A Model for the Thermal Properties of Liquid-Phase Sintered Composites

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Thermal properties are important to several applications for powder metallurgy products. For example, liquid-phase sintered tungsten-copper composites are used in microelectronic packaging to obtain a high thermal conductivity in a low thermal expansion material. This article addresses modeling the thermal properties for composites fabricated by liquid-phase sintering. A computational cell is constructed with interlinked phases, consisting of a core of low thermal expansion material (tungsten) and a edge network of high thermal conductivity phase (copper). This structure is used to calculate the composition effects on the coefficients of thermal expansion and thermal conductivity. The results are applied to prior reports on W-Cu and used as a basis to identify several candidate high thermal conductivity systems for future development.

I. INTRODUCTION

Powder processing techniques are used for the fabrication of various composite materials associated with thermal management in microelectronics. These applications require tailored materials formed to net shapes at low production costs. The objective is a high thermal conductivity with a thermal expansion matched to the semiconductor or ceramic substrate. As this application field expands, there is greater need to tailor the material properties, especially with respect to the thermal properties.

There are three thermal properties of concern—heat capacity, thermal conductivity (TC), and the coefficient of thermal expansion (CTE). The heat capacity is the easiest to model, since it is independent of microstructure and can be estimated through the rule of mixtures,

\[ C_M = \sum W_i C_i \]  

where \( C_M \) is the heat capacity of the mixture, \( C_i \) is the heat capacity for the constituent, and \( W_i \) is the weight fraction (where \( \sum W_i = 1 \)). However, appropriate models are needed for predicting the coefficient of thermal expansion and the thermal conductivity of composites. Microstructure is a factor with respect to these properties. Unfortunately, the existing models are based on idealized structures of aligned fibers, uniformly spaced particles, or laminated foils.

In contrast, the composites produced by powder metallurgy are more complicated and are not well aligned with the assumptions of these models. After liquid-phase sintering, the solid grains are interconnected and exhibit a contiguity and connectivity that depend on the dihedral angle and solid volume fraction. In addition, the solidified liquid phase is interwoven through the structure, giving interpenetrating three-dimensional networks of both phases. The solidified liquid partially penetrates the solid-solid grain boundaries and forms a structure, as exemplified by the scanning electron micrograph shown in Figure 1. Thus, the microstructure associated with liquid-phase sintered alloys is very different from the aligned fiber, laminate, or dispersed sphere models used for most composites. The actual two-phase structure is best represented by polyhedral solid grains with networks of solidified liquid, such as sketched in Figure 2.

This article develops a model for predicting thermal properties applicable to liquid-phase sintered microstructures. The model uses a polyhedron for the solid grain shape with a network of solidified liquid along the edges of the polyhedron. The model is applied to calculation of the thermal expansion and thermal conductivity. Key applications for this work are in the selection and design of thermal management materials for heat dissipation devices associated with microelectronic circuits. In these applications, the desire is to maximize thermal conductivity while avoiding debonding stresses. The modern microelectronic circuit has a high heat dissipation load that is approaching 125 W/cm² in advanced designs. These circuits require contact with a high thermal conductivity, controlled thermal expansion substrate to remove heat while avoiding stresses due to thermal cycling. Thermal fatigue is a major failure mode in microelectronic circuits, for example, failures have been reported in as few as 100 cycles with a CTE difference of 12 ppm/K between contacting materials. Accordingly, minimized thermal fatigue requires that the microelectronic package have a CTE close to that of silicon, gallium arsenide, or substrate materials, such as alumina, aluminum nitride, beryllia, or cordierite. All of these are low CTE materials, typically in the range of 3 to 7 ppm/K. However, to maximize heat removal, a high thermal conductivity is desired. Aluminum proves effective in many low power systems, but it has a very high thermal expansion, near 23 ppm/K. To tailor the match between CTE and maximize TC requires composites, such as W-Cu, SiC-Al, Mo-Cu, AlN-Y₂O₃, or AlN-Al. Such materials are candidates for liquid-phase sintering.

This article develops the model and applies it to liquid-phase sintered materials to assess the composition effects on thermal properties. The model provides a basis for first pass assessment of various candidate systems, prior to launching into expensive experimentation.
II. GEOMETRICAL MODEL

Many models for thermal properties have been advanced in the composites field. These include isolated spheres, laminates, and aligned anisotropic fibers. With respect to liquid-phase sintered microstructures, these composite models are unrealistic, since the two phases are actually intertwined; the connectivity and contiguity vary with the dihedral angle and volume fraction of solid. Beech and Price examined the electrical resistance of copper-graphite contacts and showed a major effect from the degree of connectivity in the microstructure. Unfortunately, their model lacked true interconnections between both phases. Likewise, experiments by Smugeresky and Rack with hot isostatically compacted boron carbide and copper particle composites further demonstrated the limits to existing composite models. They found the thermal conductivity of B₄C-Cu composites to be intermediate between the sphere and laminate models. Shaw-Kline and German compared the CTE of sintered iron-cordierite composites with the various models and concluded that the low ceramic content compositions followed the dispersed sphere models. However, no model was suitable at higher ceramic contents where a continuous ceramic phase exists in the microstructure. Similar observations have been made in a wide variety of particulate composites, including TiC-Ni, Mo-Cu, SiC-Al, and invar-copper, as examples.

This study starts with a simple cubic computational cell with a network of high conductivity material occupying the cell edges and the low thermal expansion material occupying the cell center. Full density is assumed for the composite. In this presentation, copper is the high thermal conductivity phase and tungsten is the low thermal expansion phase. Figure 3 shows the computational cell with the tubes of high conductivity material on the cube edges. An overall perspective is given along with views from the front face and a center cross section to aid in appreciating the intertwined nature of the phases. The unit cube can be thought of as having a dimension \( l \) with the radius of the high conductivity phase equal to \( r \). To create a nondimensionalized form, the model is constructed in terms of the ratio \( R = r/l \); essentially, the computational cell can be considered as having unit length. In this manner, the ratio of dimensions is important while the absolute dimensions are not important. Such a model is representative of the sintered structure for W-Cu, as illustrated in Figure 1. Although the actual liquid-phase sintered structure shows variation in grain size, contiguity, and connectivity, the concept of two intertwining phases is evident. Actually, based on the minimized energy grain shape accommodation calculations of Kipphut et al., the computational unit cell should vary in shape with the solid content and dihedral angle. However, the current model proves adequate for many early calculations. A tungsten grain coordination of six, as represented in Figure 3, is typical to solid contents between 65 and 80 vol pct. These compositions have thermal properties appropriate to microelectronic packaging applications. For the derivations, the W-Cu system will be used to emphasize the role of the high conductivity phase (copper) and low CTE phase (tungsten).

A link between the volume fraction of conductor phase \( V_{Cu} \) and the parameter \( R \) has been generated by nonlinear parametric least-squares regression, giving

\[
R = 0.0113 + 1.58 V_{Cu} - 1.83 V_{Cu}^{3/2} + 1.06 V_{Cu} \]  

where a pore-free structure is assumed; hence, the volume fraction of the refractory phase \( V_{w} = 1 - V_{Cu} \). The