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Technical Note

Phase Stability of Thermal Barrier Coatings Made From 8 wt.% Yttria Stabilized Zirconia: A Technical Note

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1. Introduction

Yttria stabilized zirconia is a common material used as a thermal barrier coating (TBC) for gas turbines.[1] It is advantageous because it has a high tolerance for thermal shock, low thermal conductivity, and a higher melting point than most oxides.[2] One of the limitations of pure zirconia is the phase transitions that occur at atmospheric pressure. At temperatures less than 1170 °C, the equilibrium form of zirconia is monoclinic. Between 1170-2370 °C it is tetragonal, and at temperatures above 2370 °C it is cubic.[3] The tetragonal to monoclinic transformation is accompanied by an approximate 3% volume change that causes stress in the coating and can lead to spallation. The addition of yttria or other oxides can stabilize zirconia in its cubic or tetragonal form to below room temperature[3] (Fig. 1); however, full stabilization to the cubic phase compromises the cyclic thermal fatigue life.[4] Therefore, the most common material for TBCs is partially stabilized zirconia (PSZ) with about 8 wt.% (4.5 mol%) yttria. When PSZ with 8 wt.% yttria is plasma sprayed, the molten particles are quenched to form a metastable tetragonal phase, t′,[5] with the same composition as the molten PSZ.[6] This produces a metastable t′ phase that does not transform to the monoclinic state upon cooling. However, at typical use temperatures the t′ phase can transform to the equilibrium mixture of the cubic and transformable tetragonal phases.[7,8] This technical note addresses the kinetics of the transformation from the t′ phase to the equilibrium cubic and tetragonal phases over a much longer time period than has been previously reported.

2. Experimental

The phase stability of two TBC coatings processed to achieve different microstructures was evaluated by x-ray diffraction (XRD) to determine the phases present after various time/temperature exposures. Figure 2 shows a typical cross section of each coating; coating A has vertical cracks and coating B is a porous coating.

Freestanding samples of the coatings, i.e., no bond coat or metallic substrate, were treated in air for 100, 500, 1000, 5000, and 10 000 h at 982 °C, 1204 °C, and 1315 °C. A Scintag XDS 2000 diffractometer run at 45 kV and 40 mA was used to collect two x-ray spectra for each coating. The first spectra had a 2-theta range of 27.5-32.0° (low angles) at a step rate of 0.01° per minute with a count time of 2 s, and the second had a 2-theta range of 72.5-76.0° (high angles) at a step rate of 0.005° per minute with a count time of 10 s. DMSNT Scintag software was used to locate peaks and to measure intensities, heights, and areas in the low angle range. Analysis of the high angle range was done with Grams/32 software (Thermogalactic, Salem, NH). To label the peaks, the work of Schulz [9] was referenced. Figure 3 displays a series of typical diffraction patterns for the low 2-theta range. Figure 3(a) is for coating A heated at 982 °C for 100 h. It has the cubic and tetragonal peak at 30.1°, indicating that some

