Mechanistic Investigation of Electric Field-Activated Self-Propagating Reactions: Experimental and Modeling Studies

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Abstract

The mechanism of electric field-activated self-propagating reactions is investigated using the combustion front quenching technique. In particular, previously published experimental results obtained through the Field Assisted Combustion Synthesis (FACS) of b-SiC, TaC, Ti_3Al and B_4C-TiB_2 are re-examined and compared. Pre-combustion and combustion stages involved during synthesis wave propagation are postulated for all systems. Subsequently, modeling results aimed at simulating the process where an electric field-activated self-propagating reaction takes place are presented. In particular, a one-dimensional model of FACS technique is developed to simulate the rapid quenching of the reaction during its progress as the applied field is turned off. A rate expression which accounts for the influence of temperature, particle size, compaction density, reactant stoichiometry, and inert content is included in the model.

Introduction

It is well known that relatively high exothermic reactions of either solid-solid or gas-solid type are able to propagate in the form of a combustion wave upon ignition. This area of reaction engineering is both very important and relatively poorly understood (Varma et al., 1998). The process is complex involving a wide spectrum of physico-chemical phenomena (reaction, diffusion, nucleation, grain growth, etc.).

A promising technique known under the acronym of SHS (Self-propagating High-temperature Synthesis) for the preparation of advanced materials (Merzhanov and Borovinskaya, 1972; Munir and Anselmi-Tamburini, 1989; Varma et al., 1998) as well as for other interesting applications in the field of environmental chemical engineering (cf. Orrù et al., 1999a; Cao et al., 1999) is based on the occurrence of self-propagating reactions. An empirical criterion typically adopted for determining the feasibility of self-propagating reaction is an adiabatic temperature, T_{ad}, exceeding 2000 K. But this is only one parameter affecting the occurrence of SHS reactions (Munir, 1998).

Recently, a new method, based on the use of an electric field to activate self-propagating reactions in less-exothermic systems, was developed (cf. Munir et al., 1995). Through this method, referred to in the literature as FACS (Field-Assisted Combustion Synthesis), the synthesis of materials heretofore not possible by normal SHS (e.g., SiC, SiC-AlN, TaC, B_4C-TiB_2, $MoSi_2$-SiC, and Ti_3Al) was successfully demonstrated (cf. Feng and Munir, 1995a; Xue and Munir, 1996a; Xue and Munir, 1996b; Xue and Munir, 1997; Gedevanishvili and Munir, 1998; Orrù et al., 1999b). SHS and FACS processes are typically characterized by high temperatures (up to about 3500 K), reaction waves which propagate at relatively high speeds (up to 25 cm/s), and low energy requirements, etc.

Although these processing conditions make these techniques advantageous for industrial applications, process scale-up and control may not be straightforward. In order to overcome this problem a fundamental knowledge of reaction and structure formation mechanism is necessary.

Considerable effort has been made at the experimental level in order to understand the basic mechanisms occurring during self-propagating reactions. Different and complementary approaches have been proposed in the literature, i.e. investigation of the effect of processing variables, the synchrotron radiation technique, the particle-foil technique, the combustion front quenching technique (Mukasyan and Borovinskaya, 1992; Varma et al., 1998; Gras et al., 1999). The latter one, which is based on the rapid extinction of the reaction front during its progress, is often preferred due to its simplicity and since it provides a relatively accurate picture of the physico-chemical phenomena involved during reaction evolution. By investigating product microstructure and composition at different areas relative to the location of the frozen reaction wave, it is possible to identify intermediate species and phase transformation taking place.

For those less exothermic systems which are synthesized through the FACS technique, quenching of the reaction can be obtained by turning off the electric field during front evolution. This technique has an advantage over the wedge-quench technique. The FACS quenching is due to a sudden and abrupt decrease in the energy of the wave while the other is due to a gradual increase in the heat loss to conduction.

