

# Furnace Cyclic Oxidation Behavior of Multicomponent Low Conductivity Thermal Barrier Coatings

Dongming Zhu, James A. Nesbitt, Charles A. Barrett, Terry R. McCue, and Robert A. Miller

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Ceramic thermal barrier coatings (TBCs) will play an increasingly important role in advanced gas turbine engines due to their ability to further increase engine operating temperatures and reduce cooling, thus helping achieve future engine low emission, high efficiency, and improved reliability goals. Advanced multicomponent zirconia ( $\text{ZrO}_2$ )-based TBCs are being developed using an oxide defect clustering design approach to achieve the required coating low thermal conductivity and high-temperature stability. Although the new composition coatings were not yet optimized for cyclic durability, an initial durability screening of the candidate coating materials was conducted using conventional furnace cyclic oxidation tests. In this paper, furnace cyclic oxidation behavior of plasma-sprayed  $\text{ZrO}_2$ -based defect cluster TBCs was investigated at 1163 °C using 45 min hot-time cycles. The ceramic coating failure mechanisms were studied using scanning electron microscopy (SEM) combined with x-ray diffraction (XRD) phase analysis after the furnace tests. The coating cyclic lifetime is also discussed in relation to coating processing, phase structures, dopant concentration, and other thermo-physical properties.

**Keywords** grain growth, oxide defect cluster, phase transformation and toughening, thermal barrier coatings, thermal conductivity, thermal cyclic life

## 1. Introduction

Ceramic thermal barrier coatings (TBCs) have received increased attention for advanced gas turbine engine applications. The advantages of using TBCs include increased engine efficiency by allowing higher gas temperatures and improved reliability from lower component temperatures. Future TBC systems will be more aggressively designed for the thermal protection of engine hot-section components, thus allowing significant increase in engine operating temperatures, fuel efficiency, and reliability. However, the increases in engine temperature can raise many coating durability issues.<sup>[1,2]</sup> The development of next-generation lower thermal conductivity and improved thermal stability TBCs becomes a necessity for advancing the ultra-efficient and low emission gas turbine engine technology.

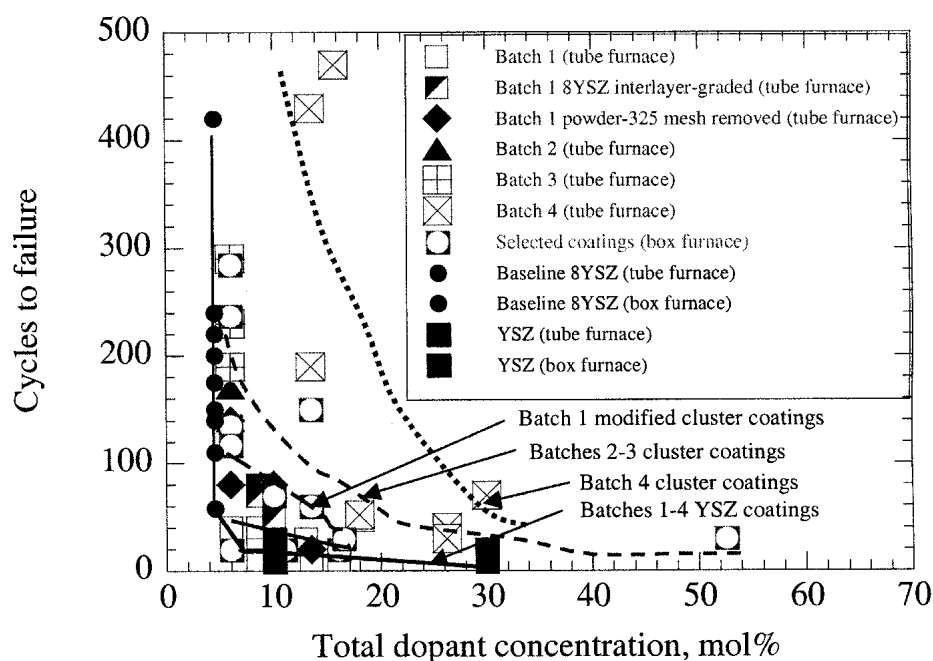
Many new TBC materials have been proposed to achieve low thermal conductivity and high-temperature capability of the coating systems.<sup>[3-20]</sup> The two most important material categories for advanced TBC applications include novel oxide compound materials such as pyrochlore-, perovskite-, and magnetoplumbite-type ceramics,<sup>[3-11]</sup> and advanced multicomponent oxide-doped  $\text{ZrO}_2$  and  $\text{HfO}_2$  solid solution based ceramics.<sup>[11-18]</sup> In particular,  $\text{ZrO}_2$  and  $\text{HfO}_2$  solid solution based thermal barrier

coatings, co-doped with the primary stabilizer  $\text{Y}_2\text{O}_3$  and additional paired rare-earth defect cluster oxides using an oxide defect clustering design approach, have been found to possess significantly lower thermal conductivity and better sintering resistance at high temperatures than current state-of-the-art  $\text{ZrO}_2$ -(7-8) wt.%  $\text{Y}_2\text{O}_3$  TBCs.<sup>[11,14-15]</sup> The solid solution based oxide TBCs may potentially also have better cyclic durability due to their possible higher toughness values, as compared with the relatively low toughness oxide compound materials.<sup>[8]</sup> The purpose of this paper is to report the furnace cyclic oxidation performance of plasma-sprayed multicomponent zirconia-based thermal barrier coatings as a function of dopant concentration and processing variations. The ceramic coating failure mechanisms were investigated using scanning electron microscopy (SEM) combined with x-ray diffraction (XRD) phase analysis after the furnace cyclic tests. The coating cyclic lifetime is discussed in relation to coating processing, phase structures, dopant concentration, and other thermo-physical properties. It should be mentioned that although these coatings were not optimized for cyclic durability in terms of the compositions and processing, the early stage furnace cyclic oxidation screening tests of a large number of the new coating systems helped to guide coating design directions using more sophisticated compositional modification and processing optimization approaches. The coating thermal conductivity and cyclic oxidation life information will be used to down-select coatings for the laser-simulated engine high-heat-flux thermal gradient cyclic testing at much higher surface temperatures, which is a critical step for the development of advanced high-performance coating systems.

