

# Finite-element analysis of thermal expansion and thermal mismatch stresses in a Cu–60vol%ZrW<sub>2</sub>O<sub>8</sub> composite

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## Abstract

Thermal mismatch stresses in the ceramic particles of a Cu–ZrW<sub>2</sub>O<sub>8</sub> composite were calculated using a finite-element model, and found to be high enough to trigger a pressure-induced phase transformation, in agreement with previous measurements by X-ray diffraction. The calculated thermal expansion/contraction curves also agree with previous experimental dilatometric results.

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## 1. Introduction

Recently, Holzer and Dunand [1] fabricated a metal matrix composite consisting of 60 vol% ZrW<sub>2</sub>O<sub>8</sub> particles within a Cu matrix, with the goal of achieving high thermal conductivity (from Cu) and low thermal expansion (from ZrW<sub>2</sub>O<sub>8</sub>) for thermal management applications. ZrW<sub>2</sub>O<sub>8</sub> was chosen because it exhibits a coefficient of thermal expansion (CTE) with a large negative, isotropic value ( $\alpha = -13.5$  to  $-5 \times 10^{-6} \text{ K}^{-1}$ ) over a very broad temperature range (4–1000 K) [2–8]. However, the composite exhibited very large dilatometric expansion on heating and contraction on cooling, much above those predicted from thermo-elasticity theory [1]. This unexpected result was justified by the formation of the high-pressure  $\gamma$ -ZrW<sub>2</sub>O<sub>8</sub> phase from the ambient pressure  $\alpha$ -ZrW<sub>2</sub>O<sub>8</sub> phase (or  $\beta$ -ZrW<sub>2</sub>O<sub>8</sub> phase above 423 K), which is associated with a substantial 5% volume change [5]. The thermal mismatch stresses developed between the matrix and the particles on cooling were hypothesized to be large enough to reach the hydrostatic pressure range (200–300 MPa [5])

at which the  $\gamma$ -phase is formed. Recently, direct evidence of this reversible stress-induced transformation in this composite was provided by X-ray synchrotron diffraction measurements during thermal cycling of this Cu–60vol%ZrW<sub>2</sub>O<sub>8</sub> composite [9,10]. The aims of the present study are to predict, using the finite-element method (FEM), the overall thermal expansion behavior of this Cu–60vol%ZrW<sub>2</sub>O<sub>8</sub> composite and to investigate the magnitude of the thermal mismatch stress in the ceramic phase to provide modeling justification to the direct and indirect experimental evidence of a phase transformation induced by thermal mismatch stresses.

## 2. Numerical modeling

The composite was modeled as a three-dimensional (3-D) infinite periodic array of unit cells. Metallography of experimental Cu–ZrW<sub>2</sub>O<sub>8</sub> composites presented in [1] shows that the ZrW<sub>2</sub>O<sub>8</sub> particles are very angular. Thus, we model the particles as tetrahedra, five of which are arranged within the unit cell in a regular manner shown in Fig. 1. The faces of adjacent tetrahedral particles are separated by channels of matrix material of constant width, determined by the volume fraction of the matrix (40%). The interface between particle and matrix is as-

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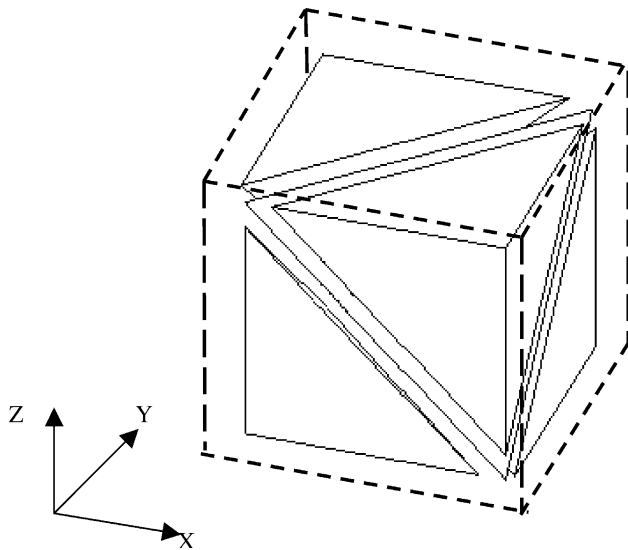


Fig. 1. FEM unit cell consisting of five tetrahedral  $\text{ZrW}_2\text{O}_8$  particles embedded in Cu matrix.

sumed to be strong and to remain bonded at all time, insuring continuity between phases. Periodic boundary conditions are used, i.e., unit cell faces are kept parallel to opposite faces, and perpendicular to adjacent faces.

