Modeling and experimental studies on the effect of thermophysical properties on field-activated combustion synthesis reactions*

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Abstract: The influence of thermal and electrical conductivities and relative density on the dynamics of self-sustaining reactions activated by an electric field was investigated by modeling. Under a given field, the variation of the wave velocity and maximum temperature with normalized electrical and thermal conductivities and density exhibited a maximum at an optimum value of each of the three parameters. The results are discussed in terms of a Fourier relationship modified by the Joule heat contribution of the imposed field. A simulation was also made to investigate the configuration of the reaction front in systems that are ignited and sustained by a current. A transition from a volume (uniform) combustion reaction to a wave-like form was found to occur as the sample size is increased. These changes are also attributed to the interrelation between the thermophysical parameters.

INTRODUCTION

In recent publications we have reported on the effect of electric fields on self-propagating synthesis reactions. Such reactions have been utilized extensively for the synthesis of a large number of materials. But the occurrence of these reactions has limitations in the thermodynamic as well as in the kinetic sense, and hence the need to activate them becomes an important consideration. The imposition of an AC field was shown to have a marked influence on the dynamics of these reactions and on the mechanism of phase formation during their progression [1,2]. The presence of a field above a threshold value was seen to make possible the initiation of such reactions in systems which normally cannot sustain them [3], increase the velocity and temperature of the reaction wave [4], and influence the nature and composition of the product [5–8].

Modeling studies were also conducted to provide an understanding for the role of the field in these reactions [9,10]. The assumption was initially made that the contribution of the field is thermal in nature, by adding Joule heat to the chemical heat of the reaction. Thus, the rate of the total heat generation in the Fourier heat balance relationship describing such moving reactions is now made up of the two terms: $\rho Q(\partial \eta / \partial t)$ and σE^2, where ρ is the density, Q is the specific enthalpy (per unit mass) of the reaction, η is the fraction reacted, t is time, σ is the electrical conductivity, and E is the field. In most (but certainly not all) self-sustaining reactions the release of the chemical heat is confined to the narrow reaction front or wave. Thus, the location of the heat release from the electrical source becomes an important consideration. If it can be concentrated in the same location as the chemical heat, a greater leverage in the activation can be realized. Experimental observations and modeling studies have shown that the localization of the contribution of the electric current depends on the electrical conductivity of the product phase forming within the receding edge of the wave [4,11]. For relatively nonconducting

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products, the electrical energy is confined primarily to the reaction wave; while in systems with a relatively conducting product, the energy is widely distributed. The implication of this is that the degree of activation by the electric field is dependent on the physical properties of the involved phases. The degree of activation is defined here as the fraction of the electrical energy imparted to the reaction zone. When more current is carried behind the wave, less activation is achieved.

Figures 1a and 1b show results of a modeling study on the effect of the electrical conductivity of SiC on the relative location of the maximum temperature and the degree of conversion, η, within the reaction wave [12]. In the model, the electrical conductivity of SiC was hypothetically changed by a factor, $F = \sigma/\sigma_o$, with σ being the assumed value and σ_o the real value. In Fig. 1a, $F = 0.4$ (i.e., the elec-
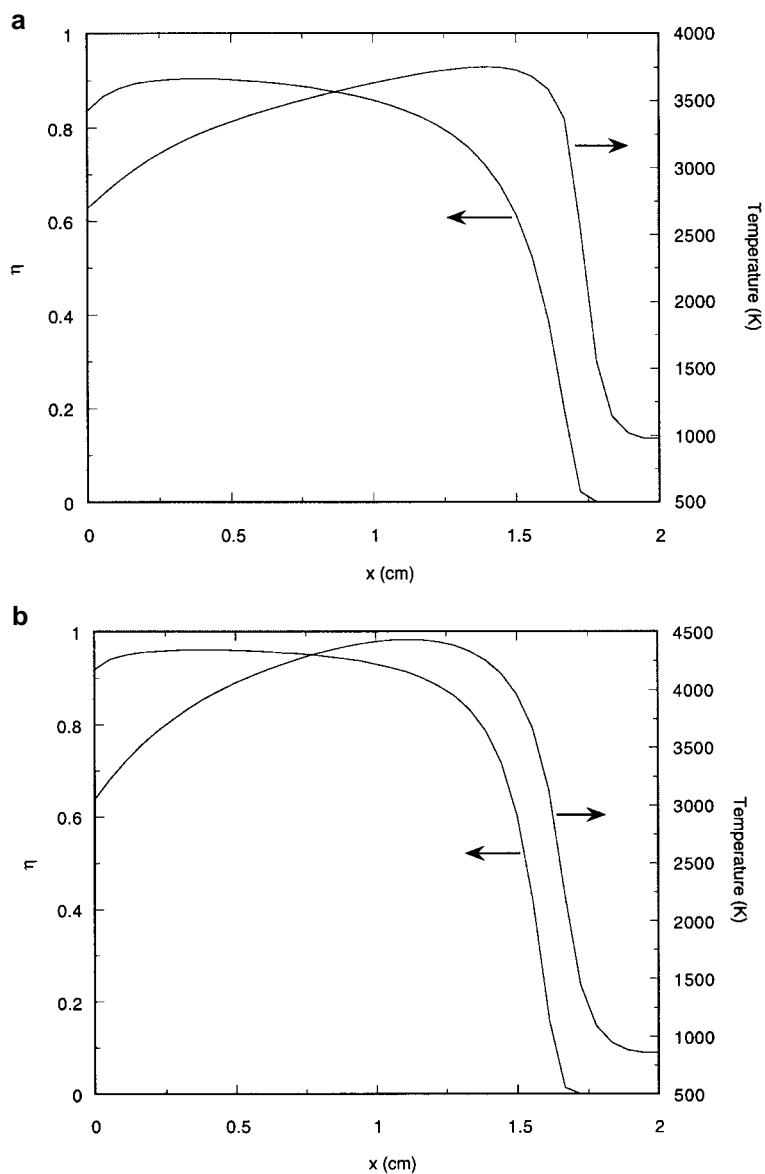

