

# Modelling of SiC Chemical Vapour Infiltration Process (CVI) Assisted by Microwave Heating

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**Abstract:** The excessive presence of residual SiC matrix inter-fiber pores is often the main cause for the very poor mechanical strength and toughness of SiC/SiC composites manufactured by CVI process. The use of numerical modeling, for optimizing both the CVI process and the material properties, poses further problems related with the presence of two very different domain scales, i.e. the reactor scale and the pore scale, which is difficult to be solved when conventional finite element codes are used.

This work presents a micro/macro microwave-assisted chemical vapour infiltration (MW-CVI) model as a strategy to attack the problems above. The proposed model couples a reactor-scale (macro) steady state electromagnetic MW-heating/heat conduction model with a pore-scale (micro) transient gas diffusion-flow/densification kinetic model. A sensitivity analysis is first accomplished to identify the most critical parameters playing a role in the MW-CVI process. Second, the densification process of the SiC/SiC composite is investigated in detail. The results show that the MW frequency is, among others, the most critical factor affecting the MW-CVI process. The predicted optimum temperature profile across the SiC preform provides a step forward to the optimum densification of SiC/SiC composites during MW-CVI.

**Keywords:** microwave-assisted chemical vapour infiltration, MW-CVI, SiC/SiC fiber-reinforced composite, MTS gas, SiC deposition, micro/macro finite element model.

## 1. Introduction

An ever increasing number of ceramic fiber-reinforced composites (e.g. C/C, cBN/C, TiC/C, SiC/C, SiC/Si<sub>3</sub>N<sub>4</sub>, SiC/Si, and SiC/SiC) [1-10] is employed in critical transport applications for resisting aggressive and/or high temperature environments. Fiber-reinforced SiC/SiC composites are especially attractive for their low density, high corrosion resistance, wear

resistance and high temperature strength. The chemical vapor infiltration (CVI) process is particularly suitable for manufacturing SiC/SiC composites since it exhibits near-net-shape features and it does not significantly degrade the SiC fibers neither thermally nor chemically or mechanically. In the CVI process a preform of desired shape is initially fabricated consisting of randomly distributed and loosely packed SiC fibers. These fibers typically form an intricate network of interconnected pores of irregular cross sections. These pores are filled by CVI using solid SiC. This is generated in-situ by the thermal decomposition of methyltrichlorosilane (MTS - CH<sub>3</sub>SiCl<sub>3</sub>) gas. The unique advantage of MTS is that it has C and Si atoms in a stoichiometric composition. This permits the solid SiC to be stoichiometrically deposited onto the pore surface. The deposition rate depends on the local preform temperature. A typical disadvantage of MTS is related to the excessively high temperatures required for its thermal decomposition. In addition, the involved reactions are endothermic [1]. To avoid these drawbacks, attempts are made to directly heat the ceramic preform with convenient heating sources. However, special care has to be taken to keep the preform temperature under control. To promote gas diffusion through the porous preform, MTS gas is frequently diluted in hydrogen (carrier gas).

An inherent critical problem often encountered is that the solid SiC preferably deposits at the hotter surface of the preform rather than inward. Consequently, the preform surface tends to be sealed faster than its inner core, thereby preventing further MTS/hydrogen gas infiltration from the surface. As a result, the final composites are excessively heterogeneous, very poor mechanically and very brittle.

The microwave-assisted CVI has been used in the last two decades as an effective means to enhance SiC matrix densification through an external control of the temperature gradient across the preform [1].

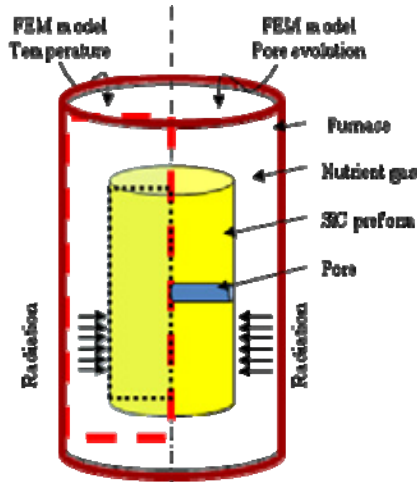
Taking advantage of this expedient, the purpose of this work is to develop a computer model which allows us to identify the most critical MW-CVI process parameters as well as to search for the optimum conditions to produce fully dense SiC/SiC composites by short times.

