Chemical Engineering Science 60 (2005) 925–933

Chemical
Engineering Science

www.elsevier.com/locate/ces

The numerical simulation of effects of the heterogeneities in composition and porosity on micropyretic synthesis

H.P. Li*

Jin-Wen Institute of Technology, Office of Research and Development, 99 An-Chung Road, Hsintien Taipei County 231, Taiwan

Received 30 December 2003; received in revised form 30 August 2004; accepted 30 September 2004
Available online 23 November 2004

Abstract

Micropyretic/combustion synthesis is a technique whereby a material is synthesized by the propagation of a combustion front across a powder. Heterogeneities in initial composition and porosity are commonly occurred during micropyretic synthesis when powders are pressed or mixed and the conventional modeling treatments thus far have only considered uniform systems. Heterogeneities in the initial composition and porosity are thought to result in local variations in reaction yield and such thermophysical/chemical parameters for the reactants as density, heat capacity, and thermal conductivity; further changing the average propagation velocity and the oscillatory pattern of an unstable combustion front. This study thus investigates the impact of heterogeneities in composition and porosity on the unstable micropyretic synthesis with Ti+2B by a numerical simulation. The heterogeneity maps, considering the composition and porosity heterogeneities concurrently, are also generated. The maps provide a better understanding of the heterogeneous composition and porosity effect on the average propagation velocity and oscillatory frequency during unstable micropyretic synthesis.

Keywords: Composition heterogeneity; Porosity heterogeneity; Micropyretic synthesis; Combustion synthesis

1. Introduction

Micropyretic synthesis/combustion synthesis (Li, 1995, 2002, 2003a, 2004a,b, 2005; Munir and Anselmi-Tamburini, 1989; Merzhanov and Khaikin, 1988; Munir, 1988) is a novel technique in which the synthesis of compounds and composites is accomplished by the propagation of a combustion front across the sample. The energy to propagate the combustion front is obtained from the exothermic heat of the reaction. The unreacted portion in front of the combustion front is pre-heated by the release energy, which initializes further reaction. A continuous cycle of reaction, heat transfer, and reaction initiation is reflected in propagation of the combustion front.

Micropyretic synthesized products have been reported to have better mechanical and physical properties (Booth, 1953; Li et al., 1992). An example is the formation of shape-memory alloys of nickel and titanium (Booth, 1953). It has been reported that those prepared by micropyretic synthesis, possess greater shape-recovery force than corresponding alloys produced by conventional methods (Booth, 1953). On account of the high thermal gradients encountered in micropyretic synthesis, it has been speculated that the products of such a process may contain a high defect concentration. The presence of high levels of defects has led to expectation of higher reactivity, namely higher sinterability. The micropyretic synthesis technique also provides rapid net shape processing. When compared with conventional powder metallurgy operations, micropyretic synthesis not only offers shorter processing time but also excludes the requirement for high-temperature sintering.

Several numerical and analytical models of micropyretic synthesis in a composite system have been well developed (Li, 2003b,c, 2004c; Lakshmikantha et al., 1992; Lakshmikantha and Sekhar, 1993, 1994; Subramanian et al.,

---

* Tel.: +886 932383482; fax: +886 223813621.
E-mail address: hli@jwit.edu.tw (H.P. Li).

0009-2509/$ - see front matter © 2004 Elsevier Ltd. All rights reserved.
doi:10.1016/j.ces.2004.09.058

1995; Dey et al., 2000). Lakshmikantha and Sekhar firstly explored the numerical model that includes the effects of dilution and porosity, and melting of each constituent of the reactants and products (Lakshmikantha et al., 1992). The analytical modeling of the propagation of the combustion front in solid–solid reaction systems has also been reported (Lakshmikantha and Sekhar, 1994). The analytical model gives good results when compared with the experimentally determined numbers and the numerically calculated values. In addition, a multi-dimensional numerical model and dynamic modeling of the gas and solid reaction have also been carried out to illustrate the effects of various parameters on the micropyretic synthesis (Lakshmikantha and Sekhar, 1993, 1994). These numerical and analytical analyses provide the better understanding of the reaction sequence during micropyretic synthesis reactions.

