Research Status of Titanium Diboride High Temperature Ceramics

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Abstract. Titanium diboride has a series of excellent physical and chemical properties, high melting point and hardness, good thermal stability and oxidation resistance. As an excellent hard phase, titanium diboride is used in new materials such as composite materials and cermet. It has a wide prospect in the application of high-temperature ceramics. In this paper, the research status, performance structure, preparation method and application of titanium diboride high-temperature ceramics are analyzed and summarized from the overall point of view, and the main problems faced by titanium diboride at present are also discussed. Finally, the future research direction of titanium diboride high temperature ceramics is discussed.

1. Introduction
Titanium diboride (TiB₂) is a compound with close-packed hexagonal lattice composed of covalent bonds and metal bonds, which has excellent physical and chemical properties. For example, high melting point, low density, high hardness, high fracture toughness and good high-temperature mechanical properties; Chemical performance is stable and oxidation resistance is good. Although oxidation starts at 800°C, the formed oxide layer is still very stable at 1200°C. Chemical corrosion resistance and melting resistance are strong, which can resist the erosion of non-alkali molten salts, including molten fluoride, molten nonferrous metals and most acids; Low friction coefficient to metal; Good wettability; Excellent thermal and electrical conductivity; Low coefficient of thermal expansion [1] Comparing the mechanical properties of boride and carbide, we can see that TiB₂ has the highest strength characteristics and thermal stability, its hardness exceeds that of all carbides, and its compressive strength is comparable to WC, especially when the temperature is higher than 1200°C, its mechanical properties are also the most wearable [2]. With the development of modern science and technology, all walks of life require higher and higher performance of materials, especially at high temperature. These requirements include high strength, high toughness, high temperature oxidation resistance, high thermal shock resistance, good wear resistance, stable chemical properties and so on.

2. Research status of titanium diboride high temperature ceramics
Although the single-phase TiB₂ material has high hardness and good electrical properties, its strength and toughness are low. At present, TiB₂ composites are mainly divided into two categories, one is TiB₂ metal composites, the other is TiB₂ ceramic composites. In TiB₂ metal composites, iron, molybdenum, chromium, nickel and other metals are additive materials that have been studied more.
3. Properties and structure of titanium boride high temperature ceramics
Titanium diboride powder is gray or gray-black, with hexagonal (AlB₂) crystal structure. Its melting point is 2980°C and it has high hardness. The antioxidant temperature of titanium diboride in air can reach 1000°C, and it is stable in HCl and HF acid. Titanium diboride is mainly used to prepare composite ceramic products. Because it can resist the corrosion of molten metal, it can be used in the manufacture of molten metal crucible and electrolytic cell electrode.

Titanium boride (TiB₂) is the most stable compound of boron and titanium, and it is a quasi-metal compound of hexagonal system. The structural parameters of the complete crystal are: A is 0.3028nm and C is 0.3228nm. In the crystal structure, the boron atom plane and titanium atom plane alternately appear to form a two-dimensional network structure, in which B and other three B are combined by covalent bonds, and an extra electron forms a large π bond. This layered structure of boron atoms similar to the stone mill and the electrons in the outer layer of Ti determine that TiB₂ has good conductivity and metallic luster, while the Ti-B bond between the boron atom plane and the titanium atom plane determines the high hardness and brittleness of this material.

4. Titanium boride and its preparation process of high temperature ceramics

4.1. Preparation process of titanium boride
The special physical and chemical properties of TiB₂ determine that this material has a very wide application prospect. However, the preparation of this material is very difficult, and the technology of preparing TiB₂ with high purity, low cost and large-scale industrialization is the subject of extensive research all over the world. At present, the main methods for preparing TiB₂ raw materials include carbothermal reduction, self-propagating high-temperature synthesis, mechanochemical reaction, vapor deposition, ball milling and so on.