## 2. The MW-CVI Physical Model

In this sections the micro/macro MW-CVI model along with its implementation within the Comsol Multiphysics environment, is presented.

The proposed MW-CVI mathematical model follows that presented by Gupta and Evans [1] although the employed numerical method, coupling strategy and algorithms differ from those in the original reference. The proposed model couples the reactor-scale model to the pore-scale model by way of the thermal field.

The geometry of the MW-CVI reactor cavity/preform system is sketched in Fig.1. The left hand side depicts the main regions of the macroscopic model (reactor-scale), whereas the right hand side depicts the main regions of the microscopic model (pore-scale).



**Figure 1.** Schematic of the MW-CVI computational domain. Left hand side: 2D axial symmetric domain used to solve the (macroscopic) electromagnetic MW-heating/heat conduction model; right hand side: 1D axial symmetric domain used to solve the (microscopic) gas diffusion through the pore and its radial evolution in time.

The reactor chamber (150 mm radius and 200 mm length) is filled with 1% mol MTS in excess

of hydrogen gas. The SiC preform (50 mm radius and 100 mm height) is fit into the MW cavity. The porous preform is assumed to be heated by a MW source and it is cooled by the flowing gas mixture.

At the microscopic scale the preform pore is described by a unit cell model represented by one single “effective” through radial cylindrical pore (Fig.1, right hand side) [1]. This unit cell model attempts to reproduce the actual complex pore network structure of the preform including the time varying change of tortuosity during MW-CVI.

As the temperature control is crucial in MW-CVI, only macroscale thermal effects are accounted. Thus the gas velocity field effects in the reactor are ignored.

For an effective SiC matrix densification the superficial pores of the preform have to close off last, i.e. after the internal pores are completely filled. Indeed, the lowest porosity that permits percolation of a fluid through the pore space is an important characteristics in CVI, since it determines the microstructure and the mechanical properties of the final composite.

### 2.1 The macroscale coupled MW heating/Heat conduction Equations

Microwaves (MW) are sinusoidally varying electromagnetic waves with frequency in the range of 0.3-300 GHz. They are especially suited for heating dielectric materials. In the MW-CVI process the SiC preform is embedded into a reflective cavity and directly exposed to a MW generating electric field. The preform heating results from the dissipation of alternate currents induced in the preform by the interaction between this electric field with the porous preform. As the preform pores are much smaller than the wavelength of the employed MW we can assume that the preform behaves as a macroscopically continuum medium with respect to electromagnetic and heat conduction phenomena. This requires the definition of suitable effective physical properties.

The coupled steady state MW electromagnetic heating and steady state heat conduction equations defined over the macroscopic reactor cavity/preform domain are expressed as:

$$\nabla \times (\mu_r^{-1} \cdot \nabla \times \vec{E}) - (\epsilon_r - j\sigma/\omega\epsilon_0)k_0^2 \vec{E} = 0 \quad [1]$$

$$Q_{MW} = \frac{1}{2} \text{Re}[\sigma \cdot E_z^2 - j \cdot \text{Re}(\omega) \cdot E_z \cdot (\bar{\epsilon} \cdot \bar{E}_z)] \quad [2]$$

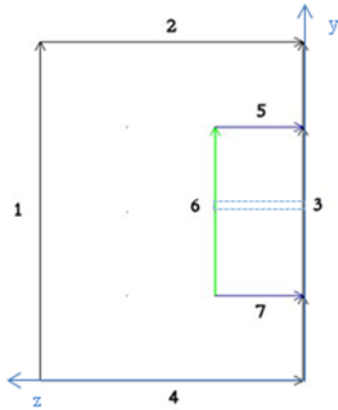
$$\nabla \cdot (-k \nabla T) = Q_{MW} \quad [3]$$

where  $E$ ,  $\mu$ ,  $\epsilon$ ,  $\omega$ ,  $Q$ ,  $k$ , and  $T$ , are electrical field, magnetic permeability, electrical permittivity, wave frequency, dissipated heat source, thermal conductivity and temperature respectively.

