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Exploration of YPO_4 as a potential environmental barrier coating

Yiguang Wang [*], Xianhong Chen, Wen Liu, Laifei Cheng, Litong Zhang

National Key Laboratory of Thermostructure Composite Materials, Northwestern Polytechnical University, Xi'an, Shaanxi 710072, PR China

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Abstract

A non-silicate material, yttrium phosphate (YPO_4), is developed for the application as environmental barrier coatings. The key issues of environmental durability, phase stability, chemical compatibility, and coefficient of thermal expansion (CTE) are considered for the selection of YPO_4. The water corrosion behaviors for the sol–gel prepared YPO_4 were investigated in an atmosphere of 50% H_2O–50% O_2 water vapor at 1350 °C. The hot corrosion study of YPO_4 was carried out at 900 °C with Na_2SO_4 melt. The results demonstrate that YPO_4 has excellent environmental durability. During these tests, YPO_4 had no phase change and decomposition. Moreover, the reactions between YPO_4 and silica at high temperatures were not detected, indicating the good chemical compatibility of YPO_4. The measured CTE of YPO_4 is close to that of SiC. The suitable CTE, good environmental durability and chemical compatibility, and excellent phase stability of YPO_4 indicate that it is a potential environmental barrier coating material.

Keywords: A. Sol–gel processes; C. Corrosion; E. Engine components; Environmental barrier coatings

1. Introduction

Silicon-based ceramics are considered as the promising structural materials for high temperature applications due to their excellent mechanical properties at elevated temperatures [1,2]. The formation of protective silica layer makes it possible for silicon-based ceramics to be used in dry air. However, when exposed to wet environments, for example combustion gas, silicon-based ceramics are oxidized and then corroded to form gaseous silica hydroxide according to reaction (1), causing weight loss and failure of ceramic components [3–8].

$$SiO_2(s) + 2H_2O(g) = Si(OH)_4(g) \quad (1)$$

In order to successfully apply silicon-based ceramics in combustion environments at high temperatures, environmental barrier coatings (EBCs) have been developed to protect them from water-vapor corrosion, improve hot-section service temperature and durability in combustion environments [9–15].

Mullite is firstly applied as environmental protection layer for silicon-based ceramics [16]. Since the corrosion resistance of mullite is limited, yttria stabilized zirconia (YSZ), is used as the overlay coating of mullite layer [11]. Such a multilayer structure consists of the first generation of EBCs. However, the big difference in coefficient of thermal expansion (CTE) of YSZ and mullite causes the cracks in coatings during thermal cycles, so that the duration of the first generation EBCs cannot meet the requirements. The second generation of EBCs, with the replacement of YSZ with BSAS ($Ba_{1-x}Sr_xO$–Al_2O_3–$2SiO_2$, $0 \leq x \leq 1$), is then developed. It has been successfully applied in engine hot-section, exhibiting long term durability in combustion environments at temperatures below 1300 °C [9,10,12]. However, the advanced turbine engines are required to work at temperatures as high as 1482 °C (2700 °F). BSAS–mullite systems are no longer available due to their poor durability and chemical compatibility at such high temperatures [11]. Consequently, more temperature-tolerance EBC materials, rare earth silicates, $RE_2Si_2O_7$ (RE = rare earth element, including Y, Sc, Yb and Lu), have been developed to meet these requirements because of their low recession rates, low mismatch with matrix, and high chemical compatibility [11,17–22].

Even though rare earth silicates exhibit excellent water vapor resistance, the Si–O bonds in silicates more or less react with water vapor to cause the material recession. Therefore,

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[*] Corresponding author. Tel.: +86 29 88494914; fax: +86 29 88494620.
E-mail address: wangyiguang@nwpu.edu.cn (Y. Wang).

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non-silicate EBC materials have been developed in recent years. The material systems focus on zirconates and hafnates [23,24]. In this paper, we report a new non-silicate material, YPO_4. Its CTE, corrosion resistance to water vapor and molten salt, and chemical compatibility with the substrate were studied according to key issues for selecting environmental coating materials [25]. The results indicate that YPO_4 can be a potential EBC material for high temperature applications.

