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Applications of additive manufacturing technologies in the production of boron-based ceramics

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ABSTRACT

Boron-based refractory ceramics, particularly boron carbide (B_4C) and boron nitride (BN), play a critical role in applications such as nuclear energy, defense, and aerospace due to their exceptional properties, including high hardness, thermal stability, and chemical inertness. While traditional manufacturing methods limit the potential of these materials, additive manufacturing (AM) technologies offer innovative solutions to overcome these constraints. Methods such as stereolithography (SLA), binder jetting, and selective laser sintering (SLS) enable the production of high-performance parts with complex geometries, reducing material waste and increasing design flexibility. This review examines the recent advancements in the AM production of boron-based ceramics and highlights future research directions and industrial potential. Furthermore, the development of sustainable and cost-effective manufacturing methods will facilitate broader use of these materials in high-performance applications.

1. Introduction

Boron-based refractory ceramics hold an indispensable place in modern engineering applications due to their extraordinary thermomechanical properties and chemical stability. These materials are particularly known for their high melting points, excellent hardness values, low density, stability at high temperatures, resistance to wear, and neutron absorption capabilities [1-4]. This versatile combination of properties makes boron-based ceramics critically important in fields such as nuclear energy, the defense industry, aerospace, cutting tools, and high-temperature applications. However, the challenges encountered in producing parts with complex geometries and precise microstructures using traditional manufacturing methods limit the potential applications of these materials. At this point, additive manufacturing (AM) techniques offer exciting opportunities to overcome these obstacles in the processing of boron-based ceramics and to fully exploit their unique properties [5-7]. Although the terms “AM” and “3D printing” are sometimes used interchangeably, they differ in technical scope. According to ISO/ASTM 52900:2021, AM generally refers to industrial-scale techniques such as selective laser melting (SLM) and binder jetting, which are suitable for advanced materials. In contrast, 3D printing typically describes desktop or consumer-friendly methods like fused deposition modeling (FDM) [8]. In this study, unless otherwise stated, the term “AM” will be used to refer to the industrial techniques applied to boron-based ceramics.

Boron carbide (B_4C) stands out as a prominent material in this field. Due to its high hardness, low density, and exceptional wear resistance, it is widely used in abrasive materials, armor panels, and as a neutron absorber in nuclear reactors. B_4C's high thermal stability and chemical inertness at temperatures up to 2450°C make it an ideal candidate for refractory applications. Detailed studies on the synthesis methods and structural properties of B_4C have revealed that the material can be produced through carbothermic reduction, magnesiothermy, and other chemical reactions [9-11]. Additionally, the mechanical properties of B_4C, particularly parameters such as Young's modulus and hardness, can vary significantly depending on the carbon content and the production method [1, 12]. The ability of AM technologies to enable the production of B_4C in complex geometries represents a significant advancement that will expand the application areas of this material [6, 13, 14].

Another important boron-based ceramic is hexagonal boron nitride (h-BN). Also known as 'white graphite,' h-BN possesses excellent thermal stability and chemical inertness, as well as a low friction coefficient at high temperatures. Thanks to these properties, h-BN finds extensive use as an insulation material in high-temperature furnaces, as a crucible and container material for molten metals and glass, and as a side dam material in thin strip casting. Additionally, h-BN is used as a sealing element in

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oxygen sensors, further demonstrating its resistance to high temperatures and chemical stability. The ability to produce h-BN in various shapes and composite forms through AM methods offers new opportunities, particularly when used as a composite with zirconium dioxide (ZrO_2) for high-temperature applications. Boron-based composite materials play a crucial role in enhancing the properties of B_4C and BN when used alone. Composites of B_4C with ZrO_2 can improve the material's mechanical properties and corrosion resistance at high temperatures. Such composites are ideal for applications where wear resistance and thermal shock resistance are critical. Similarly, composites of BN with other ceramics or metals offer the possibility of optimizing the material's mechanical and thermal properties for specific applications. AM techniques enable the precise production of these multi-phase composites, significantly expanding the application areas of boron-based ceramics [10, 15, 16].

This study will thoroughly examine the detailed properties, manufacturing challenges, and potential applications of boron-based refractory ceramics, particularly in the context of AM. The article will assess current research and development efforts to identify potential challenges in this field and future research directions. The application of AM technologies to boron-based ceramics will pave the way for their broader use in high-performance applications and make significant contributions to future materials science and engineering studies.

2. The Importance and Applications of Boron-Based Refractory Ceramics

Boron-based refractory ceramics are of critical importance in industrial applications due to their high-temperature resistance, chemical inertness, and superior mechanical properties [17]. These materials are particularly used in demanding environments such as furnaces, crucibles, armor systems, and wear-resistant components due to their high melting points and exceptional hardness [18]. While traditional manufacturing methods impose limitations on producing these ceramics with complex geometries and precise microstructures, AM techniques offer significant advantages in overcoming these challenges [17].

Through AM, boron-based refractory ceramics can be produced in complex geometries that are difficult to achieve using traditional methods [17, 18]. This is a great importance for specialized applications in the aerospace, defense, and nuclear sectors [18]. Additionally, it eliminates the need for molds, reducing production costs, and allows for the use of different materials together [17]. In this way, composite structures can be created, optimizing the material's properties [18].

Among boron-based ceramics, B_4C stands out with its high hardness, low density, and excellent wear resistance. It is widely used in armor materials, abrasives, and nuclear applications as a neutron absorber [9, 15, 17]. Similarly, BN offers high thermal stability, chemical inertness, and a low friction coefficient, making it suitable for insulation materials, high-temperature crucibles, and lubricant applications in demanding environments.

