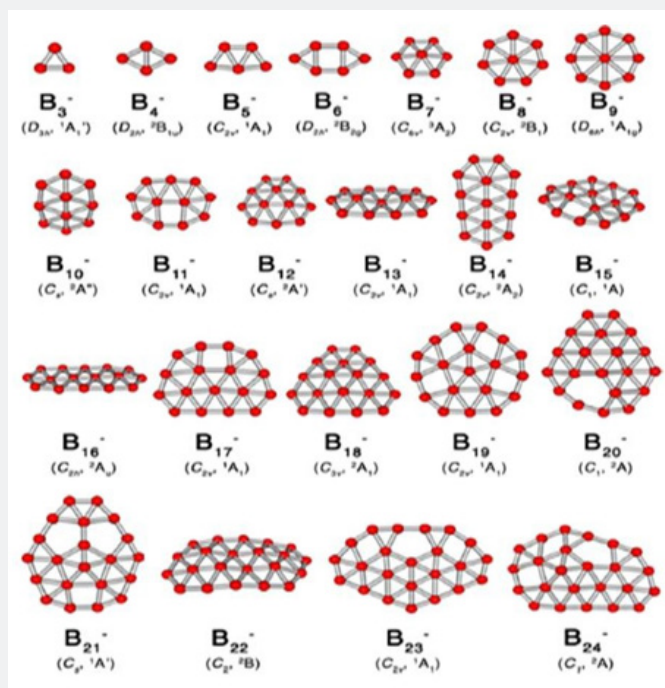

Figure 1: The structures of the main components of Bn - (n= 3−24) that contribute to the photoelectron spectra [10].

Applications of the most common derivatives Boron (B) mine

Colemanite has applications such as textile-quality glass fiber, boron alloys, and metallurgical slag-forming agents. Ulexite and Probertite have applications such as insulation glass fiber, borosilicate glass, antiseptics, boron alloys, nuclear reactors, fire retardant, nylon, photography, textile, fertilizer, catalyst, glass, glass fiber, enamel, and glaze. Anhydrous Borax has applications such as fertilizer, glass, glass fiber, metallurgical slag former, enamel glaze, and flame retardant [1]. Boron (B) applications are used such as glass and glass products, cleaning products, agrochemicals, pesticides, automotive parts, laboratory materials, metallurgy, ceramic products, textile products, sports products, aerospace products, electronic products, nuclear reactors, flame-resistant compounds, and corrosion inhibitors [4,5,6,11].

Boron carbide (B4C)

Production methods, mechanical properties, chemical at the atomic level, amorphous or crystal lattice structures, and the most common usage areas for boron carbide (B_4C) were examined in the subtitles.

Production methods and mechanical properties Boron carbide (B_4C)

B_4C is a brittle material suitable for many high-tech applications. The superior performance features of B_4C are hardness (29.1 GPa), low density (2.52 g/cm^3), high melting point 2350°C for $B_{13}C_2$ and 2450°C for $B_{12}C_3$ (B_4C), high modulus of elasticity (448 GPa), high chemical inertness, high neutron absorption cross section (600 barns), can be used in many fields besides thin films in the form of sintered powder, thanks to its excellent thermoelectric properties [12-15]. B_4C (also known as black diamond) is the third hardest material after diamond and cubic boron nitride (c-BN) [16]. It was discovered by Joly in 1883 as a by-product of the reaction involving metal borides, and various theoretical and experimental studies have been carried out on it for over 100 years. Its purity produced by the first researchers was less than 75%, and it was reported by Ridgway in 1933 that pure crystalline (90%) was produced by the carbothermic process. When the production methods of B4C are examined that

a) carbothermic reduction

b) magnesiothermic reduction

c) synthesis from elements,

d) vapor phase reactions (CVD)

e) synthesis from polymer precursors

f) liquid phase reactions

g) ion beam synthesis

h) VLS growth

i) Sintering

j) friction stir processing (FSP)

k) reactive metal infiltration

l) direct ink writing

m) sol-gel production methods are used [12,13,15,17-23].

Production of B_4C at low temperatures reduces its production cost. Homogenization provides better control over the purity, morphology, and particle size of B_4C. Conversely, the main challenge in the production of B_4C is the high purity (above 97% B_4C) liquid phase synthesis process to convert it into the final product [13]. Although it varies according to the production method, different sizes of B_4C structures are produced by using process times from 10 minutes to 18 hours, process temperatures from 1150°C to 2200°C, and various gas phase co-catalyst chemicals (such as Ar and N_2). It has been observed that above 2000°C temperature is suitable for the extremely high porosity of B_4C. Shrinkage at 1500°C, recrystallization above 1800°C, and rapid grain growth above 2200°C are observed [12,17]. The carbothermic reduction of boric acid (H_3BO_3) or boron oxide (B_2O_3) is the most widely used production method [12]. The suitable temperature range for the carbothermic reduction method is between 800 K and 2600 K [22]. Hot press and isostatic hot press applications are commonly used in the sintering method.

