HREM/SAED evidence for template-nucleation of c-ZrO_2/C inclusions in ZrB_2

R. Collins*, P. Fraundorf*, and D. Osborn*.

* Dept. of Physics and Astronomy and Center for Nano Science,
University of Missouri – St. Louis, One University Place, St. Louis, MO, 63121.

Here we discuss studies of carbon-enriched ZrB_2 ceramics for ultrahigh temperature applications. After the specimens have been sintered, the multi-micron single-crystal ZrB_2 matrix grains often show small (e.g. 250nm) two-phase inclusions, as shown in Figure 1 (a-c). Dislocation networks sometimes also present in these grains show strain-field contrast, but matrix-strain around the inclusions is remarkably absent.

SAED data taken from the inclusion shown in Fig. 1(c) are presented in Fig. 2. Naïve measurements made on the diffraction data support the presence of Graphite and ZrB_2. Graphite seems plausible due to its addition during synthesis; it seems unlikely that the inclusions within the ZrB_2 matrix are also ZrB_2. Careful inspection of the diffraction data shows that several of the reciprocal lattice points are accompanied by a closely spaced satellite point. A second phase having a reciprocal lattice of close orientation and similar spacing to that of ZrB_2 present a possible explanation of the satellite points. To resolve the question, HREM data was obtained from the inclusion. It is evident from the HREM data shown in Fig. 3 that there are two distinct spacings associated with the surrounding matrix and the high-density component of the inclusion. By computing the ratio of the 2g inter-spot distances in the power spectra, and treating the matrix grain as ZrB_2; we are able to identify the second phase as likely c-ZrO_2. This then allows the SAED data to be indexed as ZrB_2 and c-ZrO_2 with closely oriented lattices, plus several additional reciprocal lattice points attributed to Graphite.

This leaves us with two puzzles. How were inclusion strains relaxed, and why would the cubic ZrO_2 inclusion lattice be semi-coherent [1] or systematically-aligned (in multiple cases) with the hexagonal ZrB_2 matrix lattice? We might first ask about C and O solubility at the sintering temperature. If C and O reached saturation on cooling at the same time, one might expect to CO/CO_2 to evolve and diffuse away. If O reached saturation first, c-ZrO_2 might precipitate with little volume expansion if the B_2O_3 could also diffuse away [2], but subsequent C precipitation would build unreleased strain. However, if C reached saturation at the highest temperature (when the ZrB_2 lattice was most pliable), the strain that was not relaxed thereby might have been later relaxed by CO/CO_2 formation at lower T when the oxygen saturated. Moreover, template nucleation [3] of c-ZrO_2 on the ZrB_2 walls of the carbon inclusions could explain the systematic orientation-relationship between c-ZrO_2 and ZrB_2 lattices.

Further work to see if the observed orientation-relationship is consistent with: (i) an energetically-preferred nucleation sequence, (ii) the assumptions above about CO_2 and B_2O_3 mobilities, and (iii) future quench rate and O/C doping experiments to better elucidate the saturation-conditions indicated by the explanation above [4].

References:

[1] R. Guinebretière, Z. Oudjedi, B.Soulestin and A. Dauger," Semi-coherent zirconia inclusions in a ceramic matrix", *Journal of Materials Research* 15, 2482 – 2487 (2000).

[2] William G. Fahrenholtz, "The ZrB2 Volatility Diagram", *J. Am. Ceramic Soc.* **88**[12], 3509 – 3512 (2005).

