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STRUCTURE, PROPERTIES AND MODERN SYNTHESIS METHODS OF ALUMINUM BORIDES

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Abstract

Aluminum borides represent an important class of boron-containing materials owing to their combination of low density, high hardness, chemical stability, and thermal resistance. Their properties are strongly governed by the crystal structure and phase composition, making them attractive subjects for both fundamental and applied materials research. This review summarizes the current state of research on aluminum borides, with emphasis on the crystal structure and physicochemical properties of the two principal phases, AlB_2 and AlB_{12}, and the relationship between their atomic structure and material characteristics. The main synthesis approaches, including mechanical alloying, direct high-temperature synthesis, self-propagating high-temperature synthesis (SHS), plasma synthesis, molecular beam epitaxy (MBE), and electron-beam technologies, are comparatively discussed with respect to their influence on phase formation, microstructure, and structural homogeneity. Particular attention is paid to electron-beam modification, which offers unique advantages such as localized energy input, processing under vacuum, and extremely high heating and cooling rates. Although its application to the synthesis of aluminum borides remains relatively limited, the available studies indicate considerable potential for the controlled formation of Al–B boride structures. The review highlights current research trends and identifies the limited availability of experimental studies on electron-beam synthesis of aluminum borides as an important challenge for future research.

Keywords: Aluminum borides; AlB_2; AlB_{12}; electron-beam modification; synthesis; microstructure

INTRODUCTION

The development of new structural and functional materials combining low density, high mechanical strength, thermal resistance, and chemical stability is one of the leading directions in modern materials science. Of particular interest are metal borides, which, owing to the strong covalent bonds in the boron sublattice, are characterized by high hardness, good wear resistance, high melting temperature, and excellent chemical stability. These properties make them promising materials for applications under extreme operating conditions, including metallurgy, energy engineering, mechanical engineering, and aerospace technology [1].

Among the numerous metal borides, aluminum borides represent a particularly interesting group of compounds due to the combination of low density, high specific hardness, and good oxidation resistance. Their physical, mechanical, and electronic properties are largely determined by the characteristics of the crystal structure and the nature of the chemical bonds between aluminum and boron atoms. Depending on the Al:B ratio, different boride phases are

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formed in the system, exhibiting significant differences in crystal structure, phase stability, and material properties [2,3].

In recent years, increasing scientific interest has been focused on aluminum borides both as independent ceramic materials and as reinforcing phases in metal matrix composites, protective coatings, and functional surface layers. At the same time, various technological approaches for their synthesis have been developed, including mechanical alloying, high-temperature synthesis, self-propagating high-temperature synthesis (SHS), plasma synthesis, molecular beam epitaxy, and electron-beam technologies. The choice of a particular synthesis method has a significant influence on the phase composition, microstructure, and material properties of the obtained materials [3–5].

Despite the considerable number of published studies, the available information on aluminum borides remains fragmented among different research areas related to crystal structure, properties, and synthesis technologies. This makes it difficult to comprehensively evaluate the relationship between synthesis conditions, phase composition, and the functional characteristics of these materials.

The aim of this stady is to summarize and analyze the current state of research on aluminum borides, with emphasis on the crystal structure and properties of the main AlB_2 and AlB_{12} phases, the modern methods for their synthesis, and the prospects for the application of electron-beam technologies in the synthesis and modification of Al–B materials.

EXPOSITION

1. Structure and Properties of Aluminum Borides

The binary aluminum–boron (Al–B) system exhibits considerable structural complexity, with AlB_2 and AlB_{12} being among the most extensively investigated aluminum borides. In addition to these compounds, other compositions and metastable structures have been reported or theoretically investigated. Their formation and stability depend on chemical composition, crystal structure, and synthesis conditions [2,5].

The crystal structure is the determining factor for the physicochemical properties of aluminum borides. Depending on the boron content, they form layered or three-dimensional boron sublattices, which determine the nature of the chemical bonding, the electronic structure, and the mechanical properties of the individual phases [1,2,4]. Therefore, the greatest interest is focused on AlB_2 and AlB_{12}, whose crystal structure and properties are discussed in more detail in the following subsections.

1.1. Aluminum Diboride (AlB_2)

Aluminum diboride (AlB_2) is the most extensively studied compound in the Al–B system and crystallizes in a hexagonal AlB_2-type structure (space group P6/mmm).

In Figure 1 the crystal structure of AlB_2 is presented. The crystal lattice consists of two-dimensional hexagonal boron layers with aluminum atoms located between them. The strong covalent bonds between the boron atoms and the mixed metallic-covalent nature of the Al–B bond determine the high structural stability of the compound [2,4].

