Cooling rate effects on the phase transformation of ZrO₂ base thermal barrier coatings coated by APS

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The phase transformation behaviors of plasma sprayed partially stabilized ZrO₂ (PSZ) coatings were studied under the different thermal cycles. Both ZrO_2-$8Y_2O_3$ and ZrO_2-$25CeO_2$-$2.5Y_2O_3$ were isothermally heat treated at 1300°C and 1500°C for 100 hr and were cooled through four different cooling rate methods, such as water quenching, air-cooling, open furnace cooling (the furnace door was open during cooling stage) and furnace cooling. It was observed that the martensitic phase transformation from tetragonal to monoclinic was affected by the thermal cycle and stabilizer. The amount of oxygen vacancy which acts cubic as stabilizer was found to be the main factor of the phase transformation behaviors, and was strongly related to the cooling rates.

Key words: Thermal barrier coating, Partially stabilized zirconia, Martensitic transformation, Cooling rate, Oxygen vacancy.

Introduction

Thermally insulating ceramic coatings known as thermal barrier coatings (TBCs) are of great interest because of their ability to improve performance and efficiency of turbine engine by allowing higher turbine inlet temperature or reduced cooling air flow [1]. Zirconia (ZrO₂) is an attractive material for thermal barrier coating because, compared with other ceramics, it has superior mechanical properties such as high strength and fracture toughness combined with good wear resistance and, above all, a thermal expansion coefficient close to that of metallic substrates [2]. However, ZrO₂ exists in three crystallographic phases: the low temperature monoclinic phase, the intermediate-temperature tetragonal phase and the high temperature cubic phase. Especially, the phase transformation of tetragonal phase to monoclinic phase accompanies significant volume expansion (approximately 3~5 vol%), so this transition generally results in cracking and contributes to the failure of TBC system. Therefore the amount of monoclinic phase ZrO₂ is one of the important indicators of coating quality.

Addition of several oxides (Y₂O₃, CeO₂, MgO etc.) can stabilize the high temperature cubic phase in zirconia, so the occurrence of monoclinic phase zirconia can be repressed. In the case of yttria-partially-stabilized zirconia (YSZ), the rapid solidification during the plasma spray process can preserve the stabilizer content of the spray powder in the tetragonal phase and results in a significant retention of the metastable tetragonal phase (non-transformable tetragonal) at room temperature [3]. However, YSZ materials divide the yttria stabilizer between tetragonal and cubic phases in the equilibrium phase diagram at high temperature resulting in the production of low yttria tetragonal zirconia (transformable tetragonal) which can transform to monoclinic on cooling to room temperature. Therefore, the correlation between phase transformation behavior and the thermal cycle should be exactly established.

Experimental Procedure

The characteristics of the starting powders are summarized in Table 1. Commercial powders of partially stabilized zirconia, ZrO₂-8Y₂O₃(YSZ) and ZrO₂-25CeO₂-Y₂O₃(CYSZ) were used as spray materials. Both YSZ (−125 + 11 μm) and CYSZ (−90 + 16 μm) have spherical shape because these powders were manufactured by homogeneous oven spherical powder (HOSP) method. Two powders were coated on a SS41 substrate (50 × 50 × 5 mm) by atmospheric plasma spraying and the thickness of the coating was about 1 mm. Table 2 and Table 3 show the chemical compositions of substrate and the process parameters. After cutting the specimens into 10 × 10 mm pieces, the SS41 substrate was removed by soaking in a 60% HNO₃ dilute solution for several hours. The specimens were isothermally heated at 1300°C and 1500°C for 100 hr, and then cooled to room temperature through four different cooling rates: water quenching, air cooling, open furnace cooling (the furnace door is open during cooling) and furnace cool-

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Table 1. Chemical compositions of substrate (%)