2. Experimental

YPO_4 powders with atomic molar ratio Y/P = 1 were fabricated by sol–gel method. The starting materials used in sol–gel process were $Y(NO_3)_3 \cdot 6H_2O$ (99.99% purity, A&C Rare Earth Materials Center, China) and H_3PO_4 (Tianjin Tianda Chemical Co., China). $Y(NO_3)_3 \cdot 6H_2O$ and H_3PO_4 were dissolved in ethanol. The solution was stirred on a hot-plate at room temperature for 12 h, followed by heating it in an oven at 70 °C for 5 h and 120 °C for 5 h to evaporate all the solvents. The gel was then heat-treated at 1400 °C to obtain the powders. The specific area of the powders was measured by BET (NOVA1000, Quantachrome, Odelzhausen, Germany).

High temperature water-vapor corrosion tests were carried out in an alumina tube furnace. The water vapor was introduced into the tube by means of oxygen carrier gas bubbling through the distilled water heated at 81.7 °C. Heating tape was used to keep the tube at a temperature of 120 °C on the water vapor entrance side of the furnace, which prevented condensation of water vapor. The YPO_4 powders were put on an alumina boat crucible, whose sides facing to the gas flowing direction were cut off in order to avoid restricting flow over the powders. The corrosion experiment was carried out at 1350 °C in an atmosphere of 50% H_2O–50% O_2 water vapor flowing at a rate of 8.5×10^{-4} m/s (the flow rate was estimated at room temperature) with a total pressure of 1 atm. The total corrosion time was 300 h. The water vapor that condensed at the exit side of the tube was collected and used to verify our experimental conditions of 50% H_2O–50% O_2. The weight change as a function of corrosion time was measured using an electronic balance with the accuracy of 0.01 mg (Mettler Toledo AG135, Greifensee, Switzerland). When the set time was reached, the samples were taken out from the furnace directly to be held in the 200 °C zone, and then were put in the desiccators to cool down to room temperature. This avoided any absorption of water from any moisture in ambient atmosphere.

The corrosion behavior of YPO_4 under molten salt was carried out at 900 °C with a total pressure of 1 atm in an alumina tube furnace. The corrosion time was up to 100 h. The samples used in salt corrosion test were bulk YPO_4, which were sintered at 1500 °C for 5 h. One side of the bulk YPO_4 samples was polished to 1 μm. The saturated Na_2SO_4 solution was uniformly dropped on the polished surface, followed by evaporation of the solvent. The amount of Na_2SO_4 on the surface was about 8.5 ± 0.2 mg/m^2. The weight change of bulk YPO_4 as a function of corrosion time was measured using an electronic balance with the accuracy of 0.01 mg (Mettler Toledo AG135, Greifensee, Switzerland). Before weighing the corroded samples, salt was washed with distilled water. At least five samples were used for the measurement, and the average value was obtained for each point.

The CTE of YPO_4 was measured by using dilatometer (DIL 402C, Netzsch, Selb, Germany). The testing temperatures ranged from 150 to 1350 °C. The ramping rate was 5 °C/min and argon was used as protecting gas with a velocity of 50 ml/min. The phases of samples were characterized by X-ray diffraction (XRD, Rigaku D/max-2400, Tokyo, Japan) with a copper K_α radiation. Data were digitally recorded in a continuous scan in the range of angle (2θ) from 20° to 70° with a scanning rate of 0.08°/s. The microstructures of samples were observed by scanning electron microscopy (SEM, JEOL-6700F, Tokyo, Japan).

3. Results and discussion

3.1. Water-vapor corrosion behavior of YPO_4

The weight change as a function of corrosion time is plotted in Fig. 1. The powder used in the experiment is 1.1703 g with a specific area of 0.32 m^2/g. The linear weight loss constant k_l is calculated from the slope of fitting curve in Fig. 1. The value is 1.25×10^{-5} mg/(cm^2 h). In order to compare the water-vapor corrosion rates of different materials, the data acquired at different testing conditions should be normalized according to the following model [5,6]:

$$k_1 \propto \frac{{}^{1/2}P_{H_2O}^{2}}{P_{total}^{1/2}} \qquad (2)$$

where ν is the linear gas velocity, P_{H_2O} is the partial pressure of water vapor, and P_{total} is the total pressure of gaseous phase. The normalized corrosion rate constants of SiC, Si_3N_4, and BSAS are listed in Table 1. Due to lack of the corrosion data of these materials at 1350 °C, the minimum corrosion rates of them at 1300 and 1400 °C are chosen for comparison. It can be seen that the corrosion rate of YPO_4 is about 50-fold lower than those of pure SiC and Si_3N_4, and about half of BSAS.