(1) Carbothermal reduction method
In this method, oxides of titanium and boron are used as raw materials, carbon black is used as reducing agent, and carbon reduction treatment is carried out in a carbon tube furnace at high temperature for a long time. The main chemical reaction formula is 2TiO₂+2B₂O₃+5C=2TiB₂+5CO₂ or TiO₂, carbon black and boron carbide are used as raw materials to react 2TiO₂+C+B₄C=2TiO₂+2CO₂. The purity of synthesized TiB₂ powder depends on the purity of raw material powder. Thermal reduction method is a widely used process in industrial production. Its main disadvantage is that the TiB₂ powder obtained is coarse in particle size and high in impurity content.

In recent years, in order to further improve the production process of carbothermal reduction method, scientists and technicians in various countries are still exploring further. Welham [3] 2000 uses rutile, boron oxide and graphite as raw materials to prepare TiB₂. Before heating up, the mixed raw material powder is mechanically ground. With the extension of grinding time, the temperature of carbothermal reduction reaction can be reduced. For example, if the raw material mixture is ground for 1 hour, the reaction temperature is 1400°C, and if the grinding time is extended to 100h hours, the reaction temperature will be reduced to 1200°C, which is mainly due to the formation of TiB during grinding. Takeyasu et al [4] studied the precursor method of rapid carbothermal reduction method with TiO₂, HBO₃ and corn starch (chemically pure) as raw materials, and synthesized ultrafine TiB₂ powder with particle size of 80nm. After heat treatment in hydrogen atmosphere (800°C) for 9 hours, the free carbon content was greatly reduced to only 2.9%.

(2) Self-propagating high-temperature synthesis method
Self-propagating high-temperature synthesis (SHS) was first formally put forward in 1967 by Merzhanov, a former Soviet scientist, etc. [5] Its main feature is that the chemical reaction can continue automatically by using the energy of high exothermic reaction, so as to achieve the purpose of synthesizing and preparing materials. Generally, the raw material mixture to be reacted is pressed into a block, and the reaction is ignited at one end of the block, and the huge heat released by the reaction causes the adjacent materials to react, resulting in a rapid reaction! The spreading burning wave. With the advance of combustion wave, the raw material mixture is transformed into products [6]. Wang...
Weimin et al. synthesized TiB₂ powder by SHS method with chemically pure B₂O₃, TiO₂, and analytically pure magnesium powder as raw materials. The research shows that the main physical and chemical changes of B₂O₃-TiO₂-Mg system in SHS process include a small amount of reduction of B₂O₃ after melting, a large amount of reduction of TiO₂-B₂O₃ after melting magnesium and synthesis of TiB₂. In SHS synthesis, adding a small amount of magnesium as diluent reduces the synthesis temperature and combustion speed.

Fu Zhengyi et al. studied the SHS synthesis process of TiB₂ theoretically and experimentally. The research shows that the different starting temperature, diluent content and original particle size will affect the self-propagating high-temperature synthesis process, and finally affect the structure and properties of the synthesized product. Vadchenko et al. conducted an experimental study on the combustion wave mode of Ti₂B₂ self-propagating high-temperature synthesis system added with Cu and Fe, and found a low-speed reaction precursor propagation mode. The mechanism of this low-speed spread pattern needs further study. Radev et al. studied and compared some properties of TiB₂ powder prepared by SHS method and mechanochemical synthesis method. The research shows that there are some differences in some specific properties of the products obtained by different synthesis methods, and the dynamic factors in the synthesis process play a decisive role in the properties of the products. Radev et al. studied the properties of TiB₂ powder synthesized by SHS with amorphous boron powder (purity > 98%, particle size < 10um.) and high-purity Ti with purity > 99% as raw materials. The research shows that it is very important for the intermediate particles to contact each other during the synthesis process. The crystal shape of TiB₂ powder synthesized is well developed, but there is some unreacted boron in the product.

When SHS is used to synthesize different materials, the combustion wave velocity varies greatly, which mainly depends on the nature of raw materials, the chemical proportion of raw materials, the porosity of the original compacted block, and the degree of uniform mixing of raw materials.

