

Phase transformation of transient B_4C to CaB_6 during production of CaB_6 from colemanite

Ö. Yildiz*, R. Telle, C. Schmalzried, A. Kaiser

Institute of Mineral Engineering (Ceramic, Glass, Refractory and Building Materials) of RWTH Aachen, D-52064 Aachen, Germany

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Abstract

The aim of this project is the production of calcium hexaboride (CaB_6) from colemanite and petroleum coke and the determination of the temperature-dependent phase transformation of boron carbide (B_4C), which appears as an intermediate compound to CaB_6 . This process makes use of the advantages of the “ B_4C method” as a special case of the “*carbothermic method*” for the direct production of CaB_6 from natural raw materials.

Colemanite ($2CaO \cdot 3B_2O_3 \cdot 5H_2O$), taken from Eti holding Co. in Turkey, and petroleum coke are used as raw materials. As-received crushed colemanite is processed by calcination between temperatures of 400 °C and 600 °C. X-ray diffraction analyses show that the obtained material contains amorphous boron oxide (B_2O_3) and calcium oxide (CaO) as well as calcium carbonate ($CaCO_3$) and $SrSO_4$ as additional crystalline components.

The production of CaB_6 was carried out by sintering the powder mixture under argon between temperatures of 1400 °C and 2000 °C. The products were analysed with an X-ray diffractometer.

The experimental results and thermodynamic calculations show that B_4C is produced as an intermediate product and remains present up to temperatures of 1700–1850 °C as the boron source for the formation of CaB_6 . The decomposition reactions of B_4C to CaB_6 in this temperature range were recorded by X-ray diffraction analyses and agree with thermodynamic calculations.

It is concluded that the “*carbothermic method*” can be directly used for the production of CaB_6 from the as-received unmilled raw material obtained from the calcination of colemanite at 400 °C and petroleum coke.

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1. Introduction

Because of its hardness, melting point and electronic properties CaB_6 is used in a variety of industrial applications, where it is known as an abrasive and deoxydation material. It is used in large quantities as a deoxydising additive for the production of magnesia carbon bricks and for the refinement of pure iron, steel, and copper.^{1–5} Furthermore, it is used as a starting material for boron nitride synthesis.⁶ Numerous

papers have already been published on the physical, chemical and other properties,^{2,7–22} and the production^{2,8,9,23–28} of CaB_6 . New investigations in the last 15 years are concerned with the electronic structure and magnetism of CaB_6 .^{29–34} According to Kino et al.,³⁴ CaB_6 has a quasiparticle band structure and is of semimetallic character in bonding.

The high temperature oxidation behaviour of hot-pressed and sintered bodies of CaB_6 is studied by Matsushita and Komarneni.³⁵ The phase diagram of the Ca–B system is presented in “Binary Alloy Phase Diagram”³⁶ and also by Otani.³⁷

Usually, B_4C is used as a starting material for the production of CaB_6 .^{2,8,38–40} Zenk et al.³⁹ have synthesised CaB_6

* Corresponding author. Tel.: +49 1791 494621; fax: +49 1212 5137 69856.

E-mail address: o.yildiz@gmx.de (Ö. Yildiz).

powder via the reaction of CaCO_3 with B_4C and carbon. The phase transformation dependency on temperature and the quality of the raw material colemanite and on the production process of CaB_6 have not, however, been studied extensively either by means of X-ray experiments or by thermodynamic calculations.

Carbothermic reduction of a mixture of the metal oxide and boron oxide with carbon at high temperature is known as the *carbothermic method*. Carbon and/or B_4C are reducing agents in carbothermic method.^{2,8,24,28,40} When B_4C is used as a reduction material, the process is known as the *B_4C -method*. The B_4C -method is also a carbothermic process, but it provides both carbon for the reduction of the oxide as well as boron as a reactant. Therefore, B_4C is preferred in the production of CaB_6 and other borides such as TiB_2 , TaB_2 .^{2,8,26–28}

The most important methods for the preparation of borides are therefore the following:

- Synthesis of the compound through either melting, pressure sintering or hydrolysis.
- Reduction of the metal and boron oxide with carbon (*carbothermic method*).
- Reaction of the metal oxide with B_4C (*B_4C -method*)
- Reduction of the metal and boron oxide with metals Al, Si, Mg (*aluminothermic reduction*, etc.).

