Negative Thermal Expansion Materials: Thermal Stress and Implications for Composite Materials

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Introduction

The degree to which the dimensions of a material change with temperature is an intrinsic property that is quantified by the thermal expansion coefficient. The volumetric thermal expansion coefficient is defined as $\alpha_V = V^{-1}(\partial V/\partial T)_{\mathrm{P}}$. However, in cases where the change in dimension is anisotropic, a more practical expression is the linear thermal expansion coefficient $\alpha_l = l^{-1}(\partial l/\partial T)_{\mathrm{P}}$, where l is the linear dimension.

For the majority of materials, the dimensions expand as the material in heated and therefore $\alpha > 0$ since interatomic distances generally increase with increasing temperature. However, there are cases where this is not true. Zirconium tungstate, ZrW_2O_8, is an interesting example since it shows isotropic negative thermal expansion (NTE) from 0.3 to 1050 K, with $\alpha = -9\mathrm{x}10^{-6}$ K^{-1} from 2 to 350 K.[1] The magnitude of the negative thermal expansion coefficient of ZrW_2O_8 is on the order of similar ceramic materials with positive thermal expansion coefficients.

There is considerable interest in the possibility of combining NTE materials with normal (positive) thermal expansion materials, to reduce the potential of failure of a material or component due to thermal stress fracture. In this paper, we discuss the design of highly thermal shock fracture resistance materials, and consider combining positive and negative thermal expansion material to achieve low thermal expansion composites. To this end, finite element analysis (FEM) is used to explore different materials for low α composites and evaluate how parameters such as thermal and mechanical properties, rates of cooling/heating, geometry and packing fraction influence the overall expansion and thermal stress in such composites.

Use of COMSOL Multiphysics

FEM simulations were performed here using COMSOL Multiphysics v3.5. We report studies of ZrW_2O_8 in two different types of composites, ZrW_2O_8/copper and ZrO_2/ZrW_2O_8, at varying concentrations. For the simulations of composite materials, it was assumed that displacements due to thermal expansion are small and thus the materials can be treated as linearly elastic. Also, because the dynamics of the structure can be considered static compared to the time scale of the heat transfer problem, solutions can be obtained by coupling a steady-state structural mechanics problem to a transient temperature response. COMSOL Multiphysics then solves the thermal and structural problems simultaneously.

The 2D simulation geometry is shown in Figure 1. Both components were treated as isotropic and their properties at all locations were considered to be those of the bulk (*i.e.*, no interface effects). The center cell is considered representative of the bulk and was simulated with a finer mesh. It is surrounded by additional NTE/Cu cells, on a square array, placed to account for the influence of neighboring NTE particles on the center cell. A 5x5 array was used. (We found only minimal differences between 5x5 and larger arrays.)

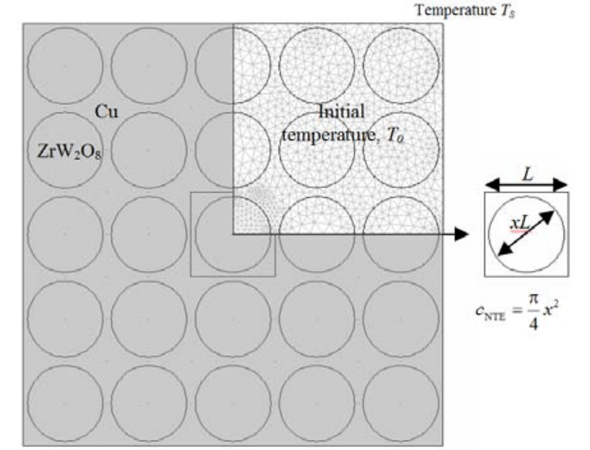

Figure 1: 2-D model of NTE in Cu composite. c_{NTE} is defined as the volume fraction of NTE material.

As shown in Figure 1, the geometry is symmetric so it is necessary to simulate only ¼ of the system. Symmetry is enforced by temperature insulation and "roller" (*i.e.*, zero displacement in the perpendicular direction) boundary conditions along the *x*- and *y*-axes. The 2D model is employed due to its simplicity in comparison to 3D models, which allows for faster solutions with finer meshes and inclusion of more neighbors. The 2D array is analogous to a 3D array of cylinders, but we found that the maximum stresses in the 2D model also are quantitatively similar to the maximum stresses in a 3D array of spheres of the same diameter. (Note, however, that a 3D array of spheres has a significantly lower c_{NTE} than a 2D array of equal diameter circles and, therefore, the overall expansion coefficient would differ.) FEM allows for the determination of stresses and overall expansion in the system.

Results

The overall thermal expansion FEM results for ZrW_2O_8/copper and ZrO_2/ZrW_2O_8 composites was determined and compared to experimental results where possible. The influence of the size of the NTE particles, concentration of NTE, and cooling rate on the maximum stresses and overall expansion for a given temperature change will be shown. Also, in order to test the influence of more closely matched thermal properties of the matrix and the inclusion, the FEM analysis of ZrO_2/ZrW_2O_8 is compared to the analysis of ZrW_2O_8/Cu.

Conclusion

The possibility of transient maxima in α at high cooling rates and large steady-state thermal stresses in the composite are a concern for the mechanical stability of the system. Thermal stresses are largest when the amount of filler is largest and hence it is advantageous to use components with similar magnitudes of α. Given the thermal stresses that can develop in a composite when subjected to a large temperature change, sufficient to cause phase transitions or brittle failure, it would be more desirable to develop pure materials with intrinsic, low expansion for applications in which potential for thermal stress is a major concern.[2]

Reference

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1. J. S. O. Evans *et al.*, Structural investigation of the negative-thermal-expansion material ZrW_2O_8, *Acta Cryst.*, **B55**, 333-340 (1999).
2. M. B. Jakubinek *et al.*, Negative thermal expansion materials: thermal properties and implications for composite materials, *Journal of Thermal Analysis and Calorimetry*, (in press, accepted March 26, 2009).