Fig. 1 Simulation results of the dependence of the temperature and conversion profiles on the electrical conductivity of SiC: (a) $F_\sigma = 0.4$; (b) $F_\sigma = 1.6$.

trical conductivity is assumed to be 0.4 σ_o), and in Fig. 1b, the conductivity is assumed to be 1.4 times the real value. In the former, the maximum temperature coincides with an η value of about 0.6 and in the latter it coincides with $\eta = 0.9$. These results thus demonstrate that as the conductivity of SiC is (hypothetically) increased, the location of the electrical energy contribution shifts toward the receding end of the wave.

EFFECT OF THE THERMOPHYSICAL PROPERTIES

Prior experimental observations

Under adiabatic conditions, the rate of heat accumulation in the reaction (combustion) zone ($\rho C_p(\partial T/\partial t)$) with ρ is density, C_p is the heat capacity, T is temperature, and t is time) is the sum of the rate of the chemical heat, $\rho Q(\partial \eta/\partial t)$, and the net rate of heat conducted thermally, $\partial/\partial x[\kappa(\partial T/\partial x)]$, where κ is the thermal conductivity and x is the coordinate along which the reaction wave is advancing. Since in nearly all self-sustaining reactions, the reactant mixtures are porous, density should play an explicit role and thermal conductivity, an implicit role. Indeed, early experimental observations have shown that both the velocity of wave propagation and the temperature of the wave are influenced by the relative density of the reactant mixtures. Figure 2 shows such a trend for reactions involving the synthesis of intermetallic compounds from early reported data [13]. The velocity exhibits a maximum at about 60% relative density. Samples with higher and lower densities propagate at much lower velocities and in the limit, at very high or low densities the reaction wave does not propagate. The implication of this and many similar subsequent observations is that thermal conductivity is being changed. At low densities, the net heat conducted is low because of the low *effective* conductivity, and thus the region ahead of the wave cannot be heated to the ignition temperature. On the other hand, at high densities, the heat is conducted so well that it is dissipated to regions far in advance of the wave, and thus the region immediately ahead of the wave is not sufficiently heated to ensure wave continuation. The effect of density has another side, that related to the decrease in the reaction enthalpy per unit volume. Thus an analysis of the effect
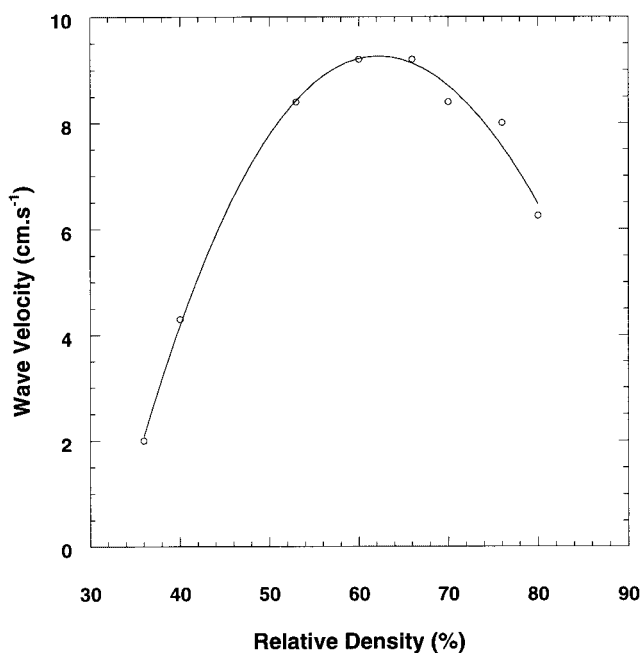