Class	Ni	Cr	Fe	Mn	C	Si	P	S
SS-41	–	–	Bal.	0.67	0.16	0.17	0.029	0.020

Table 2. Characteristics of powders

Powder	ZrO_2-CeO_2-Y_2O_3	ZrO_2-Y_2O_3
Chemical Composition (wt%)	ZrO_2-$25CeO_2$-$2.5Y_2O_3$	ZrO_2-$8Y_2O_3$
Particle Shape	Spheroidal	Spheroidal
Particle Size Range (µm)	−90+16 µm	−106+11 µm

ing (Fig. 1). An evaluation of the changes in phase fraction due to thermal cycle (heat treatment and cooling rate) was performed using X-ray Diffractometer (XRD, 40 kV, 100 mA, Cu Kα radiation). The amount of monoclinic phase zirconia in each specimen was calculated from the following equation: [4]

$$X_m = \frac{I_m(111) + I_m(11\bar{1})}{I_m(111) + I_m(11\bar{1}) + I_{c,t}(111)}$$

where I represents the diffraction intensity of different lattice planes.

Several specimens from as-sprayed state and after heat treatment at 1500°C were polished to a 1 µm diamond finish and thermally etched at 1400°C for 20 min in order to reveal the microstructure by scanning electron microscopy (SEM). Transmission electron microscopy (TEM, 200 kV) samples were prepared using a technique that involved mechanical grinding to a thickness at 100 µm, fixed on Cu grid, dimpling to a thickness of 20 µm and ion-beam milling. The extent
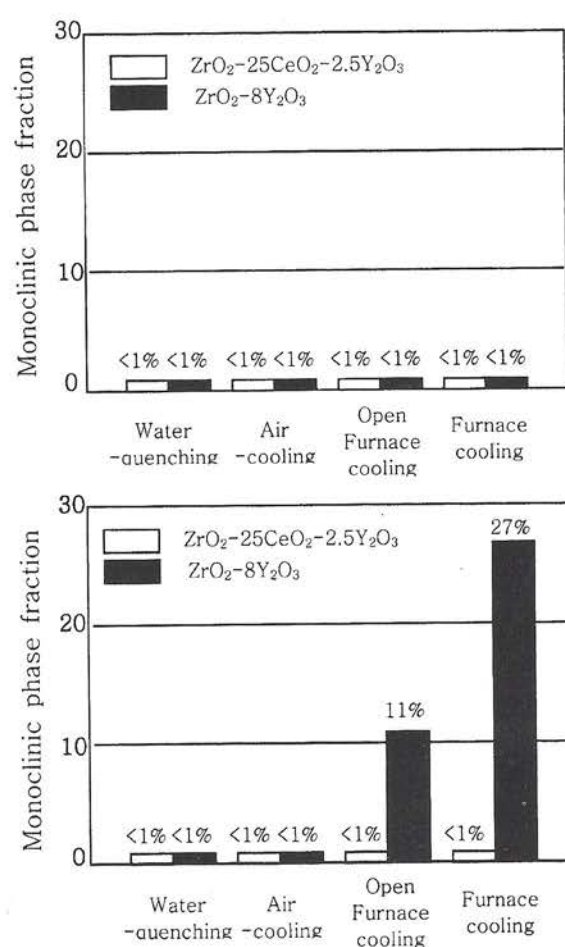
of line broadening which indicates the amount of oxygen vacancy was also evaluated by Raman spectroscopy (Jobin Yvon T64000).