AM techniques offer significant advantages in the production of boron-based refractory ceramics, enabling their expansion into a wider range of applications. Methods such as three-dimensional printing, powder bed-based printing, and direct ink printing make the production of complex parts possible. The SLA (stereolithography) method enables high surface quality and precision through light-sensitive resins, while laminated object manufacturing allows for the fabrication of large structures by layer-by-layer bonding. Direct ink writing (DIW) is particularly suitable for producing porous B_4C or BN-based structures, and filament-based writing enables the production of simpler geometries using thermoplastic-bonded boron ceramic filaments. The continuous development of these techniques improves the manufacturing processes of boron-based refractory ceramics, offering new opportunities for high-performance applications [17].

The use of boron-based refractory ceramics produced through AM will increasingly grow in high-performance fields such as defense systems, nuclear energy, and thermal insulation technologies. Additionally, research in boron-based composite materials, functional ceramics, and next-generation refractories will also accelerate.

Boron-based refractory ceramics are a crucial part of modern technology due to their unique properties in high-temperature and extreme applications. AM technologies overcome the limitations encountered in the production of these materials, allowing for the creation of more customized and high-performance parts. This enhances the potential of boron-based ceramics in both industrial and scientific fields [18].

2.1. High Performance Requirements

For boron-based refractory ceramics produced through AM techniques to be suitable for high-performance applications, they must possess superior material properties such as high hardness, thermal stability, fracture toughness, and chemical inertness, as well as be manufacturable with controlled microstructures. Among these ceramics, B_4C stands out due to its exceptionally high hardness and low density, making it highly attractive for ballistic armor, abrasive tools, and neutron-absorbing components in nuclear applications. However, B_4C's inherently low fracture toughness is a significant limitation for structural applications. To overcome this, AM approaches are being combined with reinforcement strategies. For example, the addition of tantalum oxide (Ta_2O_5) during sintering enables the formation of in-situ tantalum diboride (TaB_2) phases, significantly enhancing mechanical performance. B_4C-TaB_2 composites fabricated via pressureless sintering have achieved an elastic modulus of 312 GPa, hardness of 16.3 GPa, bending strength of 313 MPa, and fracture toughness of 6.08 MPa·$m^{1/2}$ [19].

In addition to B_4C, other boron-based refractory ceramics have drawn attention for specific high-performance applications. h-BN, for instance, exhibits excellent thermal stability, chemical inertness, electrical insulation, and a low coefficient of friction, making it suitable for high-temperature crucibles, insulating components, and vacuum processing parts [15]. Its lubricating properties are particularly valuable in applications where moving parts experience high thermal stress. AM techniques like DIW and SLA allow the production of customized BN components with intricate geometries, which are difficult to achieve via conventional manufacturing methods [20, 21].

Another important boron-based ceramic is zirconium diboride (ZrB_2), which is classified as an ultra-high-temperature ceramic due to its melting point above 3200°C, electrical and thermal conductivity, and oxidation resistance. These properties make it a strong candidate for aerospace thermal protection systems, hypersonic vehicle surfaces, and reentry vehicle nose cones. In AM, the production of ZrB_2 parts is being studied through methods such as slurry-based printing and laser powder bed fusion, which enable fine control of part geometry and porosity while addressing the challenges of densification at such high melting points [22, 23].

Titanium diboride (TiB_2) also demonstrates high hardness, good wear resistance, electrical conductivity, and chemical stability, making it suitable for electrodes in aluminum production, armor materials, and cutting tools. Its integration in AM processes allows for the fabrication of geometrically complex or functionally graded components. Techniques such as binder jetting and laser directed energy deposition have enabled the deposition of TiB_2 as a standalone material or as part of composite systems, improving toughness and machinability for targeted applications [13].

Through AM, these boron-based refractory ceramics can be produced with tailored microstructures and novel geometries, overcoming the limitations of traditional manufacturing. This flexibility allows for the incorporation of reinforcements, functionally graded structures, and hybrid materials, significantly expanding the use of these ceramics in aerospace, defense, nuclear energy, and high-temperature industrial systems. As AM technologies continue to evolve, the role of boron-based ceramics in next-generation high-performance applications is expected to grow substantially [24-26].

2.2. Industrial Applications: Aerospace, Automotive, Energy, and Biomedical Fields

Boron-based refractory ceramics, particularly BN, B_4C, ZrB_2, and TiB_2 have attracted considerable interest in various industrial applications such as aerospace, automotive, energy, and biomedical fields due to their outstanding physical, chemical, and mechanical properties. Each of these materials contributes specific advantages tailored to the extreme conditions and high-performance demands of these sectors.

BN nanostructures are especially promising due to their optical transparency, electrical insulation, biocompatibility, and thermal stability [27]. Their low density, high thermal conductivity, and low coefficient of thermal expansion make them suitable reinforcement fillers in polymer matrix composites used in the aerospace and automotive industries. Incorporating boron nitride nanotubes (BNNTs) into polymer matrices significantly improves thermal conductivity up to 20 times while preserving electrical insulation [27, 28]. These composites are ideal for heat dissipation applications such as electronic device cooling, electric motors, and lightweight structural components. Recent studies have focused on optimizing the thermal and mechanical properties of boron-modified phenolic resin composites through multi-filler systems. These investigations indicate that further optimization of filler content and processing conditions is required to enhance performance under extreme conditions for aerospace applications [29]. Furthermore, BNNTs are used in high temperature resistant coatings, energy conversion devices (e.g., solar and fuel cells), and battery systems, owing to their high electrical resistance, piezoelectric behavior, and large surface area [27, 28]. In the biomedical field, BNNTs and BN quantum dots are being investigated for drug delivery, tissue engineering, biosensing, and magnetically guided therapies, thanks to their non-toxic, biocompatible, and magnetic nature [30-34]. BNNT-reinforced hydroxyapatite composites also show improved strength and cell compatibility, making them suitable for bone implants [35]. However, more comprehensive studies are required on the long-term biocompatibility of BN in biomedical applications and its scalability for clinical use.