The selection of the production method is dependent on the properties of the raw material and the desired end product of boride. In addition, the conditions of the reaction mechanisms play a very significant role.^{10,27}

In this work, the production of CaB_6 from colemanite and petroleum coke, and the determination of the temperature-dependent phase transformation from B_4C to CaB_6 were studied. Furthermore, it was investigated whether B_4C is formed as an intermediate product and whether the advantages of the “ *B_4C method*” in the direct production of CaB_6 can also be used in the application of the “*carbothermic method*”.

2. Experimental procedure

2.1. Materials

The starting materials in this study are washed petroleum coke and colemanite processed only by calcination. The characteristics of these materials (Table 1) and the X-ray diffraction analysis of the raw and calcined material of colemanite at different temperatures are published separately by Yildiz.^{41,42}

The raw material colemanite is calcined at 600°C for 3 h in air. After calcination, the powder is dry-sieved according to the norm DIN 66165 through a sieve of Retsch type Vibro SP 1000. The petroleum coke (after drying at 60°C for 24 h) and the calcined colemanite powder (after sieving $<250\ \mu\text{m}$) are both dry-grinded (10 min) separately in a hard metal-lined

Table 1

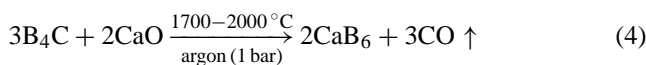
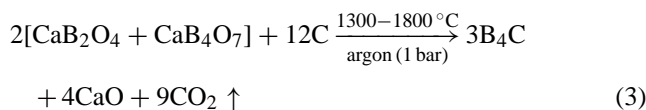
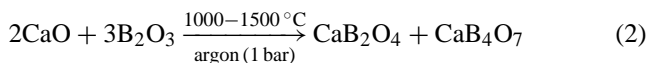
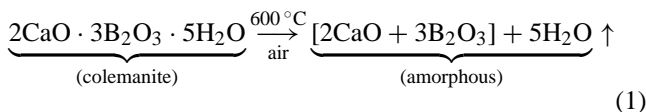
Phase composition according to the thermodynamic calculation of raw material at 600°C

Materials	Properties
Colemanite	Calcined: 600°C Particle size: $<250\ \mu\text{m}$ B_2O_3 : $\sim 58\ \text{wt.}\%$ CaO $\sim 31\ \text{wt.}\%$
Petroleum coke	Washed, dried and grinded Particle size: $<250\ \mu\text{m}$

swing mill. The properties of the used raw materials are given in Table 1.

2.2. Synthesis of CaB_6

CaB_6 is produced from a mixture of 60–95 wt.% colemanite and 4–25 wt.% petroleum coke. The application of the carbothermic method in this work is the reduction of the mixture of the calcium oxide and boron oxide by carbon through sintering at high temperature ($\leq 2000^\circ\text{C}$) in argon (1 bar) and in a graphite crucible. The reactions generally occur according to the following equations:



2.3. Characterisation of CaB_6

X-ray diffraction analyses were used in the determination of the phase formation and decomposition of B_4C to CaB_6 in products obtained at temperatures between 1500°C and 2000°C with different dwell times.

CaB_6 is obtained as a molten slag. The raw product was then broken and milled. After the preparation of powder samples ($<45\ \mu\text{m}$), the phases were analysed by a Philips PW 3020 type X-ray diffractometer using $\text{Cu K}\alpha 1$ radiation.

2.4. Thermodynamic calculations

The thermodynamic calculations, carried out by the program “Fact-Win”,⁴³ determined the particular phase compositions in temperature steps of 50°C corresponding to the same environmental conditions as those found in the experiments.

The raw material colemanite calcined at 600 °C is considered as a starting material for all thermodynamic calculations.

The raw material mixture of colemanite and petroleum coke used here contains numerous components (C, B₂O₃, CaO, CaCO₃, SO₃, SiO₂, SrSO₄, MgO, Fe₂O₃, Al₂O₃, K₂O, etc).⁴² Since some of these components were present in small quantities they were not considered in the calculations. For the theoretical calcination, petroleum coke containing some impurities (SO₃, etc.) was taken as pure carbon, and the raw material colemanite as an ideal colemanite (2CaO·B₂O₃·5H₂O), containing quartz (SiO₂) and a clay mineral (with the oxides K₂O–SiO₂–MgO–Fe₂O₃–Al₂O₃). CaCO₃ and SrSO₄ are neglected.

