MECHANISM OF THERMAL BARRIER COATING FAILURE AT HIGH TEMPERATURE

Ceramic thermal barrier coatings (TBCs) are used in gas turbine engines and other combustion components to allow operation at increased temperatures, which increases efficiency, reduces cooling requirements, and extends component life. They are currently used in aircraft engines and are expected to be adopted for energy-generating gas turbines and diesel engines in the near future. It has been estimated that for the US power generation sector alone, a one percent increase in efficiency would lead to a savings of \$140M per year.

The most common industrial TBC is yttria stabilized zirconia (YSZ), which consists of zirconia, ZrO_2 , with about 8 wt % yttria, Y_2O_3 (equivalent to 8.7 mol % $YO_{1.5}$). Many factors contribute to the stability of YSZ coatings, including particle size and homogeniety of feedstock powders, coating deposition techniques, and metallic bond coat characteristics. We have been investigating the inherent stability of the crystallographic phases present in plasma-sprayed YSZ using neutron Rietveld refinement for quantitative phase analysis.

YSZ consists of three crystallographic phases: monoclinic, tetragonal, and cubic. According to the phase diagram, the tetragonal phase is predominant at about 8 wt % yttria. However,

plasma spraying is a rapid solidification process that results in metastable phase mixtures of the monoclinic phase (0–6 wt % yttria), tetragonal phase (4–13 wt % yttria), and cubic phase (11–20 wt % yttria). It is thought that the coexistence of the tetragonal and cubic phases toughens the TBC through inhibition of crack propagation; however a presence of 5% or greater of the monoclinic phase results in coating instability because the monoclinic phase transforms to the tetragonal phase upon heating. Since this transformation is accompanied by a large volume change, thermal cycling generates stresses in the coatings leading to premature failure.

In order to simulate high-temperature operating conditions, we annealed plasma-sprayed YSZ coatings for periods of one to 100 hours at temperatures of 1000, 1200, and 1400°C. These coatings were prepared from two feedstock powders with differing characteristics; feedstock 1 was prepared by a spheroidization process and feedstock 2 by fusing and crushing. High-resolution neutron powder diffraction patterns were obtained on the NCNR 32-detector powder diffractometer at BT-1 and the data were analyzed using the Rietveld refinement technique. Results of the



FIGURE 1. Change in phase composition of YSZ coatings upon annealing. P = starting feedstock powder; A-S is the as-sprayed coating.

phase analysis of the feedstock powders, as-sprayed coatings, and annealed coatings are given in Fig. 1.

The two feedstock powders, 1 and 2, have quite different initial phase compositions: 1 has about 25 % of the monoclinic phase, whereas 2 has virtually none. The plasma-sprayed coatings are initially different as well, with coating 1 having 25 % cubic phase content and coating 2 being almost totally tetragonal. The phase content of both coatings changes gradually with annealing for longer times or at higher temperature (see Fig. 1), showing a general increase in the cubic phase content and decrease in the tetragonal phase content. However, with longer annealing times at 1400°C a significant increase in the monoclinic phase content is seen; both 1 and 2 have nearly identical phase compositions after annealing for 24, 48, and 100 hours and sufficient monoclinic phase is present to cause coating failure.

While the general phase behavior upon annealing has been known for some time from x-ray studies, the use of the neutron Rietveld technique permits us to extract more information based

TABLE 1. Yttria content of tetragonal (T) and cubic (C) phases given in mol % YO_{1.5}; estimated accuracy is ±0.2 mol % for the tetragonal phase in the annealed coatings and ±1 mol % for all other values. Yttria content of the monoclinic phase is assumed to be 3 mol % for the calculation of total yttria content.

	Feedstock 1			Feedstock 2		
Sample	т	C	total	т	C	total
Powder	7	14	8	6	7	6
As sprayed	8	15	9	8		8
1000 C/ 1h	6.6	14	9	7.4		7
10h	6.4	15	8	7.1	3	7
100h	6.2	15	8	6.9	4	7
1200 C/ 1h	6.2	15	9	7.1	5	7
10h	5.8	16	9	6.8	7	7
100h	5.0	17	9	5.3	11	7
1400 C/ 1h	5.2	14	9	5.7	8	7
10h	4.2	14	9	4.0	9	7
24h	3.8	12	8	3.5	8	6
48h	4.3	14	9	4.6	11	7
100h	6.7	14	9	7.0	10	7

upon the unit cell parameters of the tetragonal and cubic phases. It is known that the lattice parameter *a* of the cubic phase increases linearly with yttria content, and that the c/a ratio for the tetragonal phase decreases with increasing yttria content. Earlier studies, however, either underestimated the cubic phase content or assumed equal yttria content for the tetragonal and cubic phases. We were able to use the unit cell parameters obtained from the neutron data to extract the distribution of yttria in these phases assuming that the total yttria content is constant. Results are given in Table 1. Note that the nominal composition for both samples is 8.7 mol % YO_{1.5} but that sample 2 appears to be low in total yttria content.

The data given in Table 1 give an indication as to why the phase changes on annealing occur. It can be seen that even at the lower annealing temperatures the yttria is leaving the tetragonal phase and entering the cubic phase, resulting in higher yttria content of the cubic phase (coating 2) and increased cubic phase fraction (coatings 1 and 2). As the samples are annealed for longer periods at higher temperatures, the yttria content of the tetragonal phase drops below 3-4 mol % $YO_{1.5}$, and destructive transformation to the monoclinic phase occurs.

These results indicate that there is an inherent limit to the temperature and time of YSZ component operation. While technological improvements to YSZ coatings are possible, new materials will be needed to achieve significantly higher operating temperatures.