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Stoichiometric redox reaction-controlled, combustion assisted spray pyrolyzed zirconia films on stainless steel

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Keywords: zirconia, combustion, spray pyrolysis, films, YSZ

Supplementary material for this article is available online

Abstract

In this contribution, an efficient aqueous solution combustion technique was implemented to achieve zirconia films on stainless steel substrates at 400 °C, by low capital and facile spray pyrolysis of a combustible precursor comprising stoichiometric amounts of zirconium oxynitrate hydrate and glycine. Detailed derivation of stoichiometric redox reaction is emphasized in the present work. Thermal behaviour of combustible precursor revealed the combustion temperature at ∼220 °C. Crystalline tetragonal zirconia film was deposited at 400 °C with a wavy morphological surface inferred from diffraction patterns and microstructural studies, respectively. Besides, an approach to fabricate spray pyrolysed YSZ films through combustion at 400 °C was successfully accomplished. These films can have a potential impact on biomedical and thermal barrier applications.

1. Introduction

Zirconia (ZrO₂) has been explored for numerous applications due to its diverse physical, chemical, mechanical, thermal, electronic properties, and offers high melting point, chemical stability, dielectric constant, excellent wear-resistant, low thermal conductivity and biocompatibility [1, 2]. Thin films of zirconia have been extensively used in heat resistant coatings, orthopedic and dental implants, optical coatings, micro and nanoelectronics etc [2–4]. Zirconia films have been deposited by different solution-processed techniques such as sol-gel dip coating and spray pyrolysis [5–8]. Yttria (Y₂O₃) stabilized zirconia (YSZ) has been widely used as thermal barrier coatings to insulate and shield hot-section metal components in gas turbines, aircraft engines to attain durability, efficiency and performance [9]. YSZ coatings have also been fabricated through solution-processed techniques such as sol-gel dip and spin coating [4, 10].

Spray pyrolysis appears as an attractive, versatile, cost-effective, and easier process for depositing homogenous, good-quality films for large-scale production. It involves precursor spraying, droplet transport, evaporation of solvent, droplet spreading and precursor decomposition [11, 12]. Solution combustion technique achieved great attention due to the fabrication of metal oxide films at relatively low temperatures. Here, precursor comprises a redox pair of oxidizer and fuel, undergoes exothermic reaction of simultaneous reduction and oxidation, under a minimum supplied heat, resulting a localized exothermic-heat output which leads to the formation of a continuous, dense framework of metal-oxygen-metal bond [13]. Combustion-assisted spray pyrolysis (spray-combustion synthesis), invented as a fascinating route to deposit metal-oxide films on glass and Si/SiO₂ substrates [14]. However, there are no reported studies conducted on metal-oxide film deposition on metallic substrates like engineering-grade stainless steel through combustion-assisted spray pyrolysis, as per our best knowledge. In view of this, the present study aims to extend novel combustion-assisted spray pyrolysis in fabricating metal-oxide film with simple equipment on stainless steel which is widely used in industrial, marine and biomedical applications.
2. Experimental

0.1 M aqueous combustible precursor was prepared by dissolving stoichiometric quantities of ZrO(NO$_3$)$_2$·H$_2$O (99%, Sigma Aldrich, India) and glycine (99%, SRL Pvt. Ltd, India). The solution was allowed to stir for 30 min to make compositionally homogenous and optically transparent. Later, precursor was sprayed through low-cost spray gun for 30 times on polished 316L stainless steel substrates at 200, 300 and 400 °C, respectively, followed by annealing for two hours at respective temperatures. Thermal characterization of precursor, the complete procedure for fabricating films and their structural, morphological characterizations, and schematic representation (figure S1) of precursor preparation, film fabrication are detailed in supplementary information available online at stacks.iop.org/IOPSN/1/024806. Likewise, 0.1 M aqueous precursor consisting stoichiometric amounts of Y(NO$_3$)$_2$·6H$_2$O (99.8%, Sigma Aldrich, India) with ZrO(NO$_3$)$_2$·H$_2$O, glycine was used to fabricate 5 mol% YSZ film similarly on 316L stainless steel substrate at 400 °C, and the structural properties were investigated.

3. Results and discussion

3.1. Theoretical stoichiometric redox reaction

The determination of stoichiometric amounts of fuel, oxidizer is crucial in achieving high heat output from the reaction. Jain’s method (JM) systematically accounts for reducing valence (RV) and oxidizing (OV) valence of combustible reactants and incorporates them into a relationship, shown in equation (1),

$$\phi = \left( \frac{RV}{OV} \right) \times n$$

where ‘$\phi$’ is fuel to oxidizer ratio and magnitude of ‘n’ is number of moles of fuel required per mole of oxidizer [15]. Based on propellant chemistry, OV of oxidizer ZrO(NO$_3$)$_2$·H$_2$O is −10 and RV of fuel C$_2$H$_5$NO$_2$ is +9. By replacing magnitude of these values in equation (1), ‘n’ turns as ‘10 $\phi$/9’. From JM, combustion reaction is considered to be stoichiometric, if $\phi = 1$, leads to $n = 1.11$ for present redox couple. More specifically, 1.11 moles of glycine is required for one mole of zirconium oxyxynitate hydrate for complete commencement of reaction without intervention of molecular oxygen from atmosphere. Stoichiometric redox reaction as the function of ‘$\phi$’ is derived in the following manner,

