Available online at www.sciencedirect.com
ScienceDirect
Ceramics International 33 (2007) 1547–1550
CERAMICS INTERNATIONAL
www.elsevier.com/locate/ceramint

Nanosized γ-Al_2O_3 protective film for fluorescent lamps

Yiwei Ao [a], Yunxia Yang [a], Shuanglong Yuan [a], Hengyao Hu [b], Hongchen Gu [b], Guorong Chen [a,*]

[a] Key Laboratory for Ultrafine Materials of Ministry of Education, School of Materials Science and Engineering, East China University of Science and Technology, Shanghai 200237, China
[b] Nano Science and Technology Engineering Center, Shanghai Jiaotong University, Shanghai 200030, China

Received 2 March 2006; received in revised form 22 April 2006; accepted 20 June 2006
Available online 12 September 2006

Abstract

Nanosized γ-Al_2O_3 particles were prepared by the sol–gel method with aluminum ion hydrolysis control performed by nitric acid. The as-prepared particles were mixed with deionized-water and stabilizer, and cycled in a high speed sand mill to form a stable γ-Al_2O_3 suspended slurry, which was then coated on the surface of the glass substrate to form a γ-Al_2O_3 protective film. Observations of SEM and visible transmission spectra show that a well-dispersed γ-Al_2O_3 slurry could be obtained after three-cycle grinding suitable to coat fluorescent lamp glass with a dense and uniform film of visible light transmission up to 95%.

Keywords: A. Milling; B. Nanocomposites; D. Al_2O_3; E. Functional applications; Protective film

1. Introduction

It is well known that compact fluorescent lamps suffer a progressive darkening of the bulb due to sodium amalgamation under the influence of ultraviolet radiation from arc discharge together with exposure to mercury vapor [1,2]. Because black sodium amalgam absorbs both UV light at 253.7 nm and light in the visible region, photo fluorescent properties of phosphors would be badly impacted. The best way to eliminate or alleviate such a negative effect is to apply a protective film on the inner surface of the glass tube to provide a chemically inert boundary between the phosphor powders and the glass.

Nanosized γ-Al_2O_3 is one of the widely used materials for such purpose because of its high chemical inertness, good visible transmittance and high abrasive and corrosion resistance [3–5]. Corresponding to the required thickness of protective films which is normally less than 0.5 μm, nanosized (10–100 nm) γ-Al_2O_3 powders have been usually used. These in most cases were prepared by high temperature vapor phase synthesis and chemical vapor deposition. From the viewpoint of mass production, however, a more economic preparation path is highly desirable. In the present paper, the sol–gel method combined with the post-cycling treatment in high speed sand mill to prepare a stable γ-Al_2O_3 suspended slurry is described.

2. Experimental

The flow sheet of the preparation process of the nanosized γ-Al_2O_3 powders is shown in Fig. 1. Analytically pure aluminum isopropoxide (AI) was used as a raw material, isopropoxide as a solvent, and nitric acid as a catalyst. An AI solution and an aqueous solution were firstly pre-prepared separately: the former was done by dissolving AI in the solvent, and the latter by mixing a certain amount of catalyst, disperser and isopropoxide with water. These two prepared solutions were then filled simultaneously into a three-neck round bottom flask with 30 ml isopropanol. The reaction mixture was stirred with a Teflon coated paddle type stirrer at room temperature with continuous addition of reagents for 0.5 h until a transparent sol was obtained. The as-prepared sol was then kept standing at 80 °C and aged for 24 h in a loosely sealed container to obtain the gel which was finally dried for about 2 h in vacuum of 300 mbar at room temperature. Nanosized γ-Al_2O_3 powders could be obtained by treating the dry gel at 600–700 °C.

γ-Al_2O_3 films were prepared from slurries which were formed by mixing the stabilizer (citrate acid) and deionized

* Corresponding author. Tel.: +86 21 64252647; fax: +86 21 64253395.
E-mail address: grchen@ecust.edu.cn (G. Chen).

