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6. AUTHORS
Jackie Y. Ying
Justin T. McCue

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
Department of Chemical Engineering
Massachusetts Institute of Technology
77 Massachusetts Avenue, Room 66-544
Cambridge, MA 02139-4307

8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)
Office of Naval Research
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13. ABSTRACT *(Maximum 200 words)*
This report describes the synthesis, thermal stability and coating of nanocrystalline oxide composites for thermal barrier coating applications. The composites consisted of alumina-zirconia and alumina-yittria stabilized zirconia. The effect of alumina and yittria content on zirconia phase stability was examined. It was found that alumina-zirconia composites underwent phase transformation upon heat treatment at 950-1100 C. A small amount of yttria additive (1%) prevented zirconia phase transformation. Addition of alumina to the yttria stabilized zirconia system suppressed grain growth below 1100 C. The yttria stabilized zirconia powders were successfully coated onto Ni substrates using electrophoretic deposition. The composition of the coating solution was systematically varied to attain the optimal suspension for coating applications.

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Processing and Deposition of Nanocrystalline Oxide Composites
for Thermal Barrier Coatings

Technical Report on ONR Grant No. N00014-95-1-0626
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Jackie Y. Ying
Department of Chemical Engineering
Massachusetts Institute of Technology
Room 66-544, 77 Massachusetts Avenue
Cambridge, MA 02139-4307
Tel: (617) 253-2899
Fax: (617) 258-5766

Alumina-Zirconia Nanocomposites

Synthesis

As reported earlier [1], Al_2O_3-ZrO_2 nanocomposite powders were successfully synthesized via three routes: (1) co-precipitation, (2) heterogeneous precipitation, and (3) colloidal mixing. The colloidal mixing route has led to samples with the best ZrO_2 phase stability. This synthesis route was therefore used to develop various Al_2O_3-ZrO_2 nanocomposites.

In the colloidal mixing approach, commercially available zirconia and alumina sols were used as the precursors for the nanocomposite powders. Following mixing of the colloidal sols, the resulting particles were dried and calcined at 650 °C for 8 h. The nanocomposite powders were then isostatically pressed into pellets (10 mm diameter, 5 mm thick) with 50,000 psi at room temperature. The pellets were then calcined for 8 h in O_2 at temperatures varying from 650°C to 1400 °C for phase stability studies.

Thermal Stability

Figure 1 shows the X-ray diffraction (XRD) patterns of 10 wt% Al_2O_3-ZrO_2 nanocomposite after heat treatment at various temperatures. After calcining at 650 °C, 100% tetragonal phase was obtained for zirconia. Tetragonal → monoclinic phase transformation was noted in the XRD pattern of 10 wt% Al_2O_3-ZrO_2 heated to 950 °C. This phase transformation was slightly suppressed by introducing more Al_2O_3 to the Al_2O_3-ZrO_2 nanocomposites. For 30 wt% Al_2O_3-ZrO_2 samples, phase transformation was noted at a higher temperature of 1100 °C (see Table 1).

For application as a thermal barrier coating, zirconia should remain in the tetragonal phase even at high temperatures. Tetragonal → monoclinic phase transformation results in a volume expansion that is detrimental to the mechanical stability of the zirconia-based coating. To suppress this phase transformation in the Al_2O_3-ZrO_2 nanocomposites, a 1.3 wt% yttria-stablized zirconia (YSZ) colloidal sol was used instead of a pure zirconia sol in the colloidal mixing approach.

Figure 2 shows the XRD patterns of 1.3% wt% Y_2O_3-ZrO_2 after various heat treatments. The ZrO_2-based system retained a pure tetragonal phase up to 1400 °C. The small amount of yttria dopant stabilized the tetragonal zirconia phase successfully. Al_2O_3-YSZ nanocomposites showed excellent phase stability as well, with no phase transformation detected at 1400 °C. Table 1 summarizes the ZrO_2 phase transformation temperature for various ZrO_2-based nanocomposites.

Table 2 shows tetragonal zirconia grain size as a function of calcination temperature for the various Al_2O_3-YSZ nanocomposites. Below 1100 °C, alumina suppressed zirconia grain growth. At 950 °C, tetragonal ZrO_2 grain size in 20 wt% Al_2O_3-YSZ was 20 nm, compared to 33 nm for YSZ. At temperatures $\geq$ 1100 °C, significant grain growth was noted for YSZ and all Al_2O_3-YSZ composites.

