



Phase formation dynamics upon thermal explosion synthesis of magnesium diboride

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Abstract

Time-resolved X-ray diffraction was used to study the dynamics of phase formation in magnesium diboride produced by self-propagating high-temperature synthesis in the thermal explosion mode. The MgB_2 phase was demonstrated to emerge without the formation of intermediate compounds. The effect of the mixture heating rate on the formation mechanism of the MgB_2 phase was established. The presence of oxygen impurities has a significant impact on the kinetics and formation mechanism of MgB_2 . If the heating rate exceeds $150^\circ/\text{min}$, the oxide coating is not formed around the magnesium particles, which results in the solid-phase reaction of $\text{Mg} + 2\text{B} = \text{MgB}_2$ through a reaction diffusion mechanism. Moreover, the self-ignition temperature of the mixture is lower than the melting point for magnesium. Mechanical activation of the mixture leads to variations in the kinetics of MgB_2 formation, significantly increases the period of simultaneous existence of Mg and MgB_2 , and reduces the temperature at which the reaction occurs.

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1. Introduction

There are several known Mg–B derivatives: MgB_2 , MgB_4 , MgB_6 , and MgB_{12} . Magnesium diboride (MgB_2) is the most attractive of the aforementioned phases. MgB_2 is a type II superconductor, with a critical transit point of $T_c = 39\text{--}40\text{ K}$ [1]. This value is moderate compared to the T_c values of conventional low-temperature and high-temperature superconductors. Bulk MgB_2 superconductors are currently a research focus due to the high practical application potential for cryoelectronic devices at liquid hydrogen and neon temperatures. In particular, the superconductors can be used to produce electric motors, cryopumps, support-free vehicles, magnetic bearings, current limiters, and intense magnetic fields [2,3]. Additionally, MgB_2 has high practical probability for use, due

to its relevant mechanical and metal-like properties, lightness and relatively low cost [4].

Superconducting MgB_2 is generally synthesized via solid-state synthesis in accordance with the following equation: $\text{Mg} + 2\text{B} = \text{MgB}_2$. The mixture makeup, protective medium and thermal treatment conditions vary during synthesis [2]. Because magnesium is an extremely volatile active element with high oxygen sensitivity, longer processes result in magnesium oxide product contamination [5]. Therefore, it is desirable to conduct these processes within enclosures with increased inert gas pressures [3]. High pressure (up to 2 GPa) helps to suppress the uncontrolled vaporization of magnesium. The result is a material with excellent functional characteristics. The density is 98% of the expected value, and the superconducting characteristics and mechanical properties are high [3,6]. However, this method requires the use of expensive equipment (devices such as an anvil with a cavity of 100–300 cm^3 volume) to ensure continued thermal pressure exposure.

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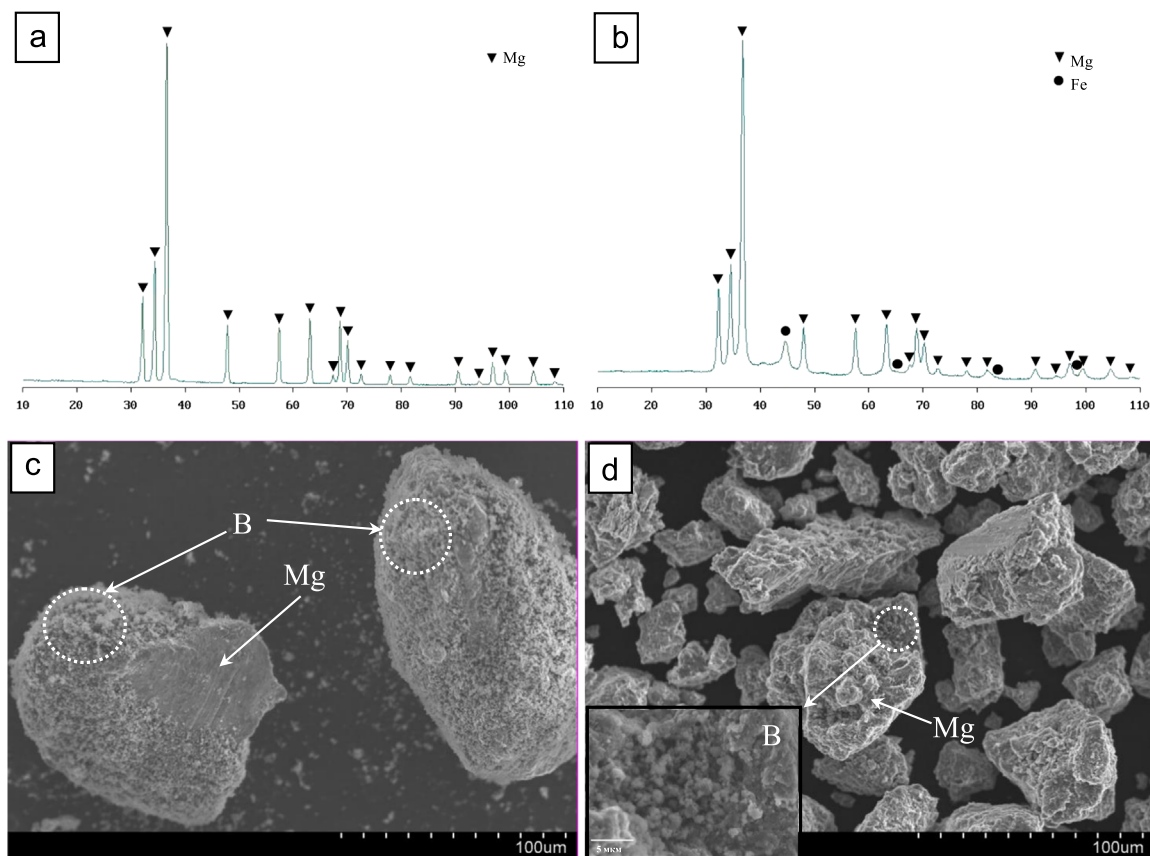