In this paper we focus on aspects related to the mechanistic investigation of electric field-activated self-propagating reactions. In the first part, we discuss previously published experimental results obtained during the FACS of b-SiC, TaC, Ti_3Al and B_4C-TiB_2 from elemental powders (Feng and Munir, 1995a; Xue and Munir, 1996a; Xue and Munir, 1996b; Orrù et al., 1999c). It should be noted that b-SiC and Ti_3Al are characterized by an adiabatic temperature less than 2000 K and thus the occurrence of a self-propagating reaction is thermodynamically limited. On the contrary, although for the other two systems T_{ad} is significantly higher of the minimum value of 2000 K, they cannot be synthesized by SHS without activation. In the second part of this paper, we present modeling results aimed at simulating the process where electric field-activated self-propagating reaction takes place. In particular, a one-dimensional model of the FACS technique is developed which is able to simulate the rapid quenching of the reaction during its progress as the applied field is turned off.

Previous Experimental Observations

In order to provide a background for the results of the FACS method, a brief description of the experimental setup and the procedure is provided here. A schematic representation of the principle of FACS and its use for the quenching of the combustion front is shown in Figure 1 (Feng and Munir, 1995a).

Typically, powders of elemental reactants are mixed in stoichiometric amounts and pressed into round-ended rhombohedral pellets. The pellets were placed between two graphite electrodes across which a voltage was applied. The sample was ignited by means of a tungsten coil placed few millimeters away from one end. The electric field was applied simultaneously with the ignition source. The latter one was turned off immediately after the reaction was initiated. The reaction front propagated through the sample only in the presence of the electric field and in a direction perpendicular to it. Since, as previously observed, the systems investigated are not self-sustaining, when the field was turned off during wave propagation, the combustion wave stopped immediately. The process evolution was recorded on a video recorder and the wave velocity was measured from video recordings using a time-code generator. Real-time current (I) and voltage (V) data were also acquired during wave propagation (Feng and Munir, 1995a).

It was reported that during the field assisted combustion synthesis of b -SiC, TaC and Ti_3Al, the propagation of the wave is only possible when the applied field is above a threshold value, E_t. For these systems, the reported values of E_t are 6.8, 8.0 and 3.8 V/cm, respectively. However, for the case of the composite yB_4C-TiB_2, the threshold field was found to depend on the value of y, i.e., the molar ratio B_4C/ TiB_2. Above the threshold, the reaction front propagates through the sample with a velocity which increases with an increase in field strength for all systems investigated. The removal of the field in such samples causes the reaction front to stop and the combustion process to extinguish.

For the case of b -SiC, Figure 2 (Feng and Munir, 1995a) shows a SEM micrograph of the quenched front. Four distinct regions can be clearly identified from this figure. XRD analysis results of samples obtained from these zones are reported in Figure 3. Region 1 represents the elemental reactants. In Region 2, in addition to Si and C along minor amounts of the product, SiC, are present. The latter compound is the major phase in Region 3 but Si and C are still present. Finally, only b -SiC was observed in Region 4. More detailed microstructural examination of these zones by SEM were accomplished. In particular, it was observed that the transition from Region 1 to Region 2 corresponds to the melting of Si (Feng and Munir, 1995a).

The results obtained by performing a layer to layer X-ray diffraction analysis at various axial locations of the quenched sample related to FACS of Ti_3Al are reported in Figure 4 (Orrù et al., 1999c). Region 1, ahead of the wave, is comprised of the elemental reactants only. Region 2 contains $TiAl_3$ together with unreacted titanium and aluminum. The latter is not detected in Region 3 where TiAl is found together with the desired phase Ti_3Al and unreacted titanium. Finally, in Region 4 only the desired phase Ti_3Al is obtained.

The phenomena involved during the progress of the combustion wave have been described in detail from SEM investigation (Orrù et al., 1999c). The first step is the melting of Al by heat conducted ahead of the wave. The molten aluminum then spreads around the Ti particles, reacting to form a layer of the first product, $TiAl_3$. No other products were observed before the aluminum is completely consumed. Then $TiAl_3$ gradually disappears and the Ti cores become surrounded by a layer of Ti_3Al which is followed by a layer of TiAl. Unreacted Ti cores are then found to gradually shrink and disappear, the layer of Ti_3Al becomes thicker and the TiAl layer becomes thinner. Finally, the only phase detected in the product region is Ti_3Al, the intended product of the synthesis.