According to Fig.2, the preform region is bounded by 5, 6, 7 boundaries. The MW source is placed at 1 surface.

Equations 1-3 are solved for the unknown electric and the temperature fields in the  $(y, z)$  reactor domain.

The boundary/interface conditions for the “In plane TE Wave” model (Fig. 2) are specified as follows: perfectly electric conductive at 2 and 4 boundaries; symmetric and perfectly magnetic conductive at 3 boundary, port condition at 1 boundary and continuity condition otherwise.



**Figure 2.** Boundary conditions in the reactor/preform system. The arrow lines in the preform represent the effective unit cell pore domain.

The boundary/interface conditions supporting the heat conduction equation (Eq.3) are defined as follows (Fig. 2): adiabatic/symmetry at 2, 3 and 4 boundaries; continuity at 5 and 7 and convection at 1 and 6 boundaries. The convection and radiation effects induced by the exchange among the gas, the outer preform surface and the reactor walls are taken into account with a suitable effective convection heat transfer coefficient ( $h$ ). In the following calculations it is assumed as a sensitivity parameter to be investigated and conveniently

optimized. Its initial value is set according to experiments [1].

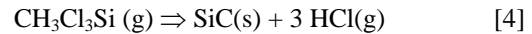
## 2.2 The microscopic diffusion/deposition model

Real preforms typically have very complicated pore structures, with very complex statistical distribution of pore shape, size and interconnections. Furthermore, these structures tend to modify dramatically during the MW-CVI process. However, the complex pore distribution of real preforms can not be analyzed with simple means neither theoretically nor experimentally.

To make the problem tractable mathematically a 1D continuum cylindrical preform pore is assumed. Essentially, it consists of one single “effective” pore capable of capturing the essential transport/deposition phenomena at the pore scale. In Fig.1 (right hand side) the pore is shown as a through radial hole across the preform. The transient SiC diffusion/deposition over the pore scale can be conveniently treated as a 1D process. In addition, it is assumed that: a) the stress relaxation time of the SiC preform is smaller than deposition time; b) the deposition reaction follows an Arrhenius-like kinetics; c) the reactant is not influenced by the heating process of the preform. The assumptions above are met in the industrial practice [1].

The infiltration process through the pore is governed by two concurrent mechanisms, i.e. gas diffusion and homogeneous/deposition reaction [1], being Knudsen diffusion negligible.

Although the actual nature of homogeneous and heterogeneous CVI reactions is rather complex, a simplified overall decomposition reaction scheme is assumed for the MTS gas:



which is associated to a first order (Arrhenius) rate equation:

$$K = K_0 \exp(-E_a / R^* T) p_{MTS} \quad [5]$$

where  $K_0$ ,  $R^*$ ,  $E_a$  and  $p_{MTS}$  are pre-exponential factor, the universal gas constant activation energy for the thermal decomposition of the MTS gas and the pressure of MTS. The rate of pore radius closure is expressed by:

$$\frac{\partial R}{\partial t} = - \frac{M \cdot K \cdot b \cdot C}{\rho} \quad [6a]$$

