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New Near-Zero Thermal Expansion [NZTE], Highly Thermal Shock Resistant Refractory Single-Phase Zirconium Phosphate

Figure 1. 3D printed parts (left) and press-formed pieces (right) after sintering at 1400°C for two hours.

Materials with near-zero thermal expansion [NZTE] have been of interest to researchers and industry for decades. Fused silica, β–eucryptite and β–spodumene, and cordierite are examples of silicates that have been found with low coefficients of thermal expansion (CTE). Unique negative thermal expansion (NTE)[1] or thermally contracting phases have been found, including phosphates and tungstates[2].

The phosphate materials in particular have been of interest recently. NASICON[3] and alkali oxide 'doped' zirconium phosphate such as sodium zirconium phosphate (NZP) are examples of modified phosphates that have led to negative or low CTE materials. Zirconium phosphate modified with barium and strontium reportedly[4] has low expansion and is usable to 1500°C. Other NZP type phases with NZTE are also reported[5].

Finding a simple, single-phase composition that exhibits CTE close to fused silica has been a persistent goal. The low CTE would allow enhanced thermal shock resistance as fabricated components are heated and cooled rapidly over an extended temperature range, since the thermal stress will be minimized.

Our studies have involved alkali-free modifications of zirconium phosphate. Sintered alkali-free zirconium phosphate displays good refractoriness as a single phase composition. That the mixture results in a single phase was confirmed through the use of both X-ray diffraction and scanning electron microscopy with energy dispersive spectroscopy.

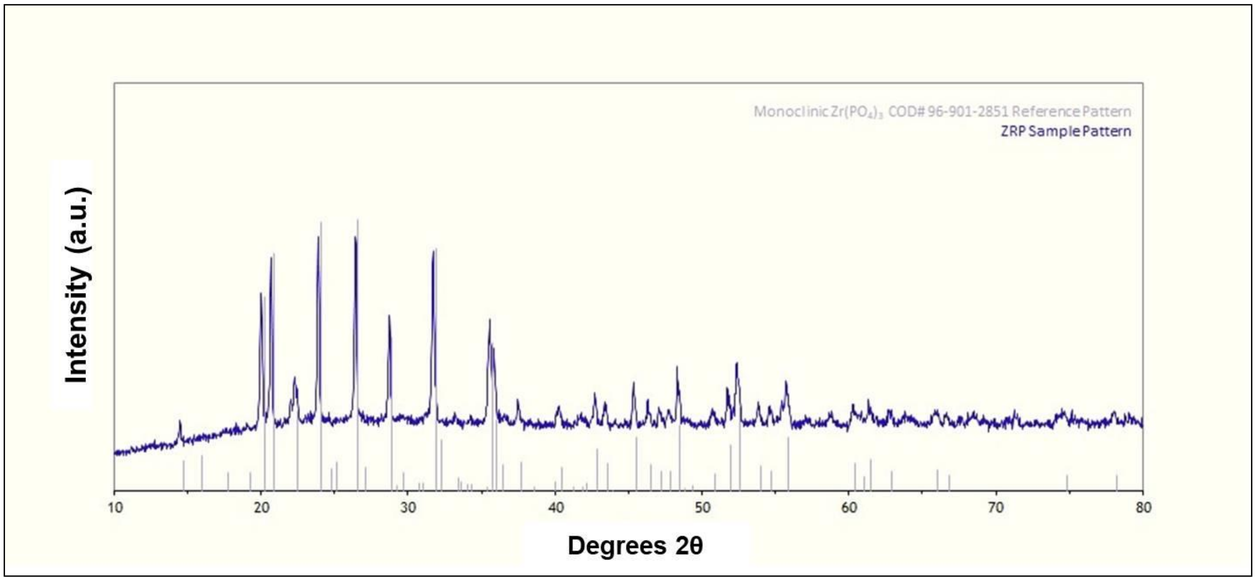

Figure 2. X-ray diffraction pattern for RefClay ZRP after sintering at 1400°C for 30 minutes in air. The monoclinic $Zr(PO_4)_3$ reference peaks (COD# 96-901-2851) are shown beneath the pattern.