In order to identify the influence of both excess carbon and boron oxide, the overall mixture was varied in the calculations by using fractions and an admixture of the experimental base material (53–95 wt.%), petroleum coke (3–31 wt.%) and B₂O₃ (7–36 wt.%).

3. Results and discussion

3.1. Calcination behaviour of the raw materials

Colemanite is a boron mineral with 5 mol of crystal water. Fig. 1 shows the X-ray powder analyses of this raw material. Colemanite loses its crystal water (~21 wt.%) by endothermic reactions between temperatures of 300 °C and 460 °C.^{41,42}

Before calcination at 600 °C the raw material possesses a particle size <250 µm (~31 wt.%), while after calcination this fraction comprises ~86 wt.%. This as-calcined fraction <250 µm shows a surface area of 2.80 m²/g and contains 52 wt.% of amorphous B₂O₃ and 30 wt.% CaO according to the chemical and the X-ray diffraction analyses (Fig. 2).

Upon heating, the combustion of petroleum coke lasts until 600 °C in air and 1000 °C in argon. After combustion of petroleum coke in air at 1000 °C, about 10 wt.% of it is left behind as ash residue.⁴²

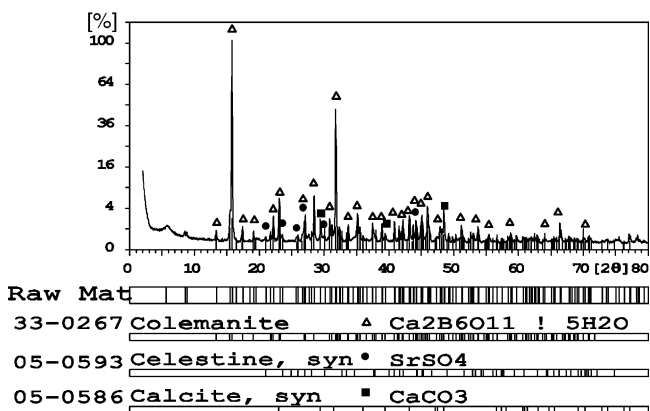


Fig. 1. XRD analysis of raw material colemanite.

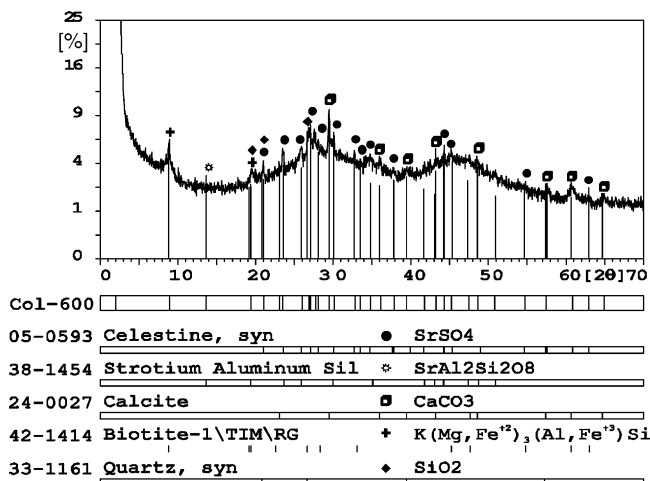


Fig. 2. XRD analysis of raw material colemanite calcined at 600 °C.

A detailed study was carried out by Yildiz^{41,42} comprising DTA-TG (in air and argon), SEM-EDX and chemical analyses of the raw materials colemanite and petroleum coke, and the influence of calcination on the particle size fraction (sieve analysis), the phase change in the colemanite (XRD) and the surface area (BET).

3.2. Thermodynamic calculation of the raw material

Thermodynamic calculations of the phase composition at 600 °C reveal the compounds listed in Table 2. In experimental studies by calcination of colemanite at 600 °C, CaB₂O₄ or CaB₄O₇ were not formed but amorphous B₂O₃ and CaO were observed (Fig. 2). CaB₂O₄ first forms at 1000 °C in air and at 1400 °C (300 min dwell time) in argon from a mixture of colemanite and petroleum coke (Figs. 3 and 4).