## 2. Experimental Materials and Methods

Plasma-sprayed multicomponent rare-earth ( $\text{RE}_2\text{O}_3$ ) oxide doped  $\text{ZrO}_2$  TBCs were used for the furnace cyclic oxidation

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**Fig. 1** Furnace cyclic oxidation test results showing the coating cycles to failure as a function of total dopant concentration for plasma-sprayed  $\text{ZrO}_2$ -based thermal barrier coatings. The coating cyclic life generally decreases with increasing total dopant concentration, and the multicomponent rare-earth cluster oxide coatings showed evidence of having better cyclic durability than yttria-stabilized-zirconia (YSZ) binary coatings at given dopant concentrations.

tests. The coatings were the  $\text{ZrO}_2$ -based oxides, stabilized with the primary yttria ( $\text{Y}_2\text{O}_3$ ) dopant and/or paired Group A (such as  $\text{Nd}_2\text{O}_3$ ,  $\text{Gd}_2\text{O}_3$ , and  $\text{Sm}_2\text{O}_3$ ) and Group B (such as  $\text{Yb}_2\text{O}_3$ ,  $\text{Sc}_2\text{O}_3$ ) rare-earth oxide co-dopants.<sup>[13-15]</sup> The total dopant concentration for the coatings ranged from 4.5 to 52.5 mol%. These multicomponent oxide cluster coatings were found to have significantly lower thermal conductivities and better thermal stability in a wide (especially in the lower) total dopant concentration range as compared with the conventional  $\text{ZrO}_2$ -8 wt.%  $\text{Y}_2\text{O}_3$  (8YSZ, or  $\text{ZrO}_2$ -4.55 mol%  $\text{Y}_2\text{O}_3$ ) coatings. The optimum thermal conductivity region was reported in the range of 6-13 mol% total dopant concentrations, believed to be near the tetragonal/cubic phase boundary region of the zirconia alloys, where 50-60% conductivity reductions have been observed for some of the best coating systems after the 20 h thermal exposure at 1316 °C.<sup>[15]</sup>

The defect cluster coating systems consisted of a 120  $\mu\text{m}$  thick NiCoCrAlY or NiCrAlY bond coat and a 180-250  $\mu\text{m}$  thick ceramic top coat, which were plasma-sprayed on to a 25.4 mm diameter and 3.2 mm thick nickel base superalloy, René N5 disk substrates. The bond coat was processed using the typical low-pressure-plasma-spray technique. The ceramic top coats with various designed compositions were air plasma-sprayed using pre-alloyed powders. The ceramic powders were first spray-dried, and then plasma-reacted and spheroidized (two passes) to ensure that the appropriate phase homogeneity and particle size distributions were obtained. Several batches of powders from different vendors were used in the studies. The plasma-spraying parameters and conditions for processing the oxide cluster top-coats were the same as those for the standard baseline  $\text{ZrO}_2$ -8 wt.%  $\text{Y}_2\text{O}_3$  coating. Some processing variations, including re-

moving very fine particles (<37  $\mu\text{m}$  in size), and plasma-spraying duplex layer ceramic coatings that consisted of a 50  $\mu\text{m}$  first-layer  $\text{ZrO}_2$ -8 wt.%  $\text{Y}_2\text{O}_3$  near the bond coat interface and a regular thickness (180-250  $\mu\text{m}$ ) cluster oxide coating, were also used to investigate the effects of processing and coating structure on the cyclic lifetime.

Furnace cyclic tests were carried out at 1163 °C (2125 °F) using either a tube or a box furnace in air with 45 min hot-time cycles. The cooling times were 15 min for the tube furnace test and 3 h for the box furnace, and the specimens were cooled to ~120 °C after each cooling cycle. The specimens were inspected in 10 or 20 cycle intervals. The coating cycle lifetime was determined by the cycle number when the coating failure occurred. The failure criterion used was the observed delamination or spallation region being equal or larger than 20% of the total coating area. The spalled coating specimens were examined using XRD for phase analysis, and SEM for detailed failure morphology analysis.

### 3. Results and Discussion

#### 3.1 Furnace Cyclic Oxidation Life of the Multicomponent Coatings

Figure 1 shows the furnace cyclic test results for the plasma-sprayed multicomponent oxide defect cluster coatings, the baseline  $\text{ZrO}_2$ -8 wt.%  $\text{Y}_2\text{O}_3$ , and other yttria-stabilized-zirconia (YSZ) binary coatings. The variation of coating cyclic lifetime from batch to batch is obvious. In addition, the cyclic life of the oxide coatings generally decreased with increasing total dopant concentration. The baseline  $\text{ZrO}_2$ -8 wt.%  $\text{Y}_2\text{O}_3$  coating gener-

**Table 1 Thermal Conductivity and Coefficients of Thermal Expansion of Baseline ZrO<sub>2</sub>-8 wt.% Y<sub>2</sub>O<sub>3</sub> and Multi-Component Defect Cluster Coatings**

	Thermal Conductivity, W/m K		Coefficient of Thermal Expansion, m/m K (Average Values From 25 to 1400 °C)
	As-Processed	After 20 h Exposure at 1316 °C	
Baseline ZrO <sub>2</sub> -8 wt.% Y <sub>2</sub> O <sub>3</sub>	1.0	1.3-1.5	10.5-11.0 × 10 <sup>-6</sup>
Oxide defect cluster coating	0.5-0.7	0.6-1.1	11.5-13.5 × 10 <sup>-6</sup>

ally showed good furnace cyclic durability. The multicomponent cluster oxide coatings showed evidence of having better cyclic oxidation durability than yttria-doped zirconia binary coatings at given dopant concentrations. The early failure and short cyclic lifetime of the first batch (batch 1) coating systems including the baseline ZrO<sub>2</sub>-8 wt.% Y<sub>2</sub>O<sub>3</sub>, was attributed to the dense top coat,<sup>[19]</sup> and also the NiCoCrAlY bond coat.<sup>[20]</sup> Both factors can result in large thermal- and oxidation-induced stresses in the ceramic coating, thus significantly weakening the ceramic/bond coat interface region due to extensive cracking during thermal cycling.

The cyclic durability of the initial batch cluster coatings was considerably improved (life increased by 2-3 times) using some processing modifications. Less dense oxide cluster coatings were processed by removing the fine particles (with the particle sizes below the -325 mesh or 37 µm) from the plasma-spraying powders. Improved interface adhesion and thermal shock resistance of the very low conductivity oxide coatings were also attempted by adding a thin intermediate layer of ZrO<sub>2</sub>-8 wt.% Y<sub>2</sub>O<sub>3</sub> coating (~50 µm) between the NiCoCrAlY bond coat and the oxide cluster top coatings. The two processing approaches proved effective in improving the coating life for the present furnace cyclic tests.

