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Thermal and crystallization behavior of zirconia precursor used in the solution precursor plasma spray process

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Abstract Yttria stabilized zirconia (7YSZ) solution precursor has been successfully used in the deposition of high durability thermal barrier coatings. In this paper, the thermal and crystallization behaviors of 7YSZ precursor were investigated by TG-DTA, FTIR and XRD. The results show that the precursor decomposition and crystallization temperatures greatly depend on heating rate e. g. 74°C for the crystallization temperature when tripping the heating rate. With a 10 °C/min heating rate, the weight loss due to precursor pyrolysis occurs predominantly at temperatures below 500 °C. A small weight loss due to the oxidation of residual carbon is detected from 800 °C to 950 °C. The complete crystallization of the tetragonal phase was determined to be around 500 °C by DTA and XRD analyses with a 10 °C/min heating rate. The crystallization kinetics and the activation energy of amorphous 7YSZ precursor were investigated by variable heating rate DTA. The calculated activation energy is 66.2 kJ/mol. The Avrami parameter value was determined to be 2.68, which indicates that crystallization nucleation and growth is diffusion-controlled. The crystalline phase of 7YSZ coatings deposited by the Solution Precursor Plasma Spray process was identified by XRD and Raman spectrum. The average YSZ grain size in the SPPS coating was determined to be 61 nm.

Introduction

Thermal barrier coatings (TBCs) are used in a number of energy-related applications, aircraft propulsion, power generation and marine propulsion, to provide thermal insulation to metallic components, and thus, protecting them from the hot gas stream in gas-turbine engines [1]. Recently, a new processing method—solution precursor plasma spray (SPPS)—has been successfully developed to deposit YSZ-based TBCs with excellent durability [2–4]. In the SPPS process, an aqueous solution precursor feedstock, instead of conventional powder, is injected into the plasma jet. The solution droplets undergo a series of physical and chemical reactions prior to deposition on the substrate as a 7YSZ coating.

The deposition mechanisms of the SPPS have been studied in detail [5–7]. In the present work, the thermal decomposition and crystallization behaviors of the 7YSZ solution precursor were investigated by TG-DTA, FTIR and XRD. A study of the thermal and crystallization behaviors of the 7YSZ precursor should provide understanding of the coating deposition mechanism and microstructure.

Experimental procedure

The precursor solutions used in the SPPS process are a zirconium metallorganic salt and an yttrium inorganic salt. The precursors are mixed according to the final composition of 7 wt% yttria-stabilized zirconia. The precursor solution was dried at ~60 °C on a hot plate. The dried precursor powder was then heated to temperatures of 350, 400, 450, 500, 600 °C with a heating rate of 10 °C/min, and then holding for 0.5 h. Both differential thermal

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analysis (DTA) and thermal gravimetric analysis (TGA) experiments were performed simultaneously on the as-dried 7YSZ precursor powders using a SDT-Q6000 thermal analyser (TA Inc.). For each thermal analysis run, ~30 mg powder was placed in an Al_2O_3 crucible. Thermal analysis was performed in flowing air by heating each sample from room temperature to 1200 °C at a rate of 10, 15, 20, 30 °C/min. $A1_2O_3$ powder was used as a reference material.

Fourier-transform infrared spectrum (FTIR) (MAGNA-IR 560, Nicolet, Madison, WI) was used to identify structural features of the precursor and the dried powders. Measurements were conducted in a wave number range of 4000–400 cm^{-1}. All samples for FT-IR measurement were well mixed with KBr in a weight ratio of 1:20 and then pressed into translucent pellets. The crystalline phase of the dried powders and the SPPS coating were identified by X-ray diffraction (Cu Kα radiation; D5005, Bruker AXS, Karlsruhe, Germany). The phase composition of the SPPS coating was also identified using a Raman instrument (Renishaw^{TM} Ramascope 2000. Renishaw, Gloucestershire, UK). An Ar-ion 514-nm wavelength laser was used to excite the Raman scattering. The coating microstructure was characterized using a JEOL JSM-6335F field emission scanning electron microscope (FESEM).

