Twin step synthesis of lanthanum zirconate through transferred arc plasma processing

To cite this article: S Yugeswaran *et al* 2010 *J. Phys.: Conf. Ser.* **208** 012119

View the article online for updates and enhancements.

Twin step synthesis of lanthanum zirconate through transferred arc plasma processing

S Yugeswaran[1], V Selvarajan[1]*, P V Ananthapadmanabhan[2] and L Lusvarghi[3]

[1] Plasma Physics Laboratory, Department of Physics, Bharathiar University, Coimbatore – 641 046, India

[2] Laser and Plasma Technology Division, Bhabha Atomic Research Centre, Mumbai – 400 085, India

[3] Department of Materials and Environmental Engineering, University of Modena e Reggio Emilia, Via Vignolese, 905, 41100, Modena, Italy

E-mail: vselvrjn47@rediffmail.com

Abstract. Low power transferred arc plasma (TAP) processing is a simple and cost-effective method for large amount of ceramic processing in a very short period of time duration. In the present work, lanthanum zirconate ($La_2Zr_2O_7$) was synthesized by transferred arc plasma (TAP) melting technique followed by mechanical milling. The mixture of La_2O_3 and ZrO_2 powders with 1:2 mole ratio were ball milled for four hours and melted for three minutes in transferred arc plasma torch at 10 kW input power with 10 lpm of argon flow rate. The phase and microstructure formation of the processed samples were analyzed by X-ray diffraction (XRD) and Scanning Electron Microscope (SEM) images.

1. Introduction

Yttria stabilized zirconia (YSZ) coatings are commonly used as thermal barrier coatings (TBC) because of their low thermal conductivity (2 W m^{-1}. K^{-1}) and high thermal expansion coefficient (11×10^{-6} K^{-1}) [1, 2]. The YSZ coatings do not fulfil the requirements for higher reliability and lower thermal conductivity at higher temperatures. The maximum surface temperature of YSZ-based TBCs is limited to 1200° C for long-term operation. Below this temperature, an important factor that influences and often determines the lifetime of the TBC system is the oxide scale formation at the bond coat-TBC interface. The higher temperatures (above 1473 K), accelerate the phase transformation of YSZ from the t' tetragonal phase to the equilibrium tetragonal and cubic phase and then to monoclinic phase, which might result in disintegration of the coating [3]. To overcome the above problems, some novel ceramic materials with lower thermal conductivity and better reliability at high temperature has been developed as candidate materials for future TBCs.

Significantly, the pyrochlore type rare earth zirconate ceramics such as $Gd_2Zr_2O_7$, $Sm_2Zr_2O_7$, $Nd_2Zr_2O_7$ and $La_2Zr_2O_7$ investigated by researchers found that $La_2Zr_2O_7$ has excellent thermal stability, (which is stable up to its melting point: 2573 K), low thermal conductivity (1.56 W·m^{-1}. K^{-1}), better chemical resistance and low sintering rate, making it a very promising candidate for TBC applications [4, 5]. $La_2Zr_2O_7$ is less oxygen transparent than YSZ, providing a possibility of better bond coat oxidation resistance. It has cubic pyrochlore structure, which consists of the corner-shared ZrO_6 octahedra forming backbone of the network and La^{3+} ions fill the holes that are formed by six ZrO_6 octahedra. It can largely tolerate vacancies at the La^{3+}, Zr^{4+} and O^{2-} sites without phase

transformation. Both La^{3+} and Zr^{4+} sites can be substituted by a lot of other elements with similar ionic radii in case where electrical neutrality is satisfied, giving rise to the possibility of tailoring its thermal properties.

Various processing routes like co-precipitation, sol-gel, hydrothermal and hydrazine and conventional solid state reaction methods can be used to prepare lanthanum zirconate [6]. However, any one of the following factors like processing cost, purity, time duration and bulk production capability limits the above processing methods. Hence, a new technique to produce bulk amount of lanthanum zirconate with time and cost effectiveness is needed. The transferred arc plasma (TAP) processing technique can be effectively used to produce high temperature compounds within a short time period in economically competitive way. Transferred arc plasma is widely used technology for melting and vitrification of hazardous wastes due to its high temperatures and simplicity of generation and control. The transferred arc plasma is assumed to be stable, steady, axi-symmetric, optically thin and in a local thermodynamic equilibrium (LTE) in an atmospheric-pressure environment [7, 8]. The process is characterized by extremely high temperatures (up to 20,000–30,000 K), excellent arc stability and low environmental impact (low oxides emissions, low percentage of ultra-fine powder). High power density allows high production rate in a short duration of time [9]. In the present work, transferred arc plasma (TAP) melting technique was successfully employed for the preparation of lanthanum zirconate from commercially available lanthanum oxide (La_2O_3) and zirconium oxide (ZrO_2).

