MULTISCALE MODELING OF INORGANIC FIBER REINFORCED CERAMICS

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Abstract

Analyses of Inorganic Fiber Reinforced Ceramics (IFRC) using multiscale modeling approach are objectives of presented paper. Ceramic specimens were prepared due to pyrolysis of fiber reinforced polymer precursor (polysiloxane resin). Next the relation between ceramic structure and properties has been studied for the purpose of exploring the changes in matrix structure due to transformation of polysiloxane precursor into silicon oxycarbide (SiOC) matrix, and its influence on final composite material. For the analysis the electrical properties of the material are used. Numerical models for prediction of specimen conductivity based on multi-scale modeling approach are used to analyse the conductivity of ceramic matrix. Measured conductivity values were compared to the numerical ones, the calibration of SiOC input parameters followed.

1 Introduction

Reinforced silicone oxycarbides (SiOC) are newly developed ceramics based on polysiloxane resin supposedly applicable as structural material possessing high heat resistance in oxygen atmosphere [1]. Their structure and properties depend on both, the type of reinforcement and matrix precursor, and time-temperature regime of polysiloxane precursor pyrolysis. The reinforcement is either particular (metals or alloys particles) or fibrous (inorganic fibers).
As for fibrous reinforcement ceramic fibers are the ones commercially applied nowadays [7]. Those are materials efficient for high-tech applications (aeronautics or astronautics) but too expensive for common use. In that case the utilization of lower cost inorganic fibers appears as most suitable approach to minimize the composite costs. The tests of glass fiber reinforcement were realized but those had proved there is impossible to reach the temperature of pyrolysis necessary for complete transformation of polysiloxane precursors (over 1000°C) into SiOC as the glass starts to melt in temperatures about 800°C [8].
Regarding this knowledge the basalt fibers were tested as potential reinforcement. Due to technical reasons the pyrolysis was realized in oxygen atmosphere. The internal structure and basic thermo mechanical properties of the composites were described in [6]. Prediction techniques for estimation of such specimen properties (mainly the transport ones) are objective of the paper. For the purpose numerical simulation of its electrical conductivity was realized with the use of multiscale-modeling approach [2]. Next estimation of matrix conductivity was performed for both, polymer precursor and final ceramic matrix. The

calibration of matrix input parameters followed using experimentally measured values of conductivity, and opportunities of material properties estimation based on chemical models of matrix structure were tested.

2 Experimental procedures

2.1 Composite specimen preparation

Inorganic fiber roving was treated by acetone to clear off the surface sizing which may undesirably affect the adhesion between the fiber reinforcement and polymer matrix. Pure fibers were impregnated by silicone resin Lukosil M130 (polymethylsilicone resin dissolved in xylene). Next the specimens were cured at the temperature of 100°C for 24 hours to prepare polymer precursors (inorganic fiber reinforced composites with cured polysiloxane resin). The fiber-polysiloxane precursors were finally pyrolysed in air at heating rate 50°C per hour. Final temperature (heat treatment temperature) was set on 1000°C, see Table 1. Within the pyrolysis cured polysiloxane resin should be transformed into heat resistant porous silicon oxycarbide glass [1].

Heating rate	**Heat treatment temperature**	**Dwell time**
50 °C per hour	1000°C	60 minute
Cooling rate		
100°C per hour	25°C	60 minute

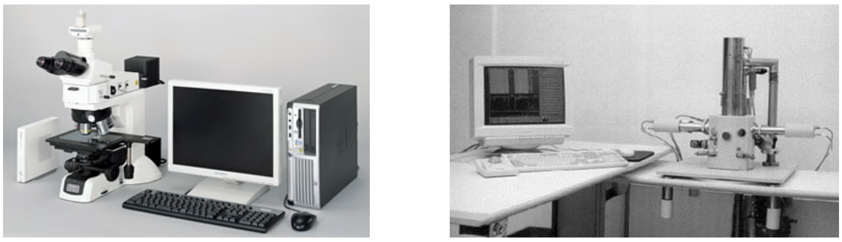
Table 1. Time-temperature regime of inorganic-polysiloxane pyrolysis

2.2 Simulation of composite specimen electrical conductivity

Numerical simulation of material properties requires the geometry description of the area or volume representing the internal structure. The geometry should be simplified to make the computation possible. To prepare geometry model suitable for numerical simulation yet to respect the real structure of composite specimen the multiscale geometry modeling approach appears as optimum for complex structures [2]. The basic structural information is acquired by the use of computer aided image analysis.