However, the heterogeneities in initial composition and porosity are commonly occurred during micropyretic synthesis when powders are pressed or mixed and the conventional modeling treatments (Li, 2003b,c, 2004c; Lakshmikantha et al., 1992; Lakshmikantha and Sekhar, 1993, 1994; Subramanian et al., 1995; Dey et al., 2000) thus far have only considered uniform systems. The occurrences of the composition and porosity heterogeneities result in local variations in the reaction yield and the thermophysical/chemical reactant parameters, such as density, heat capacity, and thermal conductivity. This changes the average propagation velocity and oscillatory nature of an unstable combustion front. Such a change may aid to the formation of rapid solidification (Li and Sekhar, 1993), and further results in the heterogeneous products. In this study, a numerical simulation is used to characterize the composition and porosity heterogeneity effects on TiB_2 micropyretic synthesis. This study also provides the heterogeneity maps, considering the heterogeneities in composition and porosity concurrently, to illustrate the influence of the heterogeneous reactions on average propagation velocity and oscillatory frequency during unstable TiB_2 micropyretic synthesis.

2. Numerical calculation procedure

During the passage of the combustion front in the reaction, the energy equation for transient heat conduction, including the source term, containing heat release due to the exothermic micropyretic reaction is given as (Merzhanov and Khaikin, 1988; Lakshmikantha et al., 1992; Lakshmikantha and Sekhar, 1994)

$$\rho C_p\left(\frac{\partial T}{\partial t}\right)=\frac{\partial}{\partial z}\left(\kappa\left(\frac{\partial T}{\partial z}\right)\right)-\frac{4h(T-T_0)}{d}+\rho Q\Phi(T,\eta). \tag{1}$$

Each symbol in the equation is explained in the nomenclature section. The reaction rate, $\Phi(T,\eta)$, in Eq. (1) is given as

$$\Phi(T,\eta)=\frac{\partial\eta}{\partial t}=K_0(1-\eta)\exp\left(-\frac{E}{RT}\right). \tag{2}$$

In this study, a numerical calculation for Eq. (1) is carried out with the assumption of the first-order kinetics. In the Eq. (1), the energy required for heating the synthesized product from the initial temperature to the adiabatic combustion temperature is shown on the left-hand side. The terms on the right-hand side are the conduction heat transfer term, the surface heat loss parameter, and the heat release due to the exothermic micropyretic reaction, respectively. The surface heat loss is assumed radically Newtonian in this study. The previous studies (Li, 2003a; Lakshmikantha et al., 1992) have shown that the surface heat loss is much less than the exothermic heat of the reaction, thus, the surface heat loss is taken to be zero in the numerical calculation.

The middle-difference approximation and an enthalpy–temperature method coupled with Guass–Seidel iteration procedure are used to solve the equations of the micropyretic synthesis problems. In the computational simulation, a one-dimensional sample of 1 cm long is divided into 1201 nodes (regions) to calculate the local temperature using an enthalpy–temperature method coupled with the Guass–Seidel iteration procedure. The choice of 1 cm sample length is only for computational purpose. It has been found that the length of sample does not affect the numerical results in this study. Thus, the simulation results are applicable to practical experimental condition. Firstly, the proper initial and boundary conditions are used to initialize the temperatures and enthalpies at all nodes. The initial conditions in the simulation are taken as follows: (1) At the ignition node, at time $t \geqslant 0$, the temperature is taken to be the adiabatic combustion temperature, ($T=T_c$ and $\eta=1$). It has been reported that the chosen temperature value at the ignition node only slightly influences the temperature profiles at the initial stage (Lakshmikantha et al., 1992; Lakshmikantha and Sekhar, 1994). (2) At the other nodes, at time $t=0$, the temperatures are taken to be the same as the substrate temperature, ($T=T_0$ and $\eta=0$). Depending on the values of the temperature and enthalpy occurred in the reaction, the proper thermophysical/chemical parameters are considered and the proper limits of the reaction zone are determined for each node in the numerical calculation. At any given time, the fraction reacted and enthalpy of the current iteration are calculated from the previous fraction reacted and enthalpy of the earlier iteration. The range of the enthalpy as well as the molar ratio among each material for each node is thus determined, and the values of temperature, density, and thermal conductivity at each node can be further calculated in appropriate zone.

Composition at each node is first calculated from the random number ($f_R(j)$ at node j) and the assigned heterogeneity ($\mathrm{Hetero}_{\mathrm{comp}}$) that determines the magnitude of the variation. The sequence of the random numbers $(-0.5$