It is known that the failure of most of the phosphates at high temperatures is due to the decomposition to form new phases. For example, $AlPO_4$ will decompose to form alumina at

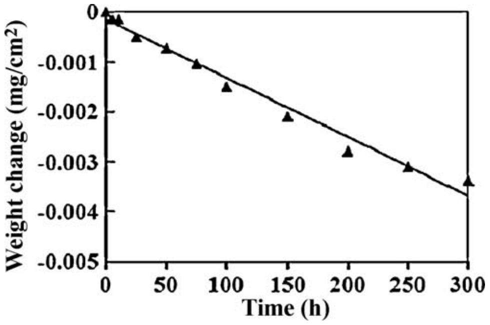

Fig. 1. Weight change of YPO_4 as a function of water-vapor corrosion time. The samples were exposed in 50% H_2O–50% O_2 at 1350 °C and a total pressure of 1 atm.

Table 1
Comparison of corrosion rate constants of different materials. The normalized conditions are 50% H_2O–balance O_2 vapor with a flow of 8.5×10^{-4} m/s at 1350 °C and a total pressure of 1 atm.

Temperature (°C)	Corrosion rate constants (g/(cm^2 h))			
	BSAS	Si_3N_4	SiC	YPO_4
1300	3.3×10^{-5}	9×10^{-4}	7.1×10^{-4}	–
1350	–	–	–	1.25×10^{-5}
1400	7.9×10^{-5}	8.6×10^{-4}	1.08×10^{-3}	–

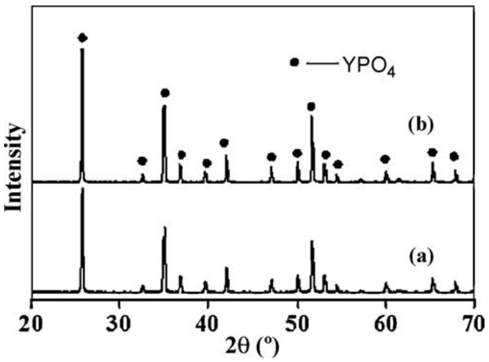

Fig. 2. XRD patterns of YPO_4 before (a) and after water-vapor corrosion for 300 h (b).

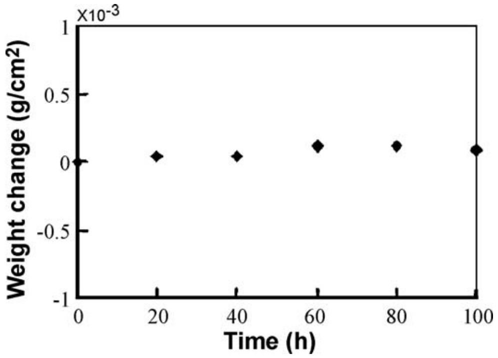

Fig. 3. Weight change of YPO_4 as a function of hot-corrosion time. The hot-corrosion was carried out in Na_2SO_4 melt at 900 °C.

temperatures higher than 1200 °C [26]. The XRD patterns of YPO_4 powders before and after water-vapor corrosion are compared (Fig. 2). The phases in both samples are only xenotime, which indicate that YPO_4 is stable in water vapor at 1350 °C, without any phase change and any obvious decomposition. Moreover, the sintering practice of bulk YPO_4 at 1500 °C shows no detectable weight loss and only xenotime phase, which demonstrates that that YPO_4 can be further stable up to 1500 °C in air.

