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Synthesis of Calcium Hexaboride Powder via the Reaction of Calcium Carbonate with Boron Carbide and Carbon

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The synthesis of calcium hexaboride (CaB₆) powder via the reaction of calcium carbonate (CaCO₃) with boron carbide (B_4C) and carbon has been investigated systematically in the present study. The influences of heating temperature and holding time on the reaction products have been studied using X-ray diffractometry, and the morphologies of CaB₆ obtained at various temperatures and holding times have been investigated via scanning electron microscopy. The interaction in the $CaCO_3-B_4C$ -carbon system by which CaB_6 is formed is a solid-phase process that passes through the transition phases $Ca_3B_2O_6$ and CaB_2C_2 . The optimal conditions for CaB_6 synthesis are a holding time of 2.5 h at a temperature of 1673 K, under vacuum (a pressure of 10^{-2} Pa). CaB₆ powder has the same morphology as B₄C, and the properties and the shape of CaB₆ powders can be improved by choosing good-quality raw materials.

I. Introduction

RARE-EARTH alkali-earth metal borides belong to a group of refractory, non-oxide-type, metal-like compounds that are characterized by a high melting point, high strength, and high chemical stability, as well as other special peculiarities, such as a low electronic work function, stable specific resistance, a low expansion coefficient in some temperature ranges, diverse magnetic orders, and high neutron absorbability. All these outstanding properties result in a wide range of applications for such materials in modern equipment.

Many countries have devoted research to these materials,¹⁻⁴ and from that research, the special properties of calcium hexaboride (CaB_6) and the resistance of its composites to neutron radiation in the nuclear industry have attracted widespread attention. In addition, a composite composed of boron carbide (B_4C) and CaB_6 can be used as abrasives, as well as in tool and structural-ceramic applications. Matsushita et al.5 investigated the oxidation of CaB₆ and a composite of titanium diboride (TiB₂) and CaB₆; a theoretical foundation for their use in oxidation-resistant materials has been established.⁶ Paderno et al.⁷ studied the emission characteristics of CaB₆ and CaB₆-TiB₂ composites. However, few papers have systematically described the synthesis of CaB₆ powder. Therefore, in this paper, the conditions that are appropriate for synthesizing CaB6 powder via the reaction of calcium carbonate (CaCO₃) with B₄C and carbon are described, as well as the effects of heating temperature and holding time on the synthesis of CaB₆ powder.

II. Experimental Procedures

The starting powders in the present study were $CaCO_3$, B_4C , and carbon powders. The characteristics of those powders are listed in Table I.

The CaCO₃, B₄C, and carbon powders were combined in the desired molar ratio (CaCO₃:B₄C:C = 2:3:1). Then, the combined powders were mixed with methanol and attrition-milled in an agate container at 600 rpm for 1 h, using agate ball media. The milled powder was dried and pressed into pellets 25 mm in diameter and 50 mm long. Next, seven or eight pellets were loaded into a boron nitride (BN) crucible 110 mm in diameter. The crucible was placed inside a vacuum resistance furnace (Model FVPHP-R-5 FRET-20, Fujidempa Kogyo Co., Ltd., Osaka, Japan), which was evacuated to a pressure of 10^{-2} Pa. The furnace was heated at a rate of 25 K/min and held for various times at different temperatures, then cooled by water circulation. The valve of the furnace was opened when the inner temperature was <373 K. The cooled pellets were removed from the crucible, and some of the pellets were ground to a powder for phase analysis via X-ray diffractometry (XRD) (Model D/max-RB, Rigaku Co., Ltd., Tokyo, Japan). The powder morphology was observed using scanning electron microscopy (SEM) (Model X-650EDAX-100, Hitachi Co. Ltd., Tokyo, Japan).

III. Results and Discussion

Different heating temperatures and holding times were used to determine the optimal synthesizing conditions for CaB_6 powder. These parameters are shown in Table II.

XRD patterns of the samples that were held for 2.5 h at various heating temperatures are shown in Fig. 1. The XRD pattern of the raw materials, which are used as a reference, is shown at the bottom of the illustration. The compositions of the raw materials remained unchanged after ball milling; however, the diffraction peaks of the carbon powder were not detected, because it is an amorphous phase. The product that was obtained at 1073 K consisted of CaO, B_4C , $Ca_3B_2O_6$, and CaB_2C_2 , which is an indication that CaCO₃ had decomposed to CaO and CO₂ and the CaO then had reacted with B_4C and carbon, or that CaCO₃ had reacted directly with B_4C and carbon. In either case, the transition phases $Ca_3B_2O_6$ and CaB_2C_2 were formed.

When the reaction temperature was 1273 K, the main phases were the same as those obtained at 1073 K, but CaB_6 diffraction peaks already existed, although they were very weak. This result indicates that CaB_6 can be formed at 1273 K. When the reaction temperature was 1473 K, the CaB_2C_2 transition phase disappeared and the intensities of the B_4C , CaO, and $Ca_3B_2O_6$ peaks decreased; accordingly, the intensity of the CaB_6 peak increased. When the heating temperature reached 1673 K, only one phase— CaB_6 —was present. Thus, only the CaB_6 phase can be obtained at 1673 K. During the formation of CaB_6 , the raw materials, transition phases, and final product were all solid, so that the interaction by which CaB_6 formed in the $CaCO_3$ – B_4C –carbon system was a solid-phase process.