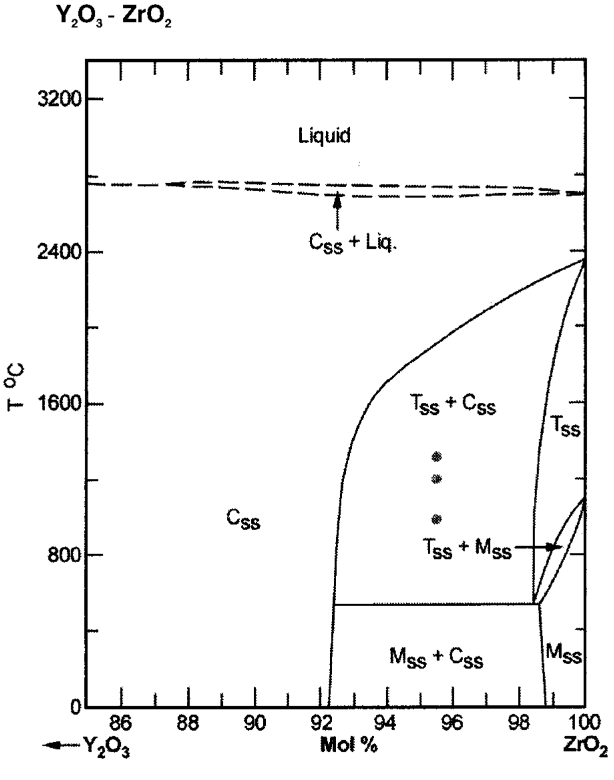

Fig. 1 The phase diagram for yttria and zirconia[3]

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of the cubic and/or tetragonal phases are present. At higher temperatures (Fig. 3b,c), the monoclinic peaks emerge at 28 and 31°. Figure 4 is a series of typical patterns for the high angle range that was used to determine the amount of tetragonal or cubic phase. Figure 4(a) shows a coating treated at 982 °C for 100 h. The two peaks present are consistent with the t′ peaks found by Schulz.[9] As the temperature and time were increased to 1204 °C for 100 and 500 h (Fig. 4b,c) there are mixtures of t′, t, and c phases present, while Fig. 4(d) and (e) shows one strong cubic peak.

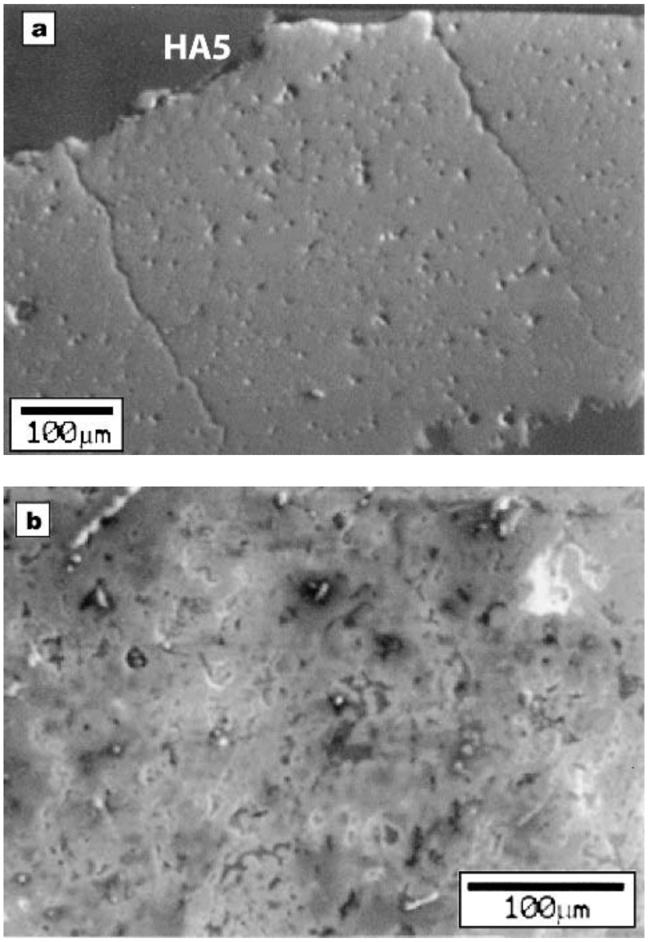

Fig. 2 Scanning electron microscope (SEM) photographs showing typical cross sections for **(a)** coating A (cracked) and **(b)** coating B (porous) coatings

