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Short communication

Prediction of the effective coefficient of thermal expansion of heterogeneous media using two-point correlation functions

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ABSTRACT

Statistical continuum mechanics is used to predict the coefficient of thermal expansion (CTE) for solid oxide fuel cell glass-ceramic seal materials with different morphology and crystallinity. Two-point correlation functions are utilized to represent the heterogeneous microstructure morphology and phase distribution. The model uses two-point correlation functions in conjunction with local properties to predict the effective CTE. Prediction results are comparable to experimental CTE results. The advantage of using the statistical continuum mechanics model in predicting the effective properties of anisotropic media is shown, using the ability to take the microstructure into consideration.

1. Introduction

Statistical continuum mechanics approaches were developed to predict properties of heterogeneous media. Adams et al. [1,2] developed a framework, called "microstructure sensitive design" (MSD), to guide information flow from materials scientists to mechanical designers. This method has been used to design and optimize materials microstructure and performance [3–6]. Using explicit mathematical relationships between the microstructure and properties, we can identify the proper processing methods to develop a material with certain desired properties. In our previous studies, the mechanical behavior of heterogeneous materials has been studied, such as elastic [7–10] and inelastic behavior [3,5,11–13].

This methodology also finds application on fuel cell industry. For planar solid oxide fuel cells (SOFCs), a hermetic seal is needed between the fuel and air sides of the cell. Seals are commonly made of glass-ceramics. An important property of these seals is the coefficient of thermal expansion (CTE), required to be close to neighboring components in the fuel cell to reduce thermal induced stress. Operated at high temperatures (800–1000 °C) in thermal cycles, a SOFC requires superior thermal performance. The seal is bonded to several other cell components, making a failure in the seal difficult to repair. Therefore, it is necessary to develop capability to predict thermal induced stress in fuel cell due to difference from thermal expansion coefficient. The glass-ceramic used in this study is G18, developed by the Pacific Northwest National Laboratory, Richland, WA [14–16]. G18 is a multi-phase material with crystalline needles formed in a glassy matrix. Crystallinity increases during aging from an initial value of 55% to approximately 72%. One advantage of using glass-ceramics as sealant is the capability to adjust CTE and corresponding thermal performance by tailoring the crystallinity.

The motivation for this work is to present a methodology to link the microstructure and all its details to properties (in this case CTE). The only other comparable technique is the use of finite element method (FEM), which is very detailed and sometimes expensive (both in terms of time and effort). In this methodology, the microstructure is reduced to a set of probability functions and then linked to properties using a statistical homogenization technique. The reduction of the microstructure to the probability functions is very similar to the mesh generation in FEM except that here, we have a mathematical relation instead of the actual microstructure.

Previous research in predicting the properties of G18 has mainly focused on the elastic modulus and creep behavior [11–13]. Although the macroscopic CTEs of G18 aged for 4 h and 1000 h are known, the mathematical relationship between the microstructure and CTE has not yet been studied to take into consideration morphology [11]. We have previously predicted the effective thermal mechanical properties using homogenization averaging schemes, based on volume fraction and local properties. These models included the Rosen–Hashin [14,15], Turner [16], Kerner [17], and

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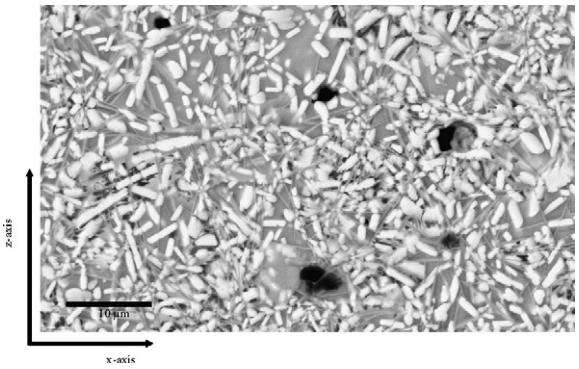

Fig. 1. SEM micrograph of G18, aged for 4 h at 750 °C after initial sintering at 850 °C.

Levin [18] models. The results agree with experimental data in isotropic media without taking into consideration anisotropy. Also, in the previous study, samples of different aging times were not studied, but rather, only one overall CTE value was used to compare. The evolution of property and microstructure was not considered.

