Study on the preparation technology and high temperature oxidation characteristics of SiB₄ powders

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Abstract. High purity SiB₄ powder is the key raw materials for high temperature resistant coating of rigid ceramic insulating tile, which plays the role of forming a dense coating and self-healing in the coating. Therefore, to obtain SiB₄ powders with high performance and high purity at the same time can solve the problem of raw materials for high temperature resistant coating in China. However, the preparation process of SiB₄ powder is complex, and no domestic manufacturer can produce it, which greatly limits the development of related industries in China. The relationship between SiB₄ phase purity and boron-silicon ratio of raw materials, particle size and sintering process parameters in the synthesis of high-purity SiB₄ powders was explored. The experimental results show that the yield of SiB₄ can be significantly improved and the decomposition of SiB₄ can be inhibited by adjusting the crystallinity of boron powder, particle size of raw material, sintering process parameters and the ratio of boron to silicon. When 1μm boron powder and 1μm silicon powder are used, the ratio of boron to silicon is 3.5:1, and the sintering process is 1320 °C - 2h, the high purity sib4 powder with only SiB₄ phase detected by XRD phase analysis can be prepared after acid washing. On this basis, the high temperature oxidation characteristics of the prepared SiB₄ powder were studied. The experimental results show that SiB₄ powder can be oxidized at 1100 °C to form B₂O₃-SiO₂ glass phase, which proves that it has better high temperature oxidation performance. In conclusion, it was proved that the prepared SiB₄ powder had high purity and excellent high temperature resistance, which could be used for further production research.

1. Introduction
When the high-speed aircraft re-flies, the surrounding air will be severely compressed, which causes the aircraft surface to bear extremely high temperature, which poses a severe challenge to the performance of anti-heat insulation materials on the surface of the high-speed aircraft. Among the thermal insulation materials, the rigid thermal insulation tile can maintain a certain shape and strength at high temperature, which is mainly used in the windward side of aircraft, and has a large thermal shock, so it needs to meet the severe requirements of temperature resistance and erosion resistance. [1] Because of the large surface area, high porosity and low emissivity of the thermal insulation tile, the surface coating plays an important role in water insulation and thermal insulation. The surface of the coating is heated and emits most of the incident heat, while the thermal insulation tile prevents most of the remaining incident heat from being transmitted inward [2]. Therefore, the preparation of surface high temperature resistant coating has become the key technology in the application of thermal insulation system. [3]
Silicon tetraborate (SiB₄) is a kind of black-gray ceramic powder, which is insoluble in water, and has the properties of oxidation resistance, thermal shock resistance and chemical attack resistance. Especially, it has high strength and stability under thermal shock. It is often used as radiation agent and sintering aid for high-temperature coatings, which mainly plays the role of sintering aid and self-healing in coatings [4-5]. The traditional glass coating reacts at high temperature to generate gas, which causes bubbles or cracks on the surface of the coating, and reduces the emissivity and strength of the coating. Adding a small amount of SiB₄ powder to the coating can effectively improve the strength of the glass coating [2]. On the one hand, in the sintering process or high temperature working environment, SiB₄ is oxidized to form SiO₂-B₂O₃ glass phase with a specific proportion, which inhibits the generation of bubbles and repairs cracks; On the other hand, the oxide of SiB₄ forms a glass phase on the surface of radiation agents such as TaSi₂ and MoSi₂, which prevents the further oxidation of the radiation agent, so that the coating can work at a higher temperature and plays an important role in the high temperature thermal protection coating [6].

Because of the special use of SiB₄ powder, there are few reports on its preparation. There are two kinds of preparation methods of SiB₄ powder. The first method is to reduce compounds of Si and B at high temperature to obtain [7-12], such as reducing SiO₂, Si(H, Br, Cl or I)₄, B₂O₃, H₃BO₃, B₂H₆ and B(Br, Cl or I)₃ or their mixture to form various borides. The biggest problem of using this kind of method to synthesize SiB₄ is that the reaction can not be controlled, and the products obtained are the mixture of various borides, boron, silicon, and unreacted raw materials, which are difficult to separate from each other. The second method is to directly synthesize SiB₄ from simple silicon and boron at high temperature in inert gas or vacuum environment [13-15]. Compared with the first method, SiB₄ synthesized by this method has fewer impurities, but the reaction process is still difficult to control.