The further modified batch 2 and 3 coatings, which used more favorable spray particle size distributions and a NASA in-house improved NiCrAlY bond coat, showed better cyclic durability than the initial processed coatings. As can be seen from Fig. 1, even the single-layered oxide cluster coatings (without the ZrO<sub>2</sub>-8 wt.% Y<sub>2</sub>O<sub>3</sub> interlayer) generally achieved better cyclic life than the duplex ZrO<sub>2</sub>-8 wt.% Y<sub>2</sub>O<sub>3</sub>/oxide cluster two-layered coatings processed in batch 1. The cyclic life improvement was more pronounced for the lower dopant (6 mol% total dopant) concentration coatings. The oxide cluster coating life reached as high as 150 cycles for the 13.5 mol% dopant coating and 300 cycles for the 6 mol% total dopant coating. The multicomponent cluster oxide coatings showed the better cyclic durability than the YSZ binary oxide coatings (solid squares) at the equivalent dopant concentrations.

The optimum processed (batch 4) coatings, which also used the improved NiCrAlY bond coat, showed excellent cyclic resistance probably due to more optimum coating processing conditions and resulting coating microstructures. It can be seen from Fig. 1 that, even for some medium high dopant concentration coatings (13.5 mol% and 15.8 mol% total dopant), the coating life reached near 450-500 cycles. Under the same furnace cyclic tests, the baseline ZrO<sub>2</sub>-8 wt.% Y<sub>2</sub>O<sub>3</sub> coatings (solid circles) under the improved processing conditions (batches 2-4) had the furnace life ranging from 140-420 cycles. The higher dopant YSZ binary coatings (ZrO<sub>2</sub>-10 mol% Y<sub>2</sub>O<sub>3</sub>, ZrO<sub>2</sub>-12 mol% Y<sub>2</sub>O<sub>3</sub>, and ZrO<sub>2</sub>-30 mol% Y<sub>2</sub>O<sub>3</sub>) showed poor cyclic resistance. The life of these binary ZrO<sub>2</sub>-Y<sub>2</sub>O<sub>3</sub> coatings seemed less depen-

dent on the processing conditions and optimizations. The failure morphologies and mechanisms for the coating will be further discussed later in this paper.

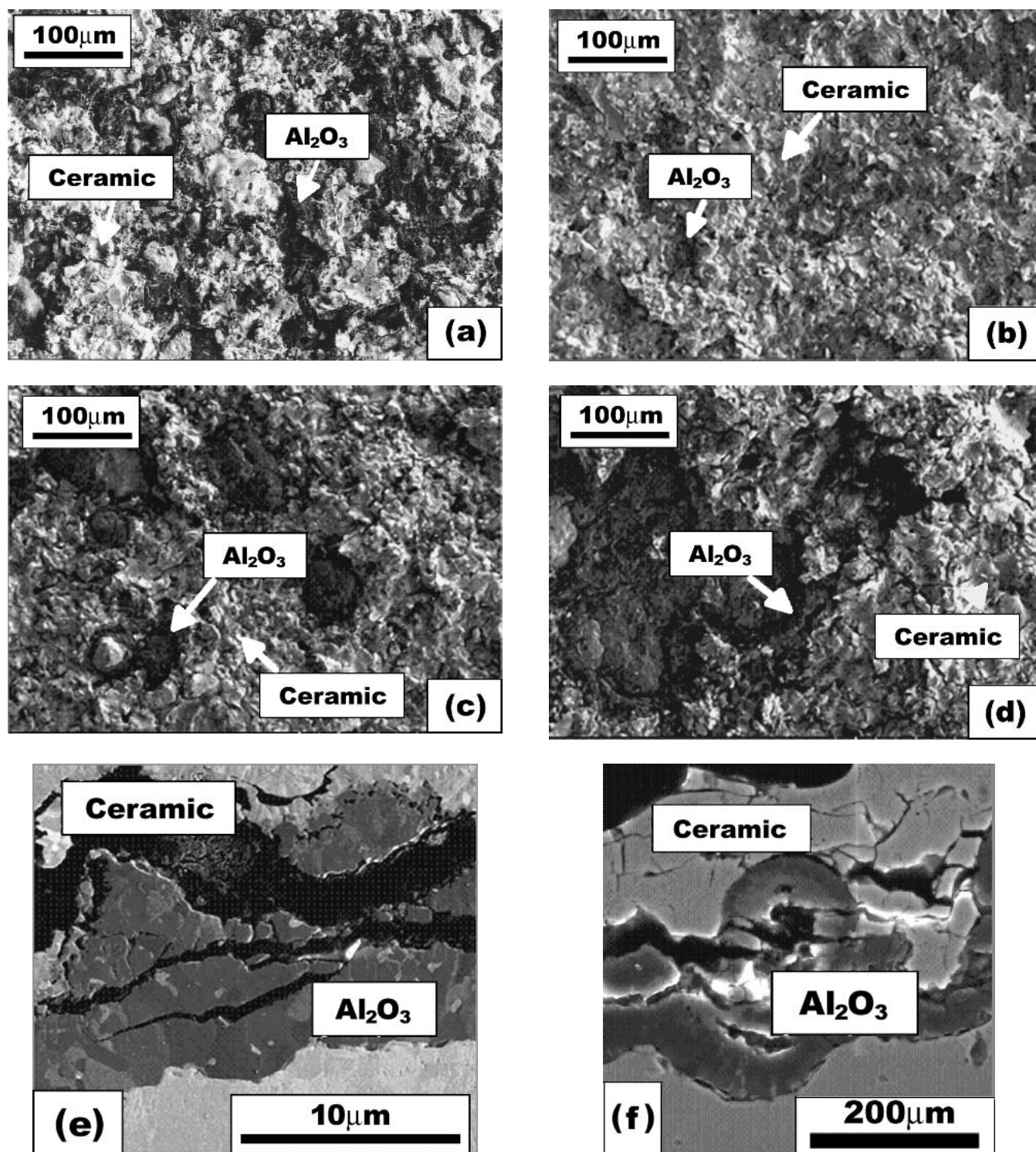
It should be mentioned that in this study, both tube furnace and box furnace tests generally showed good agreement in the coating life results. The slightly longer coating life observed in the box furnace tests may be due to the much slower cooling rate (3 h cooling for box furnace and 15 min cooling for the tube furnace), which can reduce some of the thermal shock effect for the very low conductivity and slightly higher thermal expansion cluster oxide coatings. The thermal conductivity values and thermal expansion coefficients of the multicomponent oxide cluster coating are listed in Table 1.