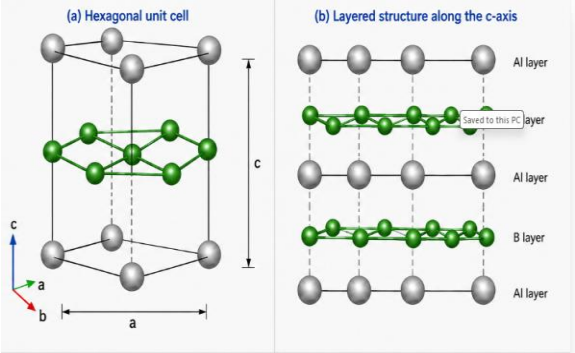


Fig. 1. *Crystal structure of AlB_2: (a) hexagonal unit cell and (b) layered arrangement of boron and aluminum atomic layers along the c-axis.*

The electronic structure of AlB_2 is formed by the interaction between the boron 2p orbitals and the valence electrons of aluminum. The electronic structure of AlB_2 is characterized by hybridization between the boron 2p orbitals and the valence electrons of aluminum, which determines the metallic character of the electrical conductivity

and the absence of superconductivity, in contrast to the isostructural MgB_2 [4,6].

The combination of a stable crystal structure, good electrical and thermal conductivity, and high thermal stability makes AlB_2 a model system in studies of metal diborides. In addition to its fundamental significance, the compound is of interest as a component of high-temperature materials, protective coatings, and composite systems where a combination of low density, structural stability, and good chemical resistance is required [1,2,7].

1.2. Aluminum Dodecaboride (AlB_{12})

Aluminum dodecaboride (AlB_{12}) is a boron-rich compound whose crystal structure differs significantly from the layered hexagonal lattice of AlB_2. The literature describes α- and γ-modifications of AlB_{12}, built from a rigid three-dimensional boron framework including interconnected icosahedral B_{12} clusters that form a three-dimensional covalent network [8].

The crystal structure of AlB_{12} consists of spatially arranged boron B_{12} icosahedra, between which aluminum atoms are located (Figure 2). The layered arrangement of the boron clusters and aluminum atoms along the crystallographic c-axis provides high structural stability and determines the characteristic mechanical and thermal properties of the compound.

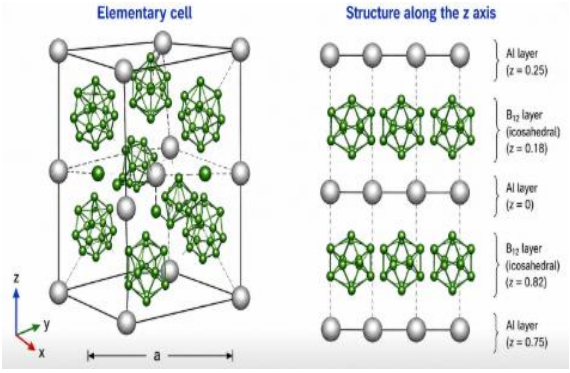


Fig. 2. *Crystal structure of AlB_{12}: (a) elementary unit cell containing B_{12} icosahedra and aluminum atoms; (b) layered arrangement of the atomic planes along the crystallographic c-axis.*

In α-AlB_{12}, the B_{12} icosahedra are interconnected through covalent B–B bonds, forming a continuous three-dimensional boron framework. Aluminum atoms occupy interstitial sites within the boron framework, and their distribution contributes to the stabilization of the crystal structure [8]. The presence of B_{12} icosahedral units makes AlB_{12} structurally similar to other boron-rich ceramics, including boron carbide [9,10].

The icosahedral crystal structure and the predominance of covalent bonding within the boron framework are responsible for the material's low density and high hardness. Reported values for α-AlB_{12} include a density of approximately 2.52–2.53 $g \cdot cm^{-3}$ and a hardness of about 22–24 GPa, although these properties depend on the phase composition, porosity, and consolidation technique employed [9–11]. However, its relatively low fracture toughness limits the use of monolithic AlB_{12} and has stimulated interest in composite materials, in which the boride phase is combined with a more ductile or fracture-resistant matrix [9–11].

Umanskyi et al. [11] investigated the high-temperature oxidation behavior of AlB_{12}–Al composites under isothermal and non-isothermal heating conditions. Their results demonstrated temperature-dependent oxidation and the formation of aluminum borate phases. These findings characterize the oxidation behavior of the composite system and should not be directly generalized to phase-pure AlB_{12}.

Overall, the properties of AlB_{12} originate directly from its three-dimensional icosahedral boron framework. The combination of low density and high hardness makes this material attractive for the development of lightweight wear-resistant ceramics, whereas its limited fracture toughness and susceptibility to high-temperature oxidation require careful control of the phase composition, grain size, and matrix selection in composite materials [9–11].

2. Methods for the Synthesis of Aluminum Borides

Aluminum borides can be synthesized

using a variety of processing routes, with the choice of method determining the phase composition, microstructure, and structural homogeneity of the resulting material. The most widely employed techniques include mechanical alloying, direct high-temperature synthesis, plasma synthesis, thin-film deposition methods, and electron beam technologies [3,12–18].

2.1. Mechanical Alloying

Mechanical alloying is one of the most widely used methods for synthesizing aluminum diboride from elemental aluminum and boron powders. During high-energy ball milling, the particles undergo repeated deformation, fracture, and cold welding, thereby increasing the contact area between the components and accelerating diffusion processes. Subsequent heat treatment (annealing) leads to the formation of AlB_2, while the final phase composition depends on the milling time, annealing temperature, and heat-treatment duration [3].