3.2. Salt corrosion behavior of YPO_4

Another barrier for the applications of silicon-based ceramics in combustion gas is the salt contaminates, which will severely deteriorate the properties of materials [27]. EBC materials should also have the ability to resist the salt corrosion. Some silicates EBC materials, such as barium aluminosilicates, exhibit excellent water-vapor corrosion resistance [11]. However, when exposed to the molten salt, the structure of materials will be destroyed by the salt and result in the failure of materials [28]. In this study, the molten salt is selected as Na_2SO_4, which is a common salt in the combustion gas. The test is carried out at 900 °C, at which Na_2SO_4 is melted. The weight change of samples as a function of corrosion time is shown in Fig. 3. It can be seen that there is no obvious weight change even after 100 h. The corroded surface of YPO_4 samples (Fig. 4) shows the same morphology as the as-sintered samples, which indicates that there is no obvious corrosion of YPO_4 samples with molten Na_2SO_4 salt. As comparison, the SiC materials are severely corroded, causing a great deal of cracks. The XRD pattern of corroded YPO_4 (Fig. 5) shows that there is only xenotime phase, similar to the pattern of YPO_4 without any corrosion (Fig. 1). The results demonstrate that the YPO_4 will not react with Na_2SO_4, or decompose with the aid of salt melt, which indicates great molten salt corrosion resistance.

3.3. Chemical compatibility of YPO_4

When exposed to the combustion environments, the silicon-based matrix will react with oxidants to form silica on its surface. The compatibility of EBC materials with substrate, or the produced silica, is an important issue to be concerned. The BSAS materials have been successfully applied in EBC materials at temperatures lower than 1300 °C. However, when the application temperatures are over 1300 °C, BSAS will react with silica to deteriorate the EBC properties, which limits it to be used at high temperatures [11,12]. For some phosphate materials, the existence of silica will accelerate their decomposition. For instance, the $AlPO_4$ mixed with silica will decompose to form mullite when annealed at high temperatures [26]. Whether the YPO_4 will react with silica, and whether silica will result in the decomposition of YPO_4 are thus highly concerned in the present study. In order to clarify the effect of silica on YPO_4 stability, 10 wt% silica is mixed with YPO_4 powders to be annealed at 1350 °C for 300 h. The XRD patterns of the mixed powders before and after annealing are shown in Fig. 6. There are no new phases formed after 300 h annealing, which indicates that silica will not react with YPO_4. The weight change of the powders is also measured. No obvious weight loss is observed after 300 h annealing, which demonstrates that the silica will not cause the decomposition of YPO_4.

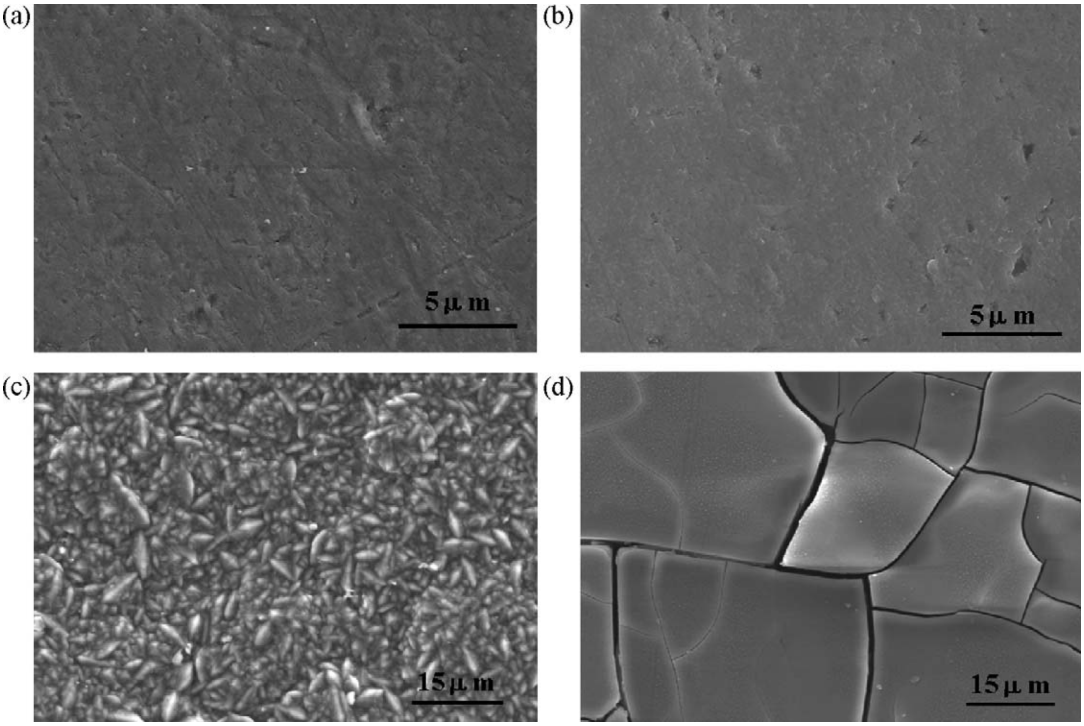

Fig. 4. SEM morphologies of YPO_4 before (a) and after hot-corrosion for 100 h (b), and as received SiC (c) and after hot-corrosion for 100 h (d). The hot-corrosion was carried out in Na_2SO_4 melt at 900 °C.