$$\nabla \cdot (R^2 D \cdot \nabla C) - 2K R = 0 \quad [6b]$$

where R, M, D, b, and C denote the local pore radius, the molecular weight of the deposited species, the stoichiometric coefficient (moles of deposited solid per mole of reacted gaseous species) and the MTS gas concentration respectively. As can be seen, Eqs. 6a and 6b are non-linearly coupled through gas concentration (C), pore radius (R) and kinetic rate constant (K). Hence, Eqs. 6a and 6b have to be integrated simultaneously with time in Eq. 6b working as a parameter. The initial condition for Eq. 6 is such that  $R = 1 \mu\text{m}$  over the whole pore length. Equation 6b's boundary conditions require a specified concentration at one end of the cylindrical pore ( $C_0 = 0.5 \text{ mol/m}^3$ ) and symmetry condition at the opposite end ( $\partial C / \partial r = 0$ ).

The infiltration process is assumed to be completed when the pore radius at the preform surface approaches zero.

### 2.3 Model Implementation in Comsol Multiphysics

The micro/macro finite element MW-CVI model is fully implemented within Comsol Multiphysics package. It is integrated in time and space using a triangular mesh. As the heat conduction equation (Eq. 3) is non linearly coupled to the electromagnetic MW model (Eq. 1) through the MW heat source (Eq. 2), these two models are solved simultaneously once for all. The former model utilizes the "General heat transfer" module (eq. 3) [11] whereas the latter utilizes the "RF module: in plane TE wave" (eqs. 1-2) [12].

The main purpose of the macroscopic model is to predict the 2D temperature field which is then used to extract the temperature profile along the preform along the z cross section (at the middle). This is relevant for the microscopic model to predict the transient pore evolution. For speeding up calculations a "weak" coupling, that is to say, one-way coupling, from the macro-model to the micro-model, is defined.

The extracted temperature profile data is interpolated by a 4<sup>th</sup> order polynomial to facilitate micro-model computations.

Equation 6a is modeled using the "PDE, general form" of Comsol Multiphysics [11] and solved using the "time dependent" solver, with the "BDF" time stepping method. Equation 6b is

integrated using the steady state "Diffusion equation" of Comsol Multiphysics [11]. These two coupled equations simulate the transient pore sealing process according to the given temperature profile across the preform.

An implied assumption in the micro/macro MW-CVI model is that pore-scale thermal effects do not affect the macroscopic thermal phenomena remarkably during CVI. This is true if the thermal effects induced by heterogeneous reactions are negligible and porosity dependent properties in the preform property changes do not noticeably affect MW heating or heat exchange among the preform surface, gas and cavity walls. The former assumption requires that the MTS dissociation enthalpy is negligible and does not significantly increase the gas temperature nearby the pore surface.

These working assumptions avoid the time consuming solution of strongly coupled micro/macro models.

The Eqs. 1 through 6 allow to predict the desired change of pore radius vs time along the preform length (z).

If the pore volume vs time is normalized a straightforward comparison against different temperature profiles is possible.

The materials properties (electrical permittivity, electrical conductivity, etc.) for SiC preform and other relevant physical data are given in Tables 1-3 (see Appendix). Gas properties, thermal and electromagnetic data are taken as default from the Comsol library.

The effective convection heat transfer coefficient (h) is set initially as high as  $500 \text{ W/m}^2 \text{ K}$ . The room temperature inside the cavity is set to  $700 \text{ K}$ .

The default "direct UMFPACK" linear system solver is selected. The default values for relative tolerance ( $10^{-6}$ ) and maximum number of iterations (25) are specified.