(3) Mechanochemical reaction method

Mechanical method (MR) is also a method developed in recent years to synthesize some refractory compounds. Include mechanochemical displacement reaction (MDR), mechanical alloying (MA) and other types. In this method, the reactant powder is placed in a high-energy ball mill, and the powder repeatedly changes from deformation to crushing under the action of extrusion and shearing of the grinding ball. The violent friction and collision of the ball milling medium causes the mechanical energy to be converted into chemical energy to synthesize the required reactants. Compared with carbothermal reduction method and SHS method for preparing TiB₂, the mechanochemical reaction method has the advantages of low synthesis temperature, wide source of raw materials and low cost. Therefore, the research on the synthesis of TiB₂ by mechanochemical reaction is also increasing. Kudaka et al. synthesized TiB₂ by mechanochemical displacement reaction. The reaction takes TiB₂ (purity > 99%), graphite (purity > 99.7%), amorphous boron powder (purity > 96.6%) and metallic calcium powder (purity > 98%) as raw materials. These raw materials are mixed with 20% of calcium exceeding the stoichiometric ratio (calcium acts as a reducing agent in the reaction process) and placed in a planetary mill, which is ground for about 1 hour under argon atmosphere. Welhum also reported that TiO₂, Mg powder and B₂O₃ were used as raw materials, and the raw material mixture was mechanically mixed and milled for 10-15h. During the milling process, the reaction of TiO₂+B₂O₃+5Mg = 5MgO+TiB₂ occurred. After the reaction product was treated by acid washing and other measures, the TiB₂ particle size was about 500nm.

In addition, Radev and others also studied the preparation of TiB₂ powder by mechanochemical reaction. As mentioned earlier, this method has the advantages of low synthesis temperature, short synthesis time and simple operation. However, in the process of mechanochemical reaction, the size, quantity and rotating speed of the abrasive have strict requirements, which have been reported in detail in the above research. The reaction mechanism and kinetics of mechanochemical reaction method need to be further studied.
4.2. Preparation of titanium boride single-phase ceramics

Because of the covalent bonding in TiB₂ and the small self-diffusion coefficient of particles, the transfer speed of particles necessary for densification of the green body is very low, which makes it difficult to densify the green body. Therefore, the research on single-phase TiB₂ ceramics mainly focuses on the sintering densification process and the selection of the best sintering additives. Sintering of TiB₂ ceramics is mainly divided into pressureless sintering and hot-pressing sintering. The hot-pressing sintering process can significantly reduce the sintering temperature and improve the densification of the green body.

(1) Pressureless sintering TiB₂ ceramics

Kang et al.[14] reported that TiB₂ green body was pressureless sintered at 1800℃ and 1900℃ for 2h with a small amount of metal Cr and elemental Fe as sintering AIDS, and its density could reach 97.6% and 98.8% of the theoretical density. The strength and fracture toughness of the sample sintered at 1800℃ were 506Mpa and 6.16MpaM1/2, respectively, which showed good performance. Einsrud[35] reported that adding a small amount of metal Ni, NiB and elemental Fe promoted the pressureless sintering of TiB₂ at 1300-1700℃. When the sintering temperature is higher than 1500℃, the density of sintered body can reach more than 94% of the theoretical density, but when the sintering temperature is too high, the abnormal growth of particles will occur.

Adding sintering AIDS in pressureless sintering can promote sintering. The reason is that with the increase of temperature, sintering AIDS melt into liquid phase. Because of the existence of liquid phase, the diffusion and migration speed of particles increases, so that the green body can be densified at a relatively low temperature. Compared with hot pressing sintering, pressureless sintering technology can reduce the cost, and the equipment is simple and easy to operate.

(2) Hot pressing sintering TiB₂ ceramics

Although TiB₂ has a series of excellent properties mentioned above, the application of TiB₂ products is still greatly restricted so far. The reason is that it is difficult to obtain dense TiB₂ products. In addition to the fact that TiB₂ is a covalent bonding material with low self-diffusion coefficient, there is a thin oxygen-enriched layer (TiO₂) on the surface of TiB₂ powder, which is very unfavorable for TiB₂ densification. Therefore, the sintering temperature of pure TiB₂ without any sintering AIDS is as high as 2200-2300℃, and such a high sintering temperature will promote the excessive grain growth.