The main reason is that SiB₄ is an intermediate phase, and its synthesis purity is very sensitive to raw material characteristics and process conditions. First of all, from the point of view of raw materials, powder particle size, mixture dispersion uniformity and B/Si ratio will all affect the B/Si ratio in the micro-area, and the fluctuation of the ratio will easily lead to the formation of SiB₆ phase. In addition, from the point of view of sintering process, the reaction temperature is too low or the reaction time is too short, which can not guarantee the full synthesis of SiB₄, and there will be residual silicon and boron; Excessive reaction time or temperature will also promote the decomposition of SiB₄ into Si and SiB₆ [16-20]. At present, there is no method to remove SiB₆ impurities from SiB₄, which makes it very difficult to synthesize high purity SiB₄ powder. In the reported research work, SiB₃ with higher purity was prepared by optimizing the reaction temperature, time and boron-silicon ratio [21-23]. In addition to the factors discussed above, the influence of crystallinity of boron powder on the synthesis purity of SiB₄ is equally important. Boron powder can be divided into crystalline boron powder and amorphous boron powder. Crystalline boron powder has low activity, and the reaction temperature required for synthesis of SiB₄ is higher, which leads to easy generation of SiB₆ impurity phase. Therefore, amorphous boron powder with high activity is generally used to react with silicon powder to synthesize SiB₄. The amorphous boron powder is not completely amorphous, and contains a part of crystalline boron, which leads to different activities of amorphous boron powder, which will have a great impact on the purity of synthesized SiB₄. There is no relevant research report on the influence of the crystallinity of boron powder on the purity of SiB₄, so it is of great significance to study the preparation of high-purity SiB₄ powder based on the crystalline state of boron powder.

In this paper, the effects of the crystallinity of boron powder, the ratio of boron to silicon, the synthesis temperature and time on the synthesis purity of SiB₄ powder and its sintering characteristics are studied, in order to obtain high-purity SiB₄ powder for subsequent high-temperature coating research and industrial production.

2. Materials and Methods
As mentioned earlier, the main factors affecting the synthesis of SiB₄ powder are the particle size and particle size distribution of raw materials, the ratio of boron to silicon, the uniformity of mixing materials and sintering process parameters. As the synthesis of SiB₄ is a sensitive process of process
parameters, it is necessary to strictly control the raw material selection, mixing and sintering process parameters in order to synthesize SiB$_4$ powder with higher purity.

In terms of raw material selection and particle size, boron powder and silicon powder with higher purity are selected. Among them, there are many preparation methods of boron powder, including magnesium thermal reduction method, BCl$_3$ and H$_2$ reduction method at high temperature and electron beam high temperature evaporation purification method. Among them, the powder purified by electron beam evaporation at high temperature has high purity and good consistency, so crystalline boron powder with particle size less than 1 μm prepared by this method is selected as raw material. 99.9% silicon powder with an average particle size of 5 μm was used as raw material. Accurate control of Sintering process parameters is the key to the synthesis of SiB$_4$. Too long reaction time or too high reaction temperature will promote the decomposition of SiB$_4$ into Si and SiB$_6$ phases. However, the reaction temperature is too low and the reaction time is too short, which cannot guarantee the full reaction. Therefore, it is necessary to strictly control the sintering process such as reaction time, reaction temperature, sintering atmosphere, temperature rise and fall rate, etc. to reduce the formation of impurities. Therefore, the silicon powder and boron powder are weighed according to a certain molar ratio, and then put into a mixing tank. At the same time, agate balls are added, the ratio of ball to material is 2:1, and the ratio of alcohol to powder is 2:1. They are evenly mixed in a mixer for 2 hours, and then dried in an oven at 70℃. Placing the dried powder in a corundum crucible, and heating to 1280-1350 DEG C at a heating rate of 5℃/min under the protection of argon. As to the prepared SiB$_4$ powder, if there are residual B and Si, it can be removed by reaction with chlorine gas at high temperature.

