Available online at www.sciencedirect.com
SCIENCE DIRECT®
Journal of Solid State Chemistry 177 (2004) 616–618
JOURNAL OF SOLID STATE CHEMISTRY
http://elsevier.com/locate/jssc

Some aspects for sintering of β-rhombohedral boron

Anatoliy Nechepurenko*

State einterprise "UNICHIM & Experimental plant", Yekaterinburg 620134, Russia

Received 26 September 2002; received in revised form 20 December 2002; accepted 29 May 2003

Abstract

The investigation of sintering conditions for magnesiothermic amorphous boron (Mg_mB_n) powder is presented. The results of chemical and X-ray analyses of magnesiothermic boron (Mg_mB_n) indicate that it consists of amorphous boron MgB_{12} and a lesser amount of β-rhombohedral boron. The Mg_mB_n-sintering process is determined by the conditions of amorphous boron transformation into β-boron (crystallization), such as the process of decomposition of MgB_{12} followed by formation of the "new" centers of active elementary boron. As a result of the experimental investigations of this process the following three stages—thermal decompositions, crystallization and Mg_mB_n sintering—were combined into one sintering process with the sintered bodies as a result of it.

Keywords: Decomposition MgB_{12}; Amorphous boron; Sintering; Crystallization β-boron

1. Introduction

The conditions and limitations of the sintering process of sintered articles (bodies) from the crystalline β-rhombohedral modification boron for neutron absorption use were investigated. The difficulties of the sintering process occur because of the rigid covalent bonds and corresponding low diffusion mobility [1, 2].

This paper contains the results of investigations on the sintering magnesiothermic amorphous boron powder process. It has been shown that, due to the liquid-phase mechanism of boron transposition, the sintering process includes the stages of MgB_{12} decomposition; α-boron crystallization into β-boron; and β-boron sintering.

2. Experimental

For manufacturing compact (high density) bodies the method of β-boron combined synthesis and its sintering in one stage was used. Magnesiothermic amorphous boron powder with a purity of 85.7 wt% was used in these investigations. β-rhombohedral boron was produced from magnesiothermic amorphous boron by crystallization during sintering under vacuum. The samples were made by cold molding under a pressure of 5 MPa and sintered at a temperature of 1470–2350 K. The decomposition of Mg_mB_n was studied by the change of the sample mass and final magnesium composition after treatment at a temperature of 1300–2300 K and pressure of 0.53 Pa. By the method of Hg-porosity measurement the porosity of the sintered β-boron sample was investigated.

3. Results and discussion

According to the results of chemical and X-ray analyses magnesiothermic boron (Mg_mB_n) contains amorphous boron, MgB_{12} and impurities of β-rhombohedral boron. Because of this process, its (Mg_mB_n) sintering has to be determined by the conditions of transformation of amorphous boron into β-boron (crystallization), such as conditions of decomposition of MgB_{12} with the formation of "new" centers of active elementary boron.

The results of experimental investigations of the process of thermal decomposition shown in Fig. 1 indicate that the mass loss of the sample begins at a temperature above 1770 K. This phenomenon may be

*Fax: 3432-71-31-01.
E-mail address: marketing@unichim.ru.

0022-4596/$ - see front matter © 2003 Published by Elsevier Inc.
doi:10.1016/j.jssc.2003.05.006

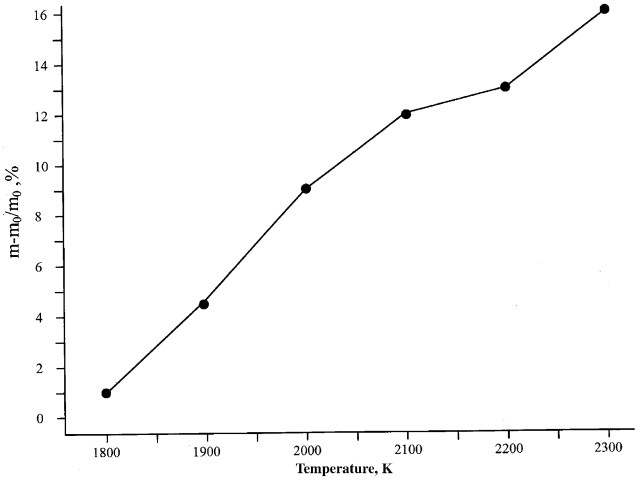

Fig. 1. Influence of sintering temperature Mg_mB_n on masses at 0.53 Pa.

