

## Phase Stability Issues in Emerging TBC Systems

N.R. Rebollo, F.M. Pitek and C.G. Levi  
University of California, Santa Barbara  
Materials Department, Engineering II  
Santa Barbara, CA 93106-5050

The high temperature stability of metastable single-phase zirconias co-doped with Y plus trivalent rare earths or pentavalent cations is discussed. The motivation arises from strategies to enhance the insulating efficiency and/or higher temperature capability of thermal barrier systems by co-doping the conventional  $\text{ZrO}_2$ -7.6% $\text{YO}_{1.5}$  composition. The fundamental issue is the partitioning of the metastable tetragonal ( $t'$ ) or cubic ( $c'$ ) phases into the equilibrium  $t+c$  compositions dictated by the phase diagram, whereupon the tetragonal phase becomes susceptible to the disruptive monoclinic transformation.

The experiments are based on compositions synthesized by precursor pyrolysis, all of which yield initially supersaturated single-phase solid solutions. Specimens are heat treated primarily in powder form, without compaction, to minimize constraint effects. The heat treatment schedule is designed to highlight differences in temperature capability, rather than maximum time at temperature without loss of stability. Phase analysis is predominantly by X-ray diffraction.

Work on the Y-Gd system [1] has shown that  $t'$  stabilized by Gd alone is significantly less resistant to partitioning at high temperature than its Y counterpart with the same amount of stabilizer (Figure 1). However, modest substitution of Gd for Y does not degrade the stability, and may improve it in some cases. Increasing the total amount of stabilizer generally enhances phase stability. It is noted, however, that such enhancement is usually not accompanied by an increase in cyclic life for the Y based compositions [2], as well as those co-doped with rare earths [3].

Results for rare-earth co-doped systems ranging from Yb to La, alone and in combination with Y, will be presented. In general, the phase stability at the same total content of stabilizer is expected to follow a pattern similar to that observed for Gd, with some important differences in the temperature capability. The thermodynamic and kinetic reasons for this behavior will be discussed.

Co-doping with pentavalent cations such as Ta compensates for the anion vacancies introduced by Y and other trivalent stabilizers. Hence, the stabilization model is different than in the case of trivalent rare earths [4] and the relative stability of the tetragonal phase (vs. the cubic form) is enhanced with increasing Ta:Y ratio (up to 1) [5]. The implications will be discussed in the context of the established phase equilibria within this system.

### References

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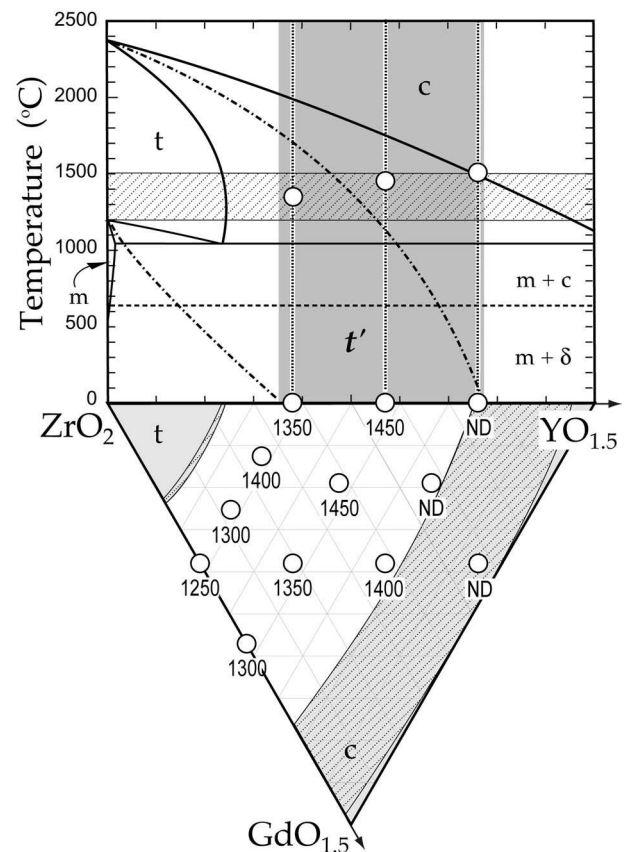


Fig. 1. The binary  $\text{ZrO}_2$ - $\text{YO}_{1.5}$  system shows the different thermodynamic scenarios that arise from varying Y content. The shaded area represents the domain in which a metastable  $t'$  phase that is thermodynamically non-transformable to monoclinic can be produced. The hatched area highlights the temperature range of interest for advanced TBCs. The leaner compositions (e.g. 7.6% $\text{YO}_{1.5}$ ) will be  $t'$  at all temperatures, while the richer composition (15.2% $\text{YO}_{1.5}$ ) will be metastable cubic ( $c'$ ). Intermediate compositions (e.g. 11.4% $\text{YO}_{1.5}$ ) can be  $t'$  at ambient but  $c'$  in the operating temperature range. The circles represent the maximum temperature prior to the step in the heat treatment schedule wherein substantial monoclinic formation was observed. The effects of Gd substitution or addition to the above compositions are summarized in the  $\text{ZrO}_2$ - $\text{YO}_{1.5}$ - $\text{GdO}_{1.5}$  ternary section under the binary. The hatched areas in the ternary represent the shift in the phase boundaries with increasing temperature (from higher to lower concentrations). The numbers next to the composition points refer to the maximum temperature before substantial monoclinic phase formation was detected. (ND = no decomposition).