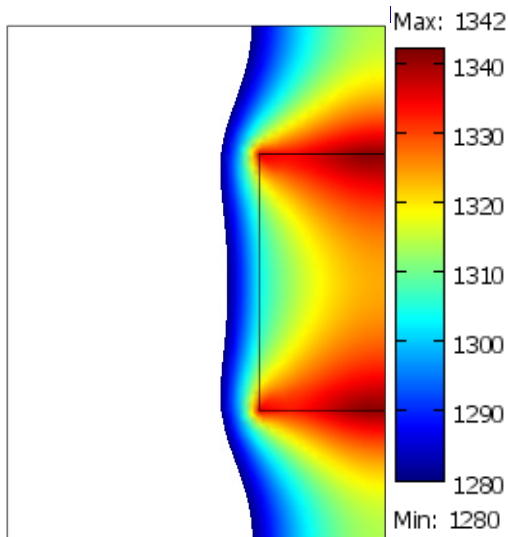
## 3. Results and discussion

### 3.1 MW heating/Heat conduction model

Experimental simulations are first performed aimed at identifying the optimum microwave frequency. Among the various MW-CVI parameters the MW frequency radiation is resulted to be the most sensitive. Accordingly to the primary objective of the work the optimum

frequency is found to be as high as 3.5 GHz whereas the MW radiation power is found to be a convenient working parameter to find the optimum temperature gradient along the pore preform. This optimum frequency is then employed in the foregoing calculations to explore the MW-CVI process behaviour for two different radiation powers.

Figure 3 shows the optimum temperature field around and across the SiC preform corresponding to the optimum frequency of 3.5 GHz and 80 kW power. The color map is properly selected to remark the temperature field in the preform and nearby it. The cooler part of the isotherms refers to the cold gas in the cavity.



**Figure 3.** Temperature field within the reactor cavity for 80 kW microwave power (the min value of the temperature range is set to 1280 °C to display the temperature field in the preform).

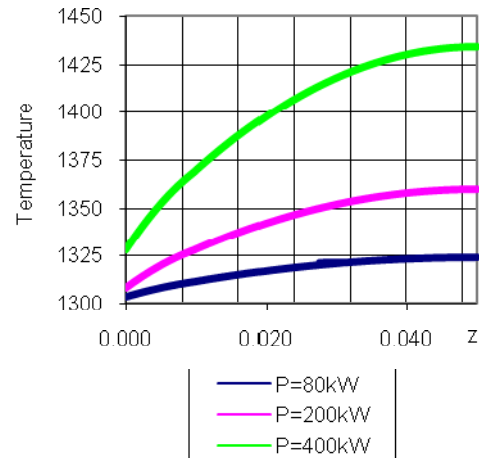
The strong thermal gradient along the z direction of the preform is clearly evidenced.

Figure 4 depicts the extracted temperature profile vs z from the 2D thermal field of Fig. 3. This is taken at the mid transversal cross section along the pore length (see Fig.2). The temperature gradient along the preform increases with increasing imposed microwave power. The temperature profile moves upward with increasing MW radiation power. Reasonably, the pore temperature is much higher at its right end than at its left end in contact with the cold gas. The latter contribute to enhance the temperature

gradient along the pore length by cooling down the preform outer surface.

### 3.2 Diffusion model

Figures 5 and 6 show the pore radius evolution vs z (along pore length) at different times for two imposed microwave powers, i.e. 400 kW and 200kW respectively.



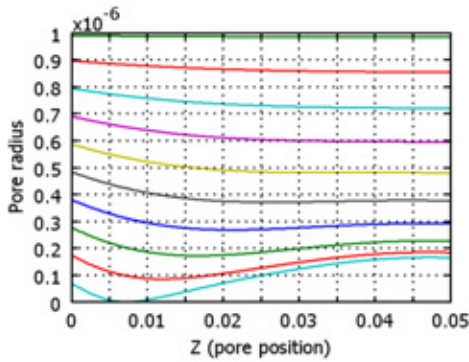
**Figure 4.** Temperature profiles at the mid section of the preform for different microwave powers.

At early deposition times, solid SiC preferably deposits inward the preform. Thus, the upper curves correspond to early deposition reaction. Only toward the very end of the infiltration process, the pore surface end appears to seal (Fig.5) before the inner regions are completely filled. The situation is worse for the 200 kW power in which the surface pore sealing occurs earlier than for 400 kW, leaving the inner pore remarkably unfilled.