- *Structural analysis of composite specimen*

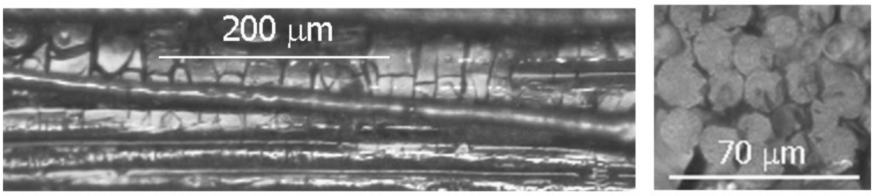
Micrographs of composite specimen were acquired by the image analysis system LUCIA (Laboratory Universal Computing Image Analysis). Complete imaging workstation is composed of microscopes, cameras, stands, illuminators, PCs and other accessories. The mezo-structure of composite was scanned by optical microscope Nikon ME600 Eclipse, the analysis of microstructure was realized with the use of scanning electrone microscope VEGA-TESCAN, see Figure 1.



(a) **(b)**

Figure 1. Image analysis workstations: (a) optical microscope Nikon ME600 Eclipse (b) scanning electrone microscope VEGE-TESCAN

The micrographs allowed us to study the morphology of cured and pyrolysed composite specimen, to analyse the influence of curing and pyrolysis on the structure of fiber reinforcement and matrix, to evaluate the development of pores and crack in final composite structure, see Figure 2 and Figure 3. Thorough structural analysis is the base for design of multiscale geometry model representing the studied composite specimen.



(a) **(b)**

Figure 2. Inorganic fiber reinforced silicon oxycarbide (optical microscope): (a) surface view, (b) cross-section view

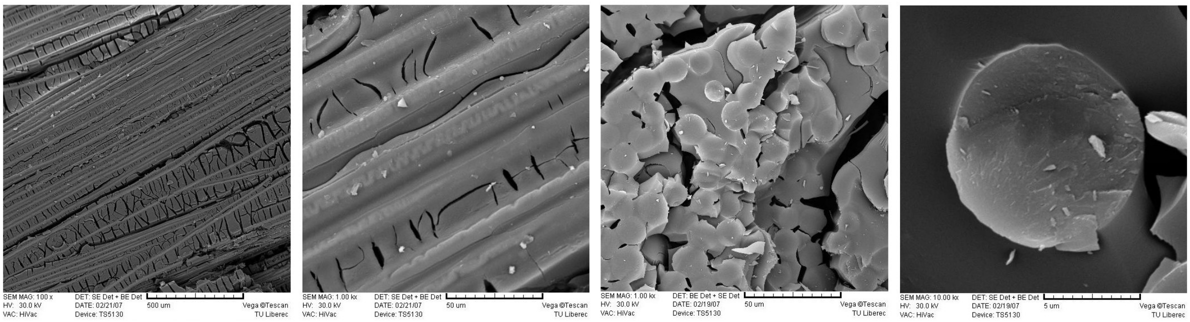


Figure 3. Surface and fracture area of basalt fiber reinforced silicon oxycarbide (scanning electron microscope)

- *Multiscale geometry model*

For numerical simulation the multi-scale geometry model of specimen was prepared with respect to structural information obtained from composite micrographs, see Figure 4. Thus were determined three levels representing the geometry of specimen in particular levels. The material parameters acquired from numerical simulation in one level are utilized as homogenized input parameters in higher levels. The parameters acquired from highest level of the model represent parameters of final composite plate.