Quantitative determination of each phase was calculated following a method similar to that described by Miller et al.[6] The difference is that these materials contained cubic c, tetragonal t, and tetragonal prime t′ phases. Therefore, the ratio of monoclinic to cubic and tetragonal includes the t′ phase. In addition, to determine the molar ratio of the cubic to the tetragonal phases, both tetragonal phases were included in the denominator. Finally, the molar ratio of t to t′ was related directly to the intensity ratios with no calibration factor due to the similarity of the structure factors for t and t′. The equations used were as follows:

$$\frac{M_{\mathrm{m}}}{M_{\mathrm{c,t,t'}}} = 0.82\frac{I_{\mathrm{m}}(11\bar{1}) + I_{\mathrm{m}}(111)}{I_{\mathrm{c,t}}(111)}$$

$$\frac{M_{\mathrm{c}}}{M_{\mathrm{t,t'}}} = 0.88\frac{I_{\mathrm{c}}(400)}{I_{\mathrm{t,t'}}(400) + I_{\mathrm{t,t'}}(004)}$$

$$\frac{M_{\mathrm{t}}}{M_{\mathrm{t'}}} = \frac{I_{\mathrm{t}}(400) + I_{\mathrm{t}}(004)}{I_{\mathrm{t'}}(400) + I_{\mathrm{t'}}(004)}$$

where M_{m}, M_{t}, $M_{\mathrm{t'}}$, and M_{c} are the molar fractions of the monoclinic, tetragonal, and cubic phases, and I represents the intensity of a given peak. The results are accurate to within ±5%.

3. Results and Discussion

Figure 5(a-d) shows the mol fraction of each phase present in coating A for each time and temperature tested. Raman spectroscopy showed that there is some monoclinic phase present in the as-sprayed powders, though the amount is quite small. The amount of each phase remains almost constant at a temperature

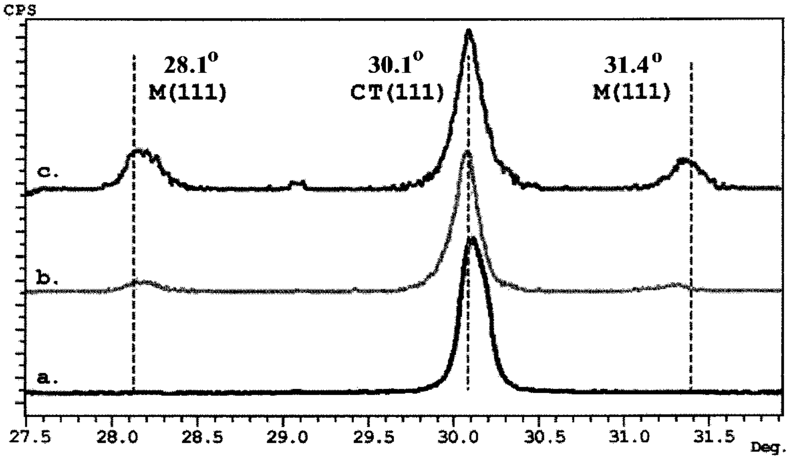

Fig. 3 Low angle XRD patterns for **(a)** 100 hours at 982 °C, **(b)** 500 hours at 1204 °C, and **(c)** 1000 hours at 1315 °C

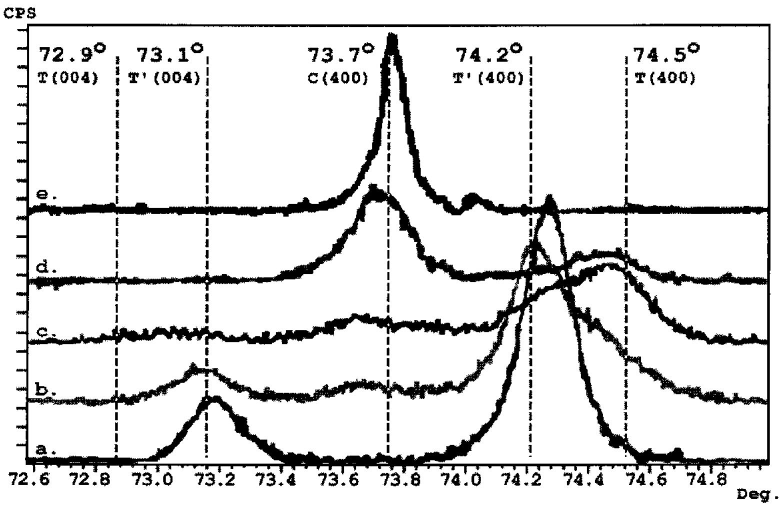

Fig. 4 High angle XRD patterns for **(a)** 500 hours at 982 °C, **(b)** 100 hours at 1204 °C, **(c)** 500 hours at 1204 °C, **(d)** 500 hours at 1315 °C, and **(e)** 10 000 hours at 1315 °C