The strong processing and composition effects on the coating cyclic life observed in this study indicate considerable challenges, but also offer great opportunities, for the development of advanced, multicomponent, high performance thermal barrier coatings. The test results demonstrate the importance of the coating processing and composition optimizations. The beneficial effects of the added rare earth cluster oxides also shows great promise in significantly improving coating cyclic durability.

### 3.2 Failure Morphologies and Mechanisms

Figure 2 shows typical SEM micrographs of spalled coating surface morphologies and cross sections for several coating systems after the furnace cyclic testing. It can be seen that the oxide coatings generally failed in a mixed mode, i.e., the coatings were spalled under thermal cycling by a combined mechanism where the coating delaminations occurred within the ceramic top coat near the ceramic/metal bond coat interface (ceramic failure), and through the thermally grown alumina scales at the interface (oxide scale failure). The oxide scale related failure was generally involved with the separation of the ceramic/alumina scale interface, as well as the cracking/delamination within the oxide scales. However, sometimes the failure occurred at the scale/bond coat interface where the bare metal surface was exposed after the coating spallation.

The ceramic coatings with optimized processing to control coating porosity demonstrated longer cyclic life. The ceramic coatings possessing a more optimum porosity were more elastically compliant but still retained adequate coating strength. The coatings can thus have reduced thermal cyclic stresses, originating either from the thermal expansion mismatch between the ceramic and metal substrate or from the bond coat oxidation during the cycling, without significantly deteriorating the coating mechanical properties. In addition to the coating processing effect, the relatively low yttria dopant ZrO<sub>2</sub>-8 wt.% Y<sub>2</sub>O<sub>3</sub> coating and certain multicomponent cluster dopant coatings exhibited excellent thermal cycling resistance, implying also a strong



**Fig. 2** SEM images of the spalled coating surface morphologies and cross sections showing a mixed failure mode involving both the ceramic failure and scale interface failure after furnace cyclic testing: (a)  $\text{ZrO}_2$ -8 wt.%  $\text{Y}_2\text{O}_3$  ( $\text{ZrO}_2$ -4.55 wt.%  $\text{Y}_2\text{O}_3$ ); (b)  $\text{ZrO}_2$ -30 mol%  $\text{Y}_2\text{O}_3$ ; (c)  $\text{ZrO}_2$ -6 mol% (Y,Nd,Yb,Sc)<sub>2</sub>O<sub>3</sub>; (d)  $\text{ZrO}_2$ -16 mol% (Y,Sm,Yb)<sub>2</sub>O<sub>3</sub>; (e) cross section of  $\text{ZrO}_2$ -8 wt.%  $\text{Y}_2\text{O}_3$ ; (f) cross section of  $\text{ZrO}_2$ -6 mol% (Y,Gd,Yb)<sub>2</sub>O<sub>3</sub>.

compositional effect on coating cyclic performance. Since the high cyclic stress region is primarily located near the ceramic/bond coat interface (the observed ceramic failure is usually within about 10-20 μm above the interface), applying a thin layer

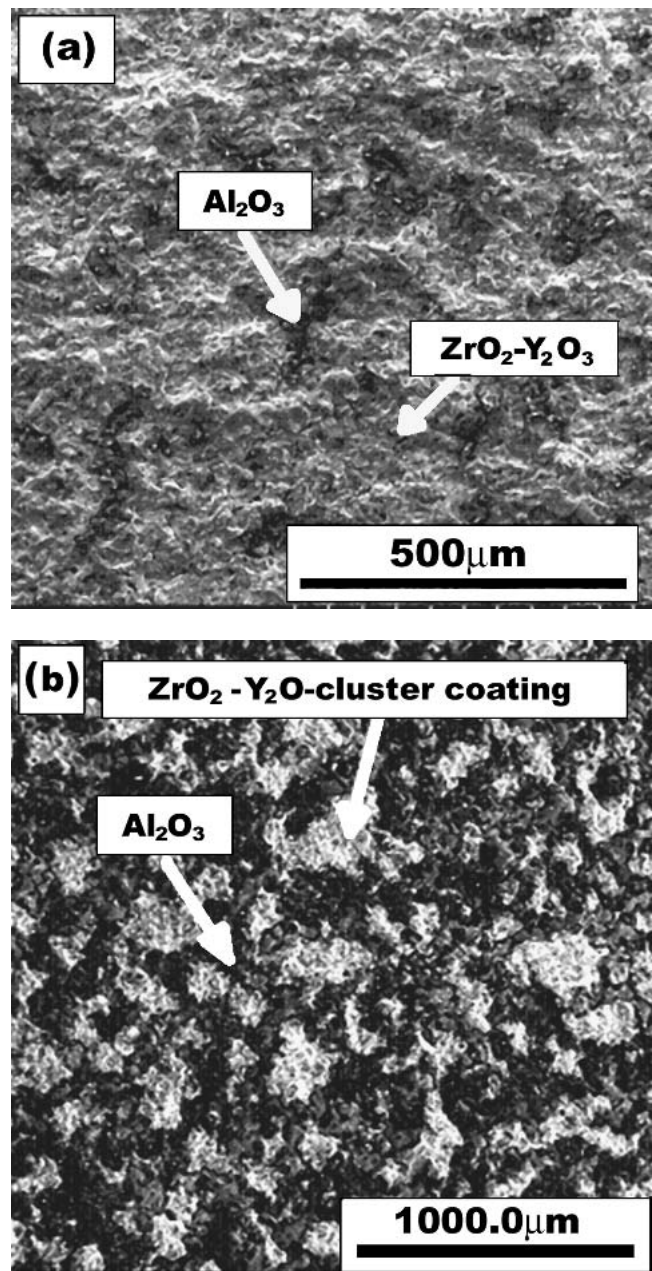
of a more cyclic stress resistant low dopant coating such as  $\text{ZrO}_2$ -8 wt.%  $\text{Y}_2\text{O}_3$  to the interface and forming a duplex coating system would greatly improve the overall coatings furnace cycling performance.