Two-point correlation functions have been used to describe the microstructure and predict properties in the past by Li et al. [6]. The use of two-point correlation functions allows the prediction to use the exact microstructure morphology, while other homogenization models are based solely on volume fraction. Predictions of the conductivity demonstrated the dependency on microstructure morphology. This formulation has been extended to predict the CTE of heterogeneous media. In this study, coefficients of thermal expansion of G18, aged for 4 h and 1000 h are predicted by a Green's function solution to the homogenization relations using two-point correlation functions.

2. Two-point correlation functions

Two-point correlation functions are used in a statistical homogenization framework to characterize different types of heterogeneous media. Correlation functions can describe the microstructure morphology, including volume fraction, clustering, and spatial relationship of the components [5,8,9,19]. Vectors with varying orientation and magnitude are sampled onto the micrograph randomly. In this system, there are three phases: barium silicate as phase 1, the matrix as phase 2, and the pores as phase 3. Hexacelsian is included in the amorphous phase due to the similarities in CTEs [20].

SEM micrographs of G18 are shown in Figs. 1 and 2. Several phases can be seen in these micrographs. The brightest phase is barium silicate; the dark gray needles are hexacelsian; the lighter gray phase is the glass matrix, and the black phases are pores.

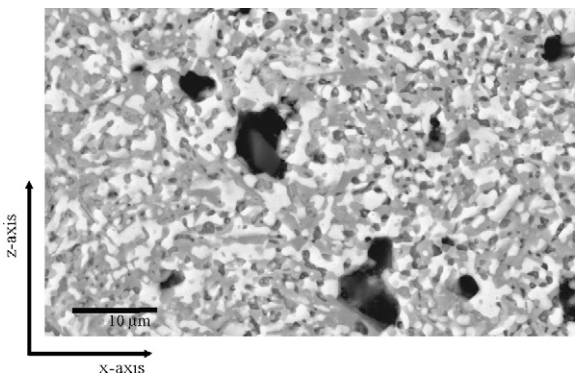

Fig. 2. SEM micrograph of G18, aged for 1000 h at 750 °C after initial sintering at 850 °C.

The minor phases, such as monoclinic celsian and other solid solutions are not observed in these micrographs and therefore ignored. Two-point correlation function is a probability function, p_{ij}, where i is the phase of the initial point and j is the phase at the vector end point. In this three phase microstructure, these operations result in nine probability variables, satisfying the normality conditions shown below, where v_i is the volume fraction of phase i:

$$p_{11} + p_{21} = v_1, \quad p_{21} + p_{22} = v_2 \tag{1}$$

$$p_{ij} = p_{ji} \tag{2}$$

$$\begin{aligned} &r \to o, \quad P_{ii}(r) \to v_i \\ &r \to \infty, \quad P_{ii}(r) \to {v_i}^2 \end{aligned} \tag{3}$$

As a result, three diagonal correlation functions will be enough to represent an anisotropic microstructure statistically. The orientation of the vector becomes important in anisotropic cases, as the two-point correlation function changes with respect to the orientation angle.

3. Statistical continuum mechanism on thermal expansion tensor

By assuming that there are three phases in the microstructure, the pore, amorphous glass and crystalline barium silicate, we will use the CTEs of these three phases to predict the overall CTE.

In our previous works, we have developed framework to predict mechanical properties and electrical properties of composites and polycrystalline materials [4,5,7,9,10]. Here, the framework is extended to predict the CTE. We assume that the heterogeneous media is composed of n constituents with different CTE tensors, α_i ($i = 1 \ldots n$) and volume fractions v_i, with i being the phase. The size of inhomogeneity is assumed to be significantly larger than the electron free path.

Effective CTE tensor α_{eff} in the heterogeneous media is then defined by the equation:

$$\left\langle \varepsilon_t(x) \right\rangle = \alpha_{eff} \left\langle \nabla T(x) \right\rangle \tag{4}$$

The brackets $\langle \cdots \rangle$ denote the ensemble average. The detailed procedure to solve α_{eff} is explained in the following. To define the relationship between the localized CTE, $\alpha(x)$, and the ensemble average of the CTE, α_0, we introduce the polarized CTE, $\tilde{\alpha}(x)$, such that:

$$\alpha(x) = \alpha_0 + \tilde{\alpha}(x) \tag{5}$$

The polarized thermal expansion is the difference from the ensemble average at location x. We define the polarized CTE tensor $P(x)$ as:

$$P(x) = \tilde{\alpha}(x) \nabla T(x) \tag{6}$$

Since the thermal expansion strain has zero divergence, we have:

$$\nabla \cdot \varepsilon_t(x) = 0 = \alpha_0 \nabla \cdot \nabla T(x) + \nabla \cdot P(x) \tag{7}$$