B_4C is another widely used boron-based ceramic in aerospace and defense due to its exceptional hardness and low density, which make it ideal for lightweight ballistic armor, wear-resistant automotive parts, and thermal protection components. However, under high-velocity impacts exceeding 900 m/s, it loses its ballistic performance due to phase transformation, and ongoing research is focused on compositional modifications to address this issue [36]. In energy systems, B_4C is utilized as a neutron absorber in nuclear reactors because of its high neutron cross-section. Boron-based ceramics serve as effective neutron absorbers in fourth-generation high-temperature nuclear reactors, underscoring their critical importance in advanced nuclear energy systems [37]. Moreover, B_4C's high thermal conductivity and chemical inertness enable its use in plasma-facing components and heat shields. In biomedicine, while less common than BN, research is ongoing into B_4C-based coatings for wear-resistant and protective biomedical tools and implants [19, 24].

ZrB_2 is a critical material in the aerospace sector, especially in thermal protection systems, hypersonic vehicles, and reentry spacecraft components, due to its ultra-high melting point, thermal conductivity, and oxidation resistance. These properties make it suitable for use in aerodynamic leading edges, nozzles, and braking systems. In automotive and energy systems, ZrB_2-based coatings improve wear resistance and thermal stability under high-load, high-speed conditions. Additionally, it is being explored for electrode materials in harsh environments [38].

TiB_2 offers high hardness, thermal and electrical conductivity, and excellent wear resistance, making it suitable for armor systems, electrical contact components, and cutting tools in the automotive and aerospace industries [39]. TiB_2 is widely used as a cathode material in aluminum electrolysis, benefiting from its chemical inertness and high current-carrying capability [40]. Despite its advantages, the high production cost and sensitivity to thermal shocks limit its applicability in industrial aluminum electrolysis. Ongoing research is focused on developing more cost-effective and durable TiB_2 cathodes to overcome these challenges [40]. In the biomedical sector, although less explored, TiB_2 composites are being studied for hard tissue replacements and load-bearing implants due to their strength and corrosion resistance [41].

Each boron-based ceramic has unique advantages that align with the high-performance requirements of modern industries. BN excels in thermal management and biocompatibility, B_4C in hardness and neutron absorption, ZrB_2 in ultra-high-temperature aerospace components, and TiB_2 in wear-resistant electrical and structural applications. AM continues to enhance the design freedom, microstructural control, and application-specific optimization of these advanced ceramics, enabling their broader integration into aerospace, automotive, energy, and biomedical systems.

3. Properties of Boron-Based Ceramics

Boron-based ceramics, particularly B_4C and BN, stand out as critical materials in advanced engineering applications due to their exceptional properties. These materials offer a unique combination of hardness, low density, thermal stability, and chemical resistance, making them ideal for extreme environments where traditional materials fall short [9]. This section examines the advantages of boron-based ceramics, focusing on their properties, mechanical and thermal characteristics, and resistance to chemical and wear-induced degradation.

Boron-based ceramics, particularly B_4C and BN, exhibit a range of exceptional properties that make them highly suitable for diverse applications, particularly in high-temperature environments. B_4C is renowned for its remarkable hardness, high melting point, and excellent chemical stability, making it essential for abrasive applications [9, 42]. The mechanical properties of B_4C can be significantly improved with various composite structures. For example, incorporating silicon carbide (SiC) into B_4C matrices enhances fracture toughness while maintaining the desired mechanical properties [43, 44]. Reaction-bonded B_4C/SiC composites exhibit high thermal stability, corrosion resistance, and structural durability, making them suitable for demanding applications [45]. In addition to its mechanical durability, B_4C possesses unique thermal and electrical properties. Due to its low thermal conductivity and suitable Seebeck coefficient, B_4C is a promising candidate for thermal energy conversion, enabling efficient energy recovery from waste heat [46, 47].

BN complements B_4C with its excellent thermal stability and electrical insulation properties. BN ceramics, characterized by high thermal conductivity and low density, offer advantages for applications requiring lightweight materials that withstand high temperatures. Composite materials combining B_4C and BN leverage the strengths of both, enhancing mechanical performance and thermal stability [48]. However, processing these boron-based ceramics presents challenges, particularly in achieving uniform microstructures and optimal mechanical properties. Variations in particle size and distribution significantly impact the final properties, requiring careful control during manufacturing [49]. Additionally, contaminants or undesirable phases can compromise mechanical integrity, emphasizing the importance of precise synthesis techniques [50].

TiB_2 based ceramics possess outstanding properties such as high hardness, high elastic modulus, excellent wear resistance, and superior thermal and electrical conductivity. These characteristics make them suitable for applications in high-temperature structural materials, cutting tools, armor, and electrodes for metal melting. TiB_2 exhibits a hardness of approximately ~35 GPa at room temperature, maintaining this property even at elevated temperatures. However, its use as a monolithic material is limited by its low fracture toughness and susceptibility to slow crack growth. To overcome these drawbacks, sintering additives are introduced to enhance density and toughness. These additives facilitate TiB_2 sintering while also influencing its chemical and thermal resistance. Microstructural analysis indicates that TiB_2's properties are significantly affected by grain size, shape, and orientation. Fine-grained microstructures generally yield higher strength and toughness, whereas coarse grains may lead to inferior mechanical properties. Additionally, TiB_2's anisotropic thermal expansion can induce microcracks within its structure, adversely affecting mechanical performance [51-53].

ZrB_2 ceramics are widely investigated for ultra-high-temperature structural applications due to their high melting point and excellent electrical conductivity [54]. The addition of SiC enhances mechanical and chemical properties such as specific strength, fracture toughness, and oxidation resistance [55]. The thermal conductivity of ZrB_2 increases from 56 W/(m K)$^{-1}$ at room temperature to 67 W/(m K)$^{-1}$ at 1675 K. However, in ZrB_2-SiC composites, a different trend is observed, where thermal conductivity decreases from 62 W/(m K)$^{-1}$ at room temperature to 56 W/(m K)$^{-1}$ at 1675 K. The thermal conductivity of polycrystalline ZrB_2 has been measured as 85 W/(m K). Additionally, the coefficient of thermal expansion (CTE) of ZrB_2 is approximately 6.8×10^{-6} K^{-1}, and adding SiC lowers the average CTE due to the lower CTE of SiC [56].