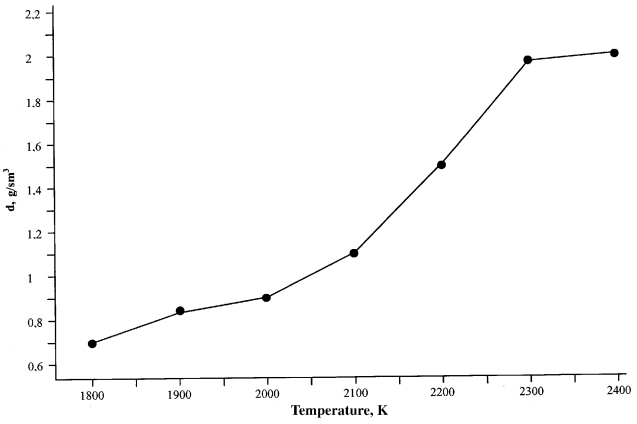

Fig. 2. Influence of sintering temperature on volume density of boron.

explained by thermal decomposition according to the reaction:

$$MgB_{12} \Rightarrow B + Mg\uparrow. \quad (1)$$

At a temperature of 2100 K the process of thermal MgB_{12} decomposition is completed. This thermal decomposition of Mg_mB_n process can be described by the following equation:

$$\Delta m/m = 4.28(Mg_o - Mg_x)\exp(-8445/T). \quad (2)$$

The combination of MgB_{12} decomposition (1470–2070 K), β-rhombohedral boron synthesis (1770–2000 K) and liquid-phase sintering (2200–2300 K) in the same process gives certain advantages in this method.

The results of X-ray analyses of sintered boron samples show that the synthesis of β-rhombohedral boron from Mg_mB_n starts at 1470 K and finishes at 2070 K. More active crystallization of Mg_mB_n in β-rhombohedral boron can be explained by the influence of β-phase and Hedvall effect (nanoamorphous "new" particles of boron). Magnesium in Mg_mB_n exists in the form of MgB_{12} and its composition in samples after the sintering process shows a degree of transformation of Mg_mB_n into β-boron: $\alpha_{\beta\text{-boron}} = (Mg_o - Mg_x)/Mg_o$. The results of the formation kinetics of β-boron indicate that the crystallization process has to be carried out at a heating rate of 10–15 K/min.

Obtaining the compact samples (density $> 2.0\ g/sm^3$) requires to combine the process of thermal decomposition with the process of sintering of the decomposition (β''-phase) products in vacuum. Fig. 2 shows the relative density dependence on the Mg_mB_n powder sintering temperature. Here, three stages of sintering can be distinguished.

In the first stage thermal decompositions of MgB_{12} with the "new" elementary boron and magnesium formation take place. Free amorphous boron starts crystallizing in the form of Mg_mB_n. The nuclei of β-boron crystalline phase play a large role in the intensification of the crystallization process. Such nuclei, amounting to 14 wt%, can be found in the raw Mg_mB_n.

The sintering kinetics ($\Delta L/L$) in the second stage are determined by conditions of phase transformation from a "new" amorphous boron into nanocrystalline and by the influence of the nanoeffect during its consolidation with larger β-boron crystals.

The third stage (2170–2270 K) is typically characterized by a small contraction rate and increasing density of the β-boron sample. In this stage phase-transformation is absent. Kinetics of the boron structure formation are determined by the law of sintering single-phase material with rigid covalent bonds and corresponding low diffusion mobility [1]. The results indicate that the best density achieved is only $2\ g/cm^3$ ($\approx 0.86\rho_{theor}$).

The process of the Mg_mB_n sintering compacted in pellets $D = 30$ mm under the induction treatment in special graphite crucible (Fig. 3) was investigated. The results of the chemical analysis and the volume density from the different zones of the sintered samples are shown in Table 1. These results show that in upper zone samples with a high content of Mg (40%) and carbon (3%) are found. The layer of half-mold pellets lies below and under it there is a void zone of the maximum temperature. Only under this zone high-quality pellets (zone 5) lay, with the form preserved and that exceeds the initial mass by 1.7–2.5 times. The density of these pellets approaches $2.2–2.3\ g/sm^3$.