The XRD patterns corresponding to five different sample layers of the quenched specimen obtained during FACS of TaC are shown in Figure 5 (Xue and Munir, 1996b). Region 1, which is located ahead of the frozen wave, is composed of reactants only. The corresponding XRD pattern displays only Ta reflections since the carbon used was amorphous. Besides the reactants, a small amount of TaC was also detected in Region 2. The degree of conversion of Ta gradually increases from Region 2 to Region 4. However, the desired phase, TaC, was accompanied by traces of Ta_2C in Regions 3 and 4. Finally, as can be seen from Figure 5, this secondary phase disappears in Region 5 where only TaC was obtained. It is worth noting that the TaC peaks were broad and had shifted from their standard 2q values as the region of analysis moves from Region 2 to 4. Specifically, the lattice parameters in Region 2, 3, 4, 5 were calculated as 4.090, 4.428, 4.442 and 4.453 Å, respectively.

XRD analyses results of the unreacted (Region 1), combustion (Region 2) and reacted (Region 3) zones of quenched samples obtained during FACS of B_4C- TiB_2 are shown in Figures 6 (Xue and Munir, 1996a). Region 1 contained the reactant elements only. The boron used was amorphous so its presence could not be identified by XRD. Unreacted carbon and TiB_2 are found in Region 2, corresponding to the combustion zone. The desired final phases, TiB_2 and B_4C, were identified in the zone behind the quenched wave, represented by Region 3.

Discussion

On the basis of the previously published experimental results (described above), it is possible to postulate the sequence of transformation during FACS of b -SiC, Ti_3Al, TaC, and B_4C-TiB_2, as summarized in Tables 1(a) to 1(d), respectively.

For the case of b -SiC, Table 1(a), it is seen that the combustion is preceded by the melting of silicon particles, a process that takes place in the leading edge of the reaction wave. This phenomenon is very important since it gives rise to an increase in the interconnectivity between particles. In addition, due to the relatively high value of the electrical conductivity of liquid silicon (relative to the corresponding values of the solid reactants and product), the current is mainly confined to this region (Feng and Munir, 1995a). From the compositional and microstructural investigation of the quenched front a gradual conversion of reactants to b -SiC is seen.

A mechanism of formation of SiC by combustion synthesis is recently proposed in the literature (Narayan et al., 1994). As observed in the previously reported FACS case (Feng and Munir, 1995a), the combustion reaction is preceded by the melting of silicon. Then, the formation of SiC involves three different steps: the first consists of the dissolution of carbon into liquid silicon, the second stage relates to the diffusion of carbon through liquid silicon, and finally the third stage relates to the formation of SiC by precipitation from a saturated liquid solution. In addition, the latter step is followed by the growth of the carbide grains.

The sequence of transformations involved in the FACS of Ti_3Al is summarized in Table 1(b) (Orrù et al., 1999c). In order to obtain the desired phase, a pre-combustion stage, i.e. the melting of aluminum, and two subsequent combustion steps are required. The first step is related to the formation of secondary (undesirable) aluminides, with $TiAl_3$ being the first phase formed. During the second combustion step these intermediate phases interact with unreacted titanium and finally forming Ti_3Al. This conclusion was also supported by the results obtained during the FACS of Ti_3Al (Orrù et al., 1999b), where the field-assisted combustion wave propagates throughout the entire sample. The corresponding temperature profiles associated with the passage of the wave showed two peaks. The first one, which is always present independently of the applied field level, corresponds to the first stage of combustion. On the other hand, the second peak, almost always absent at low fields, increased strongly with increasing field strength. Correspondingly, the formation of a mixture of phases, i.e. $TiAl_3$, TiAl, unreacted Ti, and Ti_3Al, was found to take place at low fields, while the latter phase is the only one formed when applying high fields. In particular, this is the case when using an electric field equal to 14.3 V/cm, corresponding to the conditions considered in the reported work for mechanistic investigations (Orrù et al., 1999c).

Since the adiabatic temperature of TaC is less than its melting point (4153 K) as well as the melting points of Ta (3289 K) and C (4100 K), a solid-solid mechanism is the only likely process during the combustion synthesis of this carbide phase. The transformations taking place during FACS of TaC are summarized in Table 1(c) (Xue and Munir, 1996b). The initial stage consists of the diffusion of carbon into tantalum with the formation of Ta_2C. This step is followed by the transformation of Ta_2C to TaC, which occurs as a consequence of the diffusion of C into the Ta_2C lattice. Since only trace amount of Ta_2C are found in the quenched wave, the latter step is assumed to occur relatively rapidly and therefore is not considered rate controlling. The progress of the synthesis involves also the diffusion of carbon into TaC, which is the controlling step. The fact that this slow step is limiting the process evolution, may be the reason for the relative difficulty of establishing and sustaining a combustion wave in such systems as compared to the case of other carbides, i.e. TiC, where melting phenomena are also involved.