Reduction of oxidizer:

$$\text{ZrO(NO}_3\text{)}_2\cdot\text{H}_2\text{O} \rightarrow \text{ZrO}_2 + \text{N}_2 + \frac{5}{2}\text{O}_2$$ (2)

Oxidation of fuel:

$$n \times \left( \text{C}_2\text{H}_3\text{NO}_2 + \frac{9}{4}\text{O}_2 \rightarrow 2\text{CO}_2 + \frac{1}{2}\text{N}_2 + \frac{5}{2}\text{H}_2\text{O} \right)$$ (3)

Adding (equation (2)) and (equation (3)), because redox reaction is simultaneous reduction and oxidation,

$$\text{ZrO(NO}_3\text{)}_2\cdot\text{H}_2\text{O} + n\text{C}_2\text{H}_3\text{NO}_2 + \left( \frac{9n}{4} - \frac{5}{2} \right)\text{O}_2$$

$$\rightarrow \text{ZrO}_2 + 2n\text{CO}_2 + \left( 1 + \frac{n}{2} \right)\text{N}_2 + \left( \frac{5n}{2} + 1 \right)\text{H}_2\text{O}$$ (4)

Substituting $n = \frac{10\phi}{9}$ in (equation (4))

$$\text{ZrO(NO}_3\text{)}_2\cdot\text{H}_2\text{O} + \frac{10\phi}{9}\text{C}_2\text{H}_3\text{NO}_2 + \frac{5}{2}(\phi - 1)\text{O}_2$$

$$\rightarrow \text{ZrO}_2 + \frac{20\phi}{9}\text{CO}_2 + \left( \frac{9 + 5\phi}{9} \right)\text{N}_2 + \left( \frac{25\phi + 9}{9} \right)\text{H}_2\text{O}$$

For stoichiometric reaction, $\phi = 1$,

$$\text{ZrO(NO}_3\text{)}_2\cdot\text{H}_2\text{O} + \frac{10}{9}\text{C}_2\text{H}_3\text{NO}_2$$

$$\rightarrow \text{ZrO}_2 + \frac{20}{9}\text{CO}_2 + \left( \frac{14}{9} \right)\text{N}_2 + \left( \frac{34}{9} \right)\text{H}_2\text{O}$$ (5)

It is interesting to see that redox reaction derived from JM (equation (5)) is in line with balanced redox reaction (shown in figure 1), on substituting $\phi = 1$. Note that, coefficient of molecular oxygen ‘5/2 ($\phi - 1$)’ turns
as null at $\phi = 1$; thus, the derived redox reaction matches fundamental analogy of non-requirement of molecular oxygen for combustion.

### 3.2. Thermal, structural and microstructural analysis

The thermal response of combustible precursor is represented through TGA, DTG, DTA traces, shown in figure 2(a). The TGA trace is categorized into five different zones and the temperature range, weight loss are embodied in table S1. Each slope change in TGA is designated in DTG by a peak. The initial and persistent weight loss in zone I corresponds to evaporation of aqueous solvent and corresponding endothermic peak P1 is found in DTA at $\sim 100^\circ$C. Zone II with minor weight loss can be attributed to bound water removal. Later in zone III, considerable weight loss has occurred with an exothermic response as P2 at $\sim 220^\circ$C in DTA. This phenomenon in thermal traces depicts gases evolution via an exothermic reaction. The integrated effects of mass loss (in TGA) and exothermic response (in DTA) of precursor can be ascribed to occurrence of combustion, according to balanced redox reaction shown in figure 1. A subsequent slight weight loss in zone IV can be dedicated to further escape of retained gases with increase in temperature. The exothermic response of DTA as P3 at $\sim 282^\circ$C in zone IV can be credited to the crystallization of desired oxide. Further, continual weight loss in zone V can be devoted to incineration of carbonaceous residues generating CO$_2$ evolution with a small exothermic response in DTA as P4 at $\sim 340^\circ$C. No significant weight loss in TGA curve is noticed beyond zone V.