This is a set of partial differential equations that can be solved by using Green's function:

$$T(x) = T_0 - \int dx' \nabla g(x, x') P(x') \tag{8A}$$

$$g(x, x') = \frac{1}{4\pi\alpha_0} \frac{1}{x - x'} \tag{8B}$$

where T_0 is the applied temperature, x and x' are the head and tail points of a vector in the microstructure. To obtain the temperature

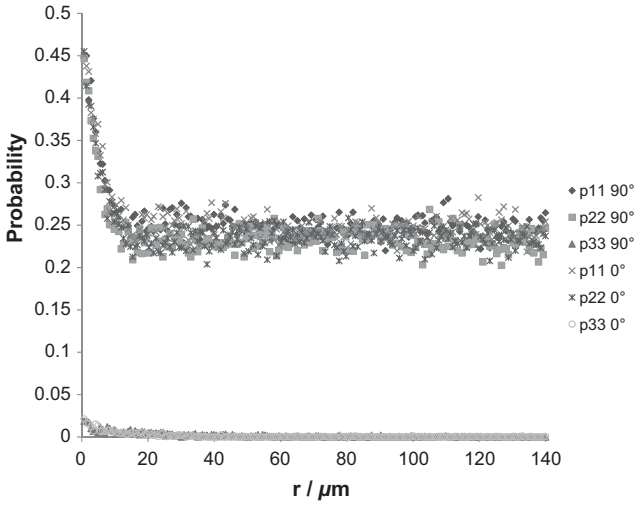

Fig. 3. Two-point correlation function results for G18 aged for 4 h with the vector orientation 0° and 90°.

gradient field ∇T, Eq. (8A) is differentiated.

$$\nabla T(x) = \nabla T_0 + \int dx' G(x - x') P(x') \tag{9}$$

where ∇T_0 is the applied temperature gradient. Here, we describe a numerical routine to perform the integration over the Green's function for an ensemble of aggregates in a heterogeneous medium. The derivation of the Green's function solution, $G(x - x')$, can be seen in Ref. [21]. Due to the singularity of the integral when $x = x'$, a spherical region around the singular point is excluded. Using integration by parts and divergence theorem, the Green's function $G(x - x')$ is expressed as:

$$G(x - x') = -D\delta(x - x') + H(x - x') \tag{10}$$

where D and H are defined by the following:

$$D = \frac{1}{3\alpha_0} I \tag{10A}$$

$$H = \frac{1}{4\pi a_0} \frac{3\hat{n}\hat{n} - I}{r^3} \tag{10B}$$

Here I is the second order identity tensor and $\hat{n}$ is the unit vector of $x - x'$.

Substitute the definition of the polarized field back to Eq. (10):

$$\nabla T(x) = \nabla T_0 + \int dx' G(x - x') * \tilde{\alpha}(x') \nabla T(x') \tag{11}$$

The average field for state h, with the state being the phase in this case, can be calculated from the above equation:

$$\left\langle \nabla T(x) \right\rangle_h = \nabla T_0 + \int dx' G(x - x') * \left\langle \tilde{\alpha}(\nabla T_0, h(x')) \right\rangle_h \nabla T_0 \tag{12}$$

Since no assumption is used on representing the statistical distribution of components in the heterogeneous media, the application of this statistical continuum model on the prediction of thermal conductivity can cover a broad range of materials systems.

4. Results and discussion

Using the two-point correlation formulation described in Section 2, two-point correlations have been used on Figs. 1 and 2, with phase 1 as the barium silicate, phase 2 as the matrix and hexacelsian needles, and phase 3 as the pores.

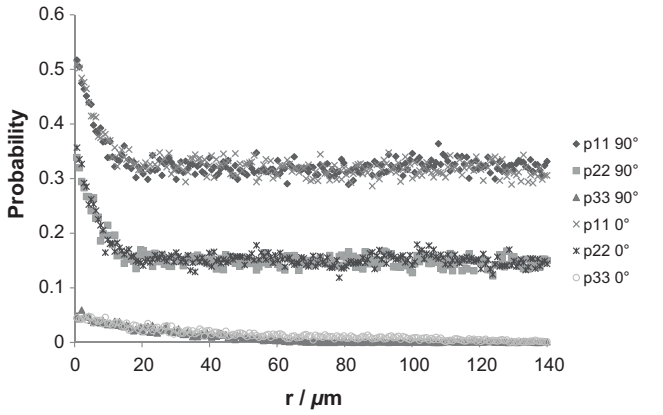

Fig. 4. Two-point correlation function results for G18 aged for 1000 h with the vector orientation 0° and 90°.