The longer life coatings, due to either improved processing or modified multicomponent rare-earth dopant compositions, typically showed a more predominant interface scale failure, as indicated by the increasing area fraction of interface scale failure region after the furnace cyclic testing. Low-magnification SEM images of the spalled surface morphologies for two distinctive performance coatings, i.e., a low toughness, poor cyclic resistance  $\text{ZrO}_2$ -30 mol%  $\text{Y}_2\text{O}_3$  (cyclic life 10-20 cycles), and a long cyclic life  $\text{ZrO}_2$ -13.5 mol% (Y, Gd, Yb) $_2\text{O}_3$  coating (cyclic life 430 cycles), are shown in Fig. 3 to exemplify the failure mechanisms.

As mentioned in the cyclic results discussion, the coatings with lower dopant concentrations generally exhibited a better cyclic resistance, suggesting a possibly more toughened phase structure in the lower concentration region. The XRD results in Fig. 4 shows the phase structure changes as a function of the dopant concentration for several oxide thermal barrier coatings. It can be seen that the  $\text{ZrO}_2$ -8 wt.%  $\text{Y}_2\text{O}_3$  and  $\text{ZrO}_2$ -6 mol% (Y,Nd/Sc) $_2\text{O}_3$  coatings had the predominant tetragonal phase structure. The  $\text{ZrO}_2$ -10 mol% (Y,Nd,Yb) $_2\text{O}_3$  and  $\text{ZrO}_2$ -12 mol%  $\text{Y}_2\text{O}_3$  coatings had mostly the cubic structure, because the tetragonal peak split of  $t(400)$  and  $t(004)$  observed for lower concentration coatings started to disappear at this composition. The higher dopant concentration coatings, such as  $\text{ZrO}_2$ -16 mol% (Y,Nd,Yb) $_2\text{O}_3$  and  $\text{ZrO}_2$ -30 mol%  $\text{Y}_2\text{O}_3$ , had a fully cubic phase structure. The fact that the coating cyclic life typically decreases with dopant concentration may suggest that the tetragonal phase has a better cyclic resistance and thus possibly higher fracture toughness; and the observed coating life decreases, corresponding to the tetragonal phase fraction decreasing, with increasing the dopant concentrations.

The better thermal cyclic resistance (thus maybe the expected higher fracture toughness) of the supersaturated tetragonal  $t'$  phase structure, as compared with the cubic phase structure, may be attributed to its long-term small grain structure and even further continuous grain size refinement due to the progressive phase transformations (tetragonal to monoclinic and/or tetragonal to monoclinic + cubic) during the thermal cycling. The refined grain sizes of the tetragonal phase can enhance the coating crack healing, which would improve the coating toughness. The martensitic phase transformation of the tetragonal phase to monoclinic phase, even at small volume fractions, may significantly toughen the ceramic coatings during the thermal cycling due to the possible crack arrest due to the formation of the monoclinic phase. The martensitic phase transformation accompanying possible favorable microcracking in the coating may also contribute to the overall coating toughening.<sup>[21]</sup>

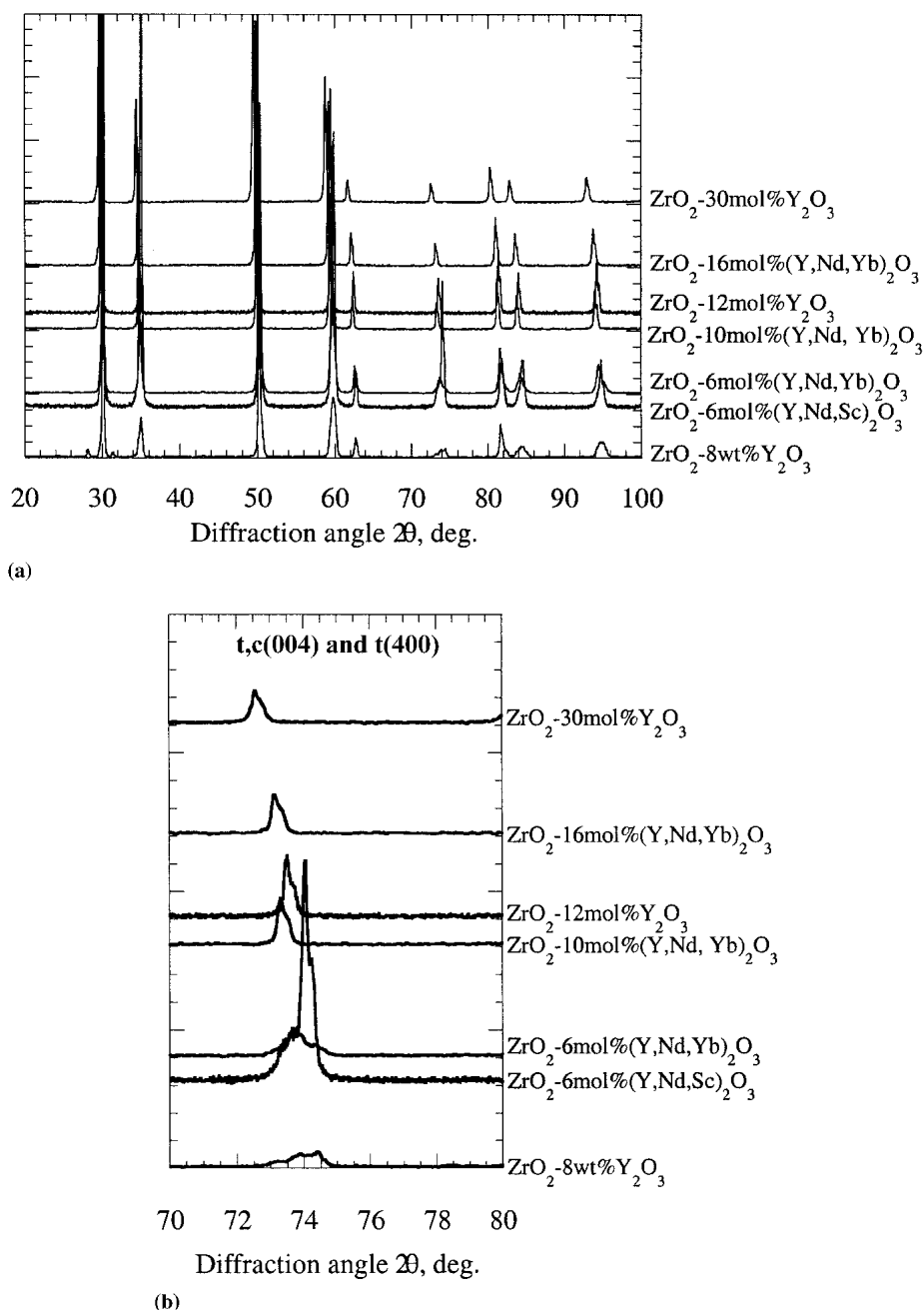
Figure 5 shows the microstructure of several coating systems after furnace cyclic testing. As can be seen from Fig. 5(a), the  $\text{ZrO}_2$ -8 wt.%  $\text{Y}_2\text{O}_3$  coating containing the partially stabilized tetragonal phase, still maintains relatively small grain sizes after extended high temperature thermal cycling testing (160 cycles). The coating also failed in a tougher mechanism, which involves severe scale interface delamination and non-brittle type ceramic coating fracture. However, as shown in Fig. 5(b) and 5(c), the higher yttria dopant content binary YSZ alloys— $\text{ZrO}_2$ -10 mol%  $\text{Y}_2\text{O}_3$  and  $\text{ZrO}_2$ -30 mol%  $\text{Y}_2\text{O}_3$  coatings that possessed the cubic phase structure—experienced significant grain growth, thus resulting in very low toughness structures. Brittle coating fracture