3.3. Phase transformation from B₄C to CaB₆ (thermodynamic calculations)

According to thermodynamic calculations, B₄C forms first in small quantities starting at 1250 °C (Figs. 5 and 6). Figs. 5 and 6 show the influence of temperature and of C- and B₂O₃-amount on the formation of B₄C. The maximum

Table 2
Phase composition according to the thermodynamic calculation of raw material at 600 °C

Components	Quantity (wt.%)
CaB ₄ O ₇	53.72
CaB ₂ O ₄	31.72
Mg ₂ B ₂ O ₅	4.09
SiO ₂ (quartz)	3.49
Ca ₃ Fe ₂ Si ₃ O ₁₂ (andradite)	2.32
KAlSi ₂ O ₆ (leucite)	2.21
CaAl ₂ Si ₂ O ₈ (anorthite)	1.23
CaSO ₄ (anhydrite)	1.22
Sum	100.00

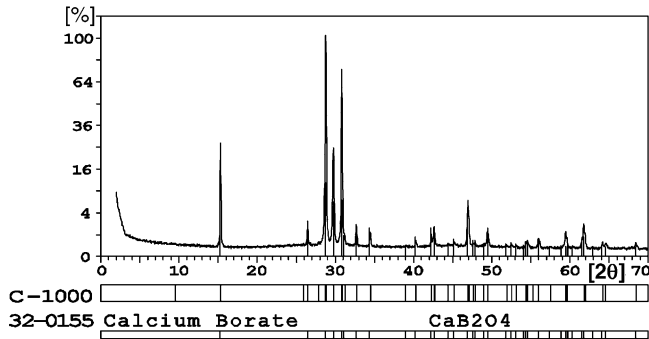


Fig. 3. XRD analysis of the mixture of colemanite and petroleum coke calcined at 1000 °C in air.

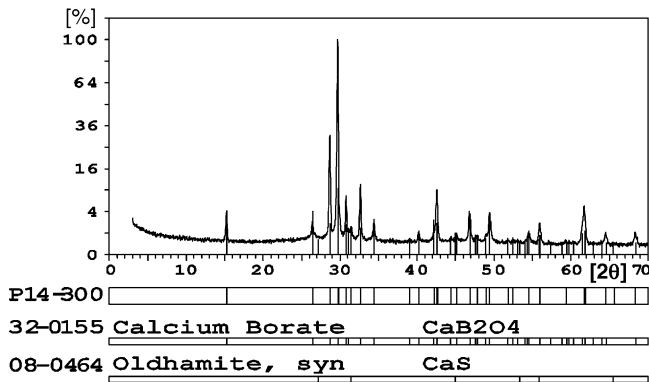


Fig. 4. XRD analysis of the mixture of colemanite and petroleum coke sintered at 1400 °C (300 min dwell time) in argon.

quantity of B_4C is formed at a temperature of 1700 °C with a mixture of 23 wt.% C without B_2O_3 or of 25 wt.% C with 13 wt.% B_2O_3 (Fig. 6).

The phase transformation from B_4C to CaB_6 begins at 1700 °C (Figs. 7 and 8) and is completed at 1850 °C (Figs. 5 and 6). It becomes clear that the formation and the quantity of B_4C and CaB_6 are dependent on quantity of C and B as well as on the reaction temperature (Figs. 5–8).

The formation of B_4C and decomposition to CaB_6 without B_2O_3 is shown in Fig. 9. By increasing the C-amount, more

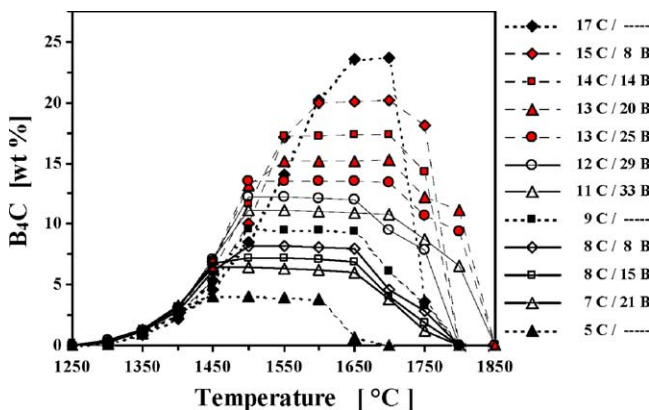


Fig. 5. Formation of B_4C as a function of temperature and quantity of added C and B_2O_3 .