As indicated above, the reported tantalum carbide peaks were shifted, indicating a change in the lattice parameter corresponding to the specific elemental ratio. Since the lattice parameter value of stoichiometric TaC, 4.455 Å, is very close to the value found in Region 5, it may be concluded that the stoichiometric phase is formed only at the end of the combustion process. This is because tantalum carbide exists in a relatively wide range of composition, as it may be seen from the Ta-C phase diagram (Thaddaeus, 1986). Thus on the basis of the general formula TaC_{1-x}, the reported lattice parameters values obtained in different zones of the quenched sample (Xue and Munir, 1996b) correspond to x values of 0.35, 0.18, 0.05 in Region 2, 3, and 4, respectively. This aspect further confirms that the stoichiometric TaC is obtained only when carbon completely disappears as a consequence of a gradual diffusion of C into the TaC_{1-x} phase.

The removal of the field, applied in a direction perpendicular to that of the combustion wave, provides an excellent means for investigating the sequence of phase formation during FACS of B_4C-TiB_2. The corresponding postulated transformation zones are summarized in Table 1(d) (Xue and Munir, 1996a). It is apparent that the synthesis of this composite occurs through two sequential reactive steps. In particular, the first stage, involving only the interaction of titanium and boron but not carbon, results in the formation of TiB_2. This combustion step provides heat to activate the second one, which leads to the formation of B_4C. Both steps take place in the combustion wave but the first one occurs near the leading edge of the wave while the second one close to the trailing edge.

FACS Modeling

As indicated in the introduction section, FACS involves complex physico-chemical phenomena, such as melting and diffusion of reactants, chemical reactions with formation of intermediate phases, nucleation and grain growth, all contributing to the formation of the microstructure of the final product. Therefore, the understanding of FACS fundamentals represents a scientific and technological challenge and, simultaneously, the key approach to develop a proper process model which can be used to address suitable control strategies. From the experimental results discussed above it has been demonstrated that by quenching the reaction front during its propagation it is possible to identify the evolution of reactants to products as well as of the structural and chemical transformations. Although this technique is able to provide detailed information of a macrokinetic type useful for process understanding, the estimate of the physico-chemical parameters involved may be obtained only by direct comparison between experimental and theoretical results. This goal cannot be achieved if the typically heterogeneous reacting mixture is considered as homogeneous, as is the case in many literature accounts. In this work, we develop a one-dimensional model of the FACS technique which takes into account the heterogeneous nature of the system and is able to simulate the rapid quenching of the reaction during its progress as the applied field is turned off. It is worth noting that, although a two-dimensional approach may be more appropriate to simulate FACS processes (Feng and Munir, 1996b; Feng et al., 1998), in this work we focus our attention on the use of heterogeneous kinetics.

By assuming that the starting powders behave like an isotropic mixture and mass diffusion of the solid reactants and products does not occur, the model consists of the following energy balance:

$$\rho C_p \frac{\partial T}{\partial t} = \frac{\partial}{\partial x}\left(k\frac{\partial T}{\partial x}\right) + (-\Delta H)\, C_B^0 \frac{\partial \eta}{\partial t} + \sigma\left(\frac{V}{L_y}\right)^2 - 2\left[\frac{h(T-T_0)+\upsilon(T^4-T_0^4)}{w}\right] - 2\left[\frac{U(T-T_0)}{L_y}\right]$$

This energy balance takes into account the rate of heat conduction and heat generation by chemical reaction, the rate of heat generation from the electric field by Joule heating as well as the rate of the heat dissipation due to radiative cooling from the sample surface. This is analogous to the model proposed by Feng et al. (1998). The energy balance is coupled with the following mass balance:

where h =1-$(d_p/d_{p0})^3$ for a>1, h =[1-$(d_p/d_{p0})^3$]/a for a<1, $C_A = C_B^0(a-\eta)$, $C_B = C_B^0(1-\eta)$ and $C_B = C_B^0(1-\eta)$, while the meaning of all symbols is reported in the Notation section. Here, the reaction rate equation is based on the model developed by Kanury (1992), in which the reaction between a low-melting-point component (A) and a high melting (solid) one (B), is considered. In particular, the model assumes that A melts and flows by capillary forces around B particles, and the reaction is proportional to the instantaneous surface area of the solid component. It should be noted that the rate expression accounts for the influence of temperature, particle size, compaction density, reactants proportion and inert content.