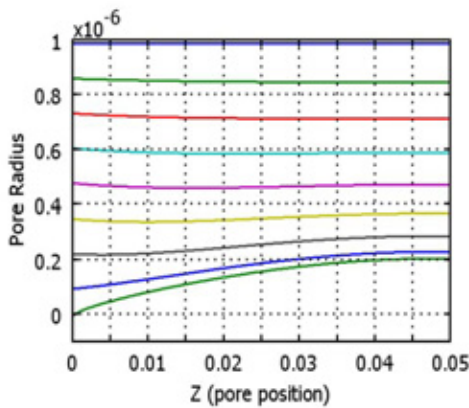
Figure 7 displays the normalized MTS gas concentration vs z for the 400 kW power. Notice that gas concentration is always higher at the preform surface and tend to decrease inward. For sake of comparison, Fig.8 shows a normalized graph of the pore volume vs time for different MW radiation powers. It is confirmed that a higher power radiation promotes higher preform density with lower processing time. A quantitative comparison of it is given in Table 1. According to the developed model, it is however difficult to attain a completely dense SiC/SiC composite. Nevertheless, the definition of the temperature profile across the preform is very

important to ensure optimum SiC matrix mechanical properties.

A refined MW-CVI model should include the gas flow inside the reactor. Although this will make the solution much more expensive than the present one it will provide a more accurate prediction of the temperature profile across the preform since its cooling will be governed by the flow field inside the reactor rather than by an empirical constant convection coefficient.



**Figure 5.** Pore radius evolution vs z (pore position) for different times at 400 kW. Surface deposition reaction starts at higher curves and completes toward lower curves.

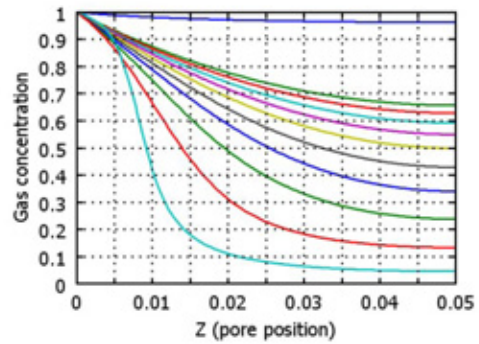


**Figure 6.** MTS gas concentration vs z (pore position) for an imposed power of 200 kW at different times.

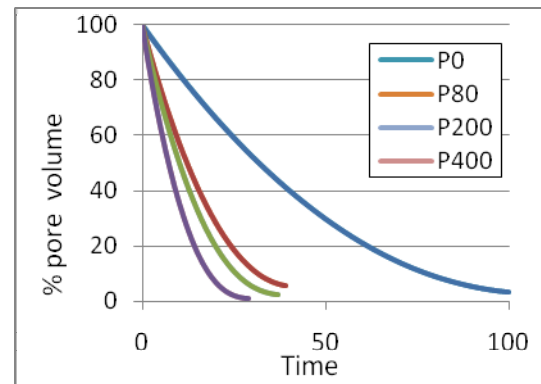
## 5. Conclusions

A micro/macro MW-CVI model based on Comsol Multiphysics package is developed. It includes the most essential phenomena and process parameters affecting the

densification process of SiC matrix at both the microscopic and the macroscopic scale.



**Figure 7.** MTS gas concentration vs z (pore position) for an imposed power of 400 kW at different times. Surface deposition reaction starts at higher line curves and completes toward lower line curves



**Figure 8.** Pore volume p.c. vs normalized time; P0: 0kW; P80: 80 kW; P200: 200 kW; P400: 400 kW.

A simulation based sensitivity analysis elucidates that, among the other process parameters, the MW frequency is the most critical factor in MW-CVI. Its optimum value is estimated as 3.5 GHz. By entering this optimum value in the built model the optimal temperature profile across the preform (i.e. along the unit cell “effective” pore) is computed as a function of power radiation. The predicted optimum temperature allows to determine the optimum densification of the SiC matrix with the minimum processing time. The 400 kW power condition retards pore closure at the preform surface and, corresponding enhanced inward deposition compared to 200 kW power condition for which pore surface sealing is anticipated and



bulk preform density is much lower. According to the developed model, however, it is difficult to attain a completely dense (100%) SiC/SiC composite. Higher temperature gradients across the preform are possible with higher MW powers or with enhanced gas cooling at the opposite end of the pore. However, it is more likely that higher SiC/SiC densification is achievable by combining microwave heating with a pressure gradient.