**Fig. 3** SEM micrographs showing the spalled thermal barrier coatings on the substrates after the furnace thermal cyclic testing (dark and bright regions are exposed alumina scales, and the remaining attached ceramic top coats, respectively): (a) low toughness  $\text{ZrO}_2$ -30 mol%  $\text{Y}_2\text{O}_3$ , cyclic life 20 cycles, showing the predominant ceramic failure; (b)  $\text{ZrO}_2$ -13.5 mol% (Y,Nd,Yb) $_2\text{O}_3$  coating, with cyclic life of 430 cycles, showing a more predominant interface scale failure.

was observed in these extensive grain growth regions after very short thermal cycles (10-30 h cycling).

The oxide defect cluster coatings showed a different grain growth behavior as compared with the binary YSZ coatings under the thermal cyclic condition. As can be seen in Fig. 5(d) and 5(e), following spalled coating interface regions of the  $\text{ZrO}_2$ -6 mol% (Y,Nd,Yb,Sc) $_2\text{O}_3$  (failed at 140 cycles) and  $\text{ZrO}_2$ -16 mol% (Y,Sm,Yb) $_2\text{O}_3$  (failed at 470 cycles), extremely fine



**Fig. 4** XRD patterns for various oxide thermal barrier coatings showing the phase structure changes as function of dopant concentration: **(a)** Diffraction patterns; **(b)** the  $\text{ZrO}_2$  (400) peak for the doped oxides.

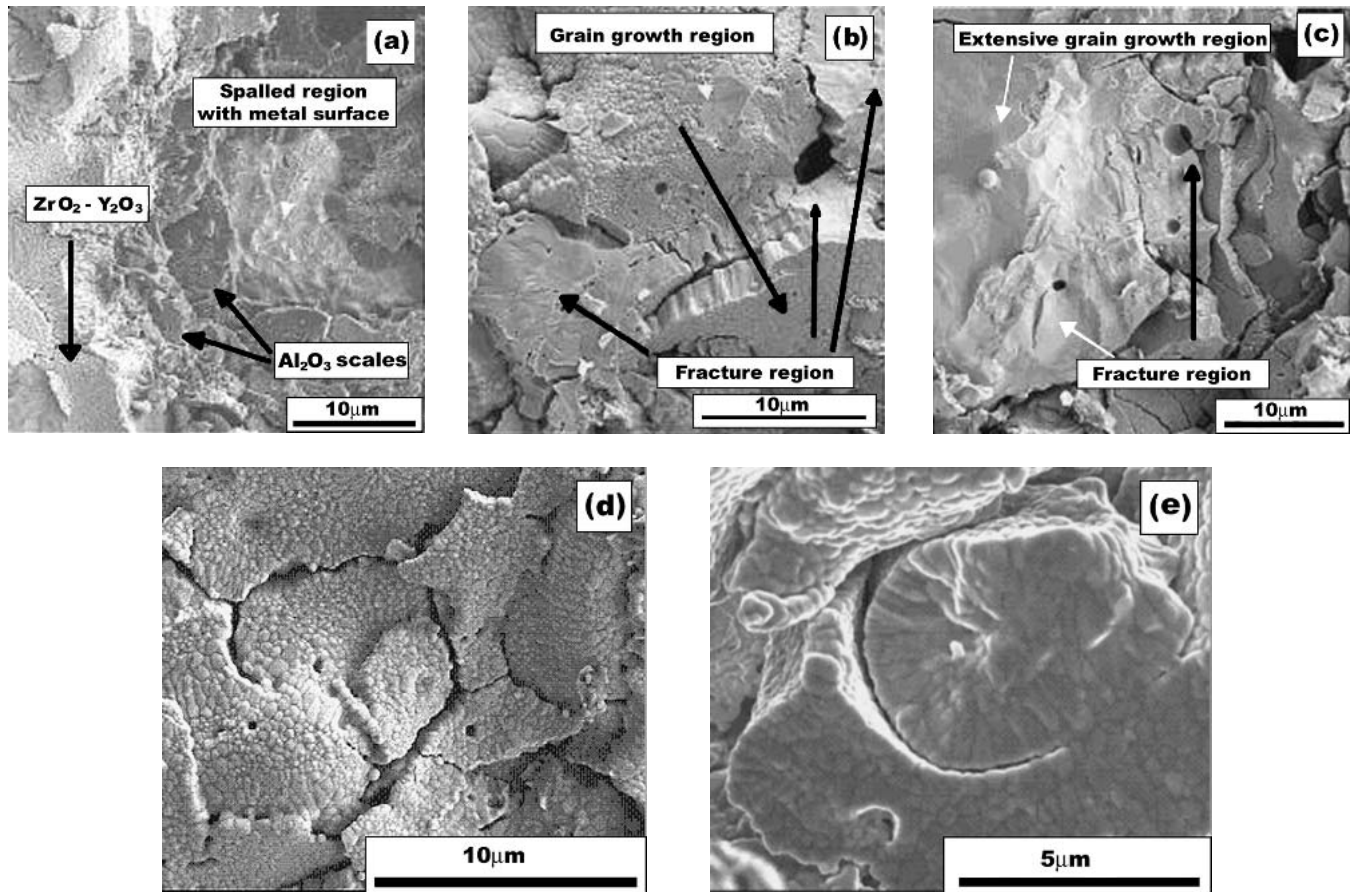
grains were observed after the long-term cyclic tests. It should be mentioned that the  $\text{ZrO}_2$ -6 mol%  $(\text{Y,Nd,Yb,Sc})_2\text{O}_3$  and  $\text{ZrO}_2$ -16 mol%  $(\text{Y,Sm,Yb})_2\text{O}_3$  coatings had a partially stabilized tetragonal structure and a fully stabilized cubic structure, respectively. The cluster dopant coatings had little grain growth even for a high dopant concentration cubic phase system.