Figs. 3 and 4 show the two-point correlation functions, p_{11}, p_{22} and p_{33}, in G18 aged for 4 h and 1000 h, respectively. Since there is no obvious oscillation period in the data, there is no clustering in the microstructure. On the other hand, correlation functions change little with respect to the orientation of vectors sampled, showing that the microstructure is very isotropic.

The formulation for the CTE formulation has been applied to the glass-ceramic described earlier, as G18. The CTE of the pores was considered as zero, while the barium silicate and the matrix phases are shown below:

$$\alpha_{BaSiO_3} = \begin{bmatrix} 12.5 & 0 & 0 \\ 0 & 12.5 & 0 \\ 0 & 0 & 12.5 \end{bmatrix} \times 10^{-6}\,K^{-1} \tag{13A}$$

$$\alpha_{matrix} = \begin{bmatrix} 9.0 & 0 & 0 \\ 0 & 9.0 & 0 \\ 0 & 0 & 9.0 \end{bmatrix} \times 10^{-6}\,K^{-1} \tag{13B}$$

These CTE properties are effective from room temperature up to 300 °C for soda-lime glass, and up to 550 °C for barium silicate. At higher temperatures, the barium silicate CTE lowers and the glass phase softens [20].

Glass-ceramic aged for 4 h, shown in Fig. 1, is composed of 49.6% barium silicate, 48.6% matrix, and 1.6% pore. After aging for 1000 h, shown in Fig. 2, the glass is composed of 56.0% barium silicate, 40.0% matrix, and 4.0% pore. As shown in Figs. 3 and 4, the correlation functions approximate to the volume fraction and regress to the square of value of volume fractions. The statistical continuum mechanics method was applied to predict the effective CTE of G18. Results from the statistical continuum mechanics model are shown below:

$$\alpha_{4\,h} = \begin{bmatrix} 10.57 & 0 & 0 \\ 0 & 10.57 & 0 \\ 0 & 0 & 10.59 \end{bmatrix} \times 10^{-6}\,K^{-1} \tag{14A}$$

$$\alpha_{1000\,h} = \begin{bmatrix} 10.52 & 0 & 0 \\ 0 & 10.52 & 0 \\ 0 & 0 & 10.76 \end{bmatrix} \times 10^{-6}\,K^{-1} \tag{14B}$$

To compare other common homogenization models, the classical upper and lower bounds, similar to the Voigt and Reuss models, were used, in addition to a self-consistent model, which is described further in Refs. [21–23]. These models are much more simple and are based on microstructure assumptions, volume fractions, and individual phase properties. The upper and lower bounds related to two extreme microstructures where the components are arranged in iso-strain and iso-stress, respectively. The simpler models allow us to see the effect of the microstructure in the effective CTE,

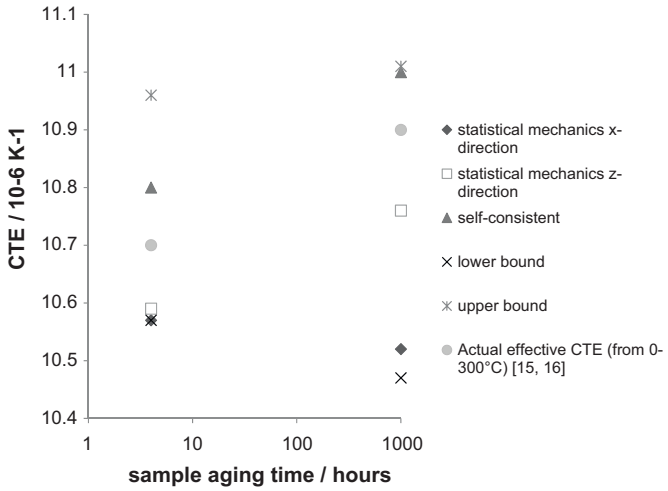

Fig. 5. Predicted CTE by statistical mechanics and by the self-consistent model of G18 at different aging times.

when comparing to the statistical continuum mechanics model. The effective CTEs predicted by these models are shown in Fig. 5.