Products in the form of B_4C black powder with 20% C content in a rhombohedral crystal lattice structure with sizes smaller than 2 μm can be produced at a temperature of between 2373 K and 2473 K, with a pressure of between 30 MPa and 40 MPa for a range from 15 minutes to 45 minutes. Produced B4C density, porosity and microstructure depend on the applied sintering process parameters (temperature, pressure, and time). These substrates and catalysts are used such as Mg, Al, V, C, Cr, Fe, Co, Ni, C, Zr, Si, and Ti. In addition, glass, BBr_3, CH_4, H_2, BN, SiC, S_3N_4, MgO, Al_2O_3, TiO_2, TiC, TiN, ZrO_2, CrB_2, TiB_2, Y_2O_3, Be_2C, Cr_3C_2, Dy_2O_3, Eu_2O_3, La_2O_3, SmO, Al-Si, WC, PMAA, PEI, PEEK, Sodium silicate + Mg (NO_3)$_2$ and Fe_2O_3, ethyl silicate, MgF_2, or AlF_3. High purity (above 96%) B_4C production is generally produced by adding between 2% to 4% concentrations at the temperature of 2000°C ± 200°C, with pressure between 200 MPa and 500 MPa, and by hot or cold pressing or sintering methods in the Ar gas environment. Although the mechanical properties of B_4C increase as the percentage of C atoms increases, difficulties arise in the industrial process due to the necessity of applying high temperature and high- pressure values. To produce B_4C with a theoretical purity of above 97%, the general situation observed is that 2200°C, or higher temperatures should be used with increasing the % C atom ratio [12-15,17-23]. An experimental study for the production of B_4C produced by the applied hot-pressing method included B/C: 4:1 ratio, 45 MPa pressure, using 1×10^{-5} mbar vacuum pressure, for 3 hours, and 1900°C temperature values were determined as the optimum result to obtain stoichiometric of above 95%

purity B_4C [14]. In an experimental B_4C production study with the precursor, boric oxide sucrose gel was produced at 873 K as a precursor. It was produced by heating this precursor at 1773 K for 3 hours. Its purity of up to 60% was achieved by this gel pyrolysis. The rate of free C atoms in B_4C was determined as 3% [24]. B4C production from the polymeric precursor with sol-gel production method included the first step, the production of the precursor by sol-gel method. The second step included thermal decomposition in air or condensation of the precursor chemical in gel form as a result of pyrolysis in an inert gas environment. The third and final step included the condensed gel precursor being subjected to heat treatment in an inert gas environment. The sol-gel method enabled the production of B_4C at a much lower temperature (such as 675°C) compared to the carbothermic reduction method [23].

The production of B_4C produced by an experimental sol-gel production method included polyhedral equiaxed particle morphology of high purity and crystalline B_4C powders were successfully produced by low-temperature sol-gel. As a result, it was provided a completed reduction of boron oxide/lower oxides for B_4C of heat treatment with Ar gas at 1500°C for 5 hours [25]. The CVD method for B_4C is the formation of the deposited material below the melting point as a result of a heterogeneous gas-solid chemical and thermodynamic reaction on a hot substrate surface slightly below 2000°C.

For orthorhombic B_8C and tetragonal $B_4.9C_3,BI_3$ (Tm = 48.5°C) and CI4 (T_m = 171°C) materials in the vapor phase and fed to the thermal furnace at certain periods, and B and C, which has a hot surface in crystalline form. Atoms begin to accumulate on the substrate surface below 1000°C thanks to vacuuming under 10^{-3} Torr pressure. The deposited B_4C structures are 1 mm diameter on T_a structure hot substrate surface electrodes. Cooling materials, on the other hand, are used for the collection of reducing chemicals in this vapor phase with volatile properties [20]. These vapor phase-reducing chemicals are suitable for low substrate surface temperature productions. In the case of working at higher temperatures, reducing chemicals in the vapor phase BBr_3, CH_4, and H_2 are used. Both T_a tubes (T_s < 1400°C) heated by direct resistances and B_4C (1000°C ≤ T_s ≤ 1800°C) are prepared in an r_f circle. B_4C structures are protected by 55 mm diameter T_a tubes or graphite substrates. The substrate surface consists of a graft disc with a diameter of 15 mm, and B_4C structures are produced by coating as a thin film layer in an amorphous structure, thanks to the pyrolysis of 2,4,6-trichloro borazine at 1200°C. Moreover, 20.4% C atoms for $B_{13}C_3$ and above 21.7% C atoms for B_4C are the lower limits. Above this ratio, free C's, namely graphite, are formed. If there is a 14% C atom ratio and the temperature is worked below 1300°C, $B_{13}C_2$ with rhombohedral crystal lattice structure and $B_{10}5C_2$ with β-rhombohedral crystal lattice structure can be produced [20]. Another experimental study included the mechanical properties of produced B_4Cs by the CVD method were investigated as a function of composition with varying B/C ratios. Maximum hardness was H and fracture toughness was K_{lc}. The reason for this situation was B/C>4 in non-stoichiometric B_4C, a decrease for H and K_{lc} with increasing B content. Because the excess B atom content reduces the bond strength in B_4C. In non-stoichiometric B_4C, if B/C<4, the decrease in H and K_{lc} means that C is released in the microstructure. In addition, the K_{lc} values of B_4C were determined as the highest values between 1800°C and 1900°C and H values at 1900°C. H and K_{lc} values decreased at values above B_4C for the B/C ratio [18].

