Self-Propagating Reactions in Finite Pellets: Synthesis of Titanium Carbide

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The preparation of advanced materials by self-propagating high-temperature synthesis (SHS) has attracted significant current interest. The basic concept is that once initiated, a highly exothermic reaction can become self-sustaining and will propagate through the mixture of initial reactants in the form of a combustion wave. The reactants are converted to the products as the combustion wave advances, as shown in Figure 1. Although known for some time, the SHS process was developed extensively by Merzhanov and coworkers starting in the 1970s (cf. Merzhanov, 1990). Since then a wide variety of advanced materials, such as borides, carbides, nitrides, silicides, intermetallics, composites, and superconductors, have been produced using this process. An increasing research effort based on experimental as well as theoretical investigations has been invested in this field, as discussed in recent review articles (Munir and Anselmi-Tamburni, 1989; Holt and Dunmead, 1991; Varma and Lebrat, 1992). Modeling of the SHS technique is necessary to develop time and space relationships between process characteristics and physicochemical parameters of the reacting systems, and for subsequent process scale-up and optimization. To date, most mathematical analyses of SHS have treated infinitely long systems, which lead to analytical expressions of the velocity of the combustion front as a function of various system parameters, such as activation energy and pellet thermal conductivity, but which are independent of position within the pellet (cf. Novozhilov, 1961; Margolis, 1983; Puszynski et al., 1987). However, as one can expect from physical intuition, for pellets of finite length the reaction front movement should be influenced by boundary conditions at the ends. The propagation rate of the reaction front should therefore be a function of position: that is, a constant-pattern behavior should not exist for finite systems.

Our recent theoretical study on this aspect has shown that for sufficiently long finite pellets, the front velocity is essentially constant along the axis of the pellet, except for end effects (Varma et al., 1990; Cao et al., 1991). In this note, results of an experimental study of TiC synthesis are described, in which an attempt was made to verify the theoretical predictions and to assess the effects of boundary conditions on the propagation of the combustion wave.

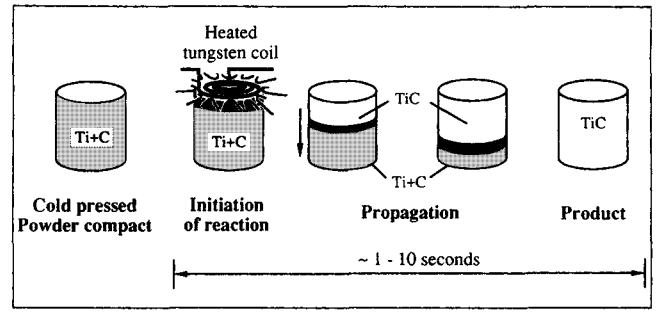

Figure 1. SHS process.

Experimental Setup and Procedure

The experimental setup (Figure 2), described previously in detail (Lebrat and Varma, 1991, 1992), consisted of a cylindrical stainless steel reaction vessel equipped with a data acquisition system and a Macintosh IIx computer. A programmable DC power supply was used as the current source. The current was passed through a tungsten coil which upon heating ignited the pellet. The data acquisition section consisted of a video system and temperature measurement devices. A video camera and recorder enabled us to record the entire combustion synthesis process, that is, ignition, propagation and completion. The sample temperature was measured continuously using a two-color pyrometer focused on the sample and thermocouples embedded in the sample. The computer was equipped with data acquisition and GPIB-compatible boards to control the power supply and to acquire signals from the pyrometer during the reaction. Equipped also with a frame grabber, it enabled us to digitize the video recording. The data

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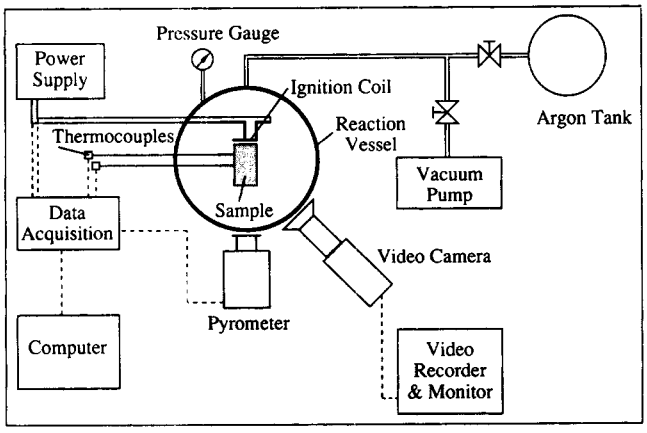

Figure 2. Experimental setup.

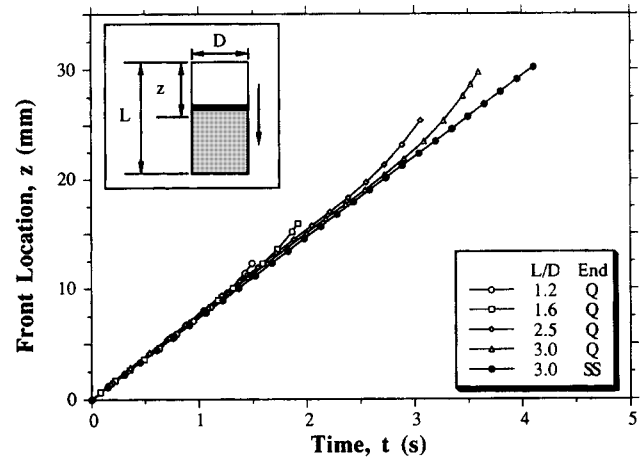

Figure 3. Experimental data for TiC synthesis: influence of sample length and end boundary on front propagation.

provided detailed information on the reaction front velocity and the pellet temperature, as a function of time.