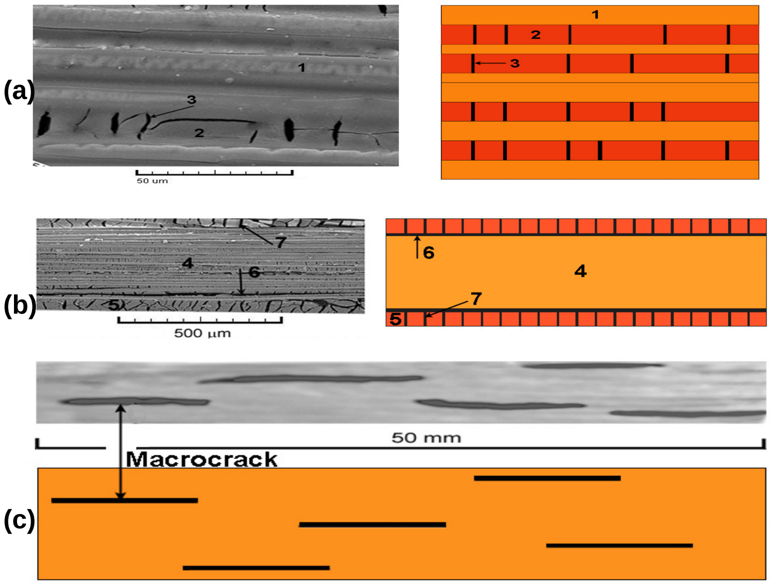


Figure 4. Multiscale geometry model of studied composite specimen:
(a) microscale level, 1 - inorganic fiber, 2 - SiOC matrix, 3 - microcracks
(b) mesoscale level, 4 - part composed of microscale particles, 5 - SiOC matrix, 6 - delamination cracks, 7 - transversal cracks, (c) composite plate with macrocracks (macroscale level)

Parameters of basic structural components are uniquely determined, see Table 2. Conductivity of inorganic fibers has been measured, obtained data are in good agreement with the ones mentioned in literature. Conductivities of SiOC and air were estimated with respect to information presented in [4,5,6].

Composite parts	*Basalt fibres*	*SiOC matrix*	*Voids filled with air*
Electrical conductivity [S.m^{-1}]	$1{,}02 \cdot 10^{-13}$	10^{-1}	10^{-10}

Table 2. Electrical conductivities of basic composite components, that are initial data for numerical simulation of composite conductivity [5,6].

- *Numerical simulation*

Numerical simulation of electrical conductivity was realized using Comsol Multiphysics software, the Electromagnetics Module that provides a unique environment for the simulation of electromagnetic wave and field propagation in conductive media. The problem of electromagnetic analysis is that of solving Maxwell's equations subject to certain boundary conditions. Maxwell's equations are a set of equations, written in differential or integral form, stating the relationships between the fundamental electromagnetic quantities. These quantities are [6]:

- *electric field intensity,* ***E****, electric displacement or electric flux density,* ***D****, magnetic field intensity,* ***H****, magnetic flux density,* ***B****, current density,* ***J****, electric charge density,* ***ρ***

You can formulate the equations in differential or integral form. The software uses differential form because it leads to differential equations that the finite element method can handle. COMSOL Multiphysics provides many tools for post-processing and visualizing model quantities. You can also compute numerical integrals of model quantities as well as display and save post-processed data. The software can post-process expressions that combine user-defined variables, application mode variables, and standard variables.

2.3 Experimental measurement of composite resistance

The HP 4339B High Resistance Meter, which is designed for measuring very high resistances and related parameters of insulation materials, has been utilized to determine the resistively of studied composite specimen, see Figure 5. Measurement features were set as follows:

Test voltage - *100 V*
Air moisture - *36 %*
Mean current - *0,8 am*

The surface resistivity [Ω.m] is calculated automatically and the result is displayed [3].

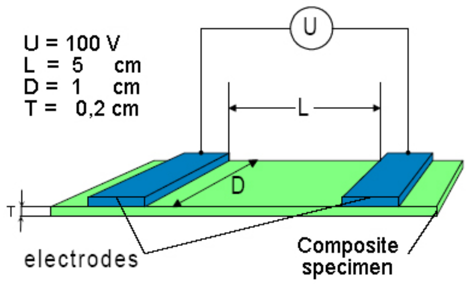


Figure 5. Scheme of specimen resistivity measurement

3 Results

The computed electrical properties of composite specimen are final results obtained within the numerical simulation. The influence of studied composite structure on charge transport in electric field is shown in Figure 6. The numerical results were verified with the aid of experimental measurement, the input parameters of SiOC ceramic matrix were calibrated with respect to the experimental results. Acquired electrical properties are displayed in following Table 3.

Electrical properties	Computed	Measured
Electrical conductivity [$S.m^{-1}$]	$1,8 . 10^{-11}$	$4,3 . 10^{-11}$
Surface resistivity [Ω.m]	$5,6 . 10^{10}$	$2,3 . 10^{10}$

Table 3. Resultant electrical properties of basalt fiber reinforced ceramics in directions parallel to composite plate. The values are valid for temperature 25°C.