Chemical, amorphous, or crystal lattice structures at the atomic level Boron carbide (B_4C)

Many studies have been carried out on the atomic chemical structure of B_4C [12-15,17-23,26,27]. Primary structural B_4C units is a 12- atom icosahedra composed of linear chains of 3 atoms connecting the icosahedra along the (111) rhombus axis and symmetry (R_3m space group) located at the corners of a triangular rhombic lattice. The basic unit lattice structure of B_4C is hexagonal B_{12} icosahedra and contains linear groups C-C-C or C-B–C [12,15,16,19]. In terms of a hexagonal lattice, the cell then corresponds to the rhombus direction [111] of the axis [111] of the hexagonal lattice.

The presence of icosahedra in the B_4C structure is a result of elemental B's ability to form latticed structures of various sizes. The icosahedra in B_4C are two interconnected pentagonal pyramids. Therefore, it corresponds to two different polar and equatorial regions connecting the icosahedra. The polar atoms in the lattice also have three atoms from each of the two opposite planes in the crystal structure. Information about the abs in the crystal symmetry of B_4C can be easily obtained from diffraction measurements. However, the full range of C and B atoms is still debated. B_4C has B-B and B-C atomic bonds in its chemical structure. B/C atom ratios are the most effective parameters on its crystal lattice structure and mechanical properties [12-15,17-23,26,27]. $B_{13}C_2$, $B_{12}C_3$, B_4C, and $B_{12}C_3$ are the most common rhombohedral crystal lattice structures [28,29]. The lower limit of the C atom ratio for the rhombohedral crystal lattice structure of B_4C is 14% C [29]. B_5OC_2, $B_{50}C$, $B_{48}C_3$, $B_{51}C$, $B_{49}C_3$ are for tetragonal. B_8C is for orthorhombic. In addition, forms $B_{12}C$, $B_{12}C_2$, and $B_{11}C_4$ are also available for orthorhombic, too [19,20]. Two stoichiometries were originally proposed for the crystal lattice symmetry considerations of the stable phase of B_4C. These are

a) carbon-rich compound B_4C (or $B_{12}C_3$), with idealized structural configuration (B_{12}) CCC where (X_{12}) represents icosahedral atoms and XXX means chain atoms.

b) If the compound $B_{13}C_2$, or $B_{65}C$ defined by an idealized (B_{12}) is in the CBC structural formula, the central chain C atom is replaced by B.

The longest rhombohedral crystal lattice unit contains 3 atoms. At the end of each chain, an atom at the end of 3 different icosahedra is connected to this chain by covalent bonds [12,17,26]. Various mechanical properties of B_4C depend on the number of C

atoms contained between 8% and 20%. The common view is the existence of a wide solid solubility range for stable phase C and the homogeneous distribution range extending from 8% C to 20% C. Although this corresponds to a single crystal lattice structure with the stoichiometry of $B_{32}C$ at 24% C. It represents the mixture of B_4C and C in the stable phase at 20% C excess. It was reported to have a eutectic point at 30% C and observed at 2350 °C, but the latter was observed at less than 2240°C. Phases with a C content of less than 8% C are generally accepted as solid solutions for B_4C and B. The rhombic lattice parameters for C-rich B_4C composite are a = 5.16 A° and a = 65.7 A°. It is also open to minor changes. It can be transformed into a more easily processed form with a hexagonal lattice. Hexagonal lattice parameters are a_o = 5.60 A°, c_o = 12.07 A° and c_o/a_o = 2.155,3 for B_4C. This is due to the slightly expanded lattices for B-rich B_4Cs and the difference in radius of C and B. Atomic bond distances depend on the number of C atoms in the B_4C structure. The bond distance is the longest at 10C, the bond distance is the shortest at 13C, and the bond distance is constant between 16C and 20C, although close to the long bond distance [26].

Homogeneity, hardness, modulus of elasticity, shear modulus, and fracture toughness increase, but thermal capacity decreases when the number of C atoms in B4C increases from 13 to 20. The thermal capacity starts to decrease in its 20°C structure [12].

Applications of the most common Boron carbide (B_4C)

B_4C is used as abrasive powder, protective thin film coating material, capacitor, electric motor, refractor, control rod, shielding material, high-temperature material, and insulation material in electronic, magnetic, defense, automotive, aerospace, and structural applications thanks to its low specific gravity, high modulus of elasticity, high hardness, high impact resistance, high chemical resistance, excellent shear strength, and high neutron capture properties [17-23,12-15,26,27].

Boron nitride (BN)

Production methods, mechanical properties, chemical at the atomic level, amorphous or crystal lattice structures, and the most common usage areas for boron nitride (BN) were examined in the subtitles.