Results and Discussion

The proportion of monoclinic phase zirconia in each top-coats through different thermal cycles is graphically shown in Fig. 2. The monoclinic phase was not discovered in either YSZ or CYSZ undergone 1300°C-100 hr heat treatment. In 1500°C~100 hr heat treated specimens, YSZ contains some monoclinic phase while none exists in CYSZ coat. The phase transformation behavior difference between YSZ and CYSZ results from the stabilization extents of these ceramic coats. This interpretation is supported by the phase fraction of as-

Fig. 1. Thermal cycles of heat treatment experiments. (heat treatment temperature, time & cooling rate)

Fig. 2. Monoclinic phase fraction after isothermal heat treatment. (a) 1300°C-100hr, (b) 1500°C-100hr

Table 3. Parameters for plasma spraying

Coating Materials	Ampere (A)	Voltage (V)	Gas Flow Rate (SCFH)			Feed Rate (g/min)	Spray Distance (mm)
			Primary Gas (N_2)	Secondary Gas (H_2)	Carrier Gas (N_2)		
ZrO_2-CeO_2-Y_2O_3	500	76	75	20	12	45	100
ZrO_2-Y_2O_3	500	76	75	20	12	45	65
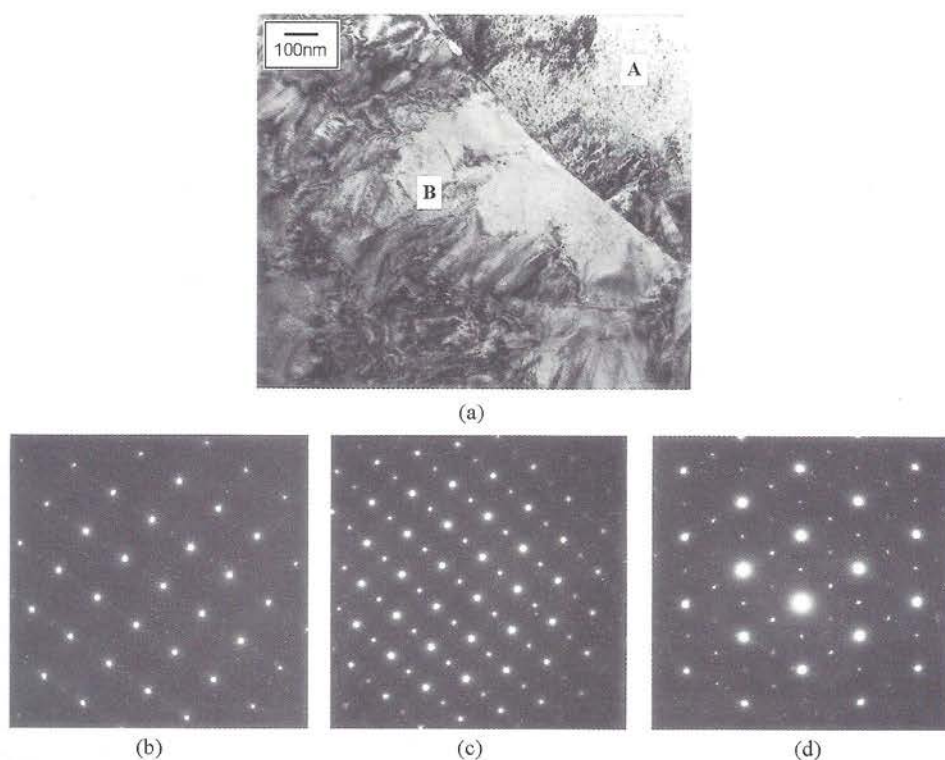
Fig. 3. BF image and SAD patterns of A area. (a) BF image, (b) Z.A = <100>, (c) Z.A = <110>, (d) Z.A = <111>

sprayed state. As-sprayed CYSZ contained about 25% cubic phase and 75% tetragonal phase, while the as-sprayed YSZ consisted of 100% non-transformable tetra-