Experimental results and discussion

Precursor crystallization and grain growth

Figure 1 shows the XRD patterns of the gel powders calcined at different temperatures for 0.5 h. From the XRD patterns, it can be seen that the gel powders calcined at 450 °C for 0.5 h are still amorphous. When the temperature is increased to 500 °C, the 7YSZ crystalline phase begins to form. However, the broad and weak peaks imply poor crystallinity and fine grains. When the calcination temperature is increased from 600 °C to 1000 °C, the peaks become sharper and stronger, which indicates increased crystallinity of the 7YSZ powders. The average grain size *D* of the heat-treated powder was calculated from the broadening of the XRD (111) peak using Scherrer's formula [8].

$$D = \frac{0.9\lambda}{B\cos\theta}$$

where λ is the x-ray wavelength (0.154 nm for Cu Kα), θ is the diffraction angle and *B* is the peak full-line width at half maximum (FWHM). The calculated crystalline size shows an increase from 8.6 nm to 20.3 nm as the calcination temperature increases from 600 to 1000 °C.

FTIR

Figure 2 shows the FTIR spectrum of the 7YSZ gel powders calcined at different temperatures in the wave number range between 400 and 4000 cm^{-1}. The precursor spectrum clearly shows broad absorption around 3450 cm^{-1}, which is characteristic of the stretching vibration of hydroxyl groups (O–H) [9]. The absorption peak at 1029 cm^{-1} in the spectrum for the gel precursor corresponds to the C–H stretching vibration [10]. The absorption peaks localized at 1567 cm^{-1} and 1451 cm^{-1} are assigned to asymmetrical

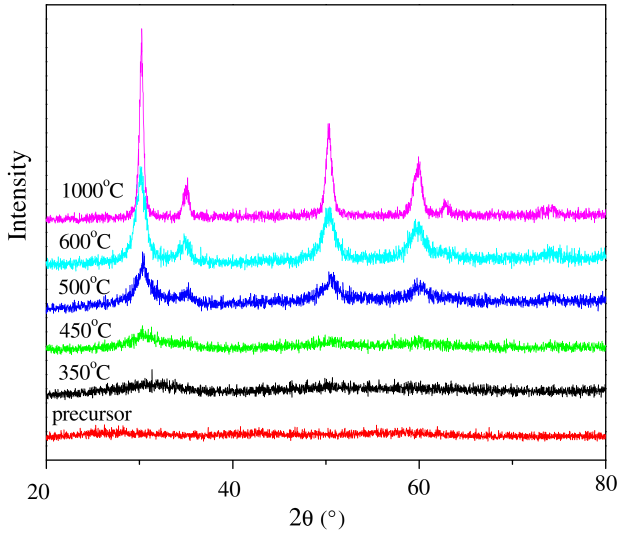

Fig. 1 XRD of 7YSZ powders calcined at various temperatures

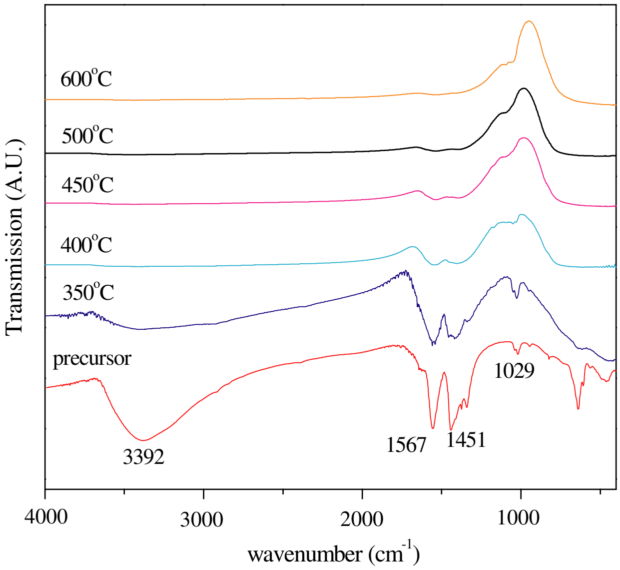

Fig. 2 FT-IR of dried 7YSZ precursor powders heat-treated at various temperatures

and symmetrical stretching vibrations of the carboxylate group (O–C = O) [9]. Those peaks are reduced to a small value as the heating temperature increases to 500 °C and disappear at 600 °C. These results provide evidence that precursor pyrolysis occurs at temperatures below 500 °C.

