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The synthesis of thermochemically stable single phase lanthanum titanium aluminium oxide

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Abstract

Lanthanum titanium aluminium oxide ($LaTi_2Al_9O_{19}$, LTA) synthesized by solid state reaction has been proven to be a promising thermal barrier material. However, LTA synthesized via solid state reaction requires a high processing temperature of at least 1500 °C for 24 h. In this paper, single phase LTA was synthesized by sol–gel at a lower temperature (1350 °C) and the process parameters, phase composition, and relative thermal properties were investigated. Two-step calcination was used to obtain fine LTA powders. According to X-ray diffraction, the best calcination temperature of sol–gel synthesized LTA is 1350 °C. XRD results also showed the thermochemical stability of sol–gel synthesized LTA, which does not react with Al_2O_3 up to 1500 °C, to be excellent. Compared to LTA synthesized by solid state reaction, sol–gel synthesized LTA has higher coefficients of thermal expansion (CTEs) which are circa 10.2×10^{-6} °C^{-1} at 950 °C, related to the size dependent characteristic of CTEs. Therefore, sol–gel synthesized LTA can be a promising candidate as a thermal barrier material on Ni-based superalloys.

Keywords: A. Sol–gel process; A. Calcination; C. Thermal properties; C. Thermal expansion

1. Introduction

Thermal barrier coating systems, mainly consisting of thermal barrier coatings (TBCs), thermally grown oxides (TGO), bond coats, and metallic substrates, are the main components of turbine blades and vanes. They can offer a 100–300 °C temperature gradient and promote the desired high operating temperatures (above 1100 °C) to significantly improve gas turbine engine efficiency [1]. However, the development of metallic bond coats has faced a bottleneck, particularly due to the cost, with the cooling systems also reaching their current technology limit. Therefore, the main focus in the development of aviation gas turbine systems is concentrated on the development of TBCs [1–4].

TBCs, as protective thermal insulation layers, are widely applied to protect gas turbine engine blades and vanes. The state-of-the-art industrial TBC material is 6–8 wt% yttria stabilized zirconia (6-8YSZ), which can be used for over the long term at temperatures below 1200 °C. At higher temperatures, sintering behavior and phase transformation will reduce the strain tolerance in combination with the increase in Young's modulus and volume change during cooling, consequently reducing the thermal cycling lifetime of TBCs [5,6]. Currently, there is a growing demand in increasing the operating temperature to increase the efficiency of gas turbine engines, hence alternative materials are required instead of YSZ. The selection of TBC materials should fulfill the following requirements: (1) high melting point, (2) low thermal conductivity, (3) no phase transformation up to operation temperature, (4) suitable CTEs matching the metallic components, (5) good thermochemical stability, (6) good sintering resistance, and (7) good corrosion and erosion resistance [7,8]. Therefore, the development of new TBC materials has been confined to doped zirconia, pyrochlores, perovskites, and aluminates [7,9].

Alternative refractory materials, such as $LaTi_2Al_9O_{19}$ (LTA), have received increasing attention and this material has been synthesized via solid state reaction. The complex crystal structure of LTA offers potentially low thermal

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conductivity (circa. 2.3 $W\,m^{-1}\,K^{-1}$ for LTA ceramic, 1400 °C). Studies of LTA prove that it has better thermochemical stability, phase stability, and sintering resistance, and lower thermal conductivity than YSZ, with comparable mechanical properties and CTEs as YSZ, except for low fracture toughness [9]. Not only can LTA be used as thermal barrier material, it can also be used as a luminescent material, such as the matrix of laser materials, due to the optical inertia of La^{3+} that does not have any electrons in the 4f shell. Nanoscience and nanotechnology offer the potential to improve the physical and mechanical properties of new and established engineering materials due to the extremely small grain size as compared to conventional materials on the micron level [10]. A significant number of studies report that nanostructured materials and coatings show an expected improvement in mechanical properties, as well as lower thermal conductivities and better sintering resistance [11–13]. Therefore, in current research, nanostructured single phase LTA was synthesized using the sol–gel method to allow control of the structure, stoichiometry and composition at a molecular level, with the relative crystal structure, thermochemical, and thermophysical properties all being investigated.