Electrophoretic Deposition

Electrophoretic deposition has been investigated as a means of depositing ZrO_2-based nanocomposite powders for thermal barrier coating applications. For the initial coating studies, 1.3 wt% Y_2O_3-ZrO_2 powders obtained via colloidal processing were used. The coating solution consisted of ethanol, water, nitric acid, and the nanocrystalline YSZ powder. Ethanol was used as the main component to provide a low electrical conductivity and a low viscosity for the electrodeposition process. A small amount of water was added to increase the dielectric constant of the solution. Nitric acid was introduced to increase the surface charge of the particles in the suspension. YSZ powder was mechanically milled for 24 h for particle deagglomeration, and then added to the coating solution to form a slurry. The slurry was ultrasonicated for 15 minutes and aged for 24 h. Ni electrodes were then lowered into the slurry and a DC voltage (~ 30 V/cm) was applied for 30-600 seconds to coat the Ni cathode with the YSZ powder. The electrodes were then removed from the slurry and the coated Ni cathode was dried at 110 °C for 2 h. Following drying, the coated sample was cold isostatically pressed at 50,000 psi to increase its mechanical stability.

The composition of the coating solution was varied systematically to attain the optimal suspension for coating applications. Uniform, mechanically stable YSZ coatings (Figure 3) were achieved using a coating solution with 0.66 g/ml ethanol, 8.2×10^{-2} g/ml water, 1.7×10^{-3} g/ml nitric acid and 5.9×10^{-2} g/ml of YSZ powder.

Future work will focus on deriving thermally stable Al_2O_3-YSZ coatings on Ni-based substrates. Prior to deposition of the Al_2O_3-YSZ thermal barrier coatings, a NiCrAlY bond coat will be applied onto the Ni substrate via electrodeposition. The coatings will be heat treated at elevated temperatures (1000 °C – 1400 °C) for extended periods and will be subjected to thermal cycles of 25 °C-1150 °C-25 °C (with ramping and cooling rates of ~300 °C/min) to examine any failure modes for the coatings. Coatings of various alumina, zirconia and yttria contents will be investigated to achieve systems with optimal thermal and mechanical stability for thermal barrier coating applications.

References

[1] Ying, J.Y. "FY98 End of Fiscal Year Letter for ONR Grant No. N00014-95-1-0626", Oct. 1998.

Table 1. Phase transformation temperatures of various zirconia-based nanocomposites.

Sample	Composition	Phase Transformation Temperature (°C)
Al_2O_3-ZrO_2#1	10 wt% Al_2O_3, 90 wt% ZrO_2	950
Al_2O_3-ZrO_2#2	20 wt% Al_2O_3, 80 wt% ZrO_2	950
Al_2O_3-ZrO_2#3	30 wt% Al_2O_3, 70 wt% ZrO_2	1100
YSZ#1	98.7 wt% ZrO_2, 1.3 wt% Y_2O_3	>1400
YSZ#2	99.4 wt% ZrO_2, 0.6 wt% Y_2O_3	>1400
Al_2O_3-YSZ#1	5.0 wt% Al_2O_3, 94 wt% ZrO_2, 1.2 wt% Y_2O_3	>1400
Al_2O_3-YSZ#2	10 wt% Al_2O_3, 89 wt% ZrO_2, 1.2 wt% Y_2O_3	>1400
Al_2O_3-YSZ#3	20 wt% Al_2O_3, 79 wt% ZrO_2, 1.0 wt% Y_2O_3	>1400

Table 2. Tetragonal zirconia grain size as a function of calcination temperatures for various nanocomposites.

Sample	Tetragonal ZrO_2 Grain Size (nm)			
	650 °C	950 °C	1100 °C	1200 °C
1.3 wt% Y_2O_3-ZrO_2 (YSZ)	13	33	75	>100
5.0 wt% Al_2O_3-YSZ	11	28	77	>100
10 wt% Al_2O_3-YSZ	8.8	22	82	>100
20 wt% Al_2O_3-YSZ	6.0	20	78	>100