TG-DTA analysis

The weight loss of the precursor as a function of temperature in air was measured using a TG-DTA instrument after the precursor was dried at 60 °C in air. Typical TG-DTA curves for the crystallization of 7YSZ precursor obtained at a heating rate of 10 °C/min in air are shown in Fig. 3. The sample weight decreases with increasing temperature continuously from room temperature to ~950 °C, and the total weight loss is about 44.3 wt%. The major weight loss (42.5 wt %) occurs below 500 °C and an additional 1.8 wt% loss occurs between 800 °C and 950 °C. There is an endothermic peak in the DTA curve around 99 °C accompanied by a simultaneous weight loss ~10.2 wt%, which can be ascribed to water evaporation. There were three exothermic peaks at 307, 354, and 496 °C. The first peak at 307 °C is due to the pyrolysis of the precursor, which accompanies a weigh loss ~16.0 wt%. The exothermic DTA peak at 354 °C, which accompanies a weight loss 8.2 wt%, is probably due to the second time decomposition of the incompletely pyrolyzed precursor, since there is still the carboxylate group peak in the FTIR spectrum when the precursor is heat-treated at 350 °C (Fig. 2). The third peak at 496 °C accompanies a 7.7 wt% weight loss and can be ascribed to the crystallization of 7YSZ from the amorphous to tetragonal phase and the burning of residual organics, as confirmed by the XRD and FT-IR. The final weight loss occurs from 800 °C to 950 °C with an exothermic peak at 935 °C. This weight loss can be attributed to the oxidation of the residual carbon which is know to burn off in that temperature range [11]. It is worth mentioning that precursor powders are white after drying at 60 °C, however, the precursor turns yellow at 350 °C, back to black at 500 °C, and then turns white above 950 °C. The black color of the sample is thought to be caused by residual carbon [11]. This color change further confirms that the weight loss between 800 °C and 950 °C is due to the complete oxidation reaction of the residual carbon.

Crystallization activation energy and mechanism

The crystallization kinetics of the as-dried 7YSZ precursor powders were studied by DTA scans at heating rates of 10, 15, 20 and 30 °C/min. The effect of heating rate on the DTA crystallization peak is shown in Fig. 4. The precursor pyrolysis and crystallization exotherm shifts to higher temperatures with increasing heating rate. The peaks of the crystallization temperature are 496, 521, 542 and 570 °C for heating rates of 10, 15, 20, 30 °C/min, respectively. The variation of the crystallization peaks according to the DTA scan rates can be used to estimate the activation energy for crystallization by using the modified Kissinger equation [12–15]:

$$\ln\frac{T_p^2}{\phi} = C + \frac{E_a}{RT}$$

where ϕ is the heating rate in degrees Kelvin per second (K/s), T_p corresponds to the crystalline peak temperature in the DTA curve, E_a is the activation energy for crystallization, R is the gas constant and C is a constant. By substituting ϕ values and corresponding T_p values into the above equation, the Kissinger plot was obtained and is

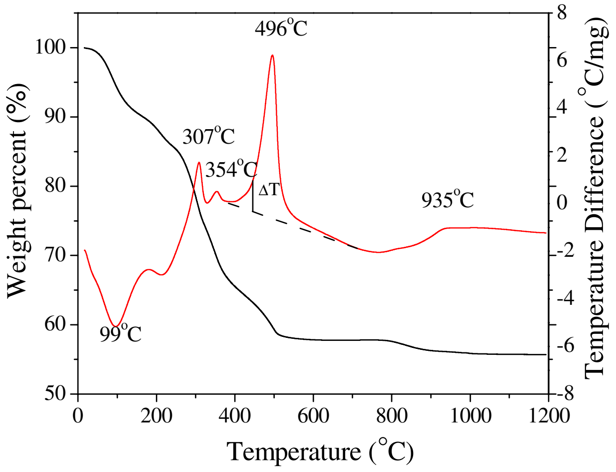

Fig. 3 Typical TG-DTA curves of dried 7YSZ precursor powders at a heating rate of 10 °C/minute

