Journal of Solid State Chemistry 188 (2012) 38–43

Contents lists available at SciVerse ScienceDirect

Journal of Solid State Chemistry

journal homepage: www.elsevier.com/locate/jssc

Hydrothermal synthesis of lutetium disilicate nanoparticles

Xiaoping Tang [a,b], Yanfeng Gao [a,*], Hongfei Chen [a,b], Hongjie Luo [c,**]

[a] State Key Laboratory of High Performance Ceramics and Superfine Microstructure, Shanghai Institute of Ceramics (SIC), Chinese Academy of Sciences (CAS), 1295 Dingxi, Changning, Shanghai 200050, China
[b] Graduate University of Chinese Academy of Sciences, 19 Yuquanlu, Beijing 100049, China
[c] Shanghai Institute of Ceramics (SIC), Chinese Academy of Sciences (CAS), 1295 Dingxi, Changning, Shanghai 200050, China

ARTICLE INFO

Article history:
Received 15 July 2011
Received in revised form
19 January 2012
Accepted 22 January 2012
Available online 30 January 2012

Keywords:
$Lu_2Si_2O_7$
Hydrothermal synthesis
Thermophysical properties
Hot corrosion

ABSTRACT

A simple, low-cost hydrothermal method was developed to synthesize irregular-and rod-shaped lutetium disilicate ($Lu_2Si_2O_7$) powders with sizes ranging from 71 to 340 nm. The synthesis temperature was 260 °C, which is nearly 1300 °C lower than that required for the solid-state reaction. The results indicated that both the hydrothermal temperature and pH values had great influences on the composition, crystalline phase and morphology of the powders. The formation mechanism, basic thermophysical properties, stability and anticorrosion properties of the $Lu_2Si_2O_7$ powders were also investigated. The obtained powders possessed low thermal conductivity, a suitable thermal expansion coefficient ($3.92–5.17 \times 10^{-6}$ K^{-1}) with the silicon-based substrate and excellent thermal and structural stability. During hot corrosion testing, the surfaces of the samples appeared to react with the water and molten salt vapors, but no serious failure occurred.

1. Introduction

Silicon-based ceramics are promising candidate materials for use in the hot section components of next-generation gas turbine engines due to their superior strength and durability at high temperatures. A major stumbling block to the application of these materials is their poor durability in high velocity combustion environments that contain high-temperature water vapor and molten alkali salts. At high temperatures, a thin silica film that forms on the surface of silicon-based ceramics can react with water vapor and dissolve in molten alkali salts to form volatile materials, which results in the failure of silicon-based ceramics. An environmental barrier coating (EBC) deposited on silicon-based ceramics helps provide protection [1–4]. Rare earth silicates, such as lutetium disilicate (i.e., $Lu_2Si_2O_7$), are potential candidates as EBC materials due to their low thermal diffusivity, excellent durability in severe environments containing both water vapor and alkali salts at high-temperatures, and desirable chemical and mechanical compatibility with the silicon-based matrix [3,5,6].

Solid-state and sol–gel syntheses are two typical routes for the preparation of lutetium silicates. However, the two methods require either annealing at a high sintering temperature (>1200 °C) or complicated processing parameters, and a pure $Lu_2Si_2O_7$ crystal is difficult to obtain. Furthermore, the produced powders usually possess large particle sizes and a wide size distribution, which hinders the formation of dense coatings [7–12]. Basically, a dense coating is required for the EBCs to obstruct the diffusion of corrosive gases. It is, therefore, necessary to develop an easy, low-cost, and efficient method to produce homogeneously dispersed lutetium silicate powders. In our previous work, nano-sized $Yb_2Si_2O_7$ powders were successfully synthesized at 200 °C via a hydrothermal process. The powders were nearly monodispersed and quite uniform in both shape and size, with a mean diameter of 20 nm [13]. In this article, we introduce a hydrothermal synthesis for the preparation of $Lu_2Si_2O_7$ powders beginning with lutetium nitrate ($Lu(NO_3)_3$) and sodium silicate ($Na_2SiO_3 \cdot 9H_2O$). Short, rod-like, pure-phase $Lu_2Si_2O_7$ powders with high crystallinity and controllable particle sizes were successfully synthesized at 260 °C. We systematically investigated the processing parameters and tested the thermal and physical properties of the products. To our knowledge, this is the first report of the synthesis of $Lu_2Si_2O_7$ by this method.