At the same time, in order to explore the best preparation conditions, this paper confirmed that the obtained high-purity Sib$_4$ powder can be used for further research and industrial production by changing the ratio of Si powder to boron powder in raw materials, the particle size of raw materials and sintering process parameters (temperature and time), and analyzing the microstructure and high-temperature oxidation performance of samples by XRD and SEM.

3. Results and Discussion

3.1. The influence of boron powder crystallinity on the purity of synthetic powder

Fig. 1 is the XRD spectrum of amorphous boron powder with different specifications. As amorphous boron powder is composed of partially amorphous and crystalline boron powder, different specifications of boron powder have different crystallinity. The crystallinity of amorphous boron powder with different specifications is calculated by XRD peak fitting method. As shown in fig. 1, the crystallinity of three amorphous boron powders is 43%, 51% and 62% respectively. Fig. 2 shows SiB$_4$ powder synthesized by amorphous boron powder with different specifications. It can be seen that the crystallinity of boron powder has great influence on the purity of synthesized SiB$_4$ powder. SiB$_4$ synthesized by boron powder with crystallinity of 43% has a high SiB$_6$ diffraction peak. With the increase of crystallinity, SiB$_6$ phase decreases. When crystallinity reaches 62%, SiB$_6$ phase disappears and silicon diffraction peak appears. This is mainly due to the high activity of boron powder with low crystallinity, which can form part of SiB$_6$ phase besides SiB$_4$. With the increase of crystallinity, the activity of boron powder decreases gradually, and the difficulty of generating SiB$_6$ increases. When the crystallinity is high, SiB$_4$ cannot be completely synthesized, which shows that there is a surplus of silicon. Therefore, selecting boron powder with appropriate crystallinity has great influence on controlling the purity of SiB$_4$. 

3.2. Effect of boron-silicon ratio on purity of synthetic powder

Fig. 3 shows XRD patterns of SiB₄ powder samples prepared with different boron/Silicon ratios. It can be seen from the figure that when B/Si ratio is low, only SiB₄ and Si diffraction peaks are found, and with the increase of B/Si ratio, silicon diffraction peaks gradually decrease. When B/Si ratio is 3.5:1, silicon diffraction peaks disappear, and only SiB₄ phase and a few impurity peaks are observed. With the further increase of B/Si ratio, the diffraction peaks of silicon and SiB₆ phase appeared, which may be due to the excessive B/Si ratio, resulting in local boron enrichment, resulting in SiB₆, a small amount of silicon failed to participate in the reaction, and finally three phases appeared.
3.3. Influence of sintering process parameters on purity of synthesized powder

Fig. 4 is an XRD pattern of SiB$_4$ synthesized at different sintering temperatures. It can be seen from the figure that there is a silicon peak in the sample sintered at 1310°C, which indicates that the reaction did not occur completely at this time; When the temperature rises to 1320°C, the diffraction peak of silicon disappears and only SiB$_4$ phase is formed. With the further increase of temperature, the diffraction peak of SiB$_6$ begins to appear, and with the increase of temperature, the intensity of diffraction peak becomes higher and higher. When the temperature reaches 1360°C, the diffraction peak of silicon appears at the same time, which is due to the decomposition reaction of SiB$_4$ phase $3\text{SiB}_4\rightarrow\text{Si}+2\text{SiB}_6$.

Fig. 4 XRD of SiB$_4$ powders after sintering at 1310 °C - 1360 °C

Fig. 5 is the XRD pattern of samples sintered at 1320°C for different times. It can be clearly seen from the figure that when the sintering time is 1 h, the phases are silicon and SiB$_4$, which indicates that only part of SiB$_4$ is formed at this time, and some silicon does not participate in the reaction. Only SiB$_4$ phase was observed when the holding time was 2 h. When the holding time is extended to 3 h, besides the main crystalline phase SiB$_4$, SiB$_6$ phase appears, which indicates that the extension of sintering time will lead to the decomposition of SiB$_4$ phase.
3.4. Oxidation characteristics of SiB₄ powder at high temperature

In the process of coating preparation and sintering, the reaction between the borosilicate glass formed by oxidation of SiB₄ powder and borosilicate glass matrix can promote the coating sintering. In addition, when the coating cracks, the exposed SiB₄ powder will also be oxidized to form borosilicate glass, which can repair the coating. Therefore, it is necessary to study the oxidation characteristics of SiB₄ powder at high temperature.