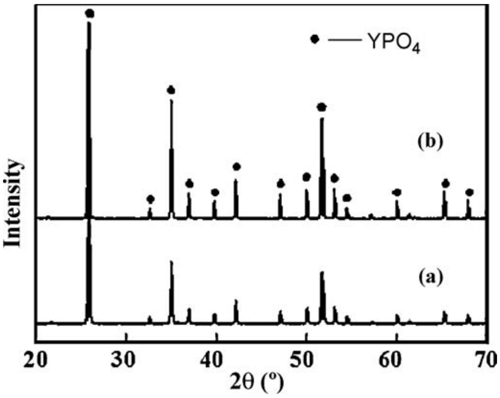

Fig. 5. XRD patterns of YPO_4 before (a) and after hot-corrosion for 100 h (b).

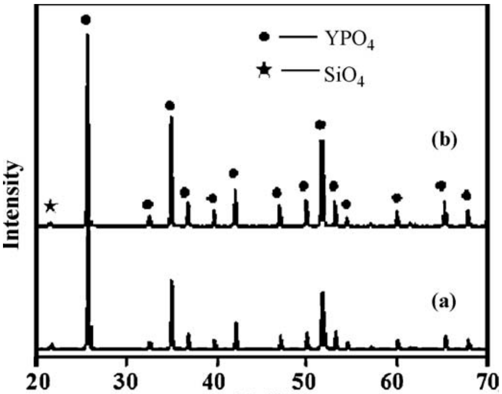

Fig. 6. XRD patterns of YPO_4 mixed with silica, as-received (a) and after heat-treatment at 1350 °C for 300 h (b).

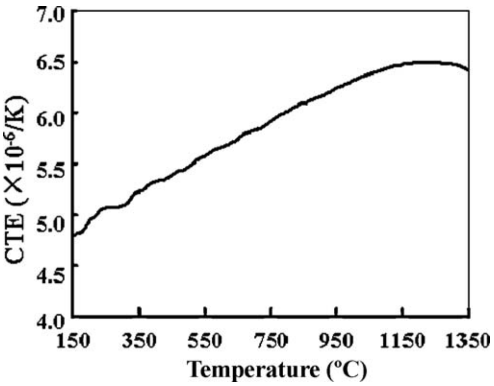

Fig. 7. CTE values of YPO_4 in the temperature range of 150–1350 °C.

3.4. Coefficient of thermal expansion of YPO_4

The engineering value of CTE for YPO_4 is shown in Fig. 7. The CTE values of YPO_4 vary from 4.8 to 6.5×10^{-6}/ °C in the temperature range of 150–1350 °C. The values are close to those for C/SiC composites ($4–5 \times 10^{-6}$/ °C) and those for mullite/BSAS ($5–6 \times 10^{-6}$/ °C). When YPO_4 is applied in the state-of-the-art of EBCs as the outerlayer or the interlayer with mullite, the cracks due to CTE mismatch will be reduced. Thus the use of YPO_4 as EBC can be beneficial in terms of performance.

4. Summary

In summary, the YPO_4 powders were synthesized by sol–gel method. Its water-vapor corrosion resistance was tested in the atmosphere of 50% H_2O–50% O_2 with a total pressure of 1 atm at 1350 °C. The molten salt corrosion was carried out at 900 °C with Na_2SO_4. The results indicate that YPO_4 has good water-vapor and molten salt corrosion resistance. YPO_4 does not react with silica or decompose with the aid of silica, which confirms that YPO_4 has good chemical compatibility with the silicon-based substrate. The suitable CTE, good water corrosion resistance and compatibility, and excellent thermal stability in molten Na_2SO_4 of YPO_4 indicate that it is a potential environmental barrier coating material.

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