In this work, the hot corrosion of $Lu_2Si_2O_7$ in a Na_2CO_3 molten salt (MS) atmosphere at various temperatures was also studied. Na_2CO_3 readily decomposes and is used to study corrosion resistance under strongly basic conditions.

$$Na_2CO_3 \rightarrow Na_2O + CO_2\uparrow(g) \tag{1}$$

This study aims to determine the hot corrosion properties of $Lu_2Si_2O_7$ in an alkaline vapor airflow environment. The results of this study are helpful for selecting candidate materials for use as environmental barrier coatings.

---

[*] Corresponding author.
[**] Corresponding author.
E-mail addresses: yfgao@mail.sic.ac.cn, yfgaosic@gmail.com (Y. Gao).

0022-4596/$ - see front matter © 2012 Elsevier Inc. All rights reserved.
doi:10.1016/j.jssc.2012.01.049

2. Experimental procedure

In a typical synthesis, 0.01 mol Lu_2O_3 was dissolved in 30 mL of dilute nitric acid (2 mol L^{-1}) to produce $Lu(NO_3)_3$ solution, and 0.02 mol $Na_2SiO_3 \cdot 9H_2O$ was dissolved in 50 mL of distilled water. The aqueous solution of Na_2SiO_3 was slowly added to the $Lu(NO_3)_3$ solution with stirring. After homogeneous mixing, the pH was adjusted to a certain value (4, 6, 8 and 10) by adding ammonia. A white emulsion formed after ultrasonication for 10 min. After stirring for more than 4 h, the emulsion was sealed in a 250 mL autoclave liner (additional distilled water was added to reach 80% capacity). The autoclaves were then slowly heated to different temperatures (230, 240, 250 and 260 °C) and held for different lengths of time (4, 6, 8, 10, and 12 h). After the reaction, the autoclave was allowed to cool naturally. The obtained powders were washed with distilled water and absolute alcohol several times before drying at 60 °C for 6 h in an oven.

The powders were granulated with 5wt% PVA solution (powder:PVA solution=9:1, mass ration), and then pressed into plates (Φ=10 mm, d=2 mm) under 10 MPa with unidirectional squash. The prepared plates were then sintered at 1200 °C for 3 h to prepare the specimens for hot corrosion tests. To increase the wettability between the plates and the salt mists, no polishing was performed. The specimens were cleaned by ultrasonication in a sequence of distilled water, acetone and alcohol before testing. Fig. 1 shows the schematic of a home-made system for the corrosion behavior tests. Compressed air flowed through a wash bottle containing deionized water and then entered into a tubular furnace. The sample and 0.05 mol of Na_2CO_3 were placed in two Al_2O_3 ceramic boats with the molten salt placed near the airflow entrance. The exhaust gas was collected by another wash bottle. This design ensures that the airflow that passes over the sample contains both water and molten salt vapors. Corrosive properties were tested at both 900 and 1000 °C for 24 and 48 h.

The crystalline structures of the resulting powders were investigated using X-ray diffraction (XRD, D/max 2550 V, RIKAKU, Tokyo), and the morphologies were characterized by scanning electron microscopy (SEM, JSM-6700 F, JEOL, Tokyo). Simultaneous thermogravimetric and differential thermal analyses (TG-DTA, STA429C, NETZSCH, Germany) were performed in air from 30 to 1400 °C with an annealing rate of 10.0 K min^{-1} to determine the thermal properties of the powders. The thermal diffusion and specific heat of the sample were measured as a function of temperature from room temperature (RT) to 1200 °C using the laser-flash method. The thermal expansion of $Lu_2Si_2O_7$ was measured via the push-rod dilatometer method at temperatures from RT to 1200 °C.