2. Experimental set up and procedures

In this work, commercially available lanthanum oxide (La_2O_3; Sigma-Aldrich) and zirconium oxide (ZrO_2; Sigma-Aldrich) were used as raw materials to prepare lanthanum zirconate. The mixture of ZrO_2 and La_2O_3 in the mole ratio of 2:1 was milled for four hours with corundum ball mill media using a planetary mill (Insmart, India). In this experiment, 10 kW plasma torch (Ion Arc Technologies, India) was used for processing the material by arc melting. The schematic diagram of the TAP experimental set up is shown in figure 1. The experimental set up consists of plasma torch, power supply, gas and water lines. A graphite bowl, 100 mm deep and 50 mm inner diameter serves as the anode of the torch as well as the melting bed. The cathode is made of a graphite rod 250 mm long and 50 mm diameter. The cathode end tapers to a conical shape for better electron emission. The cathode is enclosed in a hollow brass cylinder and provisions are made for water circulation (for cooling) and gas flow. The system has multiple inlets for plasma gas at the cathode end. The melted sample was cooled by forced air. The operating parameters are given in table 1.
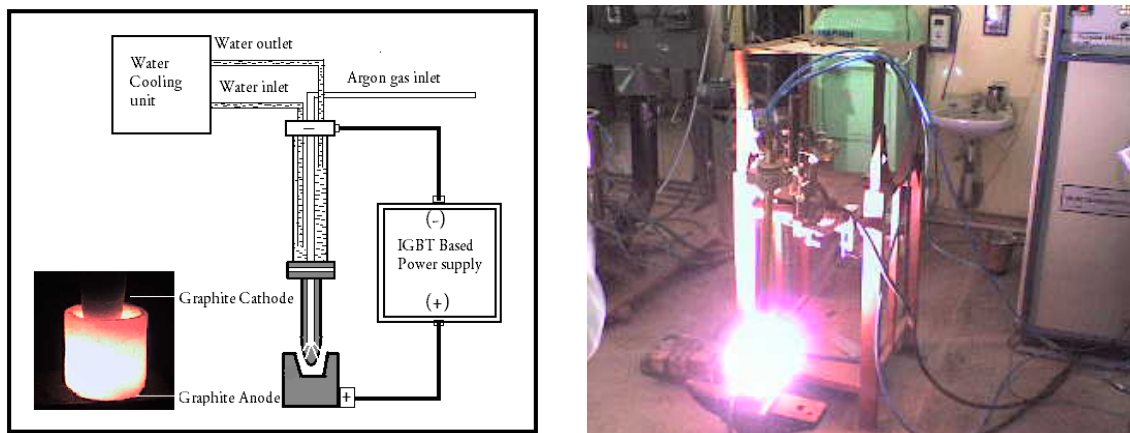

Figure 1. Schematic TAP experimental setup

Table 1: Operating parameters

Input power	: 10 kW
Plasma Gas and flow rate	: Argon; 10 lpm
Cooling water flow rate	: 10 lpm
Processing time	: 3 minutes
Cooling time	: 10 minutes
Cooling medium	: Air

The TAP processed sample was milled down to a few micrometer sized powders in an agate mortar prior to X-ray diffraction (XRD) analysis. For scanning electron microscope (SEM) investigation, the samples were polished using a set of silicon-carbide papers and finally with diamond paste. Then, the samples were chemically etched using 30 wt% HF solution for 30 seconds. The XRD pattern of the sample was recorded using a PW Philips Diffractometer with nickel-filtered Cu-Kα radiation. The microstructure of the samples was studied by the Philips XL40 SEM instrument. Density and porosity was measured respectively by a conventional method using Archimedes' principle in water medium (the theoretic density of lanthanum zirconate is 6.05 g·cm^{-3}) [10].

$$\text{Porosity (\%)} = 100 - \frac{\text{sample density}}{\text{bulk density}} \times 100 \qquad (1)$$

$$\text{sample density} = \frac{D}{W - S} \qquad (2)$$

where D, W and S are dry, saturated and suspended weights of the processed sample, respectively.

3. Results and discussion

Figure 2 shows the XRD pattern of TAP-processed lanthanum zirconate. The pattern shows a single homogeneous phase corresponding to pyrochlore structured lanthanum zirconate showing complete ness of the solid state reaction of La_2O_3 and ZrO_2 by the following reaction mechanism:

$$2\ ZrO_2 + 1\ La_2O_3 \rightarrow La_2Zr_2O_7 \qquad (3)$$

During the process, initially the plasma arc strikes the side walls of the graphite anode and the tip of cathode, then moves to all parts of the anode crucible. Consequently, the mixture of 2 mole ZrO_2 and 1 mole La_2O_3 powders got melted and formed a hemispherical shaped molten slag, the edges of which acquire more thermal energy than the centre. At the molten stage ZrO_2 and La_2O_3 react by the above reaction mechanism (Eqn. 3) and forms lanthanum zirconate.