The pellets were prepared as follows. Titanium powder (Cerac, −325 mesh, 99.5%) and carbon lampblack (Fisher) were first mixed in the stoichiometric ratio of 1.25/1 with hexane solvent. The resulting slurry was processed using an ultrasonic homogenizer to achieve uniform mixing. To maintain consistency between samples, the same powder mixture was used for all experiments. The dried mixture was then pressed into cylindrical pellets, 10 mm in diameter, using a uniaxial single-acting press at 70 MPa. The green density determined from mass and geometric measurements of the pellets was 58 ± 0.05% of TiC theoretical density ($\rho_{th} = 4.93$ g/cm^3). Previous studies of the synthesis of TiC (cf. Holt and Munir, 1986) have shown that under the high-temperature gradient present during reaction inside the pellet, substantial adsorbed gas evolution takes place leading to an elongated, porous compact. Therefore, to prevent deformation and expansion of the pellet during reaction and thus maintain a constant length, the pellet was kept constrained between two stainless steel plates. The top plate included a small hole, aligned coaxially with the longitudinal sample axis, and a thin layer of loose Ti + C powder mixture was poured between the ignition coil and the pellet. Upon ignition, this layer provided a uniform heating of the top surface of the pellet. Finally, end boundary conditions were altered by inserting, when desired, a 1.5 mm thick quartz plate, thermally insulating the pellet from the stainless steel base. The reaction vessel was evacuated to 10^{-3} torr and filled with argon prior to ignition. A preset current was sent through the tungsten coil and kept constant until ignition was detected; the current source was then immediately turned off.

Results and Discussion

Pellets with different length-to-diameter ratios, L/D, were ignited following the procedure described above. For each pellet, by analysis of the video recordings, the position of the reaction front, z was obtained as a function of time, t. To smooth out the variations, four pellets of identical L/D ratios were ignited and their average was taken. The resulting data for each L/D is presented in Figure 3. When the pellet was placed on a stainless-steel (SS) support, the velocity was constant and did not change either with position or with the length of the pellet. However, when the pellet was supported on a quartz (Q) plate, it was found that the velocity increased as the front reached the end of the pellet. This effect can be attributed to the difference in the thermal conductivity of the two supports. Stainless steel has thermal conductivity about one order of magnitude larger than quartz. When the pellet was supported on a stainless steel base, heat was transferred from the sample end more readily than when a quartz base was used. In the latter case, the heat generated at the front accumulates at the bottom of the pellet, leading to an increase in temperature and consequently faster front propagation. Thus, as suggested theoretically (Varma et al., 1990; Cao et al., 1991), the velocity of the reaction front is indeed not constant for pellets of finite length. It is, instead, demonstrated to be a function of position along the axis of the pellet.

It would be of interest to make a quantitative comparison between the theory and experiments. However, this can be done only with a full knowledge of thermophysical properties and reaction kinetics. The latter, in particular, is difficult to describe because the sequence of events leading from the initial reactants to the final product is complex (cf. Rogachev et al., 1987).

Literature Cited

Cao, G., A. Varma, and M. Morbidelli, "Remarks on Self-Propagating Reactions in Finite Pellets," *AIChE J.*, **37**, 1420 (1991).

Holt, J. B., and S. D. Dunmead, "Self-Heating Synthesis of Materials," *Ann. Rev. Mat. Sci,*. **21**, 305 (1991).

Holt, J. B., and Z. A. Munir, "Combustion Synthesis of Titanium Carbide: Theory and Experiments," *J. Mat. Sci.*, **21**, 251 (1986).

Lebrat, J.-P., and A. Varma, "Combustion Synthesis of the $YBa_2Cu_3O_{7-x}$ Superconductor," *Physica C*, **184**, 220 (1991).

Lebrat, J.-P., and A. Varma, "Self-Propagating High-Temperature Synthesis of Ni_3Al," *Combust. Sci. Tech.*, **88**, 211 (1992).

Margolis, S. B., "An Asymptotic Theory of Condensed Two-Phase Flame Propagation," *SIAM J. Appl. Math.*, **43**, 351 (1983).

Merzhanov, A. G., "Self-Propagating High Temperature Synthesis: Twenty Years of Search and Findings," *Combustion and Plasma Synthesis of High-Temperature Materials*, Z. A. Munir and J. B. Holt, eds., VCH Publisher, New York (1990).

Munir, Z. A., and V. Anselmi-Tamburini, "Self-Propagating Exo-

thermic Reactions: The Synthesis of High Temperature Materials by Combustion," *Mat. Sci. Reports*, **3**, 277 (1989).
Novozhilov, B. V., "The Rate of Propagation Front of an Exothermic Reaction in a Condensed Phase," *Dokl. Akad. Nauk SSSR*, **141**, 151 (1961).
Puszynski, J., J. Degreve, and V. Hlavacek, "Modeling of Exothermic Solid-Solid Noncatalytic Reactions," *Ind. Eng. Chem. Res.*, **26**, 1424 (1987).
Rogachev, A. S., A. S. Mukas'yan, and A. G. Merzhanov, "Structural Transitions in the Gasless Combustion of Titanium-Carbon and Titanium-Boron Systems," *Dokl. Akad. Nauk SSSR*, **297**, 1240 (1987).
Varma, A., G. Cao, and M. Morbidelli, "Self-Propagating Solid-Solid Noncatalytic Reactions in Finite Pellets," *AIChE J.*, **36**, 1032 (1990).
Varma, A., and J.-P. Lebrat, "Combustion Synthesis of Advanced Materials," *Chem. Eng. Sci.*, **47**, 2179 (1992).

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