Production methods and mechanical properties Boron nitride (BN)

BN is not found in nature and therefore can be produced synthetically by synthesizing boric acid (H3BO3) or boron trioxide (B_2O_3) [30,31]. Historically the synthesis of c-BN was initiated in 1957 by Wentorf Jr. in a laboratory in New York, USA, where a compound containing B and N was heated by electrical resistance (1350°C) under high pressure (62,000 atm-6.2 GPa). The metal capsule was produced in belt-type equipment by transforming it into a cubic crystal lattice structure (c-BN) for the first time. It is called "Borazon". In various experimental studies carried out and reported after the discovery high pressure (GPa) and temperature

(°C) are the most effective parameters in the conversion of h-BN to c-BN structure and it resembles the mechanical properties of diamond structure [32]. It was not until the early 1960s that a fixed method was available for powder forms and hot-pressed forms. Modern processing technology has made BN economically affordable thanks to advanced materials used in various forms [30,32]. In other sources, c-BN was first produced by Balmain in Tibet in 1842 by the chemical reaction between the B and N atoms between molten boric acid (H_3BO_3) and potassium cyanide (KCN). [30,31,33]. The layered structure of BN is suitable for forming nanoparticles of its different shapes such as BN nanotubes, nanosheets, and nanohorns. BN is white in color [34]. h-BN is in the stable phase at temperatures above 1000°C in air, 1400°C in vacuum, and up to 2850°C in an inert gas environment [35].

In addition, it is also possible to produce diamond-like c-BN structures by adding various catalysts (especially a 4% Zn, and Mg atoms mixture) into graphite-like h-BN under high pressure with 4 GPa and a temperature of 1000°C. c-BN, unlike diamond, maintains its stable phase at 2000°C. While diamond begins to lose its hardness at 500°C, c-BN begins to lose its hardness above 800°C. While c-BN retains its chemical inertness and machinability against steel, cast iron, and superalloys diamond cannot maintain its chemical inertness and machinability [32]. The modulus of elasticity is between 500 GPa and 600 GPa for h-BN, and thermal conductivity is 390 W/m.K for h-BN [36]. It is the second hardest material in nature with a Vickers hardness ranging from 48 GPa to 50 GPa after the diamond's Vickers hardness between 60 GPa and 120 GPa or its average above 80 GPa Vickers hardness. Also, Young's modulus is between 800 GPa and 900 GPa. [28,30,32]. An experimental study using by sintering method for c-BN production included c-BN production carried out in a vacuum environment under 8 GPa pressure and temperatures between 1800 K and 2400 K. Catalyst was not used for this study. Because it can create large and local stresses between c-BN particles under the influence of pressure and therefore cause defects and various mechanical losses. As a result, sintered c-BN products had such 3.48 g/cm³ for their density, 901 GPa was for their Young's modulus, 384 GPa for their bulk modulus, and 406 GPa was for their shear modulus produced, when 8 GPa pressure and 2300 K hot values were applied on them [28]. The general characteristics of BN structures are a large energy band gap, good resistance to oxidation, excellent thermal conductivity, thermal stability, chemical inertness, significant mechanical properties, and widespread applications [33]. Production methods of BN are mechanical exfoliation, chemical exfoliation, chemical vapor deposition (CVD), hot pressing, solid-state reactions, substitution reactions, high-energy electron irradiation, and unzipping BN nanotubes. It can be produced between 100 mTorr and 350 mTorr pressure range and in an N_2, or Ar gas environment [30,31]. Nowadays, about 50 different catalysts are used for the production of BN [32]. These substrates and catalysts used for BN production are sapphire, Ag, Au, Pt, Pd, Pr, Cu, Cr, Co, Ta, Ti, Nb, Ni, V, Fe, Ir, Ru, CNF, cellulose, ABS, PVA, PVB, HDPE, PE, PP, PI, PU, TPU, PAN, PCL,

PDDL, PDA, PVP, PMMA, PEVA, PI, PS, PPy, SAN, Fe-Cr, $NbSe_2$, GaN, AlN, SiC, WC/Co, $AgNO_3$, $AgCrO_4$, Ag_2CO_3, AgBr, Ag_3VO_4, Si/SiO_2, TiN, TiC, TiCN, HfN, Li_2O, Li_3BN_2, $Mg_3B_2N_4$, $Ca_3B_2N_4$, $Ba_3B_2N_4$, $BiOClPO_4$, NH_4BF_4, $NH_4B_5O_8$, MgO/FeO, MoS_2, WSe_2, benzene, benzyl benzoate ($C_{14}H_{12}O_2$), borazine, diborane, ammonia borane, isopropylalcohol (IPA) or NMP, methyl sulfonic acid (MSA), octadecylamine-Octadecylamine (oligomeric polyethylene glycol (PEG), trioctylamine, trioctylphosphine, ethanol, DMO, N, N-dimethylformamide (DMF), methanesulfonic acid (MSA), urea ((NH_2)2CO), sodium azide (NaN_3) sodium hydroxide (NaOH), nitric acid (HNO_3), KBH_4, potassium hydroxide (KOH), epoxy, cyanate ester, glycol-chitosan, HA, poly-L-lysine and gum Arabica.