Fig. 2 The dependence of the wave velocity in the Ni–Al system on the relative density of the reactants (data from ref. 13).

density and thermal conductivity needs to treat the two parameters separately. And when electric field application is utilized, the role of the electrical conductivity is also considered to assess the effect of these parameters on the dynamics of reaction waves. An analysis of the effect of porosity on the velocity of the combustion wave was made [14], but the conclusions are not in agreement with the experimental results of Fig. 2.

Effect of electrical and thermal conductivities

Modeling studies were made to assess the effect of these thermophysical parameters on wave dynamics utilizing a previously described method [9,10]. The model is based on a two-dimensional Fourier heat conduction with a heat source which includes the electrical energy and which accounts for heat loss. Details of this model are given in the cited references. Using the synthesis of SiC as an example, simulation computations were made to determine the effect of an electric field on the variation of wave dynamics with electrical and thermal conductivities.

Figure 3 shows the variation of the wave velocity with electrical conductivity (expressed as a ratio $F_\sigma = \sigma/\sigma_o$) for applied fields ranging from about 14 to 28 V.cm^{-1}. For any given field value, the velocity has a maximum at an optimum conductivity. This maximum increases as the field value increases, consistent with general observation on the effect of the field on velocity [4]. The occurrence of a maximum in the velocity is reconciled by two factors: the intensity of the field and the distribution of the energy. At low conductivities (low F_σ), the current is localized, but the total rate of electrical energy input to the system, σE^2, is low and hence the velocity is low. On the other end, when the conductivity is high, the electrical energy is nonlocalized, and thus the fraction of the electrical energy affecting the reaction is relatively low, leading to a low velocity. The dependence of the temperature of the reaction wave on conductivity has a similar trend to that of the velocity, as seen in Fig. 4. A maximum is observed which also increases with increasing field.
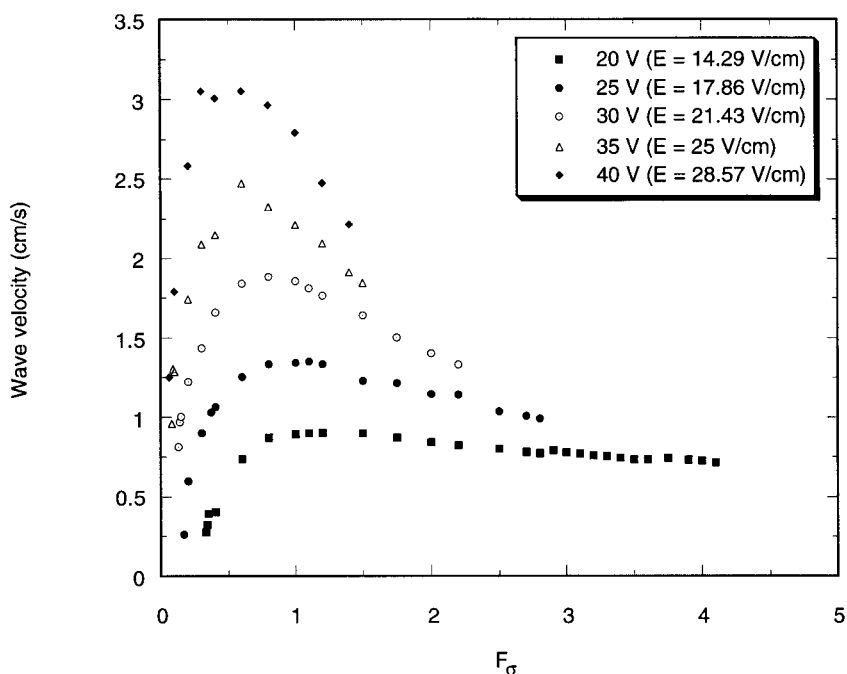