As we all know, if the grain size is too large, its strength, fracture toughness and other properties will be affected. Therefore, it is a concern of scholars all over the world to promote the sintering and densification of TiB₂ body at a relatively low temperature. In addition to the pressureless sintering process introduced earlier, at present, the hot-pressing sintering process is the most studied method to prepare TiB₂ ceramics. Park et al. studied the densification and mechanical properties of TiB₂ ceramics sintered by hot pressing with Si₃N₄ as sintering aid. The research shows that when TiB₂ ceramics are hot-pressed sintered, the green body can be hot-pressed sintered at 1800℃ by adding 2.5% Si₃N₄. The elimination of Ti₃N₄ and TiO₂ on the surface of the green body to form TiN, BN and amorphous SiO₂-TiO₂ can effectively inhibit the growth of particles, contribute to the densification of TiB₂ and greatly improve the strength of the green body. In another article, Park et al. also studied in detail the influence of hot pressing temperature on the densification and mechanical properties of TiB₂. The research shows that when TiB₂ green body with 2.5%Si₃N₄ is hot-pressed and sintered at 1500-1800℃ for 1 hour, it is found that the temperature range of the rapid increase of compactness is 1500-1600℃, and a eutectic liquid phase is formed at about 1550℃. At the same time, the bending strength, Vickers hardness and fracture toughness of the green body also increased significantly at around 1550℃. Lilonghao[18] TiB₂ ceramics were prepared by hot pressing sintering at 1800℃ with AlN as sintering aid. The research shows that when less than 5% AlN is added as sintering aid, the compactness and mechanical strength of TiB₂ green body are greatly improved due to the reaction of AlN with TiO₂ on the surface of TiB₂ to form TiN and the exclusion of Al₂O₃-TiO₂, and the green body density usually reaches more than 98% of the theoretical density.
To sum up, it is very important to choose suitable sintering AIDS whether hot-pressing sintering process or pressureless sintering process is adopted. If proper amount of Ni, NiB, Fe, Cr, Si3N4, AlN and so on are not added as sintering AIDS, pressureless sintering can't be carried out below 2000℃, and hot-pressing sintering can't be completed in a short time. Compared with pressureless sintering, hot pressing sintering TiB2 ceramics has the advantages of short sintering time, low sintering temperature and good product performance. Because of this, in recent years, the research on hot-pressing sintering TiB2 ceramics has attracted extensive attention of material science scholars all over the world. Whether there are more suitable sintering AIDS, whether the sintering temperature can be further reduced, the densification mechanism of green body in hot pressing sintering and sintering kinetics and other issues need further study.

4.3. Preparation process of titanium boride cermet

(1) Sintering method

In 1952, Nelson first made the cermet TiB2-Cr\[^{[19]}\] by sintering method. His research shows that porous TiB2-Cr composites can be obtained by sintering at 1927℃ for half an hour. This material has good oxidation resistance, and its weight gain rate is only 0.4 mg/cm\(^2\) h in air at 1039℃. Yuditsky\[^{[20]}\] and others studied TiB2-Fe cermet composites, and considered that TiB2-Fe was unstable in the presence of C impurity. This trace amount of C is mainly produced by the carbothermal reaction between TiO2, C and B2O3 or B4C. When C exists, the following reactions may occur:

\[\text{TiB}_2 + 4\text{Fe} + \text{C} \rightarrow \text{TiC} + 2\text{Fe}_2\text{B}\]
\[\text{TiB}_2 + 12\text{Fe} + \text{B}_4\text{C} \rightarrow \text{TiC} + 6\text{Fe}_2\text{B}\]

Th. Jungljon\[^{[21]}\] and others studied TiB2-Fe materials by pressureless sintering. Completely dense materials can be obtained by using tiny TiB2(2um), and it is considered that the formation of Fe2B is the result of the reaction of Fe and TiB2 with B4C or C to form Fe2B and TiC. Although Fe2B is beneficial to the densification of TiB2-Fe ceramic materials, it damages the toughness of the materials, so the formation of Fe2B must be prevented. Although TiB2. Cermet composites with high density can be obtained by pressureless sintering technology, the mechanical properties of the materials are not ideal, which is mainly due to the abnormal grain growth caused by excessively high sintering temperature in the preparation process.