The results of this extended investigation have led to the development of two unique products from ZYP Coatings:

- **3D Cer-Paste ZRP**, a solventborne ceramic paste specially made for 3D printing (additive manufacturing) in extrusion-based paste deposition modeling (PDM) 3D printers. The formed parts are sintered at 1400-1500°C in air, and can be used up to the sintering temperature. 3D printed parts made from 3D Cer-Paste ZRP sintered to full density were subjected to strenuous thermal shock testing, from 800°C in air to a water quench. The parts were subjected to 15 cycles with no observable change or deterioration.

- **RefClay ZRP**, water-based claylike material that is readily press formed or molded by clay-forming techniques into parts that can be sintered to near-full-density at 1400°C and also usable to 1500°C. The RefClay version was used to cast bars that were sintered at 1400°C for ½ hour to full density. The sintered bars were then used for measuring the thermal expansion of this new material. The CTE, measured from room temperature to 1000°C, was 0.4×10^{-6}/°C, which compares favorably to fused silica at 0.5×10^{-6}/°C. It should be noted that the density of the sintered parts is low – 2.75 g/cm^3 – and thus can be considered for aerospace applications.

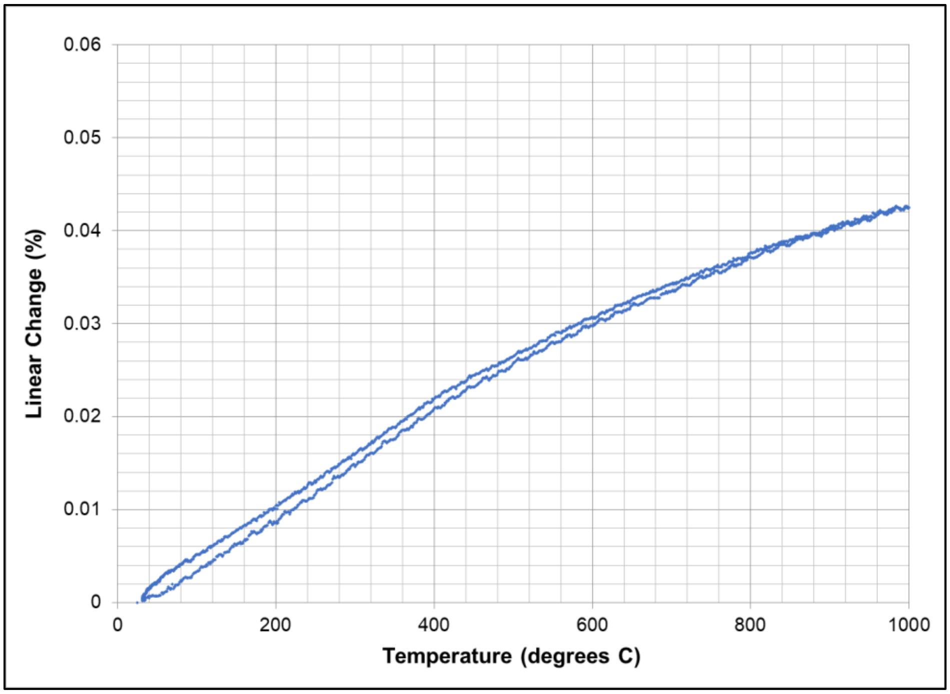

Figure 3. Dilatometry results from RefClay ZRP after sintering at 1400°C for 30 minutes in air.

The combination of NZTE and refractoriness of these single-phase zirconium phosphate ceramics is phenomenal, extending the range of usefulness of NZTE materials to 1500°C. The **3D Cer-Paste ZRP** and **RefClay ZRP** products allow easy production of parts of most any shape/configuration.

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[3] "NASICON," Wikimedia Foundation, last modified 11 March 2023, https://en.wikipedia.org/wiki/NASICON
[4] A. I. Orlova, D. V. Kemenov, V. I. Pet'kov, M. V. Zharinova, G. N. Kazantsev, S. G. Samoilov, and V. S. Kurazhkovskaya, "Ultralow and Negative Thermal Expansion in Zirconium Phosphate Ceramics," *High Temperatures – High Pressures*, **34**, 315-322 (2002).
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