ZrB_2 ceramics find applications in extreme environments such as thermal protection components in hypersonic space vehicles, advanced propulsion systems, refractory crucibles, furnace heating elements, high-temperature electrodes, and cutting tools. They are also used in microelectronics, plasma arc electrodes, solar absorbers, electrical discharge machining electrodes, and Hall-Héroult cells. Additionally, they serve as refractory protective coatings and components in continuous steel casting, reusable atmospheric re-entry vehicles, jet vanes, and nozzle parts for hypersonic vehicles. To further enhance ZrB_2 based composites, carbon additives have been extensively studied. These additives offer benefits such as low density, cost-effectiveness, and excellent thermo-mechanical stability. Their incorporation significantly improves hardness, flexural strength, and fracture toughness compared to monolithic ZrB_2 [54].

Table 1 presents a comparative analysis of the properties of B_4C, different phases of BN (hexagonal-BN and cubic-BN), ZrB_2, and TiB_2. B_4C stands out with its combination of high hardness, ranging from 30 to 42 GPa, and low density of 2.52 g/cm^3, offering excellent oxidation resistance and wear durability. This makes it widely used in armor systems, nuclear applications, and abrasive materials. Its electrical properties as a p-type semiconductor also highlight its potential in electronic applications.

h-BN, with its low density of 2.28 g/cm^3, chemical inertness, and high-temperature stability, is an important material for high-temperature insulation and lubrication applications. Its electrically insulating properties make it particularly suitable for applications that require insulation. In contrast, c-BN, with its high hardness of 49 to 76 GPa and oxidation resistance at high temperatures (up to 1200°C), is considered a promising alternative to diamond in hard cutting tools. Despite their high densities, ZrB_2 and TiB_2 are widely used in advanced engineering applications because of their exceptional mechanical and thermal properties. ZrB_2 is particularly valued in thermal barrier coatings due to its excellent chemical stability and temperature resistance, while TiB_2 is favored in armor coatings and high-temperature components for its superior hardness and wear resistance.

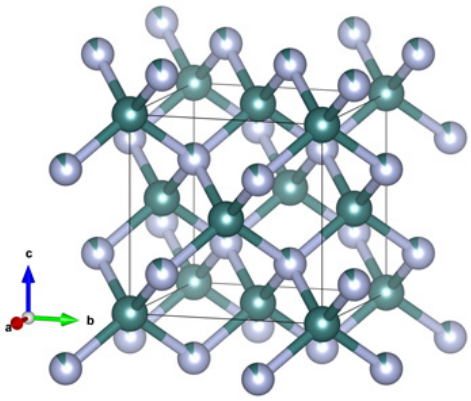
Boron-based ceramics have garnered significant interest in industrial and scientific applications due to their superior properties, such as high hardness, thermal stability, chemical inertness, and mechanical durability. Among these materials, c-BN, h-BN, Wurtzite boron nitride (w-BN), and B_4C stand out. c-BN features a diamond-like cubic crystal structure, as shown in Figure 1a, and is synthesized under high pressure and temperature. This structure imparts c-BN with hardness close to that of diamond and excellent thermal conductivity, making it ideal for cutting tools and abrasive materials. h-BN, often referred to as "white graphene" due to its layered structure (Figure 1b), exhibits high thermal stability, low friction, and electrical insulating properties, making it valuable for lubricants, thermal management systems, and protective coatings. w-BN, a rare phase, is an intermediate form between hexagonal and cubic structures (Figure 1c). This phase is stable under high pressure and holds potential for high-performance ceramic applications. However, due to its rarity, it is

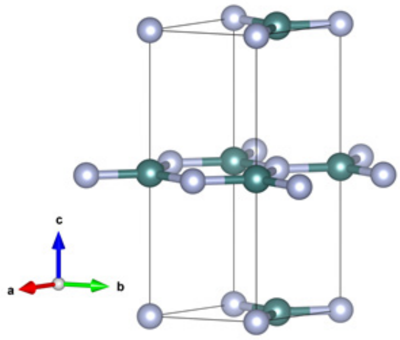
Table 1. Properties of B_4C, h-BN, c-BN, ZrB_2, TiB_2

Property	B_4C	h-BN	c-BN	ZrB_2	TiB_2
Density (g/cm³)	2,52 [57, 58]	2,28 [59]	3,487 [60]	6,1 [51, 61]	4,52 [62]
Hardness (GPa)	30-42 [1, 9]	1,5-1,3 (Vickers) [60]	49 - 76 [51]	~14 [51]	~35 [51]
Chemical Resistance	Resistant to oxidation at high temperatures [9]	Chemical inertness and high-temperature resistance [60] Resistant to acids and alkalis [35]	Resistant to oxidation up to 1200°C [60]	High chemical stability [51]	Oxidation resistance is low at temperatures above 1000°C [51]
Wear Resistance	High hardness and wear resistance [63]	Low friction coefficient (lubricant applications) [15]	Very high (hard cutting tools) [60]	High (thermal barrier coatings) [56]	Very high (hard coatings) [51]
Electrical Conductivity	p-type semiconductor [9]	Insulator [15]	Semiconductor [64]	Conductor [54]	Conductor [52]
Applications	Armor, nuclear reactors, abrasive materials	High-temperature insulation, oxygen sensors	Cutting tools, abrasive disks	Aerospace, thermal barrier coatings	Armor coatings, high-temperature components

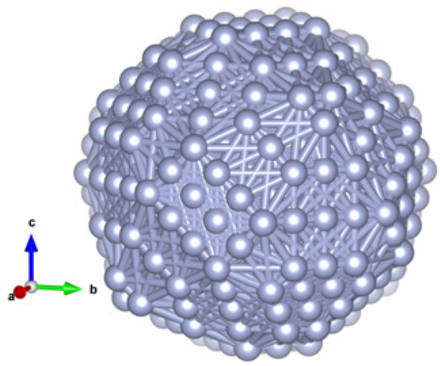
not included in Table 1. B_4C, with its hexagonal crystal structure, is among the hardest known materials after diamond. Its combination of high hardness, lightweight nature, and neutron absorption capability makes it indispensable for armor materials, nuclear applications, and abrasives (Figure 1d) [50, 63, 65-68].