(2) Self-propagating high-temperature synthesis and pressurization technology

Self-propagating high-temperature synthesis (SHS)\[^{[22]}\] is a ceramic preparation technology that uses the exothermic reaction of raw materials to make the reaction self-sustaining. It has the characteristics of fast reaction speed and high reaction temperature. After SHS reaction, due to the gasification of impurities in raw materials and the shrinkage of crystal volume, the product generally has a compactness of 40% ~ 50%. The main principle of self-propagating high-temperature synthesis and pressurization technology is that after the combustion reaction is completed, external load is applied to it to obtain high-density materials. The way of pressurization can be mechanical pressure, static pressure of liquid phase and gas phase, hot extrusion, thermal explosion, etc. Because SHS reaction is an exothermic and self-sustaining reaction process, the reaction temperature is very high (1500 ~ 4000℃) and the speed is very fast, so the sintering temperature is reduced, the reaction time is shortened, and the product is pure and dense.

(3) Mechanical alloying technology

Mechanical alloying technology is that the mixed powder is subjected to high-energy ball milling, so that the particles are repeatedly deformed, broken and welded, so that the particles are continuously refined, resulting in lattice distortion and defects, and finally the characteristics of the original particles gradually disappear, forming a uniform metastable structure. Tianyi cheng et al. prepared TiB-NiAl composites by using this technology, and then sintered at warm temperature to obtain the composites with good properties.
4. Discharge plasma sintering technology

SPS technology is a new type of material sintering technology, which uses the plasma generated by high current to heat and sinter materials. It has the advantages of fast heating speed, uniform heating and short sintering time, and the obtained materials have fine and uniform microstructure and high density, and can be used to prepare gradient materials and complex work. In addition to the characteristics of hot pressing sintering, its main feature is that the ultra-fast densification sintering of materials is realized by bulk heating and surface activation, so it has very high thermal efficiency and unique superior heat for preparing materials difficult to sinter.

5. Controlled atmosphere sintering

The sintering atmosphere has great influence on the compactness and mechanical properties of products. At present, TiB₂ cermet composites are mostly prepared by single atmosphere sintering in Ar atmosphere or vacuum. Weon-Ju Kim et al. think that a single sintering atmosphere is not conducive to the densification of materials. The reasons are as follows: when sintering in vacuum, a large amount of metal liquid phase will vaporize and evaporate; Sintering under Ar atmosphere can capture gas. Therefore, he proposed the technology of two-step sintering. For TiB₂-Ni system, he compared three processes: vacuum sintering, Ar atmosphere protection sintering and two-step sintering. Through two-step sintering, that is, sintering for 1 hour at 1600°C in vacuum, introducing Ar atmosphere, and sintering again at 1700°C for 1 hour, the material with relative density of 99% was obtained, but there was no report on the related mechanical properties of the material. It is suggested that completely dense materials can be obtained by two-step sintering.

5. Conclusion

To sum up, the research of TiB₂-based composite ceramics has aroused the interest of more and more scholars. The research and development of titanium boride-based ceramic materials is very rapid, and there are many research methods and directions. The future development directions are expected to include:

1. Studying the basic theories involved in the synthesis and preparation of titanium diboride-based composite materials, including the influence of thermodynamics and kinetics on the material preparation.

2. Study the structure of titanium diboride matrix composites, especially the formation mechanism of interface structure, and the relationship between structure and preparation process, structure and composition.

3. Develop compound adhesive with high high temperature creep resistance, in order to improve wettability and high temperature performance, and improve toughness and high temperature creep resistance of materials.

4. Reduce the production cost. Looking forward to the future, with the deepening of research and development, new titanium boride-based ceramic materials with high performance will emerge continuously, and their application fields will also expand day by day.

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