Temperature (°C), pressure (GPa), time (h), and production method vary depending on the chemical structures of the substrate and catalysts used. In addition, the physical, mechanical, and thermal behaviors of the produced BN products have changed [16,28-39]. In an experimental study for the conversion from h-BN to c-BN, the (111) plane of the h-BN reaction products synthesized with Mg as a solvent/catalyst under 6 GPa pressure and 1500°C temperature is extremely important for the conversion process. Moreover, a lattice for c-BN was determined as a = 3.615 A°. The theoretically calculated Young's modulus of h-BN is between 0.71 TPa and 0.97 TPa, and its tensile (tensile) strength is between 120 GPa and 165 GPa. These values are so close to the experimentally measured Young's modulus is 1 TPa and the tensile strength is 130 GPa of graphene [38]. Single-layer h-BN has a bulk modulus of about 160 GPa and a flexural modulus of about 31.2 GPa [29]. h-BN has between 1.5 GPa and 3 GPa Vickers hardness, Young's modulus has 36.5 GPa, electrical resistivity has 3×107 Ω.cm, dielectric constant has 3 ± 1, band gap has 5.2 eV, and thermal conductivity has 600 W/m.K. [39]. c-BN has 45 GPa Knoop hardness, Young's modulus 400 GPa, electrical resistivity 1010 Ω.cm, dielectric constant 0, band gap 6.4 eV, and thermal conductivity 740 W/m.K. [39]. Production methods for h- BN and c-BN are mechanical exfoliation, liquid exfoliation, chemical vapor deposition (CVD), physical vapor deposition (PVD), fragmentation chain transfer polymerization, chemical oxidative polymerization, casting, freeze-drying, in-situ growth method, ball milling method, solvothermal/hydrothermal method, thermal condensation process, electrospinning, microwave irradiation, boron ink method, micro fluidization, ion- intercalation assisted exfoliation, surface segregation- based method, pulsed laser deposition, vacuum-assisted filtration (VAF), vapor-liquid-solid (VLS) growth, direct growth, substitution reaction, template-directed synthesis, cross-linking, pyrolysis of compounds containing B and N elements and unzipping of BN nanotubes [16,28-39]. The CVD method is the production of a precursor containing B and N atoms on an amorphous or crystalline substrate using controlled pyrolysis depending on temperature (°C). ($HB(NH_3)$) [33]. The phase stability of c-BN depends on the applied high temperature (°C) and pressure (GPa), ie thermodynamic conditions [16,30,32,35]. Until the early 1990s, h-BN was believed to have a

more stable phase than c-BN under thermodynamically standard conditions. However, the state is reversed similarly to the graphite and diamond phases of carbon at high pressures (GPa) [30]. It was evident that c-BN was more favorable than the h-BN at temperatures below 1600 K. It was reported on transition metals at much lower temperatures. The typical growth temperatures for CVD were between 700°C and 1100°C, which were at least 300°C cooler than that observed in the general phase diagram [35].

Thermodynamic stability for the production of sintered c-BN (Pc-BN) a temperature range from 1200°C to 2000°C and a pressure range from 7 GPa to 12 GPa have also been reported [29]. Commercial products for PC-BN are BZN compact®, GE (USA), Sumboron®, Sumitomo® (Japan), Sunnit®, Amborite®, Ambrasit®, Element Six® (South Africa), Elbor®, Saint Petersburg Abrasive (Russia), Belbor®, IFTT® (Belarus), Kiborit® and ISM® (Ukraine). Various mechanical properties of PC-BN are between 28.5 GPa and 45 GPa for Knoop hardness between 3.20 g/cm^3 and 4.25 g/cm^3 for density, between 2.6 GPa and 4.6 GPa for compressive strength toughness, between 3.7 $MPa.m^{0.5}$ and 13.5 $MPa.m^{0.5}$ for K_{IC}, between 660 MPa and 910 MPa for elastic modulus. It has between 24 Btu/m.K and 110 Btu/m.K for thermal conductivity, between 0.1 mm and 4.1 for its grain size, and between 10.6 mm/W^3.m and 12.6 for wear intensity mm/W^3.m [32].

Chemical, amorphous, or crystal lattice structures at the atomic level Boron nitride (BN)

Boron nitride (BN) is a typical III-V group compound found in elemental or borate minerals in nature and is a refractory material as an element before and after C, consisting of stoichiometrically equal numbers of B and N atoms [30,31,32,34]. It can crystallize in different forms such as hexagonal (h-BN), rhombohedral (r-BN), fullerene, diamond-like cubic (c,-BN), and wurtzite (w-BN) thanks to the pressure (GPa) and temperature (°C). However, the most stable form is the hexagonal (h-BN) form at room temperature [16,28-39]. Crystal structures of BN are such as a) cubic, wurtzite, hexagonal, and rhombohedral which are presented in Figure 2 [38]. This configuration is characterized by the arrangement of B and N atoms in successive hexagonal layers, similar to the graphene structure. The hexagonal layer plane has nearly the same range of strong covalent bonds as in graphene.