2.2. High-Temperature Synthesis

Direct high-temperature synthesis is based on the reaction between aluminum and boron at elevated temperatures. One of the most widely applied variants is self-propagating high-temperature synthesis (SHS, thermal explosion), in which a mechanically activated powder mixture is heated to the ignition temperature of a self-sustaining exothermic reaction. This method enables the rapid formation of AlB_2 with high phase purity but requires precise control of both the reaction temperature and the stoichiometric composition of the starting mixture [12].

2.3. Plasma Synthesis

Pak et al. [13] reported the formation of a powder product containing aluminum and α-AlB_{12} using a high-current pulsed arc discharge in an argon atmosphere. The coexistence of metallic aluminum and aluminum dodecaboride indicates that further optimization is required to obtain phase-pure boride powders.

2.4. Thin-Film Deposition by Molecular Beam Epitaxy

Molecular beam epitaxy (MBE) enables the growth of high-quality AlB_2 thin films under ultra-high vacuum conditions. Aluminum and boron are evaporated from independent sources and condensed onto a heated substrate, where epitaxial crystal growth takes place. The use of a pre-deposited aluminum template layer provides effective control over the crystallographic orientation and improves the structural uniformity of the deposited films [14].

2.5. Electron Beam Modification

Electron beam modification is an advanced surface engineering technique for boride-based materials. The process is based on the interaction between a focused beam of high-energy electrons and the material surface, where the kinetic energy of the electrons is converted into heat. This enables localized melting, surface alloying, and electron beam physical vapor deposition (EB-PVD) while minimizing the thermal impact on the substrate [15].

The principal advantages of this technique include its high energy density, vacuum processing conditions, and extremely high heating and cooling rates. These characteristics suppress grain growth, promote the formation of a refined microstructure, and enable precise control over the structure of the modified surface layer [15].

Electron-beam surface alloying has been successfully demonstrated in the Ti–B system, where the formation of TiB_2-containing surface layers was experimentally confirmed [16]. These findings support the feasibility of electron-beam-assisted boride formation in selected metal–boron systems and provide a technological basis for further investigations of the Al–B system.

Electron-beam evaporation of boron-containing targets has been demonstrated as a deposition route for boron-containing coatings on titanium substrates [17]. Although this approach provides a basis for further development of boron-based surface layers, the formation of aluminum boride phases

requires separate experimental confirmation. Combining electron beam deposition with subsequent electron beam modification further improves the microstructure and surface properties of boron-containing coatings [18].

Although the direct electron beam synthesis of phase-pure AlB_2 and AlB_{12} remains relatively unexplored, recent studies indicate that combining electron beam processing with powder metallurgy, mechanical alloying, or coating technologies represents a promising strategy for producing Al–B materials with controlled microstructures and enhanced properties [15–18].

The synthesis methods discussed above differ in both their reaction mechanisms and their ability to control the phase composition, microstructure, and structural homogeneity of the resulting materials. The main characteristics of these technological approaches are summarized in Table 1.

Table 1. *Comparison of the main methods for the synthesis of aluminum borides.*

Method	Method	Method
Mechanical alloying	Mechanical alloying	Mechanical alloying
SHS (Self-propagating High-Temperature Synthesis)	SHS (Self-propagating High-Temperature Synthesis)	SHS (Self-propagating High-Temperature Synthesis)
Plasma synthesis	Production of ultrafine powders	Complex equipment
Molecular beam epitaxy (MBE)	Excellent control of crystal structure	Low productivity
Electron beam modification	***Localized high-energy processing under vacuum; very high heating and cooling rates***	***Still limited scientific literature on the Al–B s***

CONCLUSION

Aluminum borides represent a promising class of boron-containing materials that combine low density, high hardness, excellent chemical resistance, and good thermal stability. The two principal phases in the Al–B system, AlB_2 and AlB_{12}, differ significantly in their crystal structures, which in turn determine their distinct physical and mechanical properties. The layered hexagonal structure of AlB_2 is responsible for its good electrical and thermal conductivity, whereas the three-dimensional icosahedral boron framework of AlB_{12} provides high hardness and outstanding chemical stability.

The synthesis route has a decisive influence on the phase composition, microstructure, and structural homogeneity of the resulting materials. The processing techniques reviewed in this work—including mechanical alloying, high-temperature synthesis, plasma synthesis, molecular beam epitaxy, and electron beam technologies—offer different approaches for controlling boride phase formation and producing materials with tailored phase composition, microstructure, and structural homogeneity.

Among these methods, electron beam technologies are of particular interest because their high energy density, vacuum processing environment, and extremely high heating and cooling rates provide favorable conditions for the formation of refined boride structures with controlled microstructures. Despite these advantages, their application to the synthesis and modification of aluminum borides remains relatively limited in the available scientific literature. Consequently, electron beam processing represents one of the most promising directions for future research, highlighting the need for further investigations into the synthesis, microstructural characterization, and phase formation mechanisms of borides in the Al–B system.

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