Fig. 3 The effect of electrical conductivity on wave velocity for different applied fields. Results of simulation on SiC.
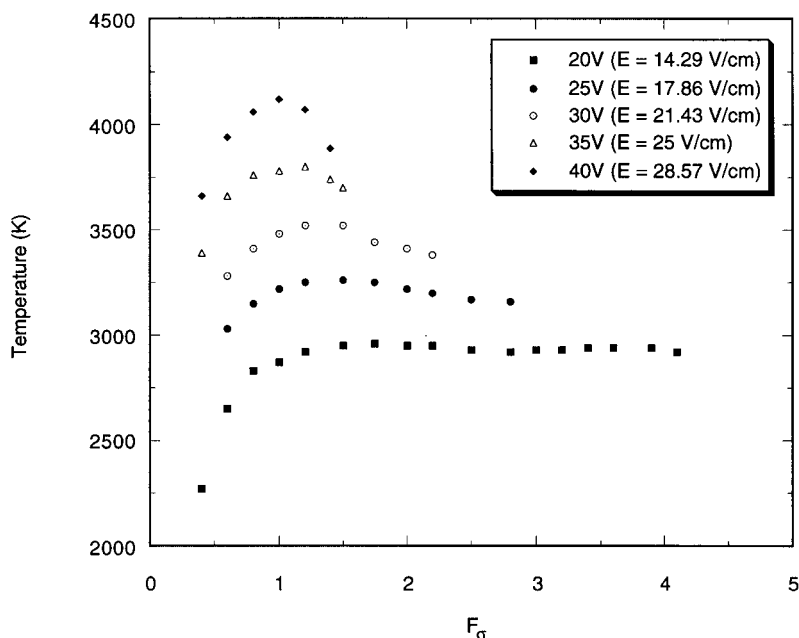
Fig. 4 The effect of electrical conductivity on temperature for different applied fields.

The modeling work shows that the effect of thermal conductivity on wave dynamics is generally similar to that of electrical conductivity. Figure 5 shows the effect of thermal conductivity on wave velocity for different fields. Here also the thermal conductivity is expressed as a ratio, $F_\kappa = \kappa/\kappa_o$, with κ_o being the real value for SiC at the temperature corresponding to the velocity value. The concept of a maximum is evident, but the curves are not as steep as those for the electrical conductivity, Fig. 3. The reason for this lies in the nature of the contribution of κ to the Fourier relationship, as modified to account for the electrical energy. As noted above, the electrical conductivity enters the analysis in two ways: its direct effect on the term σE^2 and its influence on the distribution of the current (and hence activation contribution). In contrast, the role of κ is only in the term of the net heat conducted, $\partial/\partial x[\kappa(\partial T/\partial x)]$, and thus influences the ignition of the layer just ahead of the wave. In other words, changing σ influences the amount of activation, but changing κ has no similar effect.

Effect of relative density

As was noted above, in the absence of a field, changes in the relative density of reactants undergoing self-propagating reactions are reflected in modifications in the specific reaction enthalpies (energy per unit volume) and in the effective thermal conductivity. The latter must be dominant, however, otherwise fully dense reactants should always sustain a self-propagating wave. That such waves are not sustained in highly dense samples has been amply demonstrated by experimental observations, as will be discussed further below.

Modeling studies on SiC were made to assess the effect of density, again expressed as a ratio, ρ/ρ_{th}, where ρ_{th} is the theoretical density. The effect of density on wave velocity for different values of imposed field is shown in Fig. 6. A maximum is evident at low field values but is absent at higher fields. The assumption is that it would be only apparent at very low densities. However, samples with such very low densities, <5%, do not "ignite" in the modeling simulation. Such densities, of course, are unrealistic in typical reactions of this type. The existence of a maximum, even for higher fields, is seen in Fig. 7, which depicts the influence of thermal conductivity on the maximum wave temperature.