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		Table I.	Characteristics of Starting Powders
Substance	Particle size (µm)	Purity (%)	Impurities present and quantity
CaCO ₃	0.5	99.5	Na ₂ O (0.20%), Mg (0.05%), K (0.01%), Fe (0.001%), Pb (0.002%)
B ₄ C	25-35	97.0	Si (1.58%), Fe (0.22%)
C	< 0.5		Zn (0.1%), sulfate (0.15%), Pb (0.01%), Fe (0.10%)

 Table II.
 Basic Technical Parameters of Synthesizing

 CaB₆ Powder

Sample	Holding time (h)	Reaction temperature (K)		
S1 (raw materials)				
S2	2.5	1073		
S3	2.5	1273		
S4	0.5	1473		
S5	1.5	1473		
S6	2.5	1473		
S7	6	1473		
S8	2.5	1673		



Fig. 1. XRD patterns of several samples reacted for 2.5 h at various temperatures ((a) starting mixture, (b) 1073 K, (c) 1273 K, (d) 1473 K, and (e) 1673 K).

Although CaB₆ powder can be obtained at a temperature of 1273 K, its synthesis is slow, because the reaction is a solid-phase process. To determine the optimum conditions for synthesis, various holding times at 1473 K were studied. Figure 2 shows XRD patterns of the samples reacted at 1473 K for various times. The intensities of the CaB₆ diffraction peaks in the mixture held for 0.5 h at 1473 K were stronger than those of the sample held for 2.5 h at 1273 K, and the CaB₂C₂ transition phase disappeared. This finding indicates that the CaB₆ phase formed violently at 1273–1473 K.

With a prolonged holding time, the intensities of the CaO, B_4C , and $Ca_3B_2O_6$ diffraction peaks gradually decreased and the intensities of the CaB_6 diffraction peaks increased. A limited amount of the $Ca_3B_2O_6$ transition phase formed after a holding time of 2.5 h. After holding for 6 h, the main phase was CaB_6 , although some B_4C and CaO phases still were present. All the transition phases disappeared in the temperature range of 1273–1473 K; however, complete reaction required $\gg 6$ h. In economic terms, this procedure was not feasible. The phase compositions obtained under the various conditions are listed in Table III.

To analyze the formation mechanism of CaB_6 powder, the powder obtained after holding at 1473 K for 1.5 h, after which a certain amount of CaB_6 powder has been formed, is shown in Figs. 3(a) and (b). Figures 3(d)–(f) show SEM micrographs of asreceived CaB_6 powder. As described previously, the processing temperature and holding time influences the purity and particle



Fig. 2. XRD patterns of several samples reacted at 1473 K for various times ((a) 0.5, (b) 1.5, (c) 2.5, and (d) 6 h).

Table III. XRD Analysis Results of Powder Obtained under Various Conditions

Sample	Phase composition
S1 (raw materials)	$CaCO_3$, B_4C , CaO
S 2	B_4C , CaO, Ca B_2C_2 , Ca ₃ B_2O_6
S 3	B_4C , CaO, Ca ₃ B_2O_6 , Ca B_2C_2 ,
	CaB_6 (trace)
S4	B_4C , CaO, Ca ₃ B_2O_6 , Ca B_6
S5	B_4C , CaO, Ca ₃ B_2O_6 , Ca B_6
S6	B_4C , CaO, Ca ₃ B_2O_6 (trace), CaB ₆
S7	CaO (trace), B_4C (trace), CaB_6
S8	CaB ₆

size during powder preparation. The results indicated that the powders obtained at 1473 and 1673 K had the same particle morphologies as those of the B_4C raw material; the results also show that the powder was dispersed without agglomeration (Figs. 3(a) and (c)). The CaB₆ powder obtained at 1673 K (Fig. 3(d)) was much coarser than that obtained at 1473 K (Fig. 3(b)), and many of the CaB₆ powders exhibited stratifications (Fig. 3(f)). The flat surface of the B_4C was smooth, but the surface of the powder obtained at 1473 K was coarse, because of the formation of transition phases, and the surface of the CaB₆ was much coarser, although it maintained the particle morphology of the B_4C raw material. The CaB₆ powder was dispersed, with many pores inside (Fig. 3(e)), but the faces of the stratified CaB₆ powder particles were much smoother.

The reaction of CaCO₃ (particle size of $<0.5 \ \mu$ m) with B₄C (particle size of >25–35 μ m) was the same as the reaction of a small sphere on a large plane. The reaction began from the neck that formed between the sphere and the plane. With prolonged holding time and increased heating temperature, the reaction moved continuously inside while the CaB₆ grains formed on the surface became larger. The reaction reached completion when given sufficient synthesis time. A diffuse structure was formed for gas release during the reaction.

 B_4C and CaB_6 have different crystal structures; thus, the crystal structures change during the synthesis of the CaB_6 powder. When



Fig. 3. SEM micrographs of samples obtained under various conditions ((a) and (b) 1473 K, holding time of 1.5 h and (c)-(f) 1673 K, holding time of 2.5 h).

the stress caused by the transformation of the crystal lattice is endurable, the CaB_6 maintains the B_4C morphology; however, if the stress is beyond the endurance limit, the CaB_6 becomes stratified. Thus, the morphology of the B_4C powders determines that of the CaB_6 powder, and the use of fine, high-quality, high-purity B_4C improves the properties of the CaB_6 powder more effectively.

IV. Conclusions

The synthesis of calcium hexaboride (CaB₆) powder via the reaction of calcium carbonate (CaCO₃) with boron carbide (B₄C) and carbon is a solid-phase process that passes through the transition phases Ca₃B₂O₆ and CaB₂C₂. A study of the influence of holding time and heating temperature on the synthesis of CaB₆ powder has indicated that the optimal conditions for CaB₆ synthesis are a holding time of 2.5 h at 1673 K under vacuum (pressure of 10^{-2} Pa). The morphology of CaB₆ is the same as that of B₄C; thus, choosing high-quality

 B_4C is one of the most important ways to improve the properties of a CaB₆ powder.

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