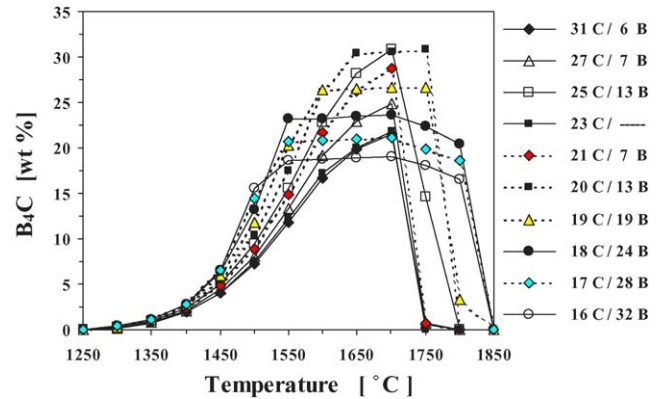


Fig. 6. Formation of CaB_6 as a function of temperature and quantity of added C and B_2O_3 .

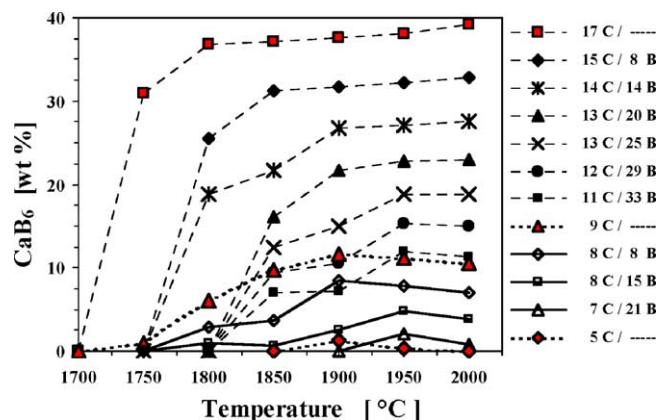


Fig. 7. Formation of CaB_6 as a function of temperature and quantity of added C and B_2O_3 .

B_4C is obtained. But starting from a certain quantity of above ~12–15% the amount of resulting B_4C is constant. Fig. 10 shows the carbon-dependent formation of B_4C at 1700 °C and of CaB_6 at 2000 °C.

According to the thermodynamic calculations the formation of CaB_6 starts at temperatures between 1700 °C and 1800 °C depending on the C/B ratio (Figs. 7 and 8). Car-

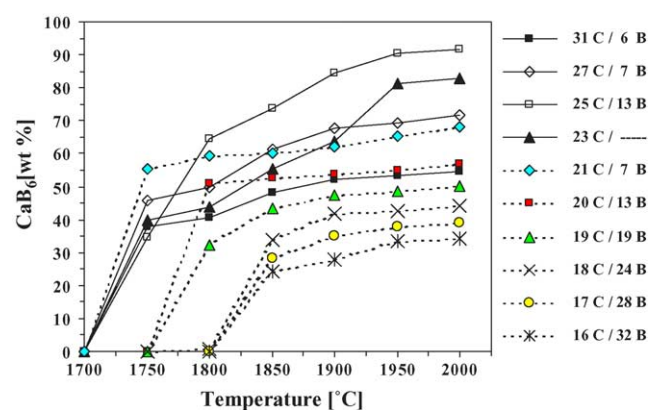


Fig. 8. Formation of CaB_6 as a function of temperature and quantity of added C and B_2O_3 .

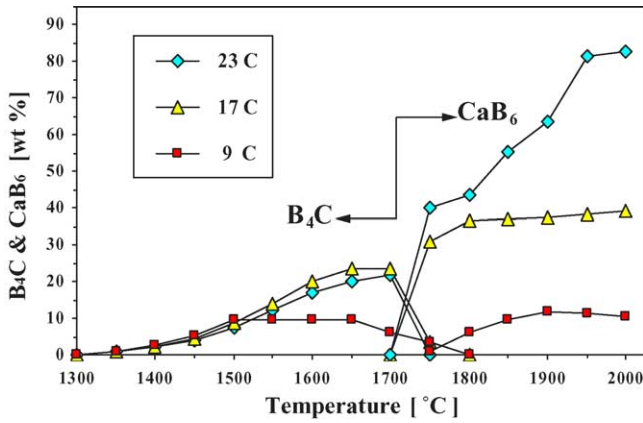


Fig. 9. Influence of C on the decomposition of B₄C to CaB₆.

bon and B₂O₃ as well as colemanite (CaO and B₂O₃) have an interdependent influence on the formation of B₄C and CaB₆. Although about 4 wt.% B₄C forms from a mixture of 5 wt.% C and 95 wt.% basis material colemanite, about 1.5 wt.% CaB₆ forms but B₄C and CaB₆ do not form from a mixture of 5 wt.% C, 90 wt.% colemanite and 5 wt.% B₂O₃ (Figs. 5–8). CaB₆ forms most favourably from a mixture of 25 wt.% C, 62 wt.% colemanite and 13 wt.% B₂O₃.