In Fig. 6 the velocity of a reaction wave in the synthesis of SiC is greater than zero even for a fully dense sample, according to the results of the modeling work. But as noted above (and shown in Fig. 2), fully dense samples using powder reactants do not sustain such waves. The important contribution of the modeling work is, therefore, the demonstration of the effect of the field. The implication
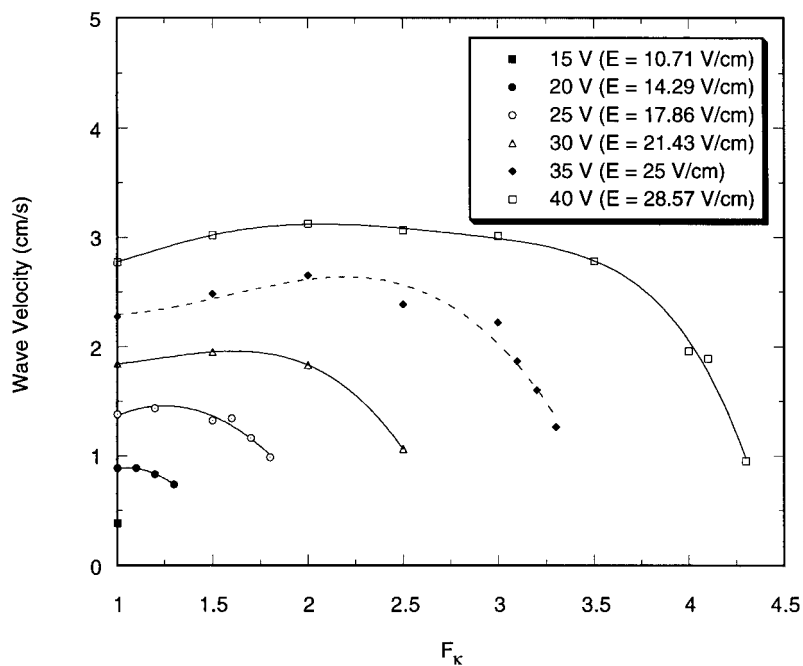
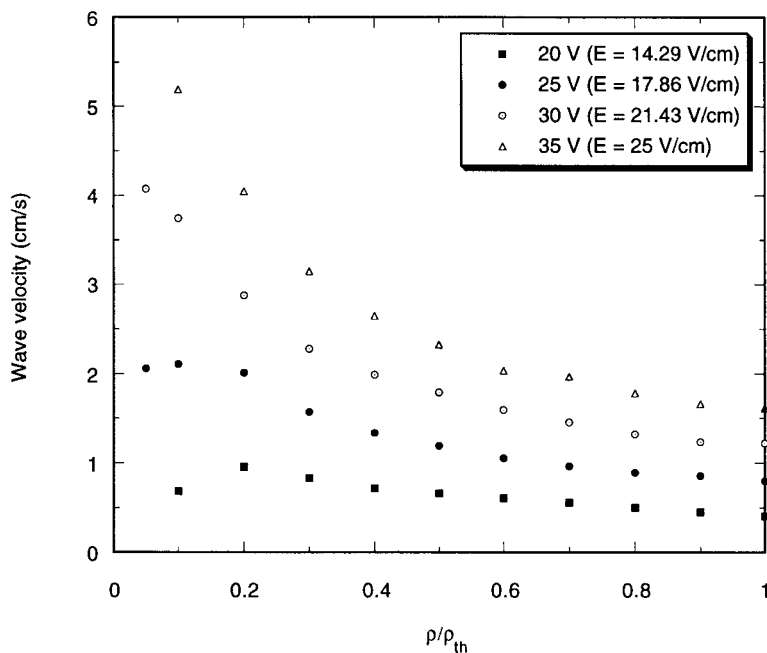**Fig. 5** The effect of thermal conductivity on wave velocity for different applied fields.

Fig. 6 The effect of relative density on the wave velocity for different fields.

is that with the application of a field, a wave can be initiated and sustained even in dense samples. Experimental work has been made recently that confirms these expectations. Figure 8 shows the effect of density on wave velocity in the synthesis of $MoSi_2$ [15]. Self-sustaining reactions between Mo and Si (in the 1:2 stoichiometry) can be initiated without a field within a density range. A maximum is seen
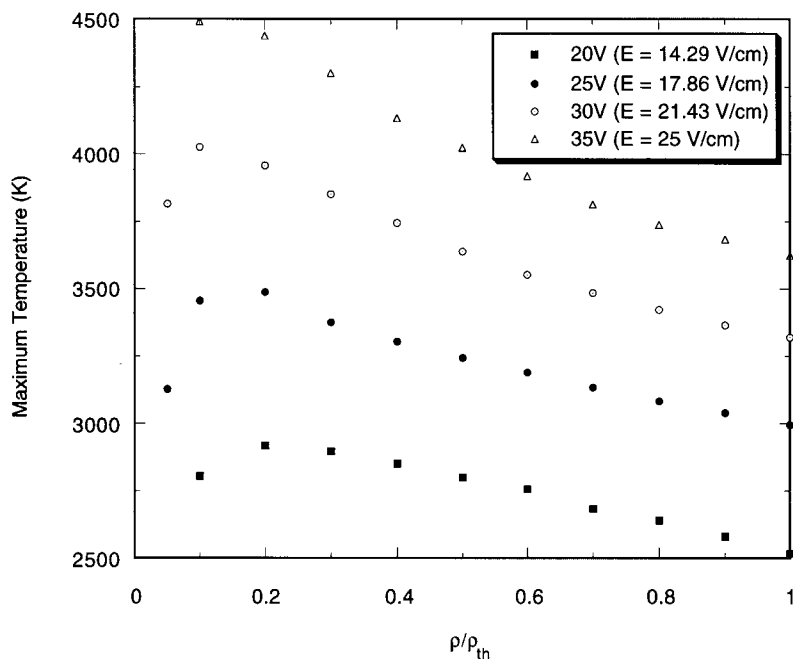

