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Effect of Al_2O_3 modification on the properties of YSZ: Corrosion resistant, wetting and thermal-mechanical properties

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ABSTRACT

Calcium-magnesium-alumino-silicate (CMAS) corrosion is one of the main failure modes of thermal barrier coatings (TBCs). Al_2O_3-modified YSZ (Y_2O_3-stabilised ZrO_2) coatings can resist it. Here, the effect of the Al_2O_3 content in YSZ on the resistance of CMAS corrosion was investigated by means of differential scanning calorimetry (DSC), X-ray diffraction (XRD) and wetting tests. The thermal properties of samples, the Young's modulus and fracture toughness of Al_2O_3-modified YSZ were studied by thermal conductivity and Vickers hardness test, respectively. The results demonstrate that when the Al_2O_3 content is 40 mol%, the Al_2O_3-modified YSZ has the best properties to resist CMAS corrosion due to the formation of anorthite which has a high melt point. Furthermore, the phase diagram and phases mole fractions with different Al_2O_3 content were calculated which match well with the experiments. With the increase of Al_2O_3 modification content, the thermal conductivity, Young's modulus and fracture toughness of the sample increase.

1. Introduction

Thermal barrier coatings (TBCs) are widely used in aero-engineering to increase the service temperature and to improve the turbine efficiency [1–3]. These coatings consist of a porous ceramic top-coat (even though new materials have emerged over time, Y_2O_3 - stabilised ZrO_2 (YSZ) is the preferred candidate), a thermally grown oxide layer, with the main composition of Al_2O_3, a MCrAlY alloy (M = Ni, Co or Fe) bond-coat (BC), and a nickel-based super-alloy substrate [4]. TBCs are generally prepared by air plasma spraying (APS) and electron-beam physical vapour deposition (EB-PVD). The former has a laminated structure and the porosities are parallel with the YSZ/BC interface, while the latter exhibits columnar grains and the intercolumnar porosities are perpendicular to this interface [5]. The polylaminate and poriferous coatings can effectively decrease the basal surface temperature.

However, the use of TBCs generally results in materials issues. When the TBC is exposed to the temperature higher than 1200 °C for some time, YSZ will sinter together due to high temperature. Densification of YSZ caused by high-temperature sintering will lead to an accompany loss in strain tolerance [6,7], and increase in thermal conductivity [8,9]. Furthermore, when the turbine is in the operating environment, fine sand in the air melts and deposits on the hot surface of TBCs and then infiltrates the coating. The composition of fusion contains mainly calcium-magnesium-alumino-silicates (CMAS) glass. The CMAS glass attacks the TBCs as a moving front by [10–14]: (i) penetrating into the TBC pores; (ii) dissolving and re-precipitation of ZrO_2 grains, leading to dilatation of the coating; and (iii) ultimately reaching the metal substrate and reacting with the substrate. Furthermore, the CMAS-impregnated TBCs have low strain-tolerance, making them highly susceptible to thermo mechanical failure during repeated heating–cooling cycles (thermal cycling) [10]. CMAS corrosion is the most serious failure mode of TBCs. The main ways to resist CMAS corrosion consist of four parts [15–21]: (1) increasing porosity or changing the geometry of pore to increase the surface area of top-coat; (2) choosing mew materials, such as gadolinium zirconate ($Gd_2Zr_2O_7$), etc., as the main composition of top coat; (3) depositing a dense layer on the surface of TBCs, filling the pores and columnar gaps of the TBC to obstruct the infiltration of CMAS; (4) making the material, including Al_2O_3, TiO_2 etc., react with CMAS before or during the infiltration, crystallizing its main constituents (mostly silicates) and increasing the viscosity of CMAS. On the practical side, an YSZ/Al_2O_3 composite which combines the properties of the individual components has a wide range of applications. For example, alumina has been widely recognized as an excellent modification material for YSZ TBCs due to its ability to shift the CMAS composition to promote crystallization and blocking further

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CMAS melt infiltration [15,22]. And it has longer thermal cycling life than a conventional YSZ. Also, an YSZ/Al_2O_3 composite has been proposed as an electrolyte for a planar Solid Oxide Fuel Cell (SOFC) because of its enhanced mechanical and thermal properties compared with conventional YSZ [23]. Al_2O_3 can react with CMAS and form anorthite phase, which is known for its stability and reported to provide sealing properties. In some studies [10,24,25], 20 mol% Al_2O_3 and 5 mol% TiO_2 were added into YSZ to resist CMAS corrosion. This composition is considered as the maximum solubility in YSZ and TiO_2 is acting as a nucleating agent. Unfortunately, the optimal composition of Al_2O_3 addition to resist CMAS is still unknown. Furthermore, during heating over 1200 °C, complex melting processes of CMAS on the surface of top coat, including melting, adhering and spreading have been observed to occur. These processes can be established association with the wetting properties of CMAS [26]. In particular, the variation of the contact angle of CMAS melt controls the infiltration and chemical reaction between CMAS and YSZ [11]. However, there are few literatures for the characterization of the CMAS wetting behaviour on the surface of Al_2O_3-modified YSZ. Therefore, it is necessary to understand the wetting and spreading dynamics of CMAS/YSZ system for CMAS resistance. Additionally, as the exist of TGO layer at the interface of bond coat and top coat, the content of Al_2O_3 is very high near the interface of TGO/top coat, especially when the top coat is also modified by Al_2O_3. The results of YSZ modified by different Al_2O_3 contents tests, including low content and high content, help for investigating the properties of TBCs from the top to bottom of the top coat. As the existing of TGO, the content of Al_2O_3 is high at the bottom of the top coat, and the high Al_2O_3 compositions were selected to investigate the properties of the top coat near the interface of TGO/top coat. However, the properties of these areas are unclear.