3.4. X-ray diffraction (XRD) analysis of products

B₄C could first be identified at 1500 °C (240 min dwell time) (Fig. 11) and continued to be present until 2000 °C (without dwell time). Although with a dwell time of 300 min at 1400 °C, B₄C could not be produced (Fig. 4), it was observed at 1600 °C (60 min)⁴² and at 1500 °C (240 min) (Fig. 11). CaB₆ first occurs experimentally at 1700 °C after a dwell time of 180 min and at 1800 °C after 60 min (Fig. 12). The identification of the compounds between temperatures of 1300 °C and 1800 °C was complicated by the fact that all phases of the borate, B₄C and other compounds were formed at the same time.

According to thermodynamic calculations, B₄C is present until 1850 °C; however, experimentally it can be seen by

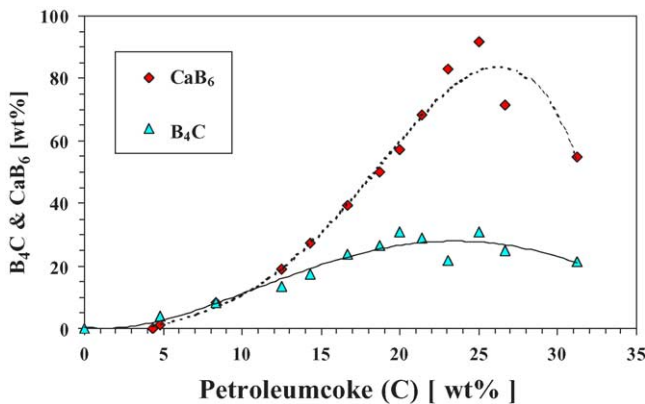


Fig. 10. Influence of C on the formation of B₄C and CaB₆.

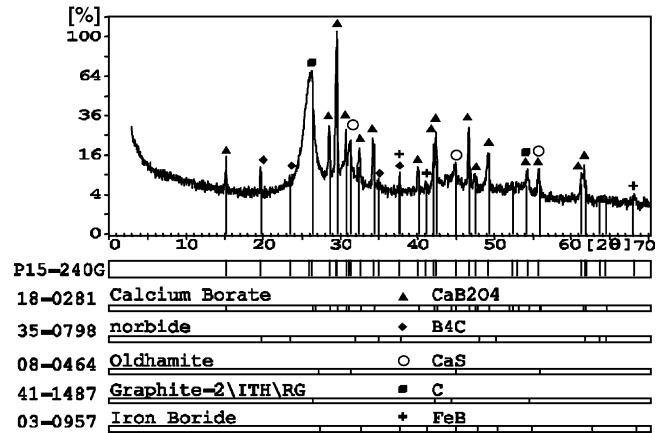


Fig. 11. XRD analysis of product (1500 °C, 240 min dwell time).

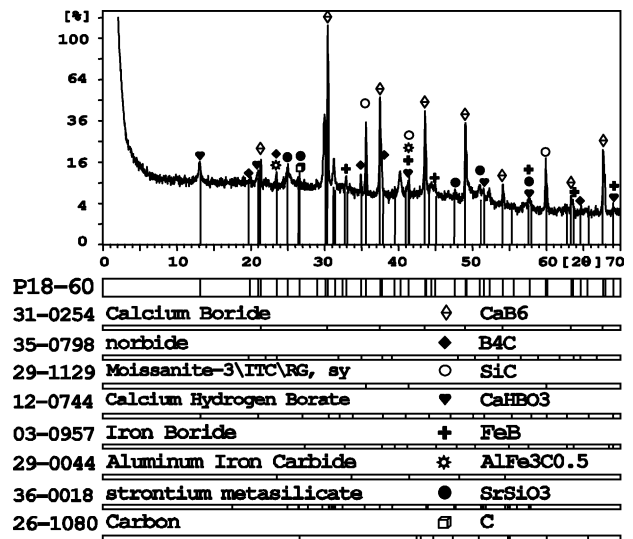


Fig. 12. XRD analysis of product (1800 °C, 60 min dwell time).