Figure 3 shows the microstructure of TAP processed lanthanum zirconate sample. The processed sample has small pores on the surface due to the release of gas during solidification. According to the Archimedes' method, the estimated density and porosity of the processed sample are 5.40 g.cm^{-3} and 11% respectively. During the solidification (after switching off the plasma arc), the edges quickly solidify than the middle of the molten mass due to the temperature gradient of the anode surface. At the same time, slowly solidifying slag produces pores due to the release of gases. Hence the solidification is a key factor, which greatly influences the microstructure formation of TAP processed lanthanum zirconate.

In the process, the stoichiometric ratio of ZrO_2/La_2O_3 in the processed sample differed from initial mixture due to the evaporation of La_2O_3 in high temperature of plasma arc. Generally the La_2O_3 evaporate predominantly than ZrO_2 [2] and causes deficiency in liquid phase concentration of La_2O_3 in ZrO_2/La_2O_3 system. However, the above variation does not affect the pyrochlore structure formation. This is plausible, since the pyrochlore structures can accommodate large deviation from stoichiometry.
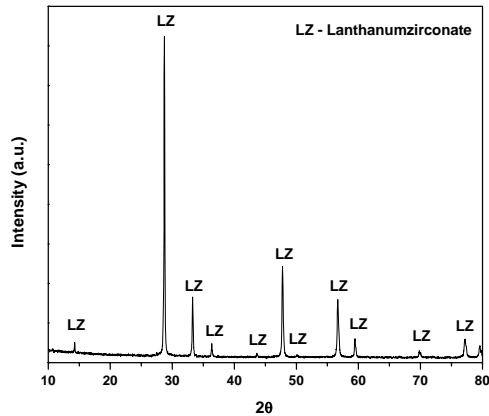
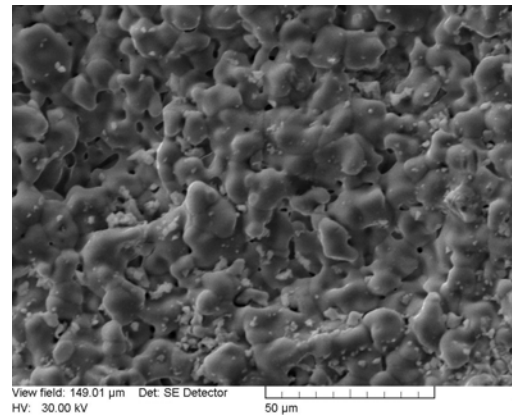**Figure 2.** XRD pattern of TAP processed lanthanum zirconate

Figure 3. Microstructure of TAP processed lanthanum zirconate

The ZrO_2 - La_2O_3 phase diagram shows considerable solubility range for $La_2Zr_2O_7$ from 0.87 La_2O_3 x 2 ZrO_2 (i.e. 53.6 wt% La_2O_3 and 46.4 wt% ZrO_2) to 1.15 La_2O_3 x 2 ZrO_2 (i.e. 60.4 wt% La_2O_3 and 39.6 wt% ZrO_2) whereby the crystal structure and properties are unaffected [11]. The above phase and microstructure formation results clearly shows that the TAP processing method is suitable for producing bulk amount of lanthanum zirconate at short time duration.

4. Conclusion
Lanthanum zirconate was successfully synthesized by low power transferred arc plasma (TAP) melting. The suggested method is competitive compared with many other methods due to its low cost and simplicity. The SEM and XRD results showed that the input power (10 kW) and processing time (3 minutes) of TAP system is enough for the preparation of pyrochlore structured lanthanum zirconate with in twin step processing.

Acknowledgements

References
[1]   Saremi M, Afrasiabi A and Kobayashi A 2008 Surf. Coat. Technol.**202** 3233
[2]   Saruhan B, Francois P, Fritscher K and Schulz U 2004 *Surf. Coat. Technol.***182** 175
[3]   Cao X Q, Vassen R and Stöver D 2004 *Eur. Ceram. Soc.* **24** 211
[4]   Cao X Q, Vassen R, Jungen W, Schwartz S, Tietz F and Stöver D 2001 *J. Am. Ceram. Soc.* **84 - 9** 2086
[5]   Bobzin K, Lugscheider E and Bagcivan N 2006 *High Temp. Mater. Process.***10** 45
[6]   Rao K K, Banu T, Vithal M, Swamy G.Y.S.K, and Ravikumar, K 2002 *Materials Letters,* **54** 205
[7]   Hsu K.C, Etemadi K and Pfender E. 1983 *J. Appl. Phys.* **54** 1293
[8]   Coudert J.F, Delalondre C, Roumilhac P, Simonin O and Fauchais P 1993 *Plasma Chem. Plasma Process.***13** 399
[9]   Deuis R L, Bee J V and Subramanian C 1997 *Scripta Mater.* **37-6** 721
[10]   Yugeswaran S, Selvarajan V and Lusvargi L 2008 *Vacuum* **83** 353
[11]   Stanek C R, Minervini L and Grimes Z R 2002 *J.Am.Cerm. Soc.* **85-11** 2792