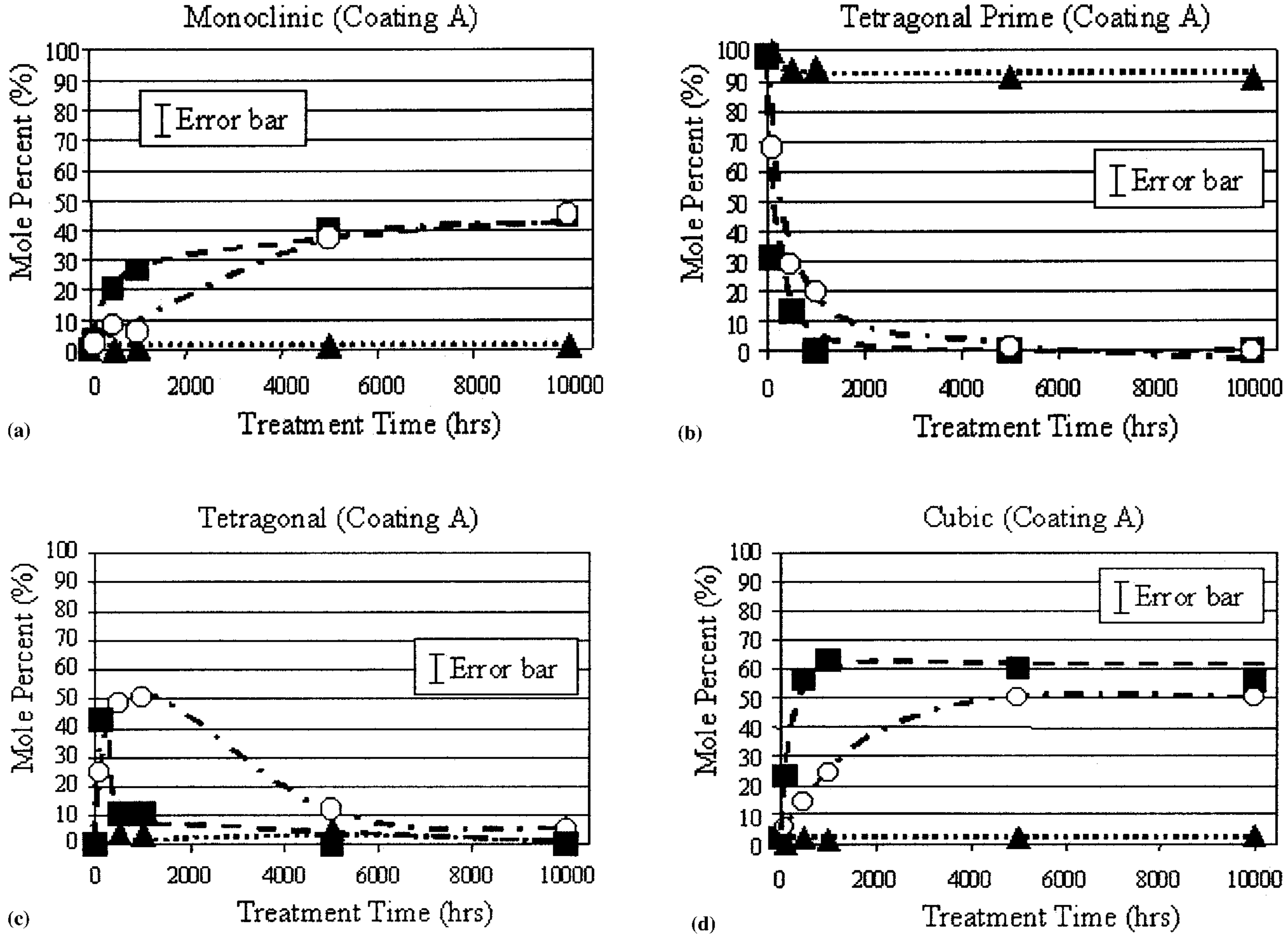

Fig. 5 **(a)** The change in mol% of the monoclinic phase for sample A as a function of time at 982 °C (▲), 1204 °C (○), and 1315 °C (■). **(b)** The change in mol% of the tetragonal prime phase for sample A as a function of time at 982 °C (▲), 1204 °C (○), and 1315 °C (■). **(c)** The change in mol% of the tetragonal phase for sample A as a function of time at 982 °C (▲), 1204 °C (○), and 1315 °C (■). **(d)** The change in mol% of the monoclinic phase for sample A as a function of time at 982 °C (▲), 1204 °C (○), and 1315 °C (■)

Table 1 The Change in mol% of Each Phase for Sample B as a Function of Time and Temperature With an Average Error of ±5%

Treatment Temperature, °C	Treatment Hours	mol% Monoclinic	mol% Tetragonal	mol% Tetragonal-Prime	mol% Cubic
982	0	2	0	91	7
982	100	0	28	34	38
982	500	19	14	5	62
982	1 000	28	10	0	61
982	5 000	36	0	0	64
983	10 000	36	0	0	64
1204	0	2	0	92	7
1204	100	0	26	62	12
1204	500	2	46	28	23
1204	1 000	2	41	21	37
1204	5 000	28	18	2	51
1204	10 000	32	5	2	61
1315	0	2	0	91	7
1315	100	0	28	34	38
1315	500	19	14	5	62
1315	1 000	28	10	0	61
1315	5 000	36	0	0	64
1315	10 000	36	0	0	64

of 982 °C for all the exposure times tested. This result is similar to that observed in Ref. 10. The small amount of monoclinic phase is desirable and typical (Fig. 5a). The tetragonal prime phase (t′) does not undergo the martensitic transformation to monoclinic upon cooling [3,5,6,11] (Fig. 5b). At an exposure temperature of 1204 °C there is sufficient cation mobility for the metastable tetragonal prime phase to transform to the equilibrium cubic and tetragonal phases. Upon cooling, the equilibrium tetragonal phase can undergo the martensitic transformation to monoclinic.