The mass and energy balances above are also coupled with the following electropotential equation:

$0< t < t_1$ $$V = \frac{V_{in}}{1+\frac{w}{L_y}R_0\int_0^{L_x}\sigma\,dx} \quad (3)$$

t ³ t_1 $V = 0$ (4)

which is derived by assuming that the electromagnetic phenomenon is static or quasi-static, i.e. by neglecting the time derivative terms in Maxwell s equations, and considering an ohmic material. The dependencies of the thermophysical properties, such as thermal conductivity, electrical conductivity, and heat capacity on temperature and composition are taken from the literature, as reported in Table 2. In order to solve the above equations, the following functional relationships have been accounted for:

$$\rho C_p = C_A M_A C_{p,A}(T) + C_B M_B C_{p,B}(T) + C_P M_P C_{p,P}(T) \quad (5)$$

$$\ln(\sigma_1) = \frac{C_A \ln(\sigma_A(T)) + C_B \ln(\sigma_B(T)) + C_P \ln(\sigma_P(T))}{C_A + C_B + C_P};\ \sigma = \left(\frac{\rho}{\rho_{th}}\right)\sigma_1 \quad (6)$$

$$k = \left(\frac{\rho}{\rho_{th}}\right)\frac{C_A k_A(T) + C_B k_B(T) + C_P k_P(T)}{C_A + C_B + C_P} \quad (7)$$

$$U = \left(\frac{s}{k_{Graphite}} + \frac{1}{h}\right)^{-1} \quad (8)$$

$t = 0 \qquad \forall x \qquad T = T_0 \qquad \eta = 0$ The following initial and boundary conditions are used:

$x = 0 \qquad \forall t > 0 \qquad T = g(t)$ (9)

(10)

$$x = L_x \qquad \forall t > 0 \qquad -k\frac{\partial T}{\partial x} = h\left(T - T_0\right) + \upsilon\left(T^4 - T_0^4\right) \quad (11)$$

It should be noted that g(t) appearing in Equation (10) is an empirical function obtained by interpolating the temperature profile at the base where the reacting sample is ignited. The equations described above are solved simultaneously by adopting a finite difference scheme at the internal node points and integrating the resulting system of ordinary differential equations using standard routines. An appropriate finite-difference scheme also applies to the boundary condition Eq (11), where non-linearities are handled with the Newton-Raphson method. During the computation, 300 discretization points was generally kept. Higher values of the internal node points did not cause any change in the results.

Modeling results and discussion

As noted in the introduction section, one of the aims of the present investigation is to contribute to the development of a model of the FACS technique which may be used to obtain macrokinetic parameters of the process by direct comparison between experimental data and model results. The model parameters reported in Table 2, are used for the computations. The reaction Si + C à SiC is considered as model system in this work. This choice is related to the results reported in the Previous Experimental Observation section (Feng and Munir, 1995a) (cf. Table 1). It was seen that the reaction is preceded by the melting of Si, and the system does not involve the formation of intermediate phases, in accordance with the adopted kinetic equation. Therefore, we took advantage of the corresponding values reported by several studies available in the literature, as indicated in Table 2. Unfortunately, to the best of our knowledge the values of the pre-exponential effective diffusivity and the activation energy are not available in the literature and therefore the corresponding values were chosen in the range of typical self-propagating reactions.

In agreement with reported experimental results, the present model predicts that in the absence of an imposed field no self-sustaining combustion waves can be initiated, but that such waves can be activated in the presence of a field above a minimum (threshold) value, i.e. 7.8 V/cm. Modeling results of outputs of current and voltage during FACS are shown in Figure 7 (dotted lines) for the case when the electropotential Eq(3) is maintained throughout the process. It is seen that when the wave is initiated, the current increases rapidly and then reaches a relatively flat level during wave propagation before the voltage is turned off when the wave reaches the opposite side of the sample. The changes in voltage correspond to those of the current, but of course are in the opposite direction.