X-rays even at 2000 °C (without dwell time) (Fig. 13). Most of the phases in small quantity (including B₄C) disappear at 2000 °C and only CaB₆ remains as a major phase (Fig. 13).

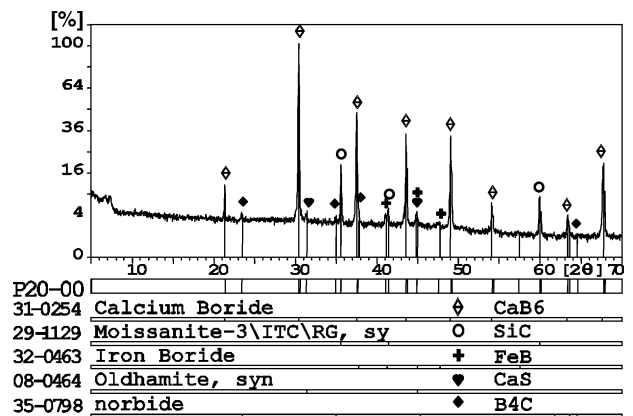
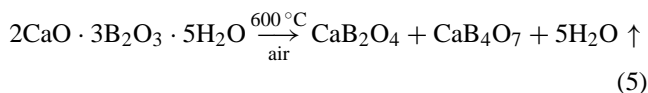
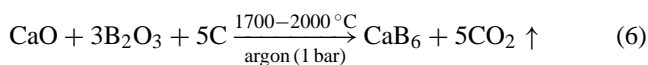


Fig. 13. XRD analysis of product (2000 °C, without dwell time).

The thermodynamic calculation of CaB₆ from the mixture of 25 wt.% C, 62 wt.% colemanite and 13 wt.% B₂O₃ at temperature of 2000 °C is in agreement with the reactions observed in the experiments. It is suggested that the reactions may occur according to the following equations:



All reactions for the formation of CaB₆ can be summarised generally as Eq. (6).



Eq. (5) goes only according to the thermodynamic calculation, whereas Eqs. (1) and (2) follow an experimental observations. Borate can be identified until 1600 °C. The reactions in the Eqs. (3) and (4) are identical for experimental observations and the thermodynamic calculations.

There are small differences between calculated and experimental formation and decomposition temperatures of B₄C, because ideal conditions and idealized components are considered for the thermodynamic calculations, whereas kinetics should be taken into account as well. Therefore the formation and decomposition temperature of B₄C in the thermodynamic calculations are lower than those obtained from experiments. With the increase of the dwell time, one may approach an equilibrium temperature. For example, B₄C can not be found after 60 min dwell time at 1500 °C, however, B₄C occurs in larger quantities after 240 min dwell time (Fig. 11).

It is clearly seen that the phase transformation from B₄C to CaB₆ is finished later (above 1850 °C) in mixtures with more B₂O₃-amount (over ~13 wt.%) compared to other mixtures, and that the amount of carbon (until ~27 wt.%) plays a positive role in the formation of B₄C as well as of CaB₆.

4. Conclusions

Because the water-containing raw material colemanite is a problem as a starting material for the production of the borides,⁴² it must be calcined at 400 °C or even better at 600 °C. A mixture from this material and petroleum coke can be used for the production of CaB₆.

It was theoretically predicted and experimentally determined that CaB₆ forms with B₄C as an intermediate product. In addition, the formation as well as the decomposition rate are mainly dependent on the reaction temperature and time, and on the stoichiometry of the raw material mixture.

B₄C begins to form theoretically at 1250 °C and experimentally starting from 1500 °C after 240 min annealing time. The decomposition of B₄C to CaB₆ begins theoretically and experimentally at 1700 °C (dwell time of 180 min).

The reaction conditions (sintering temperature and time, heating rate of the furnace, formation vapour phase, partial pressure, etc.) as well as the characteristics of the raw ma-

terials (crystal water content, quantity of other components, particle size distribution, homogeneity of mixture, etc.) play an important role on the phase formation of B₄C and CaB₆ in the carbothermic method.

The advantages of the B₄C method can clearly be used for the production of CaB₆ if the reaction conditions and the suitable processing of the raw materials can be optimally determined for the phase formation of B₄C and CaB₆, without using B₄C as a reducing agent.

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