2. Experimental

LTA powders were prepared using the Pechini sol–gel method. $La(NO_3)_3\cdot 6H_2O$ ($\geq$99.9%, Sigma Aldrich), $Al(NO_3)_3\cdot 9H_2O$ ($\geq$99.9%, Sigma Aldrich), and Titanium Butoxide [$Ti(OC_4H_9)_4$, $\geq$99.9%, Sigma Aldrich] as original materials were dissolved in absolute ethanol by stoichiometric ratio and stirred until complete light yellow transparent sol was obtained. Then, citric acid as the complexing agent and polyethylene glycol (PEG200) as the surfactant were added into the sol and stirred for another 30 min. The reaction is simply described by Fig. 1 and the following chemical reactions [14]:

$$La^{3+} + 2Ti^{4+} + 9Al^{3+} + 19O^{2-} \Rightarrow LaTi_2Al_9O_{19} \quad (1)$$

The sol was dried at 120 °C to form xerogel, calcined at the target temperature for 2 h and ball milled for 24 h to get fine white LTA powders. The as-prepared powders were pressed to corresponding bulk materials under 400 MPa of the pressure, followed by calcination at 1300 °C for 2 h to densify the bulks.

The phases were characterized by X-ray diffractometer (XRD, SIEMENS Kristalloflex 810 diffractometer) with Cu-Kα radiation at a scan rate of 1.2°/min from 20–80°. The crystallite size was obtained by the refined X-ray diffractograms by using the Rietveld method. The morphology of powders was characterized by Scanning Electron Microscope (SEM, XL-30 FEG, Philips) and Transmission Electron Microscope (TEM, JEOL 2000FX). The CTEs were measured using a high-temperature dilatometer (TA Q400, TA Instrument) from ambient temperature to 950 °C at a heating rate of 5 °C/min. The LTA powders were mixed with Al_2O_3 with the volume ratio of 1:1 and pressed under the 400 MPa of pressure, before being calcined at 1500 °C to investigate the thermochemical stability.

3. Results and discussion

3.1. The analysis of TGA-DSC curves of LTA xerogel

The calcination process of sol–gel produced LTA is determined by the DSC-TGA curves shown in Fig. 2. According to the TGA curve in Fig. 2, the weight loss of LTA xerogel begins at around 125 °C, showing a huge decrease until 621 °C and only a slight weight loss when above 621 °C. The huge weight loss starting at 125 °C can be attributed to the loss of water, the decomposition of organics, and the decomposition of nitrate ion, whilst the slight weight loss above 621 °C may be due to the effect of purged gas and the crystallization of LTA, which also indicates that the decomposition of organics has been completed at 621 °C. The DSC curve shows a small and broad endothermic peak at 125 °C, corresponding to the loss of water, with another endothermic peak around 276 °C that corresponding to the decomposition of organics where a huge weight loss is shown in the TGA curve, mainly caused by the vigorous evolution of CO_2 of citric acid decomposed to aconitic acid ($C_6H_4O_6$) and itaconic acid ($C_5H_4O_4$) according to the following equation [15–17]:

$$\text{citric acid} \xrightarrow{175^{\circ}C} \text{aconitic acid}(C_6H_4O_6) + H_2O_{(g)} \quad (2)$$

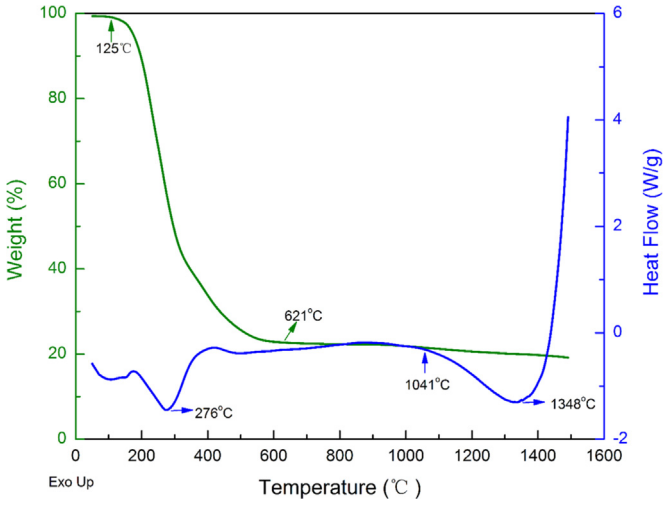

Fig. 2. TGA-DSC curves of LTA xerogel.

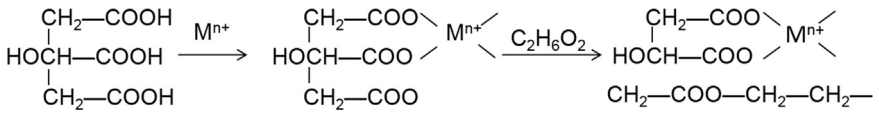

Fig. 1. The reaction process of synthesizing nanopowders by Pechini sol–gel method.