XRD patterns of films fabricated at 200, 300, 400 $^\circ$C respectively are shown in figure 2(b). It is observed that films fabricated at 200 and 300 $^\circ$C showed no traces of zirconia peaks. The former film is fabricated below the combustion temperature deduced from thermographs, so the combustion might not happen during fabrication. The cause for amorphous nature of latter film can be attributed to lack of sufficient thermal energy to crystallize at $\leq 300^\circ$C. As fabrication temperature raised above 300 $^\circ$C, i.e. at 400 $^\circ$C, the film showed the planes (111), (200) corresponding to tetragonal zirconia (ICDD: 00-017-0923) with crystallite size of 13.3 nm (calculated from Debye–Scherer’s equation). The crystallization of tetragonal zirconia film on stainless steel of the present study is in accordance with previous work [5]. From diffraction patterns, it can be deduced that the transformation to crystallized structure is happened in between 300 and 400 $^\circ$C, which is slightly higher than $\sim 282^\circ$C depicted from thermal analysis. The reason can be ascribed to the transfer of liberated heat to surroundings during fabrication because of high surface to volume ratio of the film compared to bulk precursors. Also, the byproduct gases formed might have changed their thermodynamic states (temperature) by utilizing the liberated heat during combustion reaction [16]. The heat liberated or temperature attained during combustion might not be completely used by the oxide for its crystallization which turned a little higher temperature ($> 300^\circ$C) than the temperature represented by thermal analysis. The solution-processed
technique, parameters for depositing zirconia film, zirconia phase and its evolution temperature on stainless steel reported in previous studies are given in table S2, and it can be noticed that the present work applies comparatively lower deposition temperature with usage of unsophisticated equipment.

The zirconia film fabricated at 400 °C (hereafter represented as zirconia film) analyzed under FESEM exhibited discrete particles on surface and its reason is explained by certain probabilistic assumptions. Possibly during initial spraying, most of the precursor droplets arrived at metal substrate might be wet and spread at great speed on surface of metal, as the surface tension of metal is higher than metal oxide usually. As the substrate is preheated, spread precursor droplets might be combusted, resulting in a continuous dense oxide film on the surface. As spraying continued, the successive spray droplets might fall on the surface of previously formed oxide film, which has comparatively less surface tension than the metal (here stainless steel), resulting in slow spreading. This slow spreading of droplets might lead to the formation of discrete particles on surface of film [17], as shown in figure 3(a). Also, a wavy natured morphology with tiny microscopic pores on the surface of film is observed at high-resolution (figure 3(b)). It can be ascribed to the combined effect of escape of entrapped byproduct gases from the intermediate layers leaving pores during fabrication and volume shrinkage of the upper layer occurred by evaporation of solvent at surface while spraying [18]. A continuous dense film adhering to substrate underneath the wavy surface is noticed (shown in figure 3(c)), confirms materialization of the film.

Figure 3. FESEM images of zirconia film (a) showing discrete particles on surface of film (b) representing wavy nature with pores due to escape of gases from surface during fabrication and (c) showing the presence of film.

Similarly, the way zirconia film is fabricated, as an approach, YSZ film is also fabricated on stainless steel substrate at 400 °C. The balanced redox reaction representing YSZ formation is shown in figure 4(a). The XRD pattern of YSZ film shown in figure 4(b) represents the tetragonal YSZ with diffraction plans (111), (200). The highest intense plane (111) is compared with (111) plane of zirconia film and a noticeable shift of (111) plane of YSZ film towards lower angle is observed (Shown in figure 4(c)). The shift is attributed to partial replacement of smaller Zr⁴⁺ ions (80 pm) by larger Y³⁺ ions (102 pm). In addition, calculated crystallite size is found to be 12.8 nm which is smaller than crystallite size of zirconia film (13.3 nm). The reason can be attributed to the generated retarding force by Y³⁺ ions due to replacement of Zr⁴⁺ ions present at grain boundaries might greater than the driving force for grain growth, resulting in hindrance of grain boundary movement. It has been previously demonstrated that the crystal lattice tends to convert into a structure with more symmetrical or stabilization in its phase with reduction in crystallize size [19]. Thus, it can be inferred that the tetragonal phase is successfully stabilized by introducing yttrium in the combustion-assisted spray pyrolyzed films and it coincides with the previous report [4].
4. Conclusion

In the present contribution, a novel combustion-assisted spray pyrolysis was effectively extended on stainless steel substrates for the deposition of zirconia films at 400 °C with low-cost apparatus. The theoretical redox reaction for the formation of zirconia was systematically derived and it concurred with balanced redox reaction at unit fuel to oxidizer ratio. The thermal analysis of the precursor traced combustion and phase transition at \( \sim 220 \) °C and 282 °C, respectively. The materialization of tetragonal structured wavy-morphological zirconia film of 13.3 nm crystallite size with discrete particles on surface was achieved at 400 °C. The combustion-assisted spray pyrolysis was also utilized to fabricate YSZ film, resulted in tetragonal structured crystalline film with a lower angle shift in major plane and reduced crystallite size of 12.8 nm, dedicated probably to partial replacement of \( \text{Zr}^{4+} \) by \( \text{Y}^{3+} \) and generated retarding force by \( \text{Y}^{3+} \).

Acknowledgments

This work is supported by Science and Engineering Research Board (SERB), Department of Science and Technology (ECR/2015/000339). The authors would like to thank Department of Metallurgical and Materials Engineering, NITK Surathkal, India.

Data availability statement

All data that support the findings of this study are included within the article (and any supplementary information files).

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