Coefficients of thermal expansion of the three  $\text{ZrW}_2\text{O}_8$  phases were taken as temperature independent as  $-8.7$ ,  $-4.6$  and  $-1.0 \times 10^{-6} \text{ K}^{-1}$  for  $\alpha$ -,  $\beta$ - and  $\gamma$ - $\text{ZrW}_2\text{O}_8$ , respectively [2]. The CTE of copper was given by  $\alpha_{\text{Cu}} [\text{K}^{-1}] = 16.23 \times 10^{-6} + 48.3 \times 10^{-10} T (\text{°C})$  [11]. Taking an average bulk modulus of 70 GPa for  $\text{ZrW}_2\text{O}_8$  (based on bulk modulus values of 69.4 GPa for  $\alpha$ - $\text{ZrW}_2\text{O}_8$  and 68 GPa for  $\gamma$ - $\text{ZrW}_2\text{O}_8$  [2]) and assuming a Poisson's ratio of 0.25, an elastic modulus of 105 GPa was calculated, which is also assumed to be temperature-independent. The elastic modulus and Poisson's ratio of copper were taken as 113 GPa and 0.34, respectively, at room temperature, 100 GPa and 0.33, respectively, at 573 K and assumed to vary linearly between these temperatures.

The FEM code ANSYS V 6.0 was used, assuming that matrix and particle are isotropic and deform only elastically. Three-dimensional brick elements with 20-node were chosen for meshing the unit cell. By varying the mesh size, it was determined that 13,506 nodes and 8448 elements optimized calculation time and accuracy of results. Heating and cooling cycles in the range 300–573 K were considered separately and no residual stresses were assumed at the start of the heating and cooling cycles, respectively, i.e., full relaxation was assumed. The numerical calculations were performed in an incremental manner using 10 K steps. The displacements at the edges of the cell were used to determine the thermal expansion of the composite as a function of temperature.

### 3. Results and discussion

#### 3.1. Thermal expansion curves

The validity of the FEM analysis was verified by using volume fractions  $V_f$  of each of the three  $\text{ZrW}_2\text{O}_8$  phases (measured experimentally by synchrotron X-ray diffraction [9]) to calculate the thermal expansion/contraction curves and compare it with the experimental curves [1] in the range 300–573 K. For the effective CTE value of the ceramic phase  $\alpha_p$ , a simple rule of mixtures was used

$$\alpha_p = V_{f\alpha} \cdot \alpha_\alpha + V_{f\beta} \cdot \alpha_\beta + V_{f\gamma} \cdot \alpha_\gamma - \frac{\Delta V/V}{3} \cdot \frac{\Delta V_{f\gamma}}{\Delta T}, \quad (1)$$

where  $\Delta V/V = 0.05$  is the  $(\alpha, \beta) \leftrightarrow \gamma$  polymorphic specific volume change and  $\Delta V_{f\gamma}/\Delta T$  is the change of  $\gamma$ -phase volume fraction over the temperature interval  $\Delta T$ , measured experimentally in [9]. The thermal expansion curves as calculated by FEM and as measured experimentally [1] are shown in Fig. 2. Agreement is satisfactory, given the relatively large experimental error for the phase volume fractions [9] used as input parameters, the uncertainties associated with the materials property parameters, the idealized geometry and distribution of the particles (Fig. 1), and the assumption that copper does not deform plastically and is stress-free at the start of the heating or cooling cycles. The large thermal expansion on heating observed by dilatometry is reasonably well predicted by the disappearance, upon heating, of an initial volume fraction of  $\gamma$ -phase  $V_{f\gamma} = 0.20$

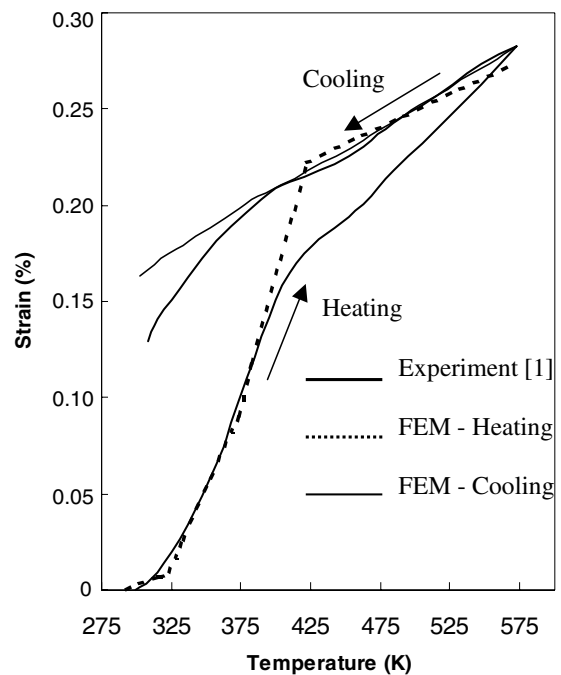


Fig. 2. Thermal expansion curves for Cu-60vol% $\text{ZrW}_2\text{O}_8$  as determined by FEM analysis and as measured experimentally [1].