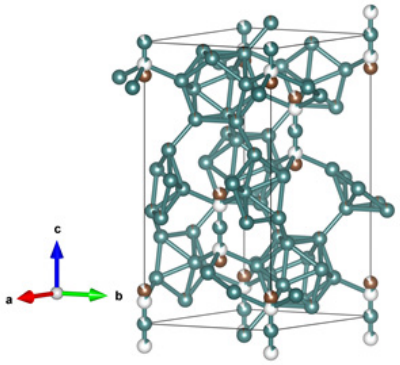
In terms of chemical durability, boron-based ceramics exhibit resistance to various chemical environments. B_4C is particularly suitable for use in abrasive environments and is resistant to oxidation at high temperatures. Additionally, some borides, such as ZrB_2 and hafnium diboride (HfB_2), show resistance to oxidation at high temperatures, and in some cases, oxidation resistance can be enhanced by forming a protective layer, such as SiC. Boron-based ceramics also exhibit good resistance to corrosive environments, making them suitable for challenging working conditions such as chemical plants. In terms of wear resistance, boron-based ceramics are particularly ideal for tribological applications. B_4C, being the third hardest material after diamond and c-BN, offers high resistance to wear due to this property. Tribological properties can be further improved with the addition of different reinforcement materials. For example, the addition of graphene nanoplatelets (GPLs) can enhance the wear resistance of B_4C composites, as GPLs can form a tribofilm that reduces wear and lowers the coefficient of friction. Wear generally occurs through mechanisms such as crack formation and propagation, and the use of reinforcement materials affects these mechanisms, thereby increasing the wear resistance of the material. As a result, boron-based ceramics, due to their chemical durability and wear resistance, are used in various applications and have the potential to be further improved with different reinforcement materials and manufacturing techniques [69].

(a)


(b)


c-BN	h-BN
Space Group: F -4 3 m	Space Group: P -6 m 2
a = 3,61000 Å α = 90°	a = 2,54000 Å α = 90°
b = 3,61000 Å β = 90°	b = 2,54000 Å β = 90°
c = 3,61000 Å γ = 90°	c = 6,59800 Å γ =120°
V = 47,0459 Å^3	V = 36,8647 Å^3

(c)


(d)


w-BN	B_4C
Space Group: P 6	Space Group: R -3 m
a = 1,00000 Å α = 90°	a = 5,65300 Å α = 90°
b = 1,00000 Å β = 90°	b = 5,65300 Å β = 90°
c = 1,00000 Å γ =120°	c = 12,15600 Å γ =120°
V = 0,8660 Å^3	V = 336,4180 Å^3

* B N C

* By Open Crystallographic Database and VESTA

Figure 1. Schematic crystal structures of (a) cubic boron nitride, (b) hexagonal boron nitride, (c) wurtzite boron nitride, and (d) boron carbide [65]

4. Challenges of Traditional Manufacturing Methods

Boron-based ceramics have attracted significant interest across various industries due to their exceptional properties, including high hardness, chemical resistance, and thermal stability. However, their widespread application is hindered by the limitations of traditional manufacturing techniques. Conventional processes such as sintering, casting, extrusion, and machining present critical challenges, including high production costs, material waste, limited shape complexity, and difficulty in achieving high precision. These limitations have fueled interest in alternative production methods, particularly AM, which offers new possibilities for fabricating complex ceramic components. Despite their favorable intrinsic properties, ceramics also possess inherent brittleness and low damage tolerance, making them difficult to process using conventional methods. Manufacturing techniques such as pressing, slurry casting, injection molding, and forging are often inadequate for producing parts with intricate geometries, small-scale features, or internal cavities [70-72]. These traditional shaping approaches typically involve multi-step procedures, including powder preparation, mold shaping, sintering, and post-machining, all of which increase time, cost, and complexity [72-74]. Sintering and pressing, widely used in ceramic part fabrication, are particularly constrained when dealing with geometrically complex or high-precision parts. Issues such as non-uniform density distribution, shape distortion after sintering, and high post-processing costs have been highlighted in recent studies. For instance, Rahaman et al. reported that density gradients in pressed alumina bodies resulted in dimensional deviations of up to 5% after sintering, particularly in large components [75]. Similarly, German found that differential shrinkage during zirconia sintering induced microcracking, reducing mechanical strength by approximately 20% [76]. Lange's findings demonstrated that variations in porosity and grain size caused by non-uniform pressing adversely affected corrosion resistance and thermal stability [77]. Richerson further emphasized that post-sintering machining can account for up to half of total production costs, casting doubt on the economic sustainability of traditional ceramic processing [78]. In addition to the above, shrinkage control remains a fundamental challenge. Sintering-induced shrinkage, especially in parts fabricated through pressing, is difficult to predict and manage due to non-uniform green body densities. These shape distortions often result in deviations from the intended design, complicating quality control in mass production [18, 74, 79]. Furthermore, due to the extreme hardness and brittleness of ceramics, post-sintering machining becomes both technically demanding and cost-prohibitive, which limits its practical application [73]. In response to these challenges, AM technologies have emerged as promising alternatives. AM enables mold-free fabrication and enhances geometric flexibility. Techniques such as FDM, DIW, SLA, and binder jetting are being explored for ceramic shaping [10, 71]. However, each AM methods presents its own set of limitations, particularly during the sintering phase. In FDM, the use of ceramic-filled thermoplastic filaments results in green parts with low ceramic content and high organic binder levels, leading to considerable shrinkage and cracking during sintering. These issues are further exacerbated during debinding, where the removal of binders generates internal stresses and dimensional instability [80, 81]. The DIW process, on the other hand, suffers from low solid content in ceramic inks, leading to green bodies with poor density. This can cause anisotropic shrinkage during sintering, resulting in uneven dimensional changes and possible structural failure [82]. Similarly, although SLA offers high resolution, it utilizes ceramic-photopolymer composites that release gases during resin decomposition. If these gases are not adequately vented, they can create internal pressure pockets, which may promote crack initiation and propagation in the final sintered component [83]. Binder Jetting also introduces issues related to green body density. The binder distribution within the powder bed is often non-uniform, which can cause differential shrinkage and compromise the dimensional accuracy and mechanical stability of sintered parts [84].