In the present work, the melting and wetting behaviour of CMAS melt on YSZ with different Al_2O_3 contents were quantitatively characterized by differential scanning calorimetry (DSC), X-ray diffraction (XRD) and wetting tests. The effect of Al_2O_3 modification on the properties of YSZ, including thermal conductivity, Young's modulus and fracture toughness were also studied. Additionally, the phase diagram and mole fraction of equilibrium phases changed with different Al_2O_3 content in CMAS were both calculated to determine the mechanism of coating's properties optimization. This most important aim for this work is to systematically study the influence of Al_2O_3 modification content on YSZ performance and reveal the appropriate Al_2O_3 modification contents range which not only can resist CMAS but also can improve the properties of YSZ. From this some reasonable suggests can be formed for people to employ in later experiments.

2. Experimental procedure

2.1. Preparation of CMAS and YSZ materials

The CMAS used in this study was obtained by laboratory synthesis. The composition is 33CaO-9MgO-13$AlO_{1.5}$-45SiO_2 (mol%). This CMAS composition has been used in previous investigations [27–29] and is a simplified version of the intruding melt found within airfoil coatings by Borom et al. [30]. The four oxides were mixed and melted at 1300 °C for 4 h. Then, the amorphous glass was ground to powder using a mortar. The radius of the particles was about 0.1–10 μm.

According to the Y_2O_3-ZrO_2-Al_2O_3 ternary phase diagram (Fig. 1) [31], the composition of 7YSZ (wt%) is located in the tetragonal zirconia + cubic zirconia phase field. With the addition of Al_2O_3 to YSZ, the composition changes to the dotted line in Fig. 1, which crosses three phase fields: tetragonal zirconia + cubic zirconia phase region, tetragonal zirconia + cubic zirconia + Al_2O_3 phase region and cubic zirconia + Al_2O_3 phase region. Powders of 7YSZ (sources were ceramic ingots from Zhongnuoxincai Company, located in Beijing, China. The purity is 99.5%) as well as 7 YSZ mixed with Al_2O_3 (99.5% purity, from Tianjin Guangfu Fine Chemical Research Institute, located in Tianjin, China) in seven compositions were chosen, as shown in Table 1. The powder samples were grinded with a Fritsch Planetary Micro Mill PULVERISETTE for 11 h. The grinding bowl is made of zirconium oxide and the diameter of the ZrO_2 grinding balls were 5, 1.5 and 0.5 mm, successively. Additionally, the difference in thermal expansion coefficients between the top-coat and substrate generates residual compressive stress in the oxide layers, resulting in coat cracking and spalling. In this study, modified YSZ content (22.5%, 40.0%, 45.0%, mol%) of Al_2O_3 and 7YSZ ceramic plates were used to resemble the TBCs top coat to negate the mechanical effect caused by the bond coat and substrate. The prepared compositions were compacted in a floating die using a hydraulic press with a compaction pressure of 220 MPa to a 10 × 10 × 3 mm plate, and then sintered in a furnace at 1400 °C for 4 h to obtain a plate.

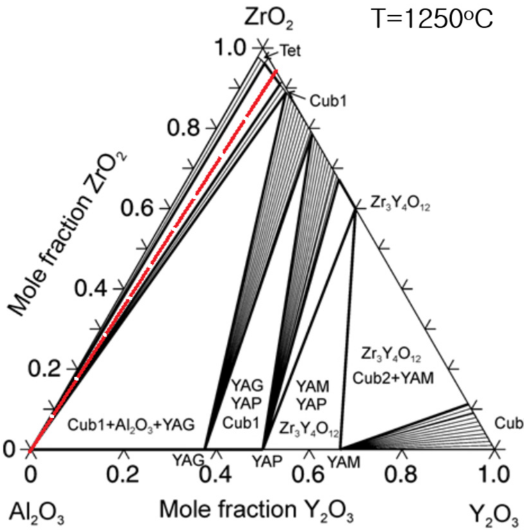

Fig. 1. The ternary phase diagram of Y_2O_3-ZrO_2-Al_2O_3 at 1250 °C, the compositions of tests are chosen through the red dotted line. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Table 1
The concentration of the samples.

No.	ZrO_2 (mol%)	Y_2O_3 (mol%)	Al_2O_3 (mol%)
1	96.0	4.0	0.0
2	95.0	4.0	1.0
3	74.4	3.1	22.5
4	67.2	2.8	30.0
5	57.6	2.4	40.0
6	52.8	2.2	45.0
7	48.0	2.0	50.0

2.2. Differential scanning calorimetry testing

Differential scanning calorimetry (DSC) was used to study the onset of the phase transformation, melting and reactions between the CMAS and YSZ. The Al_2O_3-modified YSZ powder mixed with CMAS (mass ratio of 1:1) was also selected for the DSC tests. The ratio chosen reflects the situation within TBC pores/channels where the melt is surrounded by a large amount of oxide [32]. The experiments were undertaken using a Netzsch 404F3 DSC instrument and Pt-Rh crucibles with pierced lids. Pt-Rh crucibles were used instead of alumina crucibles to ensure the minimum reaction between the crucibles and the samples. The crucibles were rested on thin Al_2O_3 washers to prevent adhesion to the instrument stage at high temperatures. With respect to the temperature profile, the samples were heated from room temperature to 1500 °C at a