The zone of the "melding" pellets is considered to be a donor for filling porosity and increasing the pellets density, pellets which lay under this zone—the main zone of pellet synthesis.

The results of the experimental investigation of the thermal decomposition process, Mg_mB_n crystallization and sintering have resulted in the following stages of

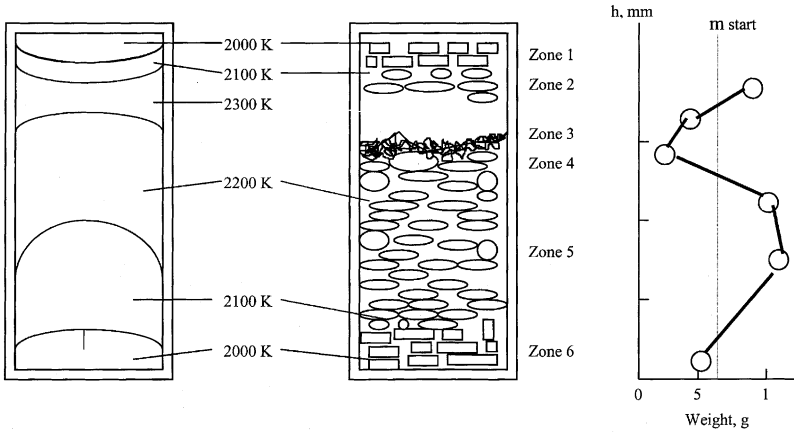

Fig. 3. Distribution of temperature zones and mass of pallets along the height of the crucible during sintering of magnesiothermic boron (Mg_mB_n).

Table 1
Chemical composition and relative density of β-boron samples sintered at $T_{\text{zone 5}} = 2270\,\text{K}$

Boron grade in the zone (Fig. 2)	B (wt%)	Mg (wt%)	C (wt%)	d (g/sm^3)
Boron-1 (1st zone)	45–54	40–45	2.5–3.5	1.3–1.5
Boron-2″ (2nd zone)	95–96	1.0–1.4	2.0–3.0	1.4–1.7
Boron-2* (6th zone)	96–97	0.5–1.0	0.3–0.8	1.2–1.3
Boron-3 (4th zone)	90–93	0.1–0.2	3.0–5.0	1.4–1.5
Boron-4 (5th zone)	97–98.5	0.3–0.5	0.8–1.3	2.0–2.3

sintered articles manufacturing from the compact crystalline β-rhombohedral boron:

The First stage is linked with sintered Mg_mB_n structure change due to the beginning of the crystallization process of amorphous boron in β-boron and the beginning of MgB_{12} decomposition into boron and magnesium, crystallization of the active centers (nanocrystalline particles β-boron) and porosity formation resulting in process of sintering β-boron activation. This reaction mechanism takes place in the temperature range of 1200–1800°C.

The Second stage is linked with β-phase recrystallization (from fine particles to larger particles) growth due to the diffusion and gas-phase processes (melting–vaporization–condensation) in local unit volume. This mechanism is the main reaction mechanism for the temperature range of 1800–2000°C.

The Third stage is linked with liquid-phase transportation of boron mass by means of capillary forces and high wettability of the hard boron surface by the liquid boron through the impregnation from the zone with a temperature higher that T_{melt} of boron to the zone of compact crystalline β-boron formation. This mechanism takes place at temperatures higher than 2000°C.

The structure and porosity of the sintered β-boron samples were investigated by the method of Hg-porosity measurement. The results show that during sintering at 1850°C most pores were 1–10 μm in size. At temperatures close to 2000°C large pores decrease and their dimensions are only 0.1–0.5 μm.

These investigations demonstrate the possibility of manufacturing compact bodies (articles) composed of β-boron (density 2.23 g/sm^3) by means of magnesiothermic amorphous boron (magnesium polyboride) powder sintering in vacuum.

References

[1] G.I. Kalandadze, S.O. Shalamberidze, A.B. Peikrishvili, J. Solid State Chem. 154 (2000) 194–198.
[2] R.A. Andrievskiy, I.A. Bayramashvily, U.I. Soliev, P.M. (1982) 27–32 (in Russian).