Although AM techniques such as FDM and SLA offer notable advantages over conventional manufacturing methods, including reduced tooling requirements and the ability to fabricate complex geometries, they still face significant challenges. Shrinkage, cracking, and non-uniform density remain critical obstacles to producing high-quality ceramic components. Nevertheless, the layer-by-layer deposition inherent to AM provides greater control over green body formation, offering better potential for achieving uniform density compared to conventional pressing. This positions AM as a compelling path forward for the production of advanced ceramic components.

4.1. Sintering and Casting Processes

The production of boron-based ceramics, such as B_4C and BN, involves significant challenges in both sintering and casting methods, particularly due to their unique material properties.

Spark plasma sintering (SPS) is an effective technique for producing high-density B_4C ceramics, achieving near-theoretical densities through rapid heating and pressure application. However, the covalent nature of B_4C necessitates high sintering temperatures and precise control to avoid adverse effects on microstructure and mechanical properties. Deviations in temperature can lead to grain coarsening or residual stresses, compromising material performance [85]. Additionally, pressureless sintering of B_4C is challenging due to its low self-diffusion coefficient, often requiring additives or high pressure, which increases process complexity and cost. The high cost of high-purity B_4C

powders and specialized SPS equipment further limits scalability, while the fabrication of complex geometries remains a significant hurdle [86, 87].

Slurry casting, also known as slip casting, is a widely used method for producing boron-based ceramics with complex shapes. This technique involves preparing a stable slurry of ceramic particles, such as B_4C or BN, in a liquid medium, which is then cast into a porous mold to form a green body. For B_4C ceramics, achieving a homogeneous slurry is challenging due to the tendency of fine powders to agglomerate, which can lead to defects in the final component. The use of dispersants and careful control of slurry viscosity are critical to ensure uniform particle distribution and minimize porosity [88, 89]. For BN ceramics, slip casting has been successfully employed to produce components with high thermal conductivity, though challenges such as mold design and drying-induced cracking must be addressed. The green bodies formed via slip casting are subsequently sintered to achieve the desired mechanical properties, but careful control of drying and sintering conditions is essential to prevent defects. While slurry casting enables the production of intricate geometries, scaling up for large components remains difficult due to limitations in mold fabrication and slurry stability [90].

4.2. Machining Challenges and Cost Increase

B_4C is considered a highly promising material for a wide range of engineering applications due to its low density, exceptional hardness, excellent neutron absorption capability, high bending strength, and outstanding wear resistance. However, its practical applications are significantly limited by poor sinterability and low fracture toughness. The primary challenge in sintering B_4C arises from its strong covalent bonding and low self-diffusion coefficient. Additionally, high-temperature processing is not only costly but also leads to excessive grain growth, which deteriorates its mechanical properties. In recent years, substantial research efforts have been directed toward reducing the sintering temperature of B_4C ceramics while simultaneously enhancing their mechanical characteristics [60, 63]. On the other hand, h-BN is a versatile material that can be utilized either in pure form or as a composite, available in powders, coatings, or sintered shapes. The mechanical behavior of h-BN is anisotropic, varying between directions parallel and perpendicular to the hot-pressing axis. In contrast, c-BN products are typically classified into dense forms for cutting and milling applications and porous forms for grinding. Polycrystalline compacts containing c-BN must be sintered under conditions that stabilize the cubic phase and prevent transformation to h-BN. This necessitates high-pressure, high-temperature sintering, with the maximum part size being constrained by the limitations of the high-pressure apparatus [15]. Dense ZrB_2 ceramics are typically produced through hot pressing or hot isostatic pressing under externally applied pressures at high temperatures. These sintering procedures require long preparation times, post-processing supplies, costly electrical energy, and complex encapsulation technology. Additionally, the extended waiting time during the sintering process leads to grain growth and microstructural coarsening, resulting in deficiencies in the structural properties [54]. The most advanced method for large-scale production of TiB_2 powder involves carbothermic reactions of titanium dioxide (TiO_2) with B_4C and C, or with boron oxide (B_2O_3) and C. Powders produced in this way are typically coarse and exhibit low sinterability, a condition that can be further worsened by the oxides on the particle surfaces. Sintering aids such as C, silicon nitride (Si_3N_4), aluminium nitride (AlN), and SiC also enhance densification, but may lead to changes in the chemical and high-temperature resistance of TiB_2 ceramics [52].

The challenges and cost increase associated with processing these materials stem from high-temperature requirements, poor sinterability, low fracture toughness, grain growth, oxide impurities, and complex manufacturing processes. To overcome these issues, continuous research is being conducted to reduce sintering temperatures, improve mechanical properties, and develop more cost-effective production methods [63].

4.3. The Potential of Additive Manufacturing

Traditional manufacturing methods offer limited design flexibility, particularly in the production of complex and precise geometries. For instance, designs such as hollow structures or intricate channel systems require additional machining steps and incur high costs when produced using conventional methods [91]. This limitation restricts the use of boron-based ceramics in advanced technology applications, such as aerospace and medicine. AM offers significant potential in producing such complex geometries, greatly enhancing design flexibility.