Generally, the CTE increases with aging. However, the CTE of the 1000-h-aged sample in the *x*-direction is lower than that of 4-h-aged sample. This is due to the higher amount of anisotropy and porosity in the 1000-h-aged sample compared to the 4-h-aged sample. The anisotropy can be seen by comparing the ratio of α_{33} to α_{11}, giving 1.00 in 4-h-aged sample and 1.02 in 1000-h-aged sample. This indicates slightly more anisotropy in the 1000 h sample. Correspondingly, the CTE along *z*-direction in 1000-h-aged sample increased slightly in comparing with that of the 4-h-aged sample. This may be due to slight anisotropy in the micrograph with some preference in the *z*-direction. Overall, the microstructure is generally isotropic, demonstrated in the correlation function and CTE results. The self-consistent and statistical continuum mechanics results fall within the classical upper and lower bounds. In general, the self-consistent model gives higher predictions than the statistical continuum mechanics model. The statistical continuum mechanics model takes into consideration the slight anisotropy of the 1000-h-aged sample. It would be more accurate to compare experimental data with effective CTE predictions calculated from the actual micrograph of the experimental data sample. The statistical continuum mechanics model provides results that can be used to predict the CTE of similar glass-ceramic materials used for SOFC seals.

Although the difference between the models is small, it is necessary for SOFC seals to be closest in CTE to neighboring components to stress in the seal. The two-point correlation model provides a method to relate the microstructure to the effective properties. Because the CTE is one of the most important qualities in an SOFC, it is necessary to find a model that would be most accurate. Therefore, it may be more beneficial to use the statistical continuum mechanics model, over the more simple models, which make assumptions about the microstructure. The results show that two-point correlation functions can serve as a tool for future development of SOFC seals.

The CTE model was also applied to these two set of samples elongated along *z*-axis Figs. 6 and 7 show the micrographs of samples which are elongated images of samples aged for 4 h and 1000 h, respectively. The anisotropy in the micrographs is demonstrated in the corresponding correlation functions. The crystalline needles, pores, and matrix phases are all elongated. The influence of microstructure evolution on the thermal behavior is reflected on

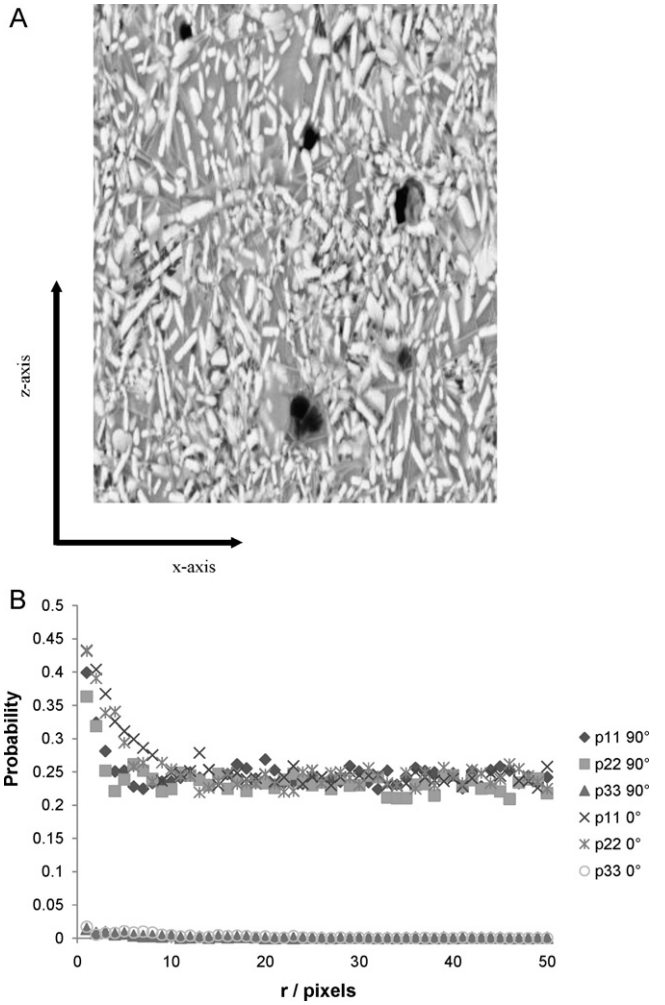

Fig. 6. (A) Microstructure A, micrograph of G18 aged for 4 h, 100% elongated in the *z*-axis and (B) the correlation function for microstructure A.