[3] K.F. Kelton and A. L. Greer (2010) Nucleation in Condensed Matter (Elsevier, Amsterdam)

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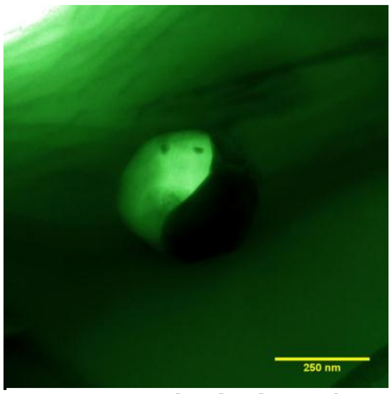

Figure 1(a) Typical Multi-Phase Inclusion

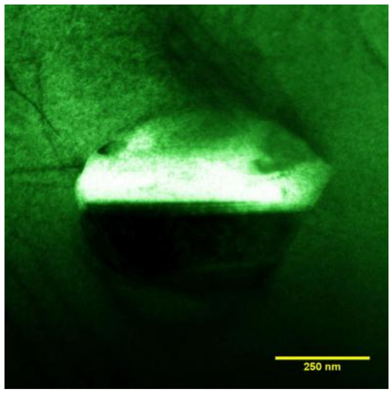

Figure 1(b) Typical Multi-Phase Inclusion

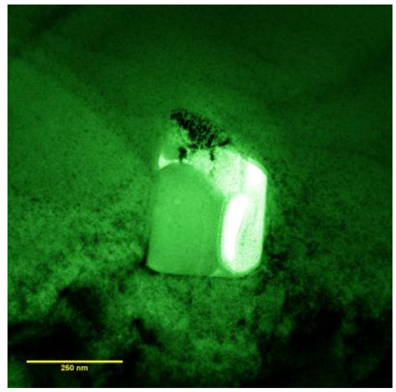

Figure 1(c) Typical Multi-Phase Inclusion

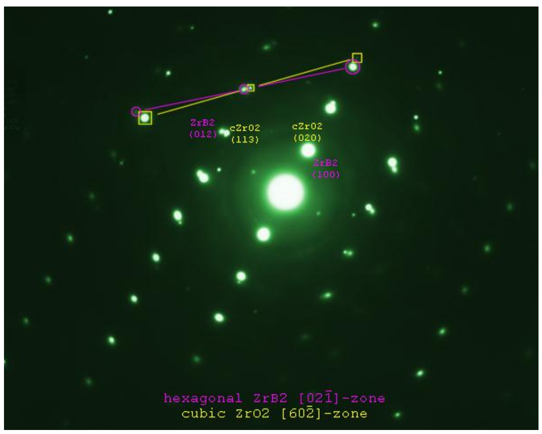

Figure 2: SAED data obtained from inclusion 1(c)

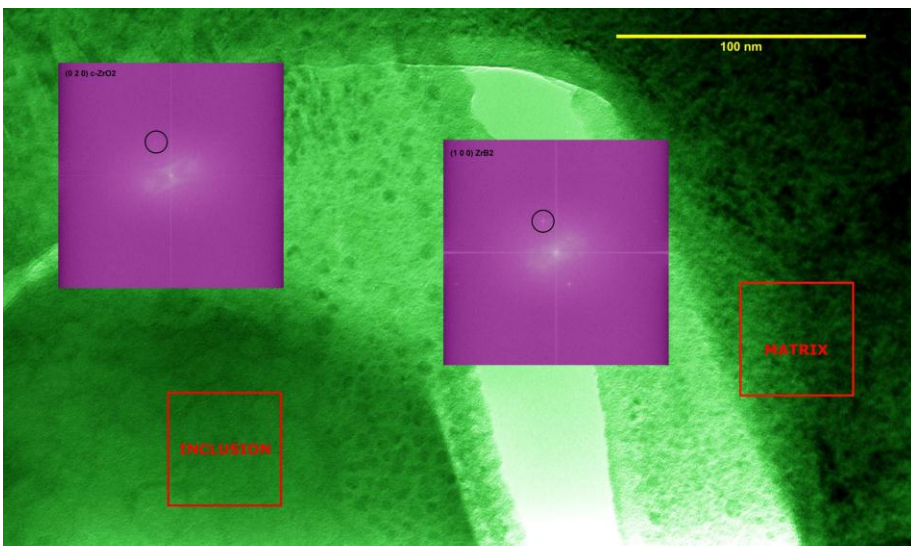

Figure 3: 240,000× HREM data from inclusion 1(c) showing power spectra associated with matrix and high-density inclusion regions.