AM provides a promising solution to the limitations of traditional techniques. Specifically, powder-based AM processes-such as SLS and binder jetting-classified under the ISO/ASTM 52900 standard, which defines seven categories of AM technologies (including material extrusion and powder bed fusion), enable the fabrication of boron-based ceramics with intricate architectures. Additionally, AM enables precise control over the material microstructure, allowing for the tailoring of mechanical and thermal properties process categories for additive manufacturing, including material extrusion and powder bed fusion, enable the production of boron-based ceramics with complex geometries [17, 91-93].

The challenges associated with traditional manufacturing methods for boron-based ceramics such as high costs, material loss, and geometric limitations during sintering, casting, and machining-have increased interest in alternative approaches. In this context, AM emerges as a transformative method capable of overcoming these barriers, thereby enabling boron-based ceramics to find broader applications across high-performance industrial sectors [18].

5. The Transformative Role of Additive Manufacturing

AM, has revolutionized traditional manufacturing methods by enabling the production of complex geometries with unprecedented precision and efficiency. Unlike conventional techniques, AM builds objects layer by layer, reducing material waste and allowing for innovative designs that were previously not possible [94]. This technology has found applications in various fields, including aerospace, healthcare, and energy, particularly in the production of advanced materials such as boron-based ceramics [17].

The adaptability of AM to various materials, such as polymers, metals, and ceramics, has accelerated research and industrial adoption. It offers cost-effective solutions for both prototyping and large-scale production, while promoting sustainability through reduced waste and energy consumption [95]. With the advancement of technology, the potential to transform production and enable new applications continues to grow, making it one of the cornerstones of modern engineering and design.

5.1. Additive Manufacturing Methods: Stereolithography, Binder Jetting, and Selective Laser Sintering

AM has revolutionized the production of complex geometries, especially in the fabrication of advanced materials like boron-based refractor ceramics. Among various AM techniques, SLA, binder jetting, and SLS are prominent methods for producing ceramic components with high precision while minimizing material waste.

SLA is a photopolymerization technique that uses a laser to cure liquid resin layer by layer. This allows for the production of complex ceramic parts with high surface quality. Recent advancements in SLA have focused on the development of ceramic-loaded resins, which enable the direct production of green bodies that can later be sintered to achieve full density. For example, Griffith et al. demonstrated the feasibility of using SLA for the production of alumina ceramics with complex geometries and highlighted its potential for boron-based ceramics [96].

However, as with all binder-based AM methods, sintering is required to achieve full density in ceramic parts produced via SLA. This also applies to other techniques such as binder jetting and FDM. The sintering process significantly affects the mechanical properties and density of ceramic components. The atmosphere and sintering methods used in the processing of boron-based ceramics play a critical role in determining the final properties of the product. Hot isostatic pressing (HIP) is typically performed in an argon atmosphere at a temperature of 2000°C and a pressure of 200 MPa. Additionally, the atmospheres used in the sintering of B_4C ceramics (e.g., argon, nitrogen, vacuum) and the chosen sintering techniques significantly influence the microstructure and mechanical properties of the final product [97, 98]. Binder jetting is a powder-based AM method that creates layered structures by selectively spraying a liquid binder onto a powder bed. This technique is particularly advantageous for ceramics due to its ability to produce parts without the need for support structures and its compatibility with a wide range of materials [99]. SLS enables the production of dense and durable ceramic components by selectively fusing powder particles. Due to its ability to achieve high mechanical strength and thermal stability, SLS has been extensively studied for use in refractory ceramics. Deckers et al. reviewed the applications of SLS in ceramic production and noted that this method is suitable for B_4C and other high-performance materials [92]. FDM is an extrusion-based 3D printing technique that utilizes thermoplastic filaments loaded with ceramic particles. This method is cost-effective and widely accessible, making it suitable for producing complex ceramic components. However, challenges such as achieving high ceramic loading in filaments and ensuring uniform dispersion remain. Recent studies have demonstrated the feasibility of using FDM for fabricating SiC and ZrO_2 ceramics with intricate geometries [100].

DIW, also known as robocasting, involves the extrusion of highly viscous ceramic pastes through a nozzle to build structures layer by layer. DIW is particularly advantageous for producing porous ceramic scaffolds and components with complex internal architectures. Its low cost and material versatility make it an attractive option for fabricating boron-based ceramics. However, achieving high density and mechanical strength in DIW-fabricated parts can be challenging due to the inherent porosity and potential for defects during drying and sintering [101, 102].

Each method has its own strengths and limitations, and ongoing research aims to address the technical challenges associated with these techniques. The continued development of AM methods will enable boron-based ceramics to find broader applications in high-temperature and high-stress environments.

6. Applications of Boron-Based Ceramics in Additive Manufacturing

Boron-based ceramics, particularly B_4C and BN, possess remarkable properties such as exceptional hardness, thermal stability, and effective neutron absorption. These unique characteristics make boron-based ceramics ideal materials for advanced applications in industries such as aerospace, defense, and nuclear [103-105]. SLS, in particular, stands out as an effective AM method for producing B_4C components with complex geometries. These components are used in high-performance applications such as lightweight armor systems and neutron shielding [106, 107]. On the other hand, binder jetting enables the production of porous structures with materials such as BN. This feature offers significant advantages, particularly in high-temperature environments, such as applications in heat exchangers and insulation materials [108, 109]. Another advantage of AM is the ability to customize the microstructure and mechanical properties of boron-based ceramics. This capability opens up new applications in the biomedical field, such as bone implants and drug delivery systems [110, 111]. The adaptability of boron-based ceramics allows for the optimization of material properties to meet specific application requirements. However, despite these advancements, challenges such as achieving full density and managing residual stress during the AM process persist. In this context, research is focused on optimizing AM process parameters and developing new raw materials to enhance the performance of boron-based ceramics [112, 113]. For example, the effects of sintering additives and the application of external pressure during the sintering process have been highlighted as key factors influencing the densification and mechanical properties of the final products. With the maturation of the AM technology, it is expected that additively manufactured boron-based ceramics will play an increasingly important role in both industrial and scientific applications [105, 109].