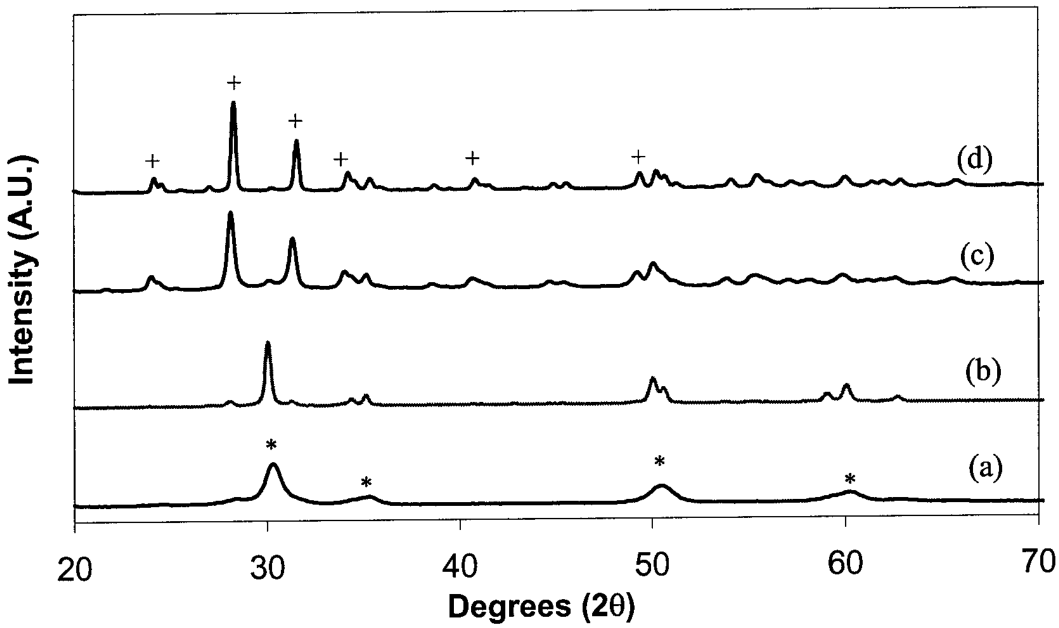

Figure 1. X-ray diffraction patterns of 10 wt% Al_2O_3-ZrO_2 after heat treatment at (a) 650 °C, (b) 950 °C, (c) 1100 °C, and (d) 1250 °C. All peaks noted correspond to the tetragonal phase (*), except for peaks noted with + (monoclinic phase).

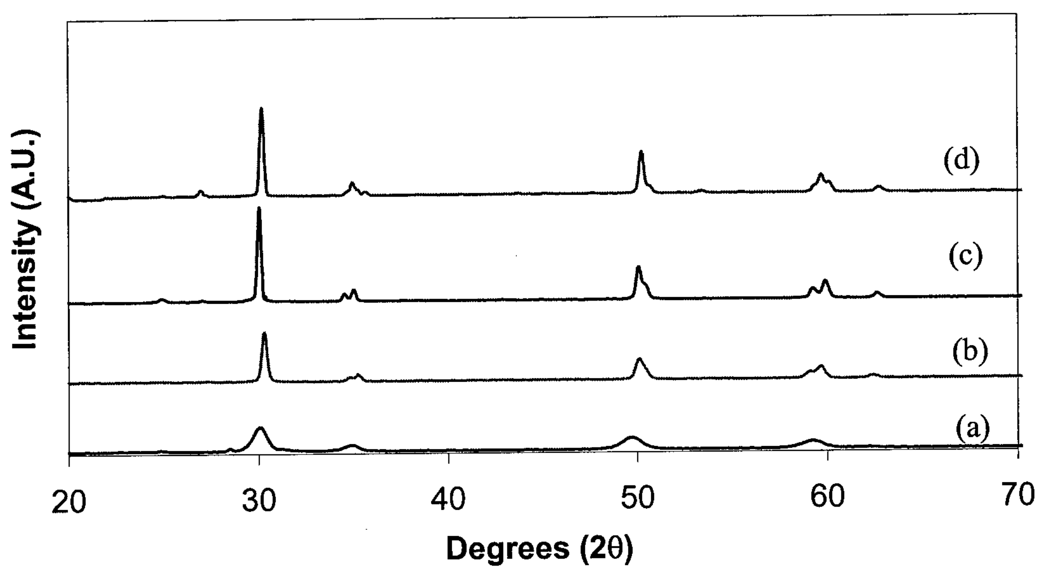

Figure 2. X-ray diffraction patterns of 1.3 wt% Y_2O_3-ZrO_2 after heat treatment at (a) 650 °C, (b) 1100 °C, (c) 1250 °C, and (d) 1400 °C. All peaks noted correspond to the tetragonal phase.

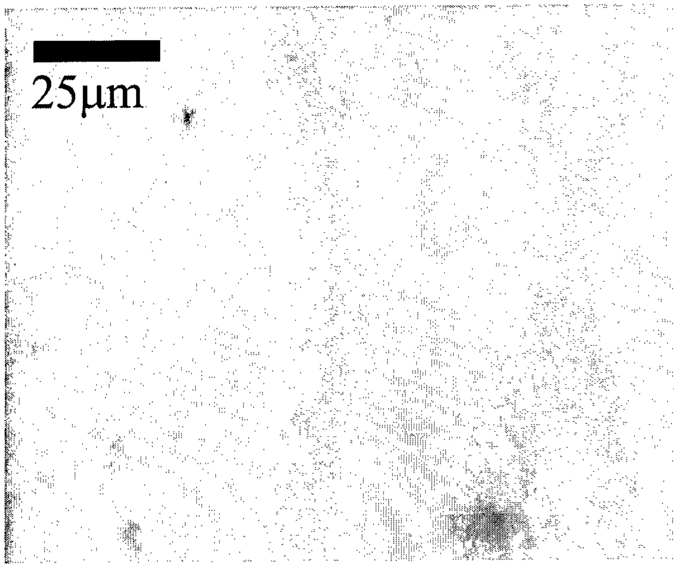

Figure 3. Optical micrograph of 1.3 wt% Y_2O_3-ZrO_2 coating on a Ni substrate.