Fig. 7 The effect of relative density on the wave temperature for different fields.
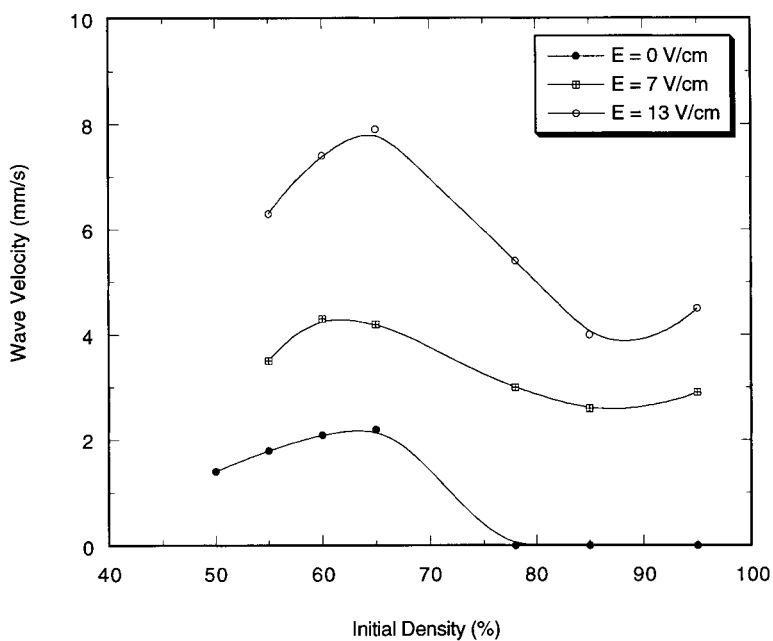

Fig. 8 Results of experimental study on the dependence of wave velocity on relative density in the synthesis of $MoSi_2$ [15].

in the velocity corresponding to a relative density of about 65%, qualitatively consistent with model predictions. In this case, however, waves cannot be initiated in reactants with a density of ≥78%. But with the application of a field, such waves are possible. Their rate of propagation increases as the field is increased for any given density. It is noteworthy that reaction waves are sustained in samples which are nearly fully dense (95%). The existence of a maximum in the velocity curves, predicted by the model is confirmed by these experimental results.

EFFECT OF THERMOPHYSICAL PARAMETERS ON WAVE CONFIGURATION

In the preceding sections we discussed the effect of the thermophysical parameters on wave dynamics in self-sustaining reaction waves. In these cases, the samples are subjected to a voltage while the reaction is being initiated by an ignition source. Another form of field activation is by igniting the reaction by the imposed voltage itself, if the room-temperature conductivity of the reactants is sufficient to promote Joule heating. This approach was used previously in the synthesis of various materials [16,17]. More recently, the approach has been utilized to densify, or simultaneously synthesize and densify a variety of materials [18,19]. Using the latter approach, it was recently demonstrated that dense nano-materials can be prepared [20].