gonal phase [5]. When the CYSZ included larger high temperature phase is annealed at 1500°C, the initial phase is hard to separate into the transformable tetra-
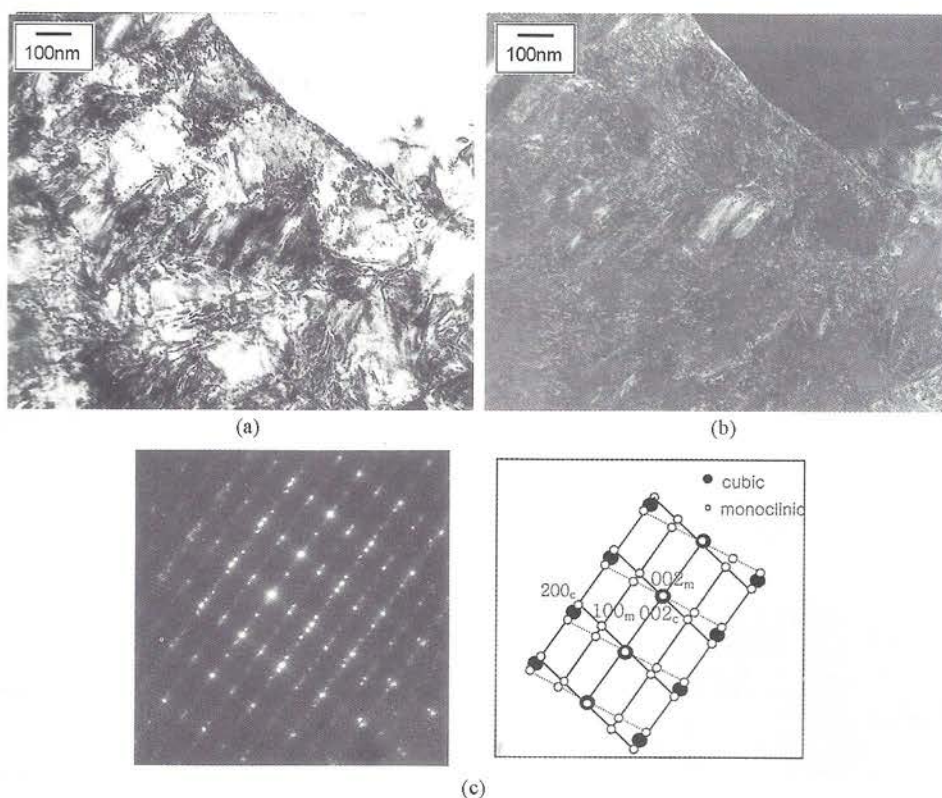

Fig. 4. BF image and SAD patterns of B area. (a) BF image, (b) DF image of B area, (c) SAD pattern of B area

gonal. Thus, CYSZ containing cubic phase is more stable than YSZ from the viewpoint of the initial chemical composition and as-sprayed microstructure.

Particularly for the YSZ with 1500°C~100 hr annealing, the amount of monoclinic phase increased with slower cooling rate. The TEM images and selected area diffraction (SAD) patterns of YSZ which was heated at 1500°C for 100 hr and cooled slowly are shown in Fig. 3 and Fig. 4. Figure 3(a) is bright field image of topcoat and A area is tetragonal phase based on SAD pattern analysis. The only way to discriminate the tetragonal phase from the cubic phase is to tilt the grain to a <111> orientation [3]. In this orientation, the tetragonal PSZ gives rise to a unique {112} reflection as shown in Fig. 3(d). We inferred from the SAD pattern analysis (Fig. 4(b)) that B area in Fig. 3(a) included monoclinic-PSZ. The monoclinic phase are identified by SAD pattern and observed in dark field image (Fig. 4(a)).

