Self-Propagating High Temperature Synthesis of Solid Materials

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Once initiated, highly exothermic reactions can become self-sustaining and will propagate through a reaction mixture in the form of a combustion wave. As the combustion wave advances, the reactants are converted to the product as shown schematically in Fig. 1 [1,2,3,4,5]. The use of such reactions to prepare solid materials has been commonly referred to as the self-propagating high temperature synthesis (SHS) method, which was developed by Merzhanov and coworkers [1]. Over the past 20 years, more than 300 solid materials have been synthesized by this method, including metallic, ceramic, and composite phases. Demonstrated advantages of SHS as a method for the preparation of materials include higher purity of the products, low energy requirements, and the relative simplicity of the process [4].

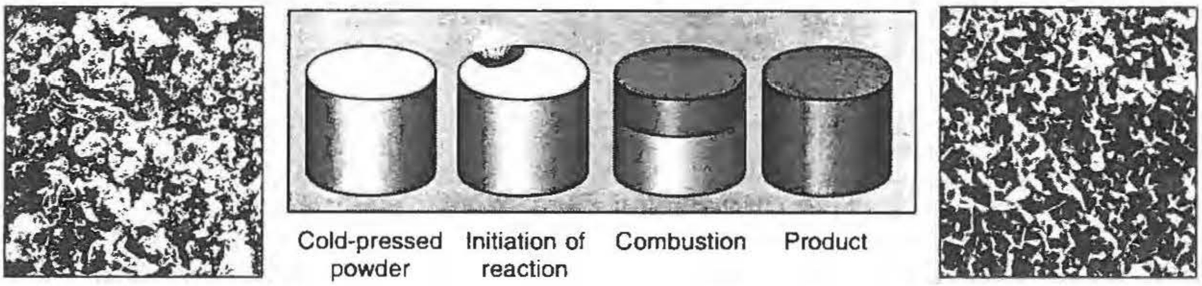

Figure 1

Two important factors in the SHS are the maximum temperature and the linear propagation rate. The maximum temperature can be calculated using the thermodynamics of an adiabatic process. Applying this concept, the maximum temperatures for the syntheses of metal carbides, borides, and nitrides could be expected to reach 1500 K to 4900 K. When the maximum temperature exceeds about 1800 K, a self-propagating reaction can occur after ignition. Below this temperature the reactants need preheating before initiating the SHS reaction. The propagating velocities vary from 6×10^{-4} to 2.5×10^{-1} m/sec. The rate can be controlled by the addition of a diluent or the variation of the particle size of the reactants [3,4].

The synthesis of titanium carbide from elemental powders has been theoretically and experimentally studied as a model system for the SHS process [6]. Thermodynamic calculations have shown that the adiabatic temperature is 3210 K, which is the melting point of TiC. The fraction of the product which has undergone melting at this temperature is 33% [7]. Investigations of the behavior of carbon-coated filaments of titanium electrically heated at different rates showed that ignition took place only when the system attained the melting point of titanium [8]. The mechanism proposed is that the high temperature generated by the exothermic reaction melts the titanium phase, which subsequently flows to and reacts with the solid carbon [9]. Scanning electron microscope(SEM) studies by using different kinds of carbon precursors showed that the products retain the morphology of carbon, which confirms the mechanism proposed above [10].

The high temperature superconductor, $YBa_2Cu_3O_{7-x}$ can be synthesized by the SHS method in less than one minute [11]. The physical properties including the critical temperature, T_c, and the superconducting phase content are comparable to the products synthesized by the furnace method [11,12]. In order to have an SHS process, the starting mixture must be composed in such a way that it contains the required amount of internal chemical energy. The use of Cu and BaO_2 instead of CuO and $BaCO_3$ produces more heat of reaction by the oxygenation of copper and the decomposition of barium peroxide to barium oxide. Heat generated by the oxidation of copper melts BaO_2, which spreads around the Cu and Y_2O_3 particles and produces the barium cuprate phase and propagates the reaction front. Further reaction between barium cuprate yttrium oxide produces $YBa_2Cu_3O_{6.85}$ [11,13].

Reactions between transition metal (V,VI) halides and alkali metal chalcogenides are highly exothermic because the reaction produces very stable, alkali metal halides [14,15,16, 17]. These metathesis reactions can produce transition metal dichalcogenides more easily than the reactions between elements. Other advantages include the control of reaction conditions and of product particle sizes by the inert additive, alkali metal halides [17]. Transition-metal mixed dichalcogenides can also be prepared from the reactions between transition-metal halides and alkali-metal mixed chalcogenides [18].

In summary, the SHS process can produce many important solid materials in a short time. The melting of less refractory materials accelerate the reaction tremendously. By choosing proper starting materials which produce enough heat to self-propagate, many solid materials can be synthesized by SHS.

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