Fig. 6 is an XRD pattern of SiB₄ powder which is kept at different sintering temperatures for 10 h. As shown in the figure, after sintering at 500°C, the diffraction peaks of SiB₄ phase are still very obvious, and the diffraction peaks of SiO₂ and B₂O₃ appear at the same time, which indicates that some SiB₄ powders have started to undergo oxidative decomposition at 500°C, but the oxidation of SiB₄ powders is slow at 500°C. When the temperature rises to 700°C, obvious amorphous features appear in the XRD pattern, but the phase of SiB₄ still exists. After further heating to 900°C for 10 h, the diffraction peaks of SiB₄ phase become very weak, and the diffraction peaks of B₂O₃ and SiO₂ are obvious. There is hardly any diffraction peak of SiB₄ phase in XRD pattern after holding at 1100°C for 10 h.

Fig. 7 is an SEM photograph of SiB₄ powder held at different sintering temperatures for 10 h. It can be seen that after holding at 500°C for 10 h, the powder remains granular, which is basically consistent with the original powder morphology. When the temperature rises, part of the powder forms a glass phase, and the powder gradually sticks together. When the temperature reaches 1100°C, a dense glass layer has been formed, indicating that SiB₄ powder has been basically oxidized into borosilicate glass phase at this time.
4. Conclusions

In this paper, the effects of crystallinity, particle size, boron-silicon ratio, mixing uniformity and sintering process parameters of raw materials on the synthesis purity of SiB₄ were studied, and the conclusions were as follows:

(1) The relationship between phase purity of synthesized SiB₄ and crystallinity of boron powder, particle size of raw materials, sintering process parameters and boron-silicon ratio was studied. The experiment showed that the purity of SiB₄ obtained by sintering at 1320°C for 2 hours was the highest when the ratio of boron powder to silicon powder was 3.5:1.

(2) Pickling the prepared SiB₄ powder to obtain high-purity SiB₄ powder with only SiB₄ phase detected by XRD phase analysis;
(3) The sintering characteristics of SiB₄ powder at different temperatures were studied, and it was found that with the increase of sintering temperature and holding time, SiB₄ gradually oxidized to form B₂O₃-SiO₂ glass phase.

Combining the experimental results, it can be proved that SiB₄ powder with high purity and high heat resistance has been synthesized in this paper. This is of great help to solve the production problems of rigid ceramic high temperature resistant coatings in China. On the basis of the work in this paper, we can further optimize the synthesis process of SiB₄ powder in the future, and gradually explore the actual industrial needs of raw materials, in order to solve the problem that the surface materials of aircraft in China are limited by foreign technology as soon as possible, and produce high-performance high-temperature resistant coatings.

