



Self-propagating high-temperature synthesis of advanced ceramics in the Mo–Si–B system: Kinetics and mechanism of combustion and structure formation

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Dedicated to the blessed memory of academician Alexander Merzhanov

Abstract

The goal of this work is to investigate the combustion mechanisms of reactions in the Mo–Si–B system and to obtain ceramic materials using the SHS method. It is concluded that the following processes are defined by the SHS for Si-rich Mo–Si–B compositions: silicon melting, its spreading over the surfaces of the solid Mo and B particles, followed by B dissolution in the melt, and formation of intermediate Mo₃Si-phase film. The subsequent diffusion of silicon into molybdenum results in the formation of MoSi₂ grains and molybdenum boride phase forms due to the diffusion of molybdenum into B-rich melt. The formation of MoB phase for B-rich compositions may occur via gas-phase mass transfer of MoO₃ gaseous species to boron particles. The stages of chemical interaction in the combustion wave are also investigated. The obtained results indicate the possibility of both parallel and consecutive reactions to form molybdenum silicide and molybdenum boride phases. Thus the progression of combustion process may occur through the merging reaction fronts regime and splitting reaction fronts regime. Molybdenum silicide formation leads the combustion wave propagation during the splitting regime, while the molybdenum boride phase appears later. Finally, targets for magnetron sputtering of promising multi-phase Mo–Si–B coatings are synthesised by forced SHS compaction method.

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1. Introduction

Designing promising heat-resistant materials and coatings to protect vital parts made of nickel, titanium, chrome, niobium alloys and molybdenum against high-temperature oxidation remains the most important task of modern materials science [1]. Materials based on molybdenum and niobium silicides are widely used for these applications, as they are characterised by high melting points and high values of strength, creep and oxidation resistance at elevated temperatures [2]. In the Mo–Si system, Mo₅Si₃ is the most refractory compound ($T_{\text{melt}}=2453$ K); it also possesses an

excellent strength at high temperature. However, its oxidation resistance is somewhat lower than that of MoSi₂ [3].

Boron doping (up to 11 at%) is used to ensure the high heat resistance of Mo₅Si₃-based materials at constant creep resistance from 800 to 1450 °C [4]. The properties of alloys in the Mo–Si–B ternary system with Si and B concentrations varied from 9 to 12 at% and 8 to 20 at%, respectively were previously studied [5–7]. In addition to high-temperature strength and oxidation stability, these materials exhibit high fracture toughness. A significant number of studies have been devoted to the investigation of alloys based on the T₂ phase (Mo₅SiB₂) [8–13], which is attractive for ultrahigh-temperature applications. The T₂ phase is formed via a pseudo-double peritectic reaction at temperatures below 2130 °C and is characterised by an appreciably

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wide homogeneity region near the stoichiometric composition (Fig. 1). Electric arc refining under argon atmosphere is conventionally used to produce various alloys based on molybdenum and boron silicides, including the T_2 phase [8–13].

This process has multiple stages, requires long-term isothermal exposure to temperatures above 1600 °C, and is highly sensitive to the slightest technological discrepancies, resulting in variation in the phase composition [8].

Self-propagating high-temperature synthesis (SHS) is an alternative method for the fabrication of ceramics in the Mo–Si–B system; this method allows for the production of various refractory compounds without high energy consumption and ensures the chemical purity of the final products due to the self-purification effect in the combustion wave [15–18]. This method employs the heat of the chemical reactions occurring between the components of the mixture. Elemental synthesis in the Mo–Si–B system at the initial room temperature may be impeded because of the low thermal effect of formation of molybdenum silicides and molybdenum borides [15–19]. However, the steady-state combustion mode can be achieved by preheating the green mixture. As opposed to the Mo–Si and Mo–B binary systems, insufficient data are available regarding the SHS fabrication of ceramic materials from the Mo–Si–B ternary mixture.

Although this analogy may seem to be rather strange, the Mo–Si–B and Ti–Ta–C ternary systems are similar in terms of the mechanism and kinetics of combustion. Two main chemical reactions occur in both systems: one occurs via the mechanism of reaction diffusion through the melt, while the other reaction is controlled to a significant degree by the gas-phase transfer of one component to the other component. Thus, temperature profiles of the combustion wave with two characteristic maxima of heat release were observed over a broad range of values of the charging parameter X of the mixture $(90\% - X)(\text{Ti} + 0.5\text{C}) + X(\text{Ta} + \text{C})$, demonstrating that combustion takes place in the splitting combustion fronts regime as a result of sequential chemical reactions [20,21]. In contrast, increasing the green parameter and the initial temperature T_0 results in the merging of the two maxima, and combustion proceeds from the splitting combustion fronts regime to the merging combustion fronts regime, in which the sequential reactions occur in parallel.