3. Results and discussion

3.1. XRD analysis

Fig. 2 shows the XRD patterns of the samples obtained under different conditions. Overall, higher hydrothermal temperatures, longer reaction times and higher pH values led to greater peak

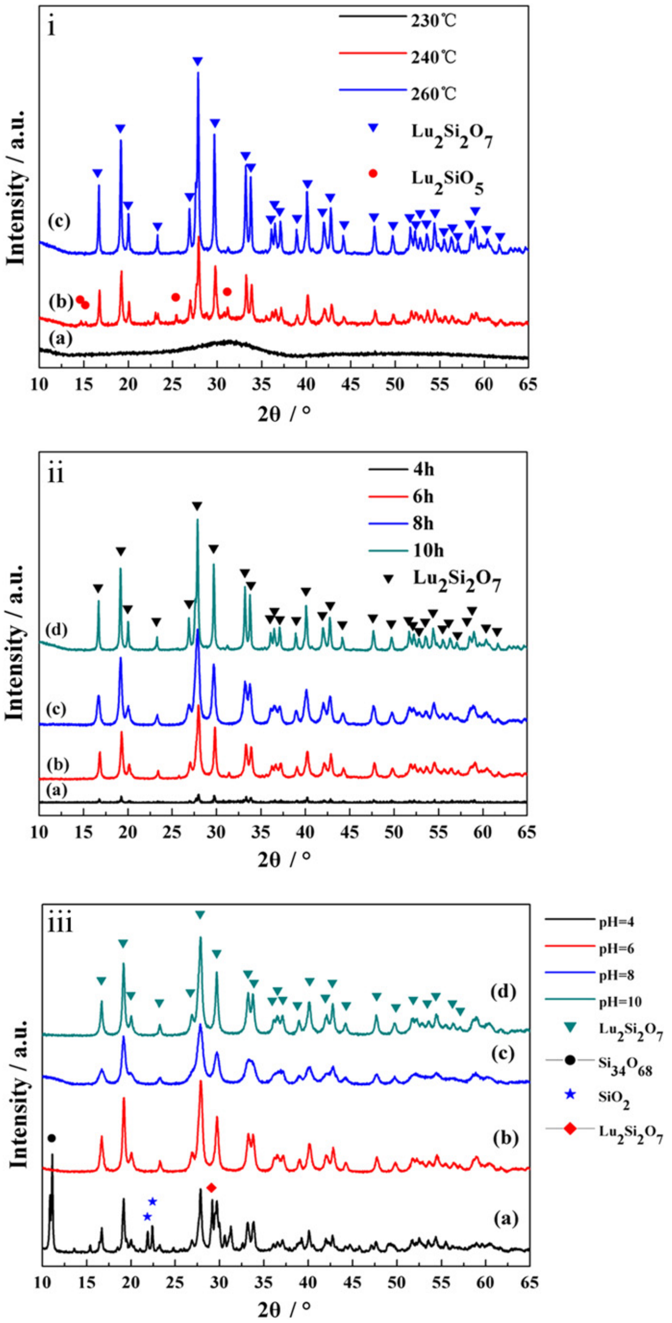

Fig. 2. (i) XRD patterns for powders obtained at different hydration temperatures with the same pH and reaction time (pH=10, 10 h): (a) 230 °C; (b) 240 °C; and (c) 260 °C. Fig.2 (ii) Different hydration times with the same pH and temperature (pH=10, 260 °C): (a) 4 h; (b) 6 h; (c) 8 h; and (d) 10 h. Fig.2 (iii) Different pH values with the same reaction time and temperature (10 h, 260 °C): (a) pH=4; (b) pH=6; (c) pH=8; and (d) pH=10.

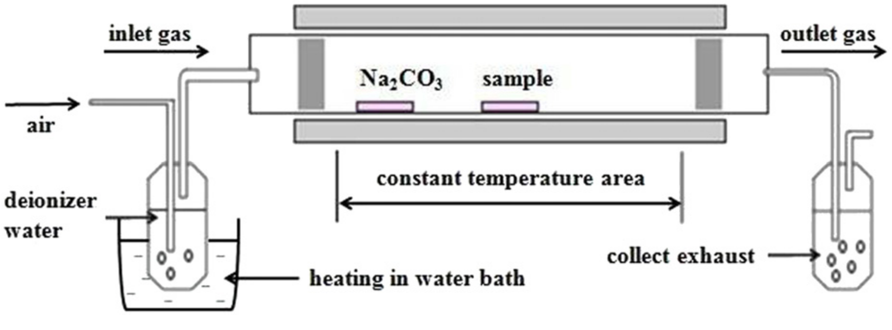

Fig. 1. Schematic drawing of the equipment used for corrosion testing.