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References
[1] Bertin, J.J., Cummings, R.M. (2003) Fifty years of hypersonics: where we've been, where we're going. Progress in Aerospace Sciences, 39: 511-536.
[2] Lu, Q., Hu, L.F., Luo, X.G., Jiang, G.Q. (2013) Development of ceramic composite and hot structures for hypersonic vehicles. Journal of the Chinese Ceramic Society, 41: 251-260.
[3] Laub, B., Venkatapathy, E. (2004) Thermal protection system technology and facility needs for demanding future planetary missions. Proceedings of the International Workshop Planetary Probe Atmospheric Entry & Descent Trajectory Analysis & Science, 544: 239-247.
[4] Li, Y., Wang, R.G., Rong, R.F., Gu, Z.G., Liao, M. (2003) Research of silver metalization on the surface of AlN composite based cofire at low temperature. Journal of Functional Materials, 34: 338-341.
[5] Cline, C.F., Sands, D.E. (1960) A New Silicon Boride, SiB₄. Nature, 185: 456-456.
[6] Wu, Y.B., He, X.D., Li, J. (2012) Preparation and properties of SiO₂-B₂O₃-MoSi₂-SiB₄ coating for ceramic insulation tile. Aerospace Manufacturing Technology, 5: 6.
[7] Tremblay, R., Angers, R. (1992) Mechanical characterization of Dense silicon tetraboride (SiB₄). Ceramics International, 18: 113-117.
[8] Jumper, E.J., Seward, W.A. (1994) Model for oxygen recombination on reaction-cured glass. Journal of Thermophysics and Heat Transfer, 8: 460-465.
[9] Gambaryan-Roisman, T., Shapiro, M., Litovsky, E., Shavit, A. (2003) Influence of gas emission on heat transfer in porous ceramics. International Journal of Heat & Mass Transfer, 46: 385-397.
[10] Tao, X., Xu, X.J., Guo, L.L., Hong, W.H., Guo, A.R., Hou, F., Liu, J.C. (2016) MoSi₂-borosilicate glass coating on fibrous ceramics prepared by in-situ reaction method for infrared radiation. Materials & Design, 103: 144-151.
[11] Tao, X., Liu, J., Xu, X., Hong, W., Feng, H. (2016) Comparative study of MoSi₂-Borosilicate glass coatings on fibrous ceramics prepared by in-situ reaction method and two-step method. Journal of Alloys & Compounds, 684: 488-495.
[12] Luo, L.M., Zhang, Y.X., Zan, X., Liu, J.Q., Zhu, X.Y., Wu, Y.C. (2018) Status and development of self-propagating high-temperature synthesis of high melting point powders. Chinese Journal of Rare Metals, 42: 1210-1220.
[13] Wu, Y.B., He, X.D., Li, M.W., He, F., Zhong, Y.S. (2012) Microstructure and properties of high emissivity coating for fibrous insulation composites. Rare Metal Materials & Engineering, 41: 323-325.
[14] Kher, S.S., Romero, J.V., Caruso, J.D., Spencer, J.T. (2008) The formation of neodymium boride thin film materials from polyhedral boron clusters and metal halides by chemical vapor deposition. Applied Organometallic Chemistry, 22: 300-307.
[15] Zou, J., Zhang, G.J., Fu, Z.Y. (2019) Pressureless densification of ultra-high temperature ceramics and microstructure tailoring. Chinese Journal of Rare Metals, 43: 1221-1235.
[16] Mukaida, M., Goto, T., Hirai, T. (1992) Preparation of SiB<sub>4</sub> and SiB<sub>6</sub> plates by chemical vapour deposition of SiCl<sub>4</sub> + B<sub>2</sub>H<sub>6</sub> system. Journal of Material science, 27: 255.
[17] Goto, T., Mukaida, M., Hirai, T. (1989) Chemical Vapor Deposition of Silicon Borides. Mrs Proceedings, 168, 1124-1131.
[18] Wuchina, E.J. (1995) Thermochemical modeling and chemical vapor deposition of two-phase borides in the hafnium-silicon-boron-chlorine-hydrogen system. Commonwealth of Virginia: Virginia Polytechnic Institute and State University
[19] Rizzo, H.F., Bidwell, L.R. (1960) Formation and structure of SiB<sub>4</sub>. Journal of the American Ceramic Society, 43: 550-552.
[20] Real, T., Roch, A. (1989) Preparation of High Purity SiB<sub>4</sub> by Solid State Reaction between Si and B. Ceramics International, 15: 73-78.
[21] Tremblay R, Angers R. (1992) Mechanical characterization of dense silicon tetraboride (SiB<sub>4</sub>). Ceramics International, 18: 113-117.
[22] Lim, G., Kar, A. (2009) Radiative properties of thermal barrier coatings at high temperatures. Journal of Physics D: Applied Physics, 42: 155412-155417.
[23] Goldstein, H.E., Leiser, D.B., Katvala, V.W. (1978) Reaction cured glass and glass coatings. U.S. Patent: 4093771, 1978-6-6.
[24] Søren, K. (2015) Quantitative analysis of silica aerogel-based thermal insulation coatings. Progress in Organic Coatings, 89: 26-34.
[25] Stewart, D.A., Leiser, D.B. (2008) Toughened uni-piece, fibrous, reinforced, oxidization-resistant composite. U.S. Patent: 7314648, 2008-1-1.