Fig. 1. X-ray diffraction patterns and morphology of the reaction mixtures treated in the ball rotating mill (a, c) and exposed to MA for 60 min (b, d).

Recently, multiple synthesis methods have been tested, including mechanochemical [7] and electrochemical [8], as well as various self-propagating high-temperature synthesis (SHS) technologies [4,9–14]. The products obtained using these methods have a fine-grain structure consisting of nanoparticles. The products are also characterized by a high level of chemical purity, better sinterability and compactibility at relatively lower temperatures than their coarse-grained analogues. These properties determine the practical applications of the end product.

Meanwhile, the SHS reaction for the formation of magnesium diboride ($\text{Mg} + 2\text{B} = \text{MgB}_2$) is characterized by a relatively low enthalpy of product formation ($-\Delta H_{298}^{\circ} = 112$ kJ/mol) and a low adiabatic combustion temperature ($T_c^{\text{ad}} = 1615$ K). Therefore, the initiation of combustion in the powder mixture is impeded. For this reason, magnesium diboride can be synthesized by one of the following two methods:

- Thermal explosion synthesis [4,10–12], which consists of preheating a mixture of reactants to their spontaneous self-ignition temperature, where an exothermic reaction occurs almost simultaneously over the entire bulk sample. The exothermic reaction between Mg and B begins at a temperature close to the melting point of magnesium ($T_{\text{Mg}}^{\text{melt}} = 650$ °C);
- Synthesis with preliminary mechanical activation (MA) of the reaction mixture [4,13–15], which results in a

significant reduction of mixture heterogeneity, enhancement of the reaction surface area, accumulation of reactant structure defects, increased rate of reaction and conversion, and a lower ignition temperature [16].

In a previous study [9], the phase transformation behaviour of Mg–B in the combustion synthesis regime was investigated using a combustion front quenching test. The reaction starts with solid-phase diffusion when the chemical reaction occurs on the Surface of a Mg particle and propagates toward its centre. When magnesium is melted, boron particles are dissolved in the resulting liquid melt. As the melted magnesium saturates with boron, fine particles of MgB_2 are disengaged. The formation of a small amount of MgB_4 is possible following the decomposition of MgB_2 due to the partial evaporation of Mg in the heating zone before the reaction with boron begins. In previous research, [17] it was assumed that MgB_4 is formed at a combustion temperature of 1200 °C through the decomposition reaction: 2MgB_2 (s) \rightarrow Mg (g) + MgB_4 (s), which may occur at low magnesium partial pressures and temperatures below 1000 °C. Despite the aforementioned publications, the dynamics of the structural phase transformations during the combustion of the $\text{Mg} + 2\text{B}$ mixture in the thermal explosion mode have not been sufficiently studied to determine the conditions under which a single-phase product of the required phase and chemical purity can be obtained and where reproducibility is ensured.

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