By using the field to initiate reactions, it was understood that the current heats the reactants to the ignition point, and then the reaction occurs everywhere in the sample. The mode of such reactions is referred to as volume or simultaneous combustion. The difference between this form of reaction and the self-propagating form relates to the temperature profiles during the reaction. Self-propagating waves are associated with steep temperature gradients, a circumstance that has implications on product phase evolution. In order to understand reaction processes initiated and propagated by the presence of a field, we have carried out simulation studies using cylindrical samples for reactions to form SiC and $MoSi_2$ [21]. The model used in these simulations is the same as that cited above, but it is now converted to cylindrical coordinates. Analyses were made to determine the nature of the reaction by developing profiles for conversion, temperature, and current density as a function of sample size (i.e., radius). Figures 9a
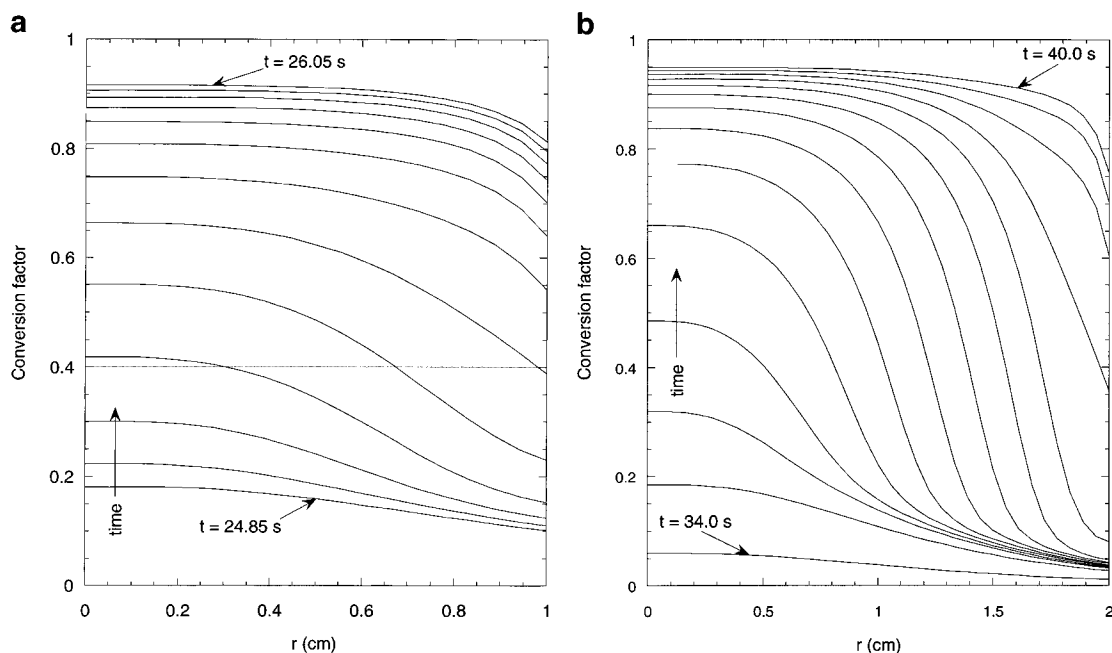