The SEM images of as-sprayed state and 1500°C~100 hr annealing are shown in Fig. 5. The range of grain size distribution is very broad and the anisotropic feature distinguishes TBC structure. The average grain size for the as-sprayed state is 0.5~1.6 μm and the heat treatment at 1500°C for 100 hr results in a grain growths to 1.5~2.8 μm. During grain growth, the diffusion and stabilizer redistribution must have occurred. The original non-transformable tetragonal phase (t' phase) decompose into a cubic phase (c phase) and a low yttria transformable tetragonal phase (t phase). In order to identify the phase separation into t phase and c phase, the water-quenched YSZ was reheated at 400°C for 1 hr, a temperature which tetragonal-monoclinic phase transformation is known to occur. Figure 6 shows XRD pattern after the reheat-treatment, and the $(111)_m$ and $(-111)_m$ peaks are observed. About 6% monoclinic phase, which was not found in the water-quenched YSZ, can be detected. On the assumption that a negligible diffusion occurs in ceramic at 400°C, this situation involves that the rapid cooling rate of water quenching suppressed the phase transformation of tetragonal to monoclinic phase. In other words, other factors which control phase transformation behavior, such as a diffusion during high temperature holding and grain size, were sufficient for monoclinic phase formation, but the effect of rapid cooling suppressed the martensitic transformation.

One of the reason that a rapid cooling rate suppressed phase transformation (t → m) is a high degree of anion vacancy from rapid quenching. It is said that a oxygen vacancy raises a stabilization extent. Zirconia has a CaF_2 structure, but the tetragonal ZrO_2 structure is not simply a tetragonally distorted CaF_2 structure. In the tetragonal ZrO_2, Zr and O atoms occupy the following positions.

$$2Zr\ (0\ 0\ 0)\ (1/2\ 1/2\ 1/2)$$
$$4O\ (0\ 1/2\ z)\ (1/2\ 0\ -z)\ (0\ 1/2\ 1/2\ +z)\ (0\ 1/2\ -z)$$
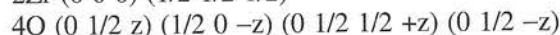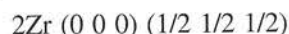
The z value is slightly less than 0.25 in the tetragonal ZrO_2, and approaches 0.25 in the cubic ZrO_2. The effect of raising the anion vacancy concentration is to increase the value of z towards 0.25, so that the lattice may be considered to approach the cubic structure [6]. Figure 7 shows the results of Raman spectra obtained from YSZ with different cooling rates (air-cooled and furnace-cooled). The full-width half maxima (FWHM)
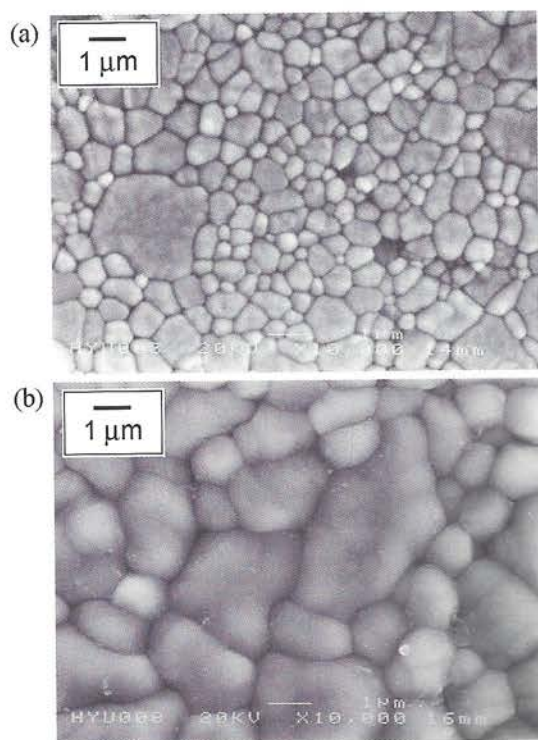