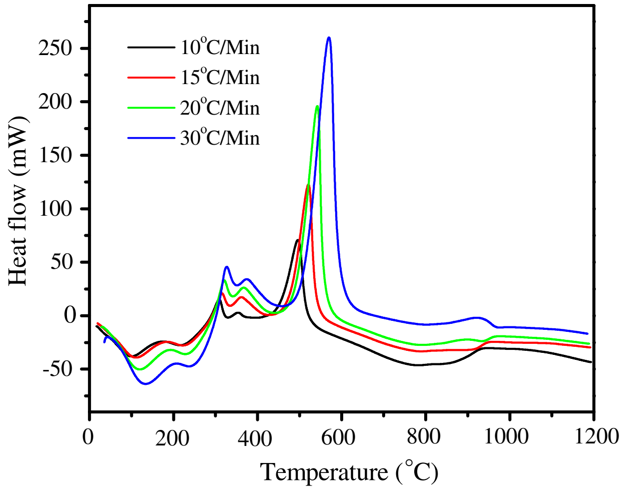

Fig. 4 Differential thermal analysis (DTA) scan curves of dried 7YSZ precursor powders observed at various heating rates

presented in Fig. 5. From the slope of the Kissinger plot, the activation energy for crystallization of the 7YSZ dried powders was determined to be E_a = 66.2 kJ/mol.

The Avrami parameter (n) is related to the nucleation and growth mechanism of a new phase [13, 16], and can be estimated from the DTA curves. In a given DTA curve, the temperature differential ΔT at any given instant can be estimated as being proportional to the instantaneous reaction rate. Then, the Avrami parameter can be derived from the following equation [13, 14, 16]:

$$\frac{d(\ln \Delta T)}{d(\frac{1}{T})} = -\frac{nE_a}{R}$$

or

$$\ln \Delta T = -\frac{nE_a}{RT} + C'$$

where ΔT is the vertical displacement at temperature T of the DTA crystallization exotherm from the baseline (Fig. 3), n is the Avrami parameter, C' is a constant independent of the temperature T. Figure 6 shows a plot of lnΔT as function of the inverse temperature estimated from a DTA curve recorded at 10 °C/min. The Avrami parameter n was estimated from the slope of the plot and the value of E_a (66.2 kJ/mol), and it is equal to 2.68. Very similar values are obtained for the higher heating rate data. Values of n = 1, 2 and 3 have been assigned to one-, two-, and three-dimensional crystal growth. A value of n = 2.68, which is close to 3, suggest a constant number of nuclei growing spherically at a constant rate in three dimensions, and that crystal growth is a diffusion controlled process.

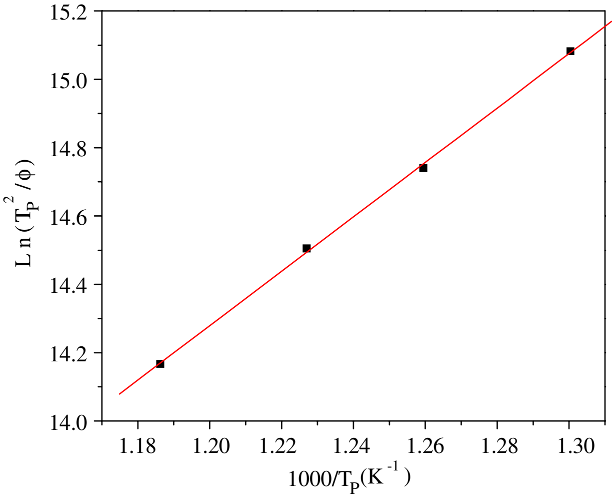

Fig. 5 Kissinger plot of 7YSZ precursor powders with DTA heating rates of 10, 15, 20 and 30 °C/minute

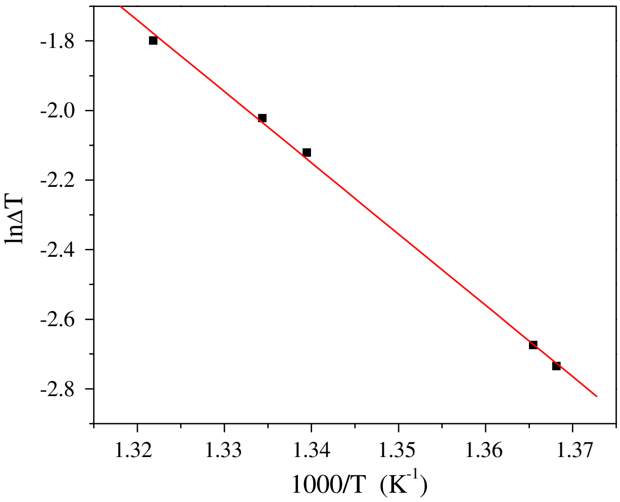

Fig. 6 Plot of the lnΔT vs. 1/T (the values of ΔT and T were derived from DTA curves recorded at a heating rate of 10 °C/minute

Pyrolysis of 7YSZ solution precursor and coating deposition

As indicated in the TG-DTA analysis, the solution precursor will undergo water vaporization, precursor pyrolysis and combustion of residual organic groups, crystallization to tetragonal Zirconia and finally the carbon is burned off. During the SPPS process, which involves high plasma temperatures (about 10.000 K) and short residence times (few milliseconds) [17], the solution precursor droplets are assumed to undergo the same physical and chemical changes as was observed in the laboratory experiments performed under near equilibrium conditions.