The Ti–C and Mo–Si systems are similar in the fact that combustion occurs via the reaction–diffusion mechanism after the melt is formed (carbon is dissolved in the titanium melt [15,22], while molybdenum and silicon are dissolved in the silicon and molybdenum melts, respectively [23,24]). Solid-phase diffusion through the newly formed product layer is the limiting stage of the combustion of the Ta–C and Mo–B mixtures; however, the reagent is fed via the gas phase. In the case of Ta–C, carbon is transferred to the surface of tantalum particles via circulation of CO and CO₂ by the Buduar–Bell cycle [25,26], consisting of the following steps: interaction of a CO₂ molecule with carbon, yielding two moles of CO; gas-transport transfer of 2CO to the surface of a tantalum particle; chemisorption of 2CO on the surface; two-stage interaction between tantalum and carbon, yielding tantalum semicarbide and subsequently tantalum carbide according to the scheme $\text{Ta} + 2\text{CO} \rightarrow \text{TaC} + \text{CO}_2$; desorption of a

CO₂ molecule from the surface of the resulting tantalum carbide layer; transfer of CO₂ to the surface of a carbon particle; interaction between CO₂ and carbon, yielding 2CO, etc. In the case of Mo–B, molybdenum undergoes gas-phase transfer (in the form of volatile molybdenum suboxide MoO₃) to the boron surface, where chemisorption occurs, giving rise to molybdenum boride [15,19].

Thus, similar observations can be expected in the Mo–Si–B system: the effects of detachment and/or merging of combustion waves depending on the mixture composition, the dispersibility of powders, the heterogeneity of the mixture, and the initial temperature T_0 .

This work focuses on studying the kinetics and the mechanism of elemental synthesis in the Mo–Si–B ternary system, and on analysing the stages of chemical conversion and structure formation of SHS products. The experiments were carried out for three compositions (shown in Fig. 1 as compositions 1, 2, and 3), which are of interest not only in terms of studying combustion but also for the production of composite targets for ion plasma (magnetron) sputtering of heat-resistant coatings with different ratios of silicon, boron, and molybdenum.

2. Materials and methods

Molybdenum powder PM-99.95 with an average particle size of 5 μm; silicon powder obtained by grinding KEF-4.5 single crystals (orientation 100) with a final particle size below 63 μm; and black amorphous boron powder (grade B-99A) with a specific surface area of 13 m²/g and an average particle size of 0.2 μm were used as the starting reagents in this study. The powders were mixed in a ball mill for 8 h using hard metal milling agents with a 1:8 ratio between the green mixture and the balls. Table 1 lists the compositions of the green mixtures studied here, where composition no. 3 corresponds to Mo₅SiB₂ (T_2 phase).

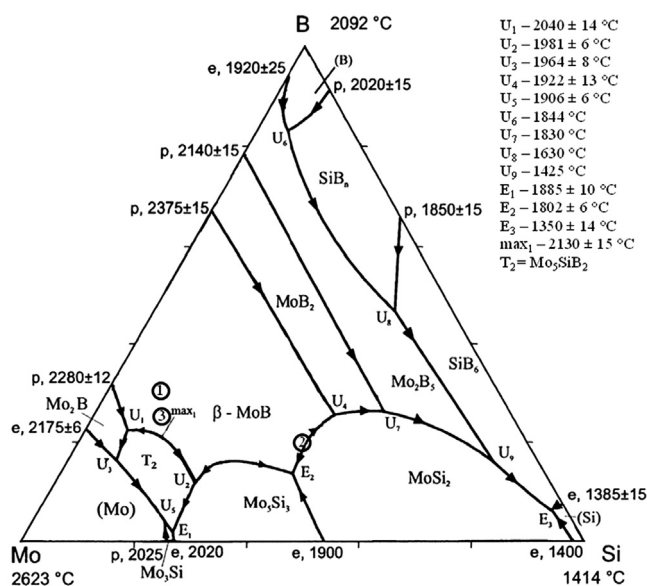


Fig. 1. Melting diagram of Mo–Si–B system [14].

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