The model calibration using experimental data serves for precision of input parameters representing the properties of individual composite compounds. This is mostly important in estimation of matrix properties, which is formed within the composite preparation, and it is hardly possible to measure its properties separately. The resultant values of pure matrix properties also indicate possible order of matrix structure. With respect to acquired results we may assume the resultant matrix is semiconductor with high fraction of free carbon with sp2-hybridization [5]. This is basis for estimation of presumable order of SiOC structure, as mentioned in [4] by examining electrical conductivity of pure SiOC, which correlates to volume fractions of SiO2- and C- groups in the matrix structure. The knowledge led us to analyse the structural transformation of polysiloxane precursor into SiOC matrix within the process of pyrolysis using molecular modeling methods. The results of pilot test are shown below. The validation of these assumptions, and its utilization into pyrolysis process description are subject for further research.

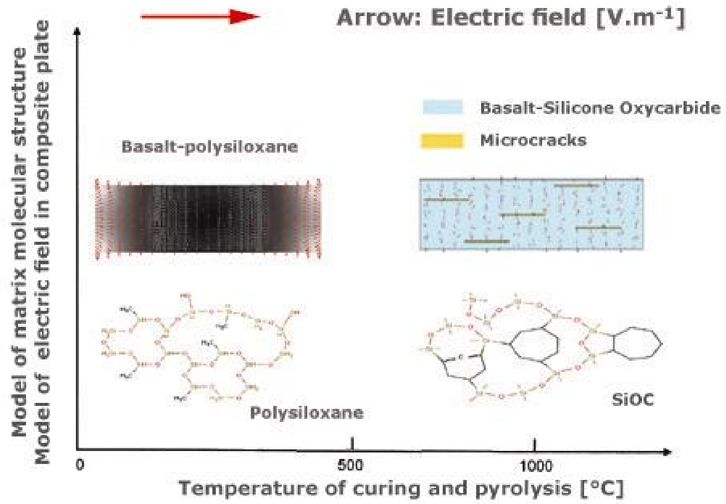


Figure 6. Model of studied composite structure influence on charge transport in composite plate and model of presumable order of matrix molecular structure, inspired by Cordelair in [5]

Electrical conductivity [$S.m^{-1}$]	Initial data from literature [5,6]	Data acquired from numerical model	Data acquired from pilot molecular models
Polysiloxane matrix	10^{-12}	$4,2*10^{-12}$	$6,8*10^{-12}$
SiOC matrix	10^{-1}	$3,6*10^{-1}$	$0,8*10^{-1}$

Table 4. Electrical conductivities of basic composite components, that are initial data for numerical simulation of composite conductivity [5,6].

4 Conclusions

Development of new composite material in general, it is project combining the material design based on prediction of final material properties, design of technology, and practical preparation of composite specimen to verify the theoretical expectations. Thorough study of real specimen structure and properties is essential part of the research. As not all properties may be reliably measured, and not each of material response on certain type of load may be studied experimentally, the tests of new material properties are the combination of experimental measurement and numerical simulations. Numerical simulation requires the geometry description of area or volume representing studied specimen, and estimation of particular input parameters.

There is no universal geometry model for complex composite specimen. The models are prepared individually with respect to real structure of studied specimen, and properties of basic composite compounds. It is necessary to verify the reliability of suggested models using the comparison of particular numerical results with available experimental data. Such models may be used for prediction of other material properties.

In present paper the geometry model, representing the structure of newly developed inorganic fiber reinforced SiOC composite, was generated, and applied for prediction of electrical

conductivity of studied specimen. The comparison of numerical results to the experimental ones enables us to specify conductivity of pure SiOC matrix, and estimate probable order of SiOC structure. Obtained results are comparable to data mostly mentioned in the literature [4,5,6], and give us new information how to evaluate the structure and properties of ceramic matrix itself (e.g. using molecular modeling methods), and within the scope of whole inorganic fiber reinforced SiOC composite.
Good agreement between the computed values of electrical conductivity and the experimental ones indicates the geometry model of composite structure may be used for prediction of other material properties of studied composite, and for technology optimization. These are objectives for future research.

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