The combination of the inherent superior properties of boron-based ceramics with modern AM techniques makes these materials increasingly feasible for a wide range of industrial applications. Ongoing research holds great promise for overcoming existing challenges, further solidifying their role in meeting high-performance requirements across various industrial sectors.

6.1. Turbine Blades and Aerospace Components

Boron-based ceramics, particularly B_4C and BN, are gaining increasing recognition for their exceptional properties, including high thermal stability, an excellent strength-to-weight ratio, and resistance to extreme environmental conditions. These attributes make them ideal candidates for applications such as turbine blades and aerospace components. Due to their resistance to high temperatures and abrasive environments common in turbine engines, these materials offer significant advantages in aerospace applications [105]. The integration of AM techniques, particularly methods like SLS and binder jetting, has revolutionized the production of these ceramics. It has made possible the creation of complex and lightweight designs that enhance the performance and efficiency of aerospace systems [25, 114]. For example, BN components produced through AM are successfully used in turbine engines due to their excellent thermal conductivity and oxidation resistance, which contribute to improved operational lifetimes under high-temperature conditions [103]. Similarly, B_4C composites produced through AM techniques have shown potential in creating lightweight, high-strength components. These composites provide superior protection against micrometeoroid impacts and radiation, making them crucial for spacecraft components [115]. Ongoing research focuses on improving AM parameters and developing new raw materials to enhance the performance of boron-based ceramics produced through AM [103]. For example, SPS is being studied to enhance the densification and mechanical properties of B_4C ceramics. These enhancements are essential for the application of these materials in structural components [106]. As research progresses in addressing these challenges, the adoption of 3D-printed boron-based ceramics in turbine blades and aerospace components is expected to increase significantly, fostering innovations in future aerospace and space technologies.

6.2. Armor Systems and Electronic Devices

Boron-based ceramics, especially B_4C and BN, are increasingly being used in critical applications due to their unique properties, such as high hardness, light weight, and excellent thermal conductivity. The emergence of AM technologies has significantly enhanced the performance of these materials, making it possible to produce complex geometries necessary for optimizing their functional capabilities. For instance, B_4C armors produced via SLS maintain their lightweight characteristics while providing optimized ballistic resistance, making them ideal for military and security applications [1, 9]. The lightweight structure and high hardness of B_4C provide effective protection against the weight disadvantages typically associated with traditional armor materials [116].

Similarly, the high thermal conductivity and electrical insulation properties of BN make it suitable for high-power electronic devices, such as AM-produced cooling grids and thermal management solutions. The ability to customize the microstructure and properties of these ceramics through AM enhances not only thermal management performance but also improves protection levels in armor systems. For example, the integration of BN in electronic applications can lead to more efficient heat distribution, increasing the lifespan and reliability of electronic devices [45, 103].

Ongoing research in these areas will expand the use of additively manufactured boron-based ceramics, driving future technological advancements. Researchers are focusing on optimizing AM processes to control porosity and improve the mechanical properties of the final products [117].

7. Future Potential and Research Directions

Boron-based refractory ceramics, especially B_4C and BN, play a critical role in modern engineering applications due to their high temperature resistance, chemical inertness, and superior mechanical properties. However, several important areas require focus in future research to fully realize the potential of these materials. First, AM technologies need to be further developed. Although layer-by-layer production techniques have made it possible to produce boron-based ceramics in complex geometries, optimizing sintering processes for the production of fully dense and high-performance parts is of paramount importance. In this context, emphasis should be placed on the use of sintering aids and the optimization of AM parameters. Additionally, utilizing boron-based ceramics in composite forms with other ceramics or metals could further enhance their material properties. Specifically, composites of B_4C with ZrO_2 or SiC can enhance thermal shock resistance and corrosion durability. The production of such composites through AM methods may open up new application areas. Microstructural control should also be an important focus of future research. The mechanical properties of boron-based ceramics can vary significantly depending on their microstructure. Therefore, it is crucial to develop methods for controlling the microstructure to enhance properties such as fracture toughness and wear resistance. The exploration of new application areas could further boost the potential of boron-based ceramics. Their use in fields such as biomedical implants, energy storage systems, and high-temperature applications is promising, particularly with the utilization of structures like BNNTs and BN quantum dots in drug delivery systems and biosensors for biomedical applications. Finally, making the production processes of boron-based ceramics more sustainable and cost-effective could facilitate their more widespread use in industrial applications. The potential of AM techniques to reduce material waste offers a significant advantage in this regard. Future research focusing on these areas could further enhance the potential of boron-based ceramics and enable their broader application in modern engineering.

8. Conclusions

This study emphasizes the critical role of boron-based refractory ceramics, particularly B_4C and BN, in modern engineering applications. Due to their unique properties, such as high hardness, low density, thermal stability, and chemical inertness, these materials hold an important place in fields such as nuclear energy, the defense industry, aerospace, and space. However, conventional manufacturing methods restrict the potential applications of these materials.

In recent years, AM technologies have revolutionized the production of boron-based ceramics. Methods such as SLA, binder jetting, and SLS enable the fabrication of high-performance parts with complex geometries. These technologies reduce material waste, increase design flexibility, and lower production costs. Furthermore, future research should focus on optimizing AM processes, developing composite materials, and exploring new application areas. Producing boron-based ceramics using more sustainable and cost-effective manufacturing methods will enable their widespread use in industrial applications.

Boron-based refractory ceramics stand out as an essential component of modern technology, offering unique properties for high-performance applications. AM technologies help overcome the limitations of conventional production methods, enabling the creation of more customized and complex parts. These advancements significantly enhance the industrial and scientific potential of boron-based ceramics.

9. Author Contribution Statement

Ece Kalay: Conceptualization, visualization, resource provision, data analysis.

İskender Özkul: Data curation, supervision, validation, review, and editing.

Both authors have contributed to all stages of the study, evaluated the results, and approved the final manuscript.

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