Fig. 5. SEM images of ZrO_2-Y_2O_3 coating. (a) as-sprayed state, (b) after heat-treatment (1500°C~100 hr)
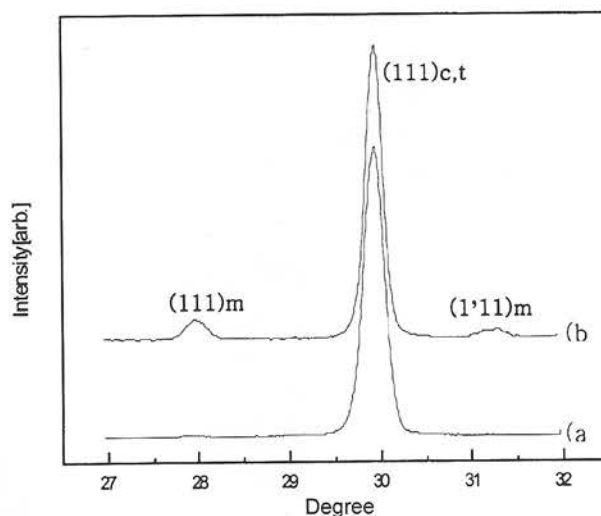

Fig. 6. X-ray diffraction pattern after reheat treatment (400°C~1 hr). (a) before reheat treatment (water quenching), (b) after reheat treatment
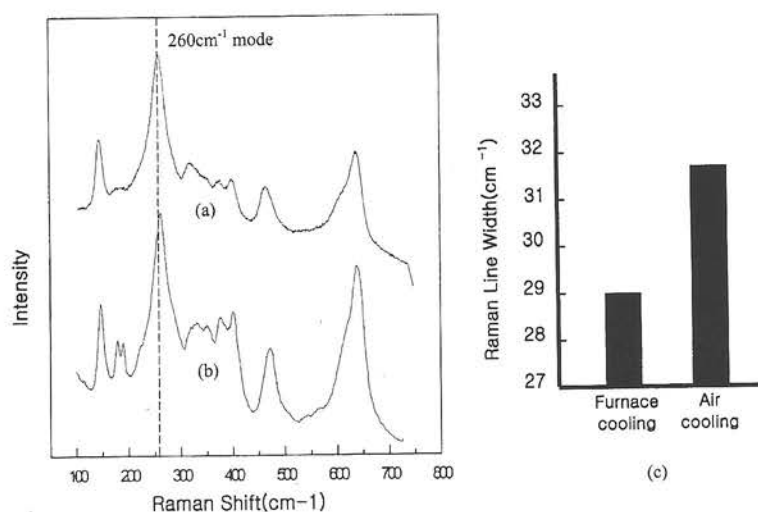
Fig. 7. Raman spectrum from zirconia coating. (a) air-cooled, (b) furnace cooled, (c) Raman line width

of the Raman lines near 260 cm^{-1} which represents tetragonal phase were measured to compare the amount of oxygen vacancy. As shown in Fig. 7(c), the FWHM of air-cooled YSZ is approximately 32 cm^{-1} and this value of furnace-cooled YSZ is 29 cm^{-1}. The broader Raman line width indicates an increased structural disorder, viz oxygen vacancy [7].

That is to say, high oxygen vacancy formed during high temperature holding remained to room temperature due to a fast cooling rate. The extra oxygen vacancy at the room temperature displaced oxygen ion from the equilibrium position on the tetragonal phase and functioned as cubic stabilizer, so the martensitic transformation was believed to be suppressed. On the other hand, in the YSZ cooled slowly, the anion vacancy was reduced during cooling stage, and was sufficiently low for the phase transformation to monoclinic phase.

Conclusions

The phase transformation behavior of partially stabilized zirconia TBC was affected by the kind of stabilizer and thermal cycle (holding temperature and cooling rates). From the view of composition, ZrO$_2$-25CeO$_2$-8Y$_2$O$_3$ was less susceptible to the phase transformation of tetragonal to monoclinic phase than ZrO$_2$-8Y$_2$O$_3$. In

case of YSZ annealed at 1500°C for 100 hr, the stabilizer redistribution and grain growth satisfied the monoclinic phase formation, but was suppressed by the rapid cooling. The faster cooling rate, the less phase transformation occurred. The oxygen vacancy concentration was one of the factors affecting this phenomenon. The extra oxygen vacancy formed with quenching functions as a cubic stabilizer in PSZ and inhibited the martensitic transformation.

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