The observed grain growth behavior as a function of the dopant concentration for the YSZ binary and multicomponent oxide defect cluster coatings is plotted in Fig. 6. The data show the grain growth generally increases with increasing total dopant concentrations. Significant grain growth (up to 2-5  $\mu\text{m}$  in size)

was observed for the higher yttria concentration, cubic phase structured YSZ coatings after the furnace cyclic testing. However, the multicomponent cluster oxide coatings showed much smaller grain sizes (typically less than 1  $\mu\text{m}$ ) at given dopant concentrations. This experimental evidence strongly suggests that the rare-earth dopants added to the  $\text{ZrO}_2$ -based coating systems can significantly suppress the grain growth at high temperatures, and thus can potentially greatly improve the coating toughness and thermal cycling resistance.

Figure 7 is a high-resolution SEM image of a cross section from a plasma-sprayed  $\text{ZrO}_2$ -8 wt.%  $\text{Y}_2\text{O}_3$  coating, showing fur-

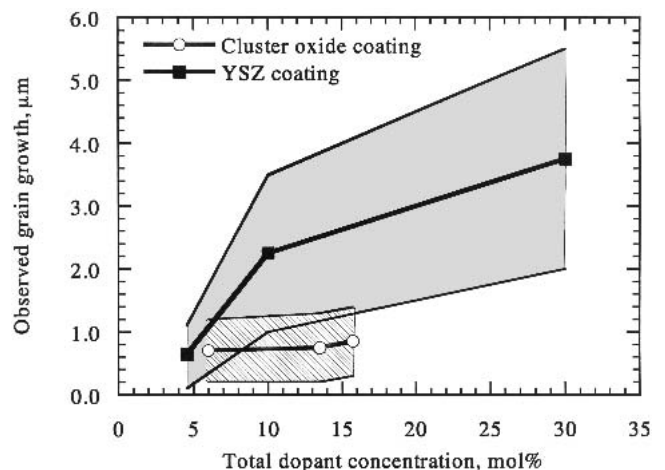




**Fig. 5** SEM showing the ceramic coating spalling/fracture morphologies near the ceramic/bond coat interface region after furnace thermal cyclic testing: (a)  $\text{ZrO}_2$ -8 wt.%  $\text{Y}_2\text{O}_3$ , 160 cycles; (b)  $\text{ZrO}_2$ -10 mol%  $\text{Y}_2\text{O}_3$ , 30 cycles; (c)  $\text{ZrO}_2$ -30 mol%  $\text{Y}_2\text{O}_3$ , 10 cycles; (d)  $\text{ZrO}_2$ -6 mol%  $(\text{Y,Nd,Yb,Sc})_2\text{O}_3$ , 140 cycles; (e)  $\text{ZrO}_2$ -16 mol%  $(\text{Y,Sm,Yb})_2\text{O}_3$ , 470 cycles.

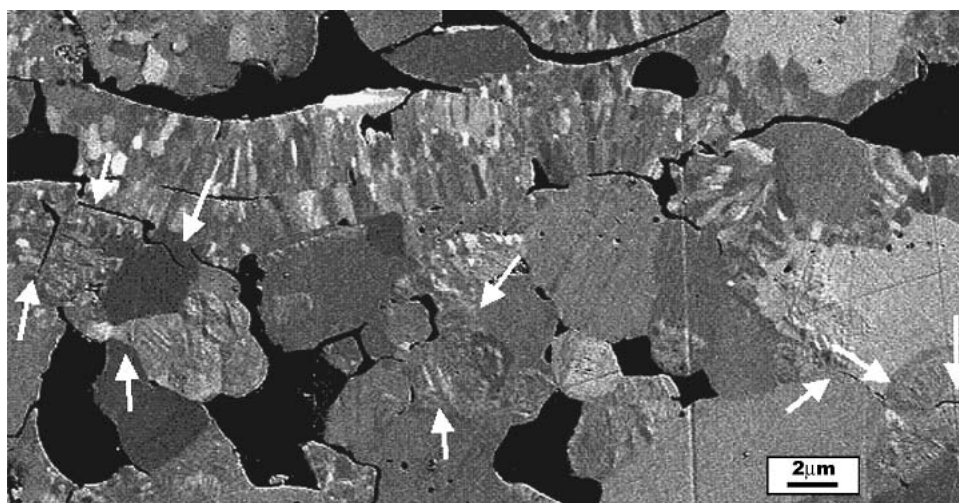
ther grain refinements and toughening by a small amount of monoclinic phase transformations (tetragonal to monoclinic and/or tetragonal to monoclinic+cubic) during the thermal cyclic testing. The grain refinements and phase transformation toughening can greatly contribute to the generally observed excellent cyclic life performance of the  $\text{ZrO}_2$ -8 wt.%  $\text{Y}_2\text{O}_3$  (at least at moderately high testing temperatures) and the lower dopant  $t'$  phase structured defect cluster coatings containing some transformable tetragonal phase. The monoclinic phase content of the plasma-sprayed  $\text{ZrO}_2$ -8 wt.%  $\text{Y}_2\text{O}_3$  coating as a function of cycle time at 1163 °C, derived from the XRD analysis based on the phase calculation approach described in literature,<sup>[22]</sup> is shown in Fig. 8. It can be seen that the monoclinic phase progressively increases with the cycle time, which may help to continuously toughen the coating structure and thus provide the excellent cyclic performance.