## 6. References

1. D. Gupta and J.W. Evans, A mathematical model for chemical vapor infiltration with microwave heating and external cooling, *J. Mater. Res.* **6(4)** 810-818 (1991).
3. M. Jacob, *Heat transfer*, I-180-193, Chapman & Hall, London (1959).
3. MPDB v6.51, Jahm Software Inc.
4. C.W.Manke, and L.F.Donaghey, Analysis of transport processes in vertical cylinder epitaxy reactors, *J. Electrochem. Soc.*, **124(4)** 561-569 (1977).
5. S.V. Patankar, Computational modeling of flow and heat transfer in industrial applications, *Int. J. Heat and Fluid Flow*, **23**, 222–231 (2002).
6. W. Zhang, and K.J. Hüttinger, Simulation studies on chemical vapor infiltration of carbon, *Composites Sci. and Tech.*, **62**, 1947–1955 (2002).
7. A. Li, and O. Deutschmann, Transient modeling of chemical vapor infiltration of methane using multi-step reaction and deposition models, *Chem. Engng Sci.*, **62**, 4976–4982 (2007).
8. V.I. Kulika, A.V. Kulikb, M.S. Rammc, and Y.N. Makarovd, Modeling of SiC-matrix composite formation by isothermal chemical vapor infiltration, *J. Crystal Growth*, **266**, 333–339 (2004).
9. T. Tago, M. Kawase, Y. Ikuta, K. Hashimoto, Numerical simulation of the thermal-gradient chemical vapor infiltration process for production of fiber-reinforced ceramic composite, *Chem. Engng Sci.*, **56**, 2161-2170 (2001).
10. R.Naslain, F. Langlais, *Material Science Research*, **20** 145 (1986)
11. COMSOL Multiphysics, Model Library (2008)
12. COMSOL Multiphysics, RF Module Model Library, (2008)

14. M.D. Allendorf and C. Bernard, *EUROCVI-11*, Electrochemical Society, publisher (1997).

## 7. Appendix

### 7.1 Physical data

Thermal conductivity	$K=90 \text{ W/m}\cdot\text{K}$	[3]
Density	$\rho=2960 \text{ kg/m}^3$	[3]
Heat capacity at constant pressure	$c_p=810 \text{ J/kg}\cdot\text{K}$	[3]
Electrical permittivity (complex form)	$\epsilon=60-35i$	[1]
Electric conductivity	$\sigma=10^{-12} \text{ S/m}$	[3]
Molecular weight	$M=60 \text{ uma}$	[1]

**Table 1.** Materials properties of SiC.

Heat transfer coefficient	$450 \text{ W/m}^2\cdot\text{K}$
MW Electric field	$10 \text{ V/m}$
MW Power	$80 \text{ Kw}$
Cavity pressure	$1 \text{ atm}$

**Table 2.** Physical data for the heat conduction and electromagnetic MW-heating model.

Reaction activation energy	$E_a=120 \text{ kJ/mol}$	[1]
Arrhenius pre-exponential coefficient	$K_0=2.62 \text{ m/s atm}$	[14]
Moles of deposited solid per mole of reacted gaseous species	$b=1 \text{ mol/mol}$	[1]
Diffusion coefficient of MTS in $\text{H}_2$ at 1000 K	$D_0=0.05 \text{ m}^2/\text{s}$	[1]

**Table 3.** Physical constants used in the microscopic deposition model: MTS- $\text{H}_2$  gas mixture and interaction between solid SiC and SiC preform.