[3] At 1204 °C and short exposure times, the amount of the tetragonal phase increases, but begins to decrease after 1000 h. The tetragonal phase is possibly stable at room temperature at short exposure times due to the small size of the phase regions. For heat treatments of 1315 °C, the amounts of the t′ and t phases rapidly decrease accompanied by increases in monoclinic and cubic phases until 5000 h when no further transformation occurs. The final monoclinic fraction at long exposure time is what would be predicted by the phase diagram.

Table 1 shows the fraction of each phase present in coating B for each time and temperature tested as calculated from the XRD data. At 1204 °C there is less t′ than in coating A for 100 h, but by 500 h the mol% are approximately the same. The increase in amounts of monoclinic phase is somewhat slower and accompanied by less t phase than in coating A. The cubic phase appears at an earlier time in coating B and there is significantly more cubic phase after 1000 h at 1204 °C. At 1315 °C, coating B seems to transform at the same rate as coating A. The reasons for these differences are not clear.

4. Summary

In summary, the phase stability in plasma sprayed 8 wt.% PSZ coatings with a porous and cracked microstructure were studied for times of up to 10 000 h at temperatures of 982 °C, 1204 °C, and 1315 °C. The two coatings behaved similarly and exhibited minimal change in the monoclinic content at exposures of 982 °C, while exposures at 1204 °C and 1315 °C resulted in increasing amounts of monoclinic phase versus time; the monoclinic phase reached a maximum of 40% at longer time exposures at the highest temperature as predicted by the phase diagram.

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