measured by diffraction [9]. The most sensitive parameter in the calculations is the ceramic CTE (Eq. (1)) which, in the temperature range where the  $\gamma$ -phase exists, is dominated by the value of  $\Delta V/V$  and the initial volume fraction of the  $\gamma$ -phase  $V_{f\gamma}$ . Some of the discrepancy may be due to the fact that the input parameters  $\Delta V_{f\gamma}/\Delta T$  was measured in [9] under a heating/cooling rate different from that used in the dilatometry experiment [1]. We also note that the FEM curve is very close to a predicted curve using a rule-of-mixture equation for the composite CTE, as reported in [9].

The above observations thus confirm that the highly-variable and anomalously-large CTE of the Cu-60vol%ZrW<sub>2</sub>O<sub>8</sub> composite recorded in [1] is due to the reversible formation of  $\gamma$ -phase. Therefore, as suggested by these authors, inhibition of this transformation by reduction of mismatch stresses and/or alteration of the ZrW<sub>2</sub>O<sub>8</sub> critical transformation stress should result in composites with high thermal conductivity and low, uniform CTE (which could become zero or even negative with a higher ceramic content).

### 3.2. Internal stresses

Fig. 3 shows hydrostatic stress contours on the surface of a ceramic particle at room-temperature after cooling from 573 K (assuming no residual stresses at that temperature). As expected from the large mismatch in CTE values between matrix and ceramic, these stresses are strongly compressive. They are also highly non-uniform, varying between  $-190$  MPa at the face center and  $-310$  MPa at the tip of the particle. Thus, the FEM model predicts that the pressure-induced phase transformation of the ceramic particles should begin at

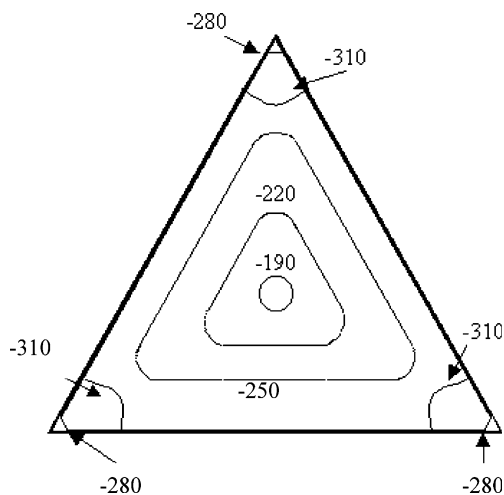


Fig. 3. An example of contour plots of hydrostatic stress ( $\sigma_h$  (MPa)) distribution in a surface of a tetrahedral ceramic particulate at room temperature after cooling is shown schematically. The hydrostatic stress ( $\sigma_h$  (MPa)) distribution at other surfaces of tetrahedral is similar.

its sharp corners even if the average stress is not sufficient for a complete transformation. A recent neutron diffraction study of unconstrained  $\alpha$ -ZrW<sub>2</sub>O<sub>8</sub> showed that the transformation to the  $\gamma$ -phase starts at a hydrostatic compressive pressure of 200 MPa and that the  $\gamma$ -phase volume fraction increases linearly to 100% over a relatively broad range of 100 MPa [5].

In Fig. 4, the calculated minimum, mean and maximum hydrostatic stresses in the particles are plotted with respect to temperature on cooling from 573 K. The mean hydrostatic stress, found by summing the hydrostatic stress of each element and dividing by the number of elements, has a standard deviation of ca. 13%. The average stress values, determined from the result of experimental diffraction measurements given in [10], are also shown in Fig. 4, and is in good agreement with the calculated mean stress, given the experimental error (estimated as 20% [10]) associated with the X-ray stress measurements. At room temperature after cooling, the mean FEM hydrostatic stress of the ceramic is 235 MPa, which is above the minimum stress value of 200 MPa necessary to trigger the pressure-induced  $\alpha \rightarrow \gamma$ -phase transformation in loose ZrW<sub>2</sub>O<sub>8</sub> powders [5]. This prediction is in agreement with formation of high-pressure  $\gamma$ -phase produced on cooling from indirect dilatometric measurements [1] and direct synchrotron X-ray diffraction measurements [9,10].