the CTEs simulated by statistical continuum mechanics:

$$\alpha_A = \begin{bmatrix} 10.2 & 0 & 0 \\ 0 & 10.2 & 0 \\ 0 & 0 & 11.6 \end{bmatrix} \times 10^{-6}\,\mathrm{K}^{-1} \quad (15A)$$

$$\alpha_B = \begin{bmatrix} 9.9 & 0 & 0 \\ 0 & 9.9 & 0 \\ 0 & 0 & 12.0 \end{bmatrix} \times 10^{-6}\,\mathrm{K}^{-1} \quad (15B)$$

The large difference in CTE along different directions is due to the anisotropy that was introduced to the microstructure. The anisotropy is reflected in the ratio of α_{33} to α_{11}, increasing dramatically from 1.22 in elongated 4-h-aged sample to 1.37 in elongated 1000-h-aged sample. There is an increase from the original anisotropy indicators. The results show that the CTE has lowered in the *x*-direction, while increasing in the elongated *z*-direction. These examples show that the statistical continuum model takes into account the morphology of the microstructure, as well as the volume fraction, as opposed to other homogenization models, such as the self-consistent, which only considers the volume fraction. In the future, this method can be used on other heterogeneous materials to predict the CTE. This model can also be used for polycrystalline materials, which can take each crystal as a different phase, with anisotropic individual properties.

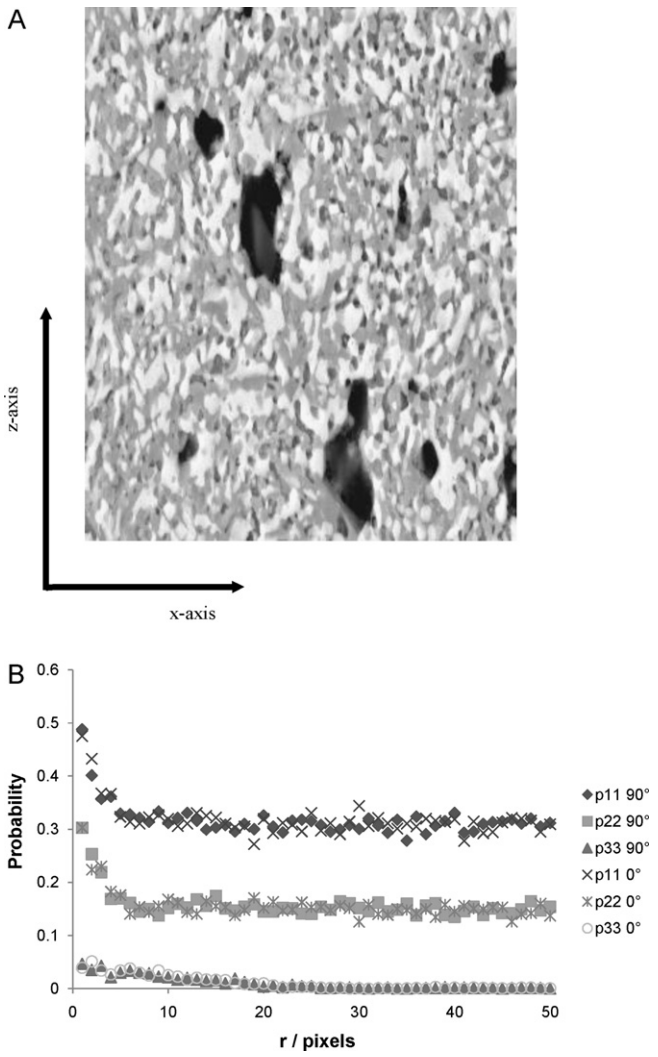

Fig. 7. (A) Microstructure B, micrograph of G18 aged for 1000 h, 100% elongated in the *z*-axis and (B) the correlation function for microstructure B.

5. Conclusions

A statistical continuum mechanics model was developed to predict the CTE of heterogeneous media composed by isotropic phases. Two-point correlation models were used to describe the microstructure's morphology, volume fractions, and phase distribution. This model was applied to predict the CTE of glass-ceramic SOFC seal G18. This model can be used on other heterogeneous materials, including anisotropic materials, to predict the effective CTE. Results show the change in effective CTE with increased barium silicate. Also, for anisotropic microstructures, thermal expansion was greater in the elongated direction. To cross validate the accuracy of statistical continuum mechanics, predicted results were compared with experimental data and prediction results from other models. Reliability of statistical continuum mechanics was demonstrated.

Acknowledgements

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