The layered structure of BN creates and protects the layered 3D structure by the alternating alignment of B and N atoms with each other in the vertical direction with the help of Van der Waals forces [16,30,31,34-36,39]. BN can be isomorphic to C in any lattice structure. It has zero- dimensional (0D), one-dimensional (1D) nanotubes, two- dimensional (2D) nanotubes, and three-dimensional (3D) nanotubes (similar to diamond-like crystal lattice structures). In addition, 2D hexagonal BN (h-BN) structures similar to graphene can be produced [31]. The main allotropes of BN are c-BN and h-BN. c-BN is a sp³ hybridized dense phase with B-N bonds. h-BN is a low-density phase sp² hybridized

with B-N bonds [30]. The bond length between the B-N atoms of h-BN is 1.44 A°. It is 1.42 A° in graphene [38]. h-BN consists of a planar alignment of B and N atoms in hexagonal rings. This h-BN structure is a multilayered structure separated by weak interaction Van der Waals forces with a distance of 0.335 nm, positioned perpendicular to the planar layer called graphene formed by only C atoms. Crystal lattice parameters of h-BN are about 1% larger than its C-only counterpart, called graphene. The bond distances are a = 0.25038 nm and c = 0.6661 nm for h-BN [A-6]. The bond angles are $\alpha = \beta = 90°$, $\gamma = 120°$. The bond distances are a = 0.2464 nm and c = 0.6738 nm for graphite [16]. h-BN production can be produced in an inert gas (N_2, or Ar) environment with a temperature range from 985°C to 2000°C and high pressure (GPa). In this way, it provides excellent dielectric, thermal, and UV emission properties. The band gap for h- BN is between 5 eV and 6 eV. It is specifically 5.9 eV. c-BN is a hard and dense phase sp^3 hybridized (111) with bonds of N atoms. It is suitable for use in insulators with the highest hardness, and electrical and thermal conductivity. It is very difficult to produce pure [16]. However, c-BN has a thermodynamically more stable phase up to relatively high temperatures (°C) at 0 pressure (depressurized) in terms of transformation temperature compared to h-BN nowadays. The purity of h-BN to c-BN conversion depends on material parameters such as particle size and defect concentration. An h-BN layer can be represented as a graphene layer. The C atoms are completely replaced by alternating B and N atoms. Similar to graphene, the atoms in each h-BN layer are bound together by strong covalent bonds, while Van der Waals forces exist between weaker layers [30]. The parameters of crystallographic h-BN and graphite are almost the same [30,33]. Unlike the popular graphene monolayers, their corresponding BN sisters have rarely been observed due to the alignment properties of B-N. The hexagonals in h-BN are superimposed on adjacent planes. That is, B and N atoms alternate along the c axis (AA0 stack). Moreover, graphite is shifted by a half- hexagonal (AB alignment). N-N or B-B bonds are very low compared to B-N bonds when considering bond energy costs due to AB alignment. Two adjacent Bs are replaced by N atoms, starting from an isolated h-BN plane. That is, two B-B bonds and two N-N bonds are formed.
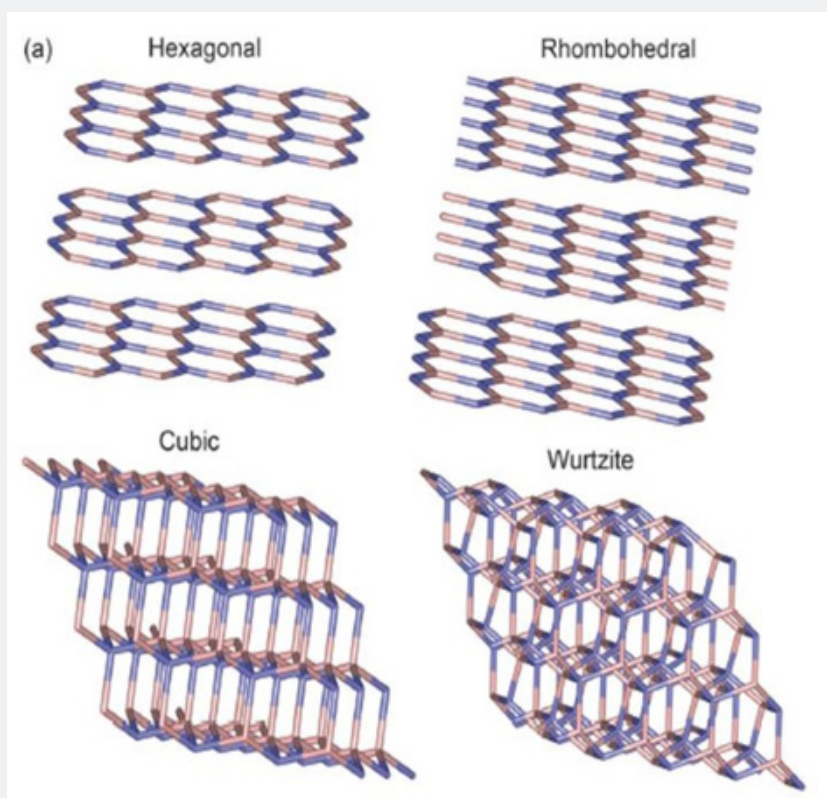

Figure 2: Crystal structures of BN are such as a) cubic, wurtzite, hexagonal, and rhombohedral [38].

The calculated defective bond energy cost of this antisite is 7.1 eV after atomic relaxation [30]. Moreover, the difference in electronegativity of B and N is partially ionic for B-N bonds as opposed to C-C bonds in graphite and is estimated at 22% [16,30-32]. These features can lead to "lip- lip" interactions. It occurs as bridges or "point sources" between neighboring

layers in BN nanostructures, that is, between chemical atoms. (between adjacent layers). This phenomenon contributes to a metastable state. By using B- B and N-N bonds instead of B-N bonds, the number of these suspended bonds can be reduced and the minimum bond energy can be achieved in the formation of a metastable phase. Therefore, multilayer BN formation stabilizes the entire structure [30].