From Fig. 4, the maximum hydrostatic stress values (at the particle corners) exceed the critical value (200 MPa) for initiation of the transformation to the  $\gamma$ -phase at ca. 480 K, and they reach 540 MPa at room temperature. It is thus very likely that phase transformation

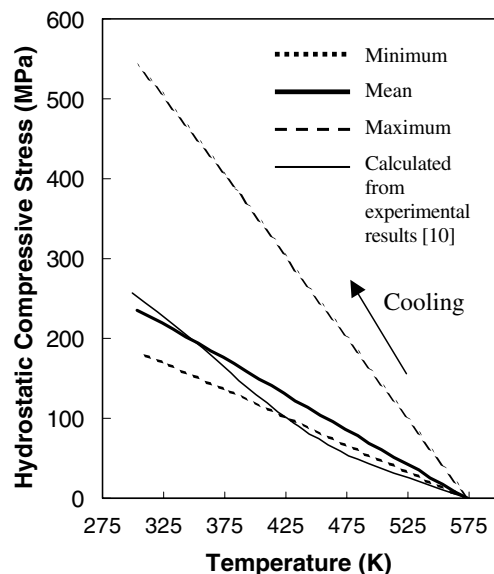


Fig. 4. Minimum, mean and maximum hydrostatic stress values in  $\alpha$ -ZrW<sub>2</sub>O<sub>8</sub> particle as a function of temperature. The average stress values in ZrW<sub>2</sub>O<sub>8</sub> particles calculated from experimental diffraction measurements [10] is also shown.

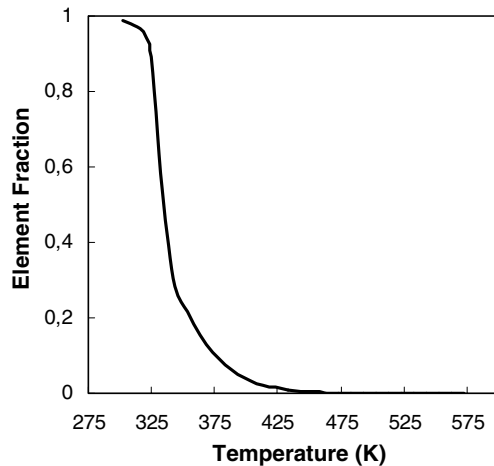


Fig. 5. Temperature dependence of volume fraction of  $\alpha$ -ZrW<sub>2</sub>O<sub>8</sub> particle with hydrostatic stress exceeding the critical value for onset of  $\gamma$ -phase formation (200 MPa).

initiates at the particle sharp corners early during cooling and propagates into the particle center. The volume change ( $\Delta V/V = 0.05$ ) associated with the transformation will however alter the local state of stress of the particle, an effect which is taken into account only in an average manner in the present calculations, by using an average CTE given by Eq. (1). The minimum value of hydrostatic stress is lower than 200 MPa, indicating that transformation of the particle to the  $\gamma$ -phase will only be partial.

In Fig. 5 the volume fraction of ceramic particle above the critical stress value for transformation to the  $\gamma$ -phase (200 MPa) at room temperature is shown as a function of temperature. This represents an upper limit for the volume fraction of  $\gamma$ -phase, since the transformation occurs over a range of 200–300 MPa [5]. Also, if transformation is sluggish (as reported in [1]) and nucleates first at the highly-compressed corners of the particle, the  $\gamma$ -phase produced in those regions will reduce the hydrostatic stress of the nearby particle volume before it transforms, until the critical value is not exceeded anywhere in the particle. So the true value of  $\gamma$ -phase is expected to be lower than predicted the curve in Fig. 5. Indeed, direct measurements of the  $\gamma$ -phase fraction using synchrotron radiation [9] showed that its volume fraction at ambient temperature was ca. 20%.

Also, the experimental dilatometric curve [1] in Fig. 2 shows a hysteresis of 0.13% at room temperature, which corresponds to a volume fraction of 13%  $\gamma$ -phase produced during the thermal excursion, as estimated by [1].

#### 4. Conclusions

Finite-element method was used to study the thermal expansion behavior of a metal matrix composite, consisting of 60 vol% ZrW<sub>2</sub>O<sub>8</sub> particles in a Cu matrix, upon cycling between 300 and 573 K. The dilatometric curve calculated by FEM using ceramic volume fraction independently measured by X-ray diffraction [9] is in reasonable overall agreement with an experimental dilatometric curve reported in [1]. This agreement confirms the earlier hypothesis [1] that the anomalously-high thermal expansion/contraction of these composites is due to the volume change of the ceramic particle associated with the stress-induced formation of the allotropic  $\gamma$ -ZrW<sub>2</sub>O<sub>8</sub> phase. The average particle hydrostatic pressure calculated by FEM after cooling to room temperature was found to exceed the critical value for stress-induced formation of  $\gamma$ -ZrW<sub>2</sub>O<sub>8</sub>. Hydrostatic stresses are highest at particle corners, where transformation is likely to occur first, thus relaxing the internal mismatch stresses within the particles.

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