The coating phase composition was identified by XRD and Raman Spectrograph. Figure 7 shows the XRD and Raman spectrum of the SPPS 7YSZ coating. A sharp and strong peak XRD shows the well-crystallized 7YSZ phase (Fig. 7a). The Raman peak is characteristic of the tetragonal phase (Fig. 7b) [18]. The average grain size calculated using Scherrer formula from (111) XRD peak is about 61 nm, thus, producing a nano-grained coating. In the SPPS process, the droplet dwell time in the plasma flume is very short and the crystallized grains cool quickly. The grains do not have enough energy and time for growth, so a nano-grained structure results. A typical coating microstructure is shown in Fig. 8a. Spherical particles, ultra-fine splats can be observed on the coating top surface, which indicate the precursor droplets undergo pyrolysis, melt, and solidification in the plasma. Figure 8b shows the coating surface morphology after heat-treatment at 1450 °C for 2 h. The grain size is increased from the original 61 nm to 300 nm due to the grain growth under thermal energy. The nearly spherical grains shape is consistent with the three-dimensional grain growth mechanism obtained by the

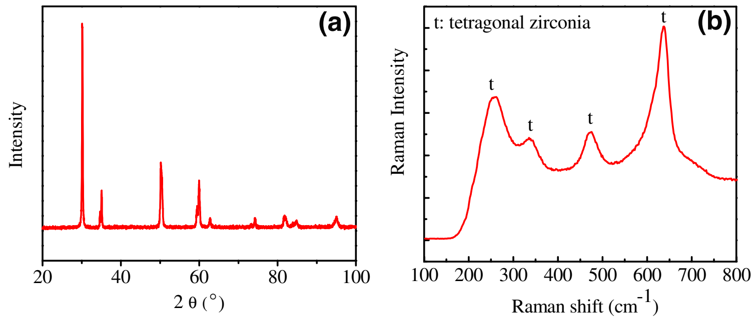

Fig. 7 (**a**) XRD and (**b**) Raman spectrum of the SPPS coating

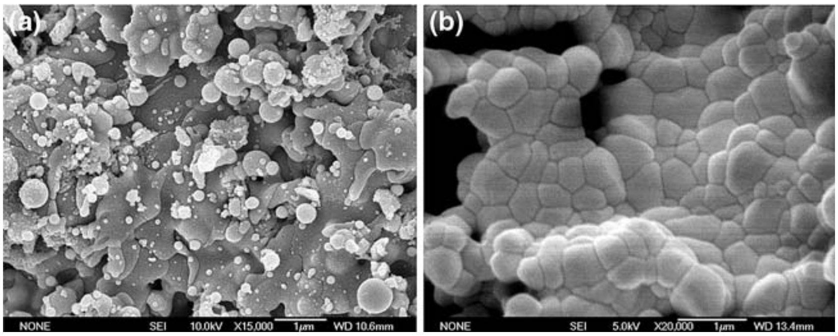

Fig. 8 Surface morphology of the SPPS 7YSZ coating: (**a**) as-sprayed; (**b**) heat treated at 1450 °C for 2 h

Avrami parameter determined in Section ''TG-DTA analysis''.

Conclusions

The detailed thermal and crystallization behaviors of the 7YSZ gel used to make SPPS TBCs were studied and characterized by XRD, FT-IR and TG-DTA. With a 10 °C/min heating rate, complete precursor pyrolysis occurs below 500 °C; a small amount of residual carbon is detected from 800 °C to 950 °C. The complete crystallization to the tetragonal phase occurs around 500 °C. The calculated activation energy is 66.2 kJ/mol. The Avrami parameter value is 2.68, which indicates a three-dimensional, diffusion-controlled nucleation and growth crystallization mechanism. The deposited coating consists of ultra-fine splats and pores, a tetragonal crystal structure and a 61 nm grain size.

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