Fig. 9 Conversion profiles for the simulated combustion synthesis of SiC under 25 V: (a) sample radius = 1 cm, (b) sample radius = 2 cm.
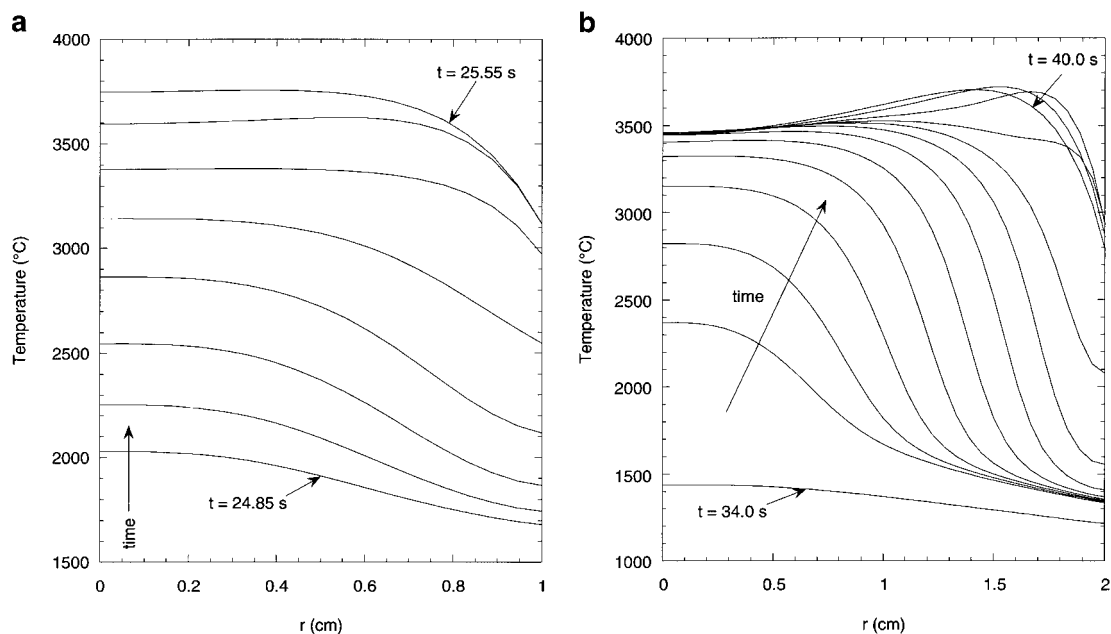
Fig. 10 Temperature profiles for the simulated combustion synthesis of SiC under 25 V: (a) sample radius = 1 cm, (b) sample radius = 2 cm.
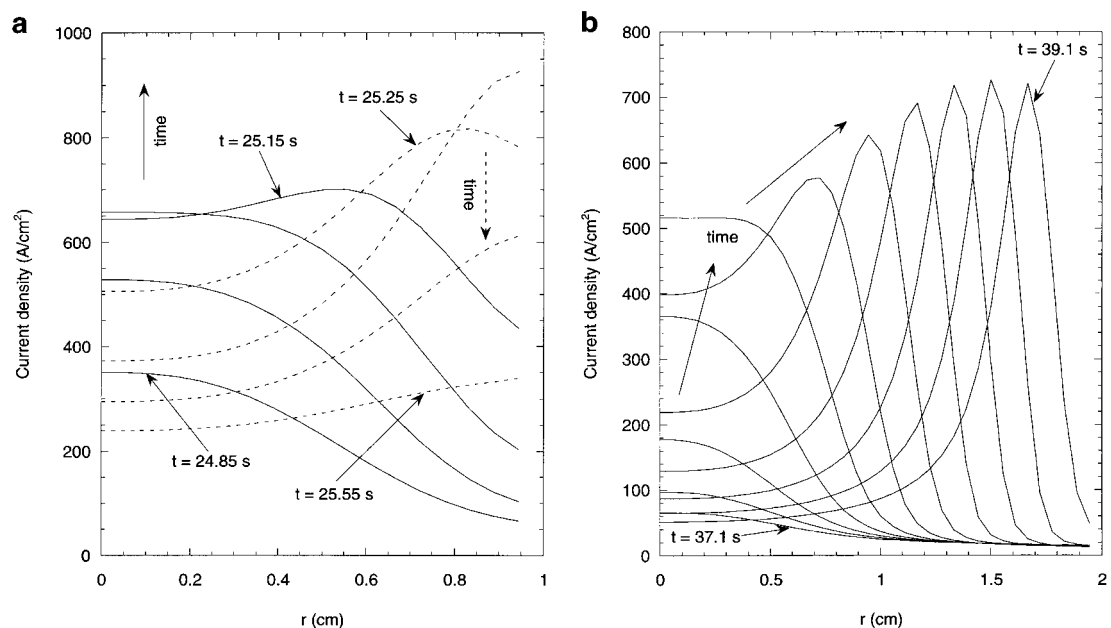

Fig. 11 Current density profiles for the simulated combustion synthesis of SiC under 25 V: (a) sample radius = 1cm, (b) sample radius = 2 cm.

and 9b show the conversion profiles during the synthesis of SiC for 1- and 2-cm radius samples, respectively. Corresponding temperature and current density profiles for the two sizes are shown in Figs. 10a and 10b and Figs. 11a and 11b, respectively. All these and subsequent results were obtained with an applied voltage at 25 V on 2.5-cm-high cylindrical samples.

The results depicted in these figures show a marked change in the mode of the reaction as the sample size is increased from 1 to 2 cm. For the smaller size, the conversion and temperature profiles show that the reaction is fairly uniform across the sample (Figs. 9a and 10a), indicating a volume mode of combustion. But as the sample size increases to 2 cm, the profiles are markedly changed. Now they exhibit steep gradients in both conversion and temperature, Figs. 9b and 10b. Under these conditions, the reaction proceeds as a wave, analogous to the case of self-propagating reactions discussed in the previous section. The profiles of current density, Figs. 11a and 11b, provide additional confirmation of the nature of the reaction front. For a 1-cm radius sample, the current is widely distributed but becomes highly localized in the larger sample. The profiles in the latter are similar to those obtained in the modeling of wave propagation in the synthesis of SiC [1].

The difference in the reaction mode between small and large samples for SiC is dictated by heat generation, heat flow, and heat loss contributions to the model. A detailed analysis shows that thermal conductivity plays a major role in the setting up of temperature profiles which is the prerequisite for the occurrence of a wave form [21]. Results on $MoSi_2$ are qualitatively similar to those of SiC except that the transition from volume combustion to waveform reaction takes place as the sample size is increased from 2 to 3 cm. The difference in behavior with regards to the dependence of the transition on size relates to the electrical and thermal conductivities of the components in both reaction systems.

ACKNOWLEDGMENTS

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