Applications of the most common Boron nitride (BN)

BN applications are medicine, orthopedic implants, biosensing, drug and gene delivery, composite, cosmetics, hydrogen storage, electricity, electronics, optics, optoelectronics, microelectronics, UV emission, piezoelectric, abrasive material, cutting material, motor coating, protective film coating, gas sensor, ultrafiltration, water desalination, renewable energy, mechanics, field emission, magnetism, dye adsorption, 3D-printing, memory storage, capacitors, gate dielectrics, adsorption, lubrication, packaging, automotive, battery electrode, chemical detector, insulating cable, photocatalysis, catalysis, ecology, and biology [16,28-39].

Boron Fibers (BF)

Production methods, mechanical properties, chemicals at the atomic level, amorphous or crystal lattice structures, and the most common applications for boron fibers (BF) were examined in the subtitles.

Production methods and mechanical properties Boron fibers (BF)

Pure B consists almost entirely of slightly deformed icosahedra arranged in a highly complex array. The BF has both a high tensile strength of 2.07 GN/m^2 or 3.5×10^5 psi and a high Young's modulus of 418 GN/m^2 or 60.5×10^6 psi. The mechanical properties of BF are dependent on residual stress distribution. They are volume expansion in the core due to B diffusion and formation of tungsten boride for the first step, thermal expansion mismatch between borate core and outer B mantle for the second step, B elasticity process during storage for the third step, and reactor outlet quenching process at the mercury electrode for the fourth step in the production process [40]. BF samples used for property measurements were commercially produced with average tensile strengths above 3 GN/m by Avco Systems Division at nominal diameters of 102 μm (4 mils), 142 μm (5.6 mils), 203 μm (8 mils), and 375 μm (15 mils). These fibers were produced by CVD in a single-stage reactor by hydrogen reduction of B tri-chloride on a continuously passing resistively heated (1300 °C) wire substrate.

For two larger diameter fibers, induction heating coils need to be added near the exit end of the reactor. The substrate for most samples is 13 μm (0.5 mils) and 17 μm (0.67 mils). After deposition, the remaining fibers 3 μm (0.1-mil) pyrolytic graphite layer were formed to form the ammeter core on a substrate consisting of a 34 μm (1.3 mils) C monofilament of fully botrytized tungsten wire. The tungsten substrate is available for all four diameters, while the C substrate is only available in fiber sizes of 102 μm and 142 μm. The elasticity modulus is between 397 GN/m^2 and 402 GN/m^2 for a temperature of 295 K. The shear modulus is approximately between 176 GN/m^2 and 179 GN/m^2 for a temperature of 295 K. The Poisson ratio is A = 0.11-0.14 for a temperature of 295 K. The theoretical amorphous density for a temperature of 295 K is between 2.29 g/cm^3 and 2.48 g/cm^3. Amorphous BF is usually used with B, SiC, Si$_3$N$_4$, Mg, Ni, Al, Ti, TiB, TiC, SiC, B$_4$C, BN, TiB$_2$, TiO$_2$, Ti$_6$Si$_3$, TiSi$_2$, Ti$_6$Si$_3$, W, W$_2$B$_5$, WB$_4$, Li$_2$S, TiL$_3$M$_2$,3M$_2$,3, and L$_3$M$_2$,3M$_4$ on substrate surfaces in the form of glass or graphite filaments. It is generally produced by chemical vapor deposition (CVD), laser-assisted chemical vapor deposition (LCVD), or gas phase chemical deposition (GPCD) methods by heating with the help of catalysts such as in thermodynamic conditions [34,15,25,41,40,42-48]. It can also be produced by plasma torch spraying, diffusion bonding, or hot-pressing methods [47]. The mechanical properties of BF vary depending on the BF diameter (μm). As the diameter of the BF decreases, tensile strength and modulus of elasticity increase [15,25,34,41,43,45,46]. As the pressure increases, the boron (B) fiber gets thinner and the tensile strength increases. Although its high costs limit aviation applications, mainly is used because of its properties such as low density, high tensile strength, high modulus of elasticity, and excellent buckling resistance [40,42]. 2.57 g/cm^3 is for its density, 400 GPa is for its Young's modulus, 0.13 is for its Poisson's ratio, between 3 GPa and 4 GPa is for its tensile strength, but specifically 3.6 GPa and 165 GPa is for its shear modulus [41]. Commercially available BF is produced in the USA (Specialty Materials, Inc.) and France (SNPE) [42]. Special SiBCN fibers have high thermal stability up to 1800 °C as they remain amorphous in an inert environment [44].

Chemical, amorphous, or crystal lattice structures at the atomic level Boron fibers (BF)

Three well-known polymorphs of pure B in an almost regular icosahedral crystal lattice structure formed by the grouping of 12 atoms are used. They are α-rhombohedral boron, which has the unit cell, a$_o$ = 0.505 rim, a = 58.06 ~ space group R3m, contains 12 atoms with an icosahedron at each of its lattice sites with a density of 2.46 g/cm^3. Tetragonal boron has the unit cell, a$_o$ = 0.875 nm, c$_o$ = 0.506 nm, space group P$_{42}$/nm, containing 50 atoms distributed among four icosahedra and two individual atoms, with a density of 2.31 g/cm^3.