The test results demonstrate that the design of optimum composition and microstructured thermal barrier coatings can yield excellent cyclic performance. The ceramic coatings using improved oxide cluster compositions may potentially achieve a better toughness and cyclic life, even in a composition region which contains a fully cubic phase, due to their ability to maintain long-term fine grain structures and sintering resistance from low mobility oxide defect clusters.<sup>[15]</sup> The crack propagation in

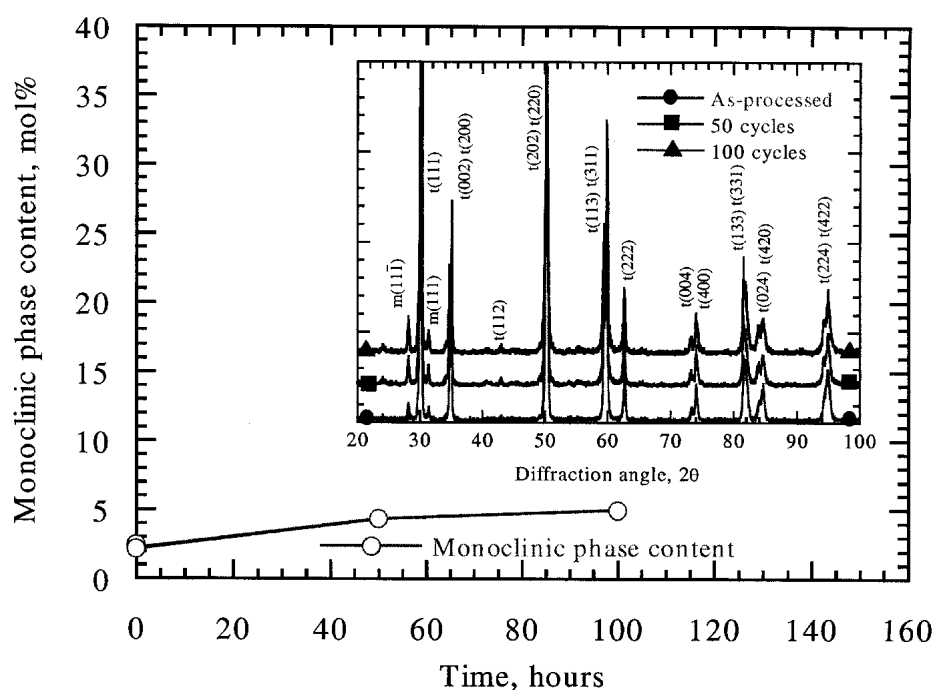


**Fig. 6** Ceramic coating grain growth after the furnace cyclic oxidation testing for the multicomponent oxide cluster coating systems and the yttria-zirconia binary coating systems. The shadowed areas in the plot show the approximate grain size distribution bands observed in many noticeable coating grain growth regions.

the coating may also be hindered by the complex stress fields associated with lattice distortions from the nano-sized oxide defect clusters. Since the tetragonal to monoclinic phase transfor-



**Fig. 7** High-resolution SEM images showing the overall fine grain structures of  $\text{ZrO}_2$ -8 wt.%  $\text{Y}_2\text{O}_3$ . Further grain refinements and toughening by a small amount of monoclinic phase transformations (tetragonal to monoclinic and/or tetragonal to monoclinic + cubic) during the thermal cyclic testing can contribute to the excellent cyclic life performance of this baseline coating and other lower dopant oxide defect cluster  $t'$  phase structured coatings. The arrows in this micrograph indicate the possible crack arrests and the ceramic toughening by the formation of the monoclinic phase (seen as rippled needle-like structure).



**Fig. 8** The monoclinic phase content of the plasma-sprayed  $\text{ZrO}_2$ -8 wt.%  $\text{Y}_2\text{O}_3$  coating as a function of cycle time at 1163 °C, derived from the XRD analysis. Insert is the XRD patterns for  $\text{ZrO}_2$ -8 wt.%  $\text{Y}_2\text{O}_3$  coating specimens under conditions of as-processed, and after testing for 50 and 100 cycles at 1163 °C in a tube furnace, respectively, showing the monoclinic phase increases progressively with the cycle time.

mation may further refine the grain structures and toughen the coating systems, a small amount of the tetragonal phase transformation may be incorporated into the coating systems under the thermal cycling conditions by utilizing advanced compositional and structural heterogeneity design approaches, thus significantly improving the coating delamination and spallation resistance.

#### 4. Concluding Remarks

The durability of plasma-sprayed  $\text{ZrO}_2$ - $\text{Y}_2\text{O}_3$  binary coatings and advanced low conductivity multicomponent cluster oxide coatings was evaluated using conventional furnace cyclic oxidation tests at 1163 °C. The results have shown that the oxide defect cluster coatings have the potential to achieve significantly



better cyclic performance than the binary  $\text{ZrO}_2\text{-Y}_2\text{O}_3$  coatings due to their improved high temperature stability, reduced grain growth, and thus increased toughness structures.

The ceramic coating cyclic life generally decreases as the dopant concentration increases presumably due to the reduced fraction of tetragonal phase and the increased fraction of the cubic phase. The fully stabilized cubic phase usually shows an enhanced grain growth behavior, and also lacks the further grain-refining and toughening mechanisms by the tetragonal to monoclinic phase transformation present in a partially stabilized tetragonal phase. Therefore, very low toughness coating structures are often observed in high-dopant-concentration coatings, and especially for the  $\text{ZrO}_2\text{-Y}_2\text{O}_3$  binary coatings.

Although the advanced multicomponent oxide defect cluster coatings followed a similar trend as the  $\text{ZrO}_2\text{-Y}_2\text{O}_3$  binary coating systems in the furnace cyclic behavior (where the coating cyclic life decreases with increasing the total dopant concentration), the oxide cluster coatings showed promise for achieving better cyclic life than the binary  $\text{ZrO}_2\text{-Y}_2\text{O}_3$  coatings with equivalent dopant concentrations. Cyclic life comparable to (or better than) that of the low dopant  $\text{ZrO}_2\text{-8 wt.% Y}_2\text{O}_3$  coating has been observed even for some medium-high-dopant-concentration, and very low-conductivity coating systems. Advanced processing and composition optimization will be used to further improve the durability of the high performance ceramic thermal barrier coating systems.

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