On the other hand, when the field is turned off during wave propagation (cf. Figure 7 solid line), i.e. both the electropotential Eqs (3) and (4) are used with t_1 = 2 s, the front becomes quenched during its progress as it can be seen from Figure 8 where the time-space conversion profiles are depicted. It is clear from Figure 8 that the velocity of the wave rapidly decreases after the time when the field is turned off, until the front is stopped.

The variation of the calculated ratio d_p/d_{p0} and the corresponding extent of conversion as a function of the spatial distance along the pellet axis at t = 2.2 s is shown in Figure 9. This figure is representative of the sample portion were the combustion wave is frozen. In particular, moving from the region on the right corresponding to the reactants, the particle diameter of the solid component first sharply decreases in a relatively narrow region (about 1 mm thick) and then continues to decrease at a much slower rate, until the product region is approached.

Ideally, by taking advantage of the experimental information obtainable through FACS quenching and relating it to the spatial evolution of the particle diameter of the solid reactant, it is possible to obtain reliable model kinetic parameters following standard fitting procedures. The proposed model appears then to be able to capture the essential features related to the microstructure evolution observed experimentally during FACS. Thus, it may represent a good starting point towards the development of a more accurate description of the phenomena taking place during electric field-activated self-propagating reactions. It should be noted that for this type of reactions the relevant physico-chemical phenomena cannot be uncoupled, as performed when evaluating, for example, kinetic parameters of a classical heterogeneous chemical reaction, and thus the development of a comprehensive model of the type proposed here and in previous studies available in the literature (cf. Feng and Munir, 1996b; Feng et al., 1998), where mass, energy, and electropotential equations are solved simultaneously, is mandatory.

Concluding remarks

In the present work we devote our attention to the mechanistic investigation of electric field-activated self-propagating reactions. These reactions have in general received less attention in the chemical engineering literature (cf. Luss, 1990) despite their dramatic level of application in the field of inorganic and organic chemistry as well as material science and technology (Munir and Anselmi Tamburini, 1989; Varma et al., 1998). After the discussion of previously published experimental results obtained during the FACS of b-SiC, TaC, Ti_3Al and B_4C-TiB_2 from elemental powders, we devote our attention to provide a contribution towards the development of a reliable model of FACS quenching technique which might be used to quantitatively describe the evolution of either the reaction front or the product microstructure. The main idea is to couple the proposed model with a physico-chemical description of appropriate mechanism of structure formation. The final goal will be the possibility to predict the microstructure of final products so that to synthesize materials with tailored properties using the FACS method, whose advantages over conventional techniques are reported in the literature (cf. Feng and Munir, 1995a; Xue and Munir, 1996a; Xue and Munir, 1996b; Xue and Munir, 1997; Gedevanishvili and Munir, 1998; Orrù et al., 1999b).

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Notation

a moles of melting reactant, A per mole of nonmelting reactant, B in the initial mixture

b moles of inert diluent, P per mole of non melting reactant in the initial mixture

C Concentration, *mol/m³*

C_p heat capacity, $J\ mol^{-1} K^{-1}$

d_p average particle diameter of the solid reactant, B, m

D pre-exponential effective diffusivity of the melting reactant, A, $m^2 s^{-1}$

E activation energy, $J\ mol^{-1}$

g(t) function appearing in equation (10), K

h natural convection heat transfer coefficient, $W\ m^{-2} K^{-1}$

L_x sample length, m

L_y sample height, m

k thermal conductivity, $W\ m^{-1} K^{-1}$

M molecular weight, $g\ mol^{-1}$

R universal gas constant, $J\ mol^{-1}\ K^{-1}$

R external circuit resistance, Ω

R_0 external circuit resistance, Ω

s graphite electrode thickness, m

T temperature, K

T_0 initial temperature, K

t time, s

t_1 time at which the field is interrupted, s

V voltage, V

w sample width, m

x longitudinal coordinate, m

Greek letters

b ratio between the thickness of product and the initial particle diameter on the nonmelting reactant

-DH reaction heat, $J\ mol^{-1}$

h extent of conversion of the nonmelting reactant

r density, $g\ m^{-3}$

s electrical conductivity, $\Omega^{-1}\ m^{-1}$

n Stefan-Boltzmann constant, $J\ s^{-1}\ m^{-2}\ K^{-4}$

Superscripts and subscripts

A melting reactant

B nonmelting reactant

in applied value

P reaction product

th theoretical

0 value at t = 0

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