β-rhombohedral boron has the unit cell a$_o$ = 1.017 nm, c~ = 65.2 ~ space group R$_3$m, and contains 105 atoms with a density of 2.35 g/cm^3 [25].

Applications of the most common Boron fibers (BF)

Boron fibers (BF) applications are widely used in textile, defense, automotive, energy, space, and composite material sectors [40-44]. Fairings, flight control surfaces, landing gear doors, leading and trailing edge panels on the wing and stabilizer, interior components, floor beams, floorboards, vertical and

horizontal stabilizer primary structure on large aircraft, primary wing, and fuselage structure on new generation large aircraft are turbine engine fan blades and propellers in the space sector [43].

Conclusion

Boron (B) element is found in various mineral types in Turkey (72.2%), which is the most common deposit in the world. Boron (B) mineral derivatives (Borates) found in Turkey are colemanite ($Ca_2B_6O_{11}5(H_2O)$), borax-tincal ($Na_2B_4O_710(H_2O)$), and ulexite ($NaCaB_5O_98(H_2O)$) minerals. Turkey is abundant in Bursa, Balıkesir, Eskişehir, and Kütahya. In its chemical structure, it has abundant B-B bonds, and as the atomic number (n) increases, the particle size (nm) and crystal lattice structure change, and various mechanical properties such as hardness, Young's modulus, and tensile strength also change. It has chemical formation in monoclinic and triclinic crystal lattice structures. Its density ranges from 1.95 g/cm^3 to 2.43 g/cm^3. It is also an extremely hard and room temperature solid element thanks to its hardness in the between 2 Mohs and 5 Mohs hardness range. Generally, in the production of boron (B) minerals by purification; concentration, crushing (grinding), sintering (at high pressures and temperatures), or thermal processing (usually between 1000°C and 2500°C at high temperatures), washing and classification are carried out. The most common types used in these applications are boron carbide (B_4C) boron nitride (BN) and boron fibers (BF). Briefly, the element Boron (B) is a valuable element found in various mineral forms in nature in monoclinic and triclinic forms with an almost regular icosahedral crystal lattice structure formed by the grouping of 12 atoms. By using B-B and N-N bonds instead of B-N bonds, the number of these suspended bonds can be reduced and the minimum bond energy can be achieved in the formation of a metastable phase. B_4C can be produced in rhombohedral and hexagonal crystal lattice structures. B-C bonds are chemically bonded to each other by strong covalent bonds and weak Van der Waals forces. The B/C ratio must be 4/1. B_4C particulates can be stored by applying a vacuum to the substrate surfaces in a chemically inert gas environment and optionally catalysts can be used. BN can be produced in hexagonal (h-BN) and cubic (c-BN) crystal lattice structures. B-N bonds are chemically bonded to each other by strong covalent bonds and weak Van der Waals forces [49].

CVD can be used in production methods such as sintering, carbothermic reduction, and sol-gel under high temperatures and pressure, in a certain process time. BN particulates can be stored by applying a vacuum to the substrate surfaces in a chemically inert gas environment and optionally catalysts can be used. BF can be produced in α-rhombohedral, tetragonal, and β-rhombohedral crystal lattice structures. B-N bonds are chemically bonded to each other by strong covalent bonds and weak Van der Waals forces. It can be produced under high temperatures and pressure with CVD and LCVD production methods in a certain process time. BF can be stored by applying a vacuum on substrate surfaces in a chemically inert gas environment and optionally catalysts can

be used. Quality (purity) regardless of the B element and its derivatives (B_4C, BN, and BF) can be produced with smooth and homogeneous surface morphology and particle size thanks to B/C ratio, applied temperature, pressure, time, catalyst type, and concentration used. Their process types and parameters should be applied such as above 2000°C temperature, 8 GPa pressure, Ar gas environment, C solid substrate surface, and CVD production method to create the most suitable conditions. Regardless of the B element its derivatives (B_4C, BN, and BF) are widely used in fields such as textile, health, defense, space, aviation, electronics, agriculture, sports, nuclear, and metallurgy. Experimental productions should be done by applying various ratios and using various production methods for future experimental studies thanks to the B/C ratio, applied temperature, pressure, time, catalyst type, and concentration. Comparative analyses should be made by applying various characterizations and tests such as XRD, SEM, FT-IR, TGA, DSC, hardness, and tensile strength, and appropriate applications should be determined specifically.

The future perspective for boron and its derivatives is that various Boron (B) and its derivatives (especially in c- BN form and cubic crystal lattice structure) are very rich in mineral deposits in Turkey. They are manufactured using CVD, or sintering methods at high pressure (between 200 MPa and 500 MPa) and temperature (2000°C ± 200°C). So, they can be produced with small particle sizes (<6 mm) thanks to their production in fiber or ceramic plate forms that produce conditions. They have superior and high mechanical properties in their areas such as textile, health, defense, space, aviation, electronics, agriculture, sports, nuclear, and metallurgy. It is thought that they can be widely used in those areas.

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