0272-8842/$32.00
doi:10.1016/j.ceramint.2006.06.003

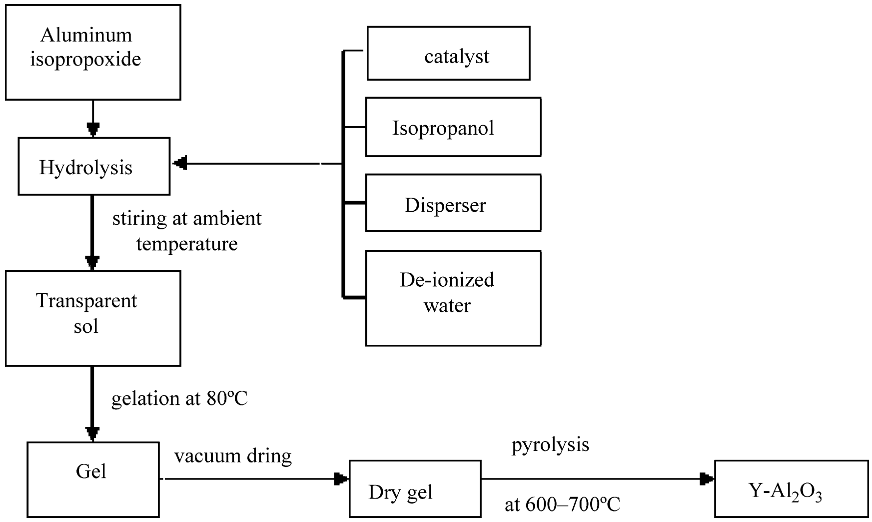

Fig. 1. Flow diagram for preparation of γ-Al_2O_3.

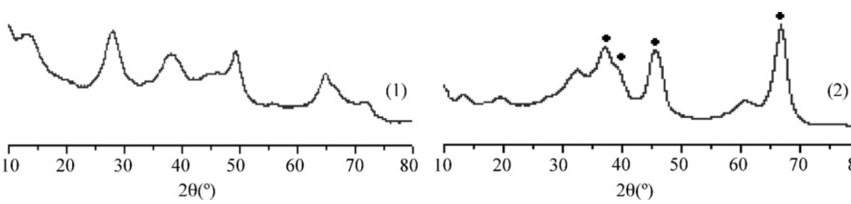

Fig. 2. X-ray diffractogram of dry gel (1) and alumina powders (2).

water (pH 7) with the nanosized γ-Al_2O_3 powders in the mass ratio of 0.01/90/10, respectively. The mixture of active materials and water was carefully ground in a high speed sand mill for 1–4 cycles. The γ-Al_2O_3 films were prepared by spinning the γ-Al_2O_3 slurry on a glass substrate at a speed of 2000 rpm. The coatings were then dried at room temperature for 2 h, subsequently heated very slowly (1 °C/min) to 80 °C and held at this temperature for several hours to get dense and uniform γ-Al_2O_3 films.

Transmission electron microscopy (TEM, JEM-200CX) and X-ray diffraction (XRD, D/max-RA) analysis were used to clarify morphology and phase composition of the nanosized γ-Al_2O_3 powders. The particle size distribution of γ-Al_2O_3 powders was measured with a Malvern particle size analyzer (HPPS—5001). The morphology of the γ-Al_2O_3 films was observed by scanning electron microscopy (SEM, JSM-6360LV). UV Spectromatography (UNICOUV-2102PC) was used to measure the visible light transmission of the γ-Al_2O_3 films.

3. Results and discussion

3.1. Nanosized γ-Al_2O_3 powders

In the present work, aluminum ions as alumina precursors were formed by rapid neutralization of aqueous acidic aluminum salts while the precipitates were amorphous hydroxides with different water contents. It is known that these products could transform into either crystalline hydroxides, $Al(OH)_3$ (bayerite), or oxide hydroxide, AlOOH (boehmite) [6], depending on the thermal treatment conditions. For example, at a high heating rate (above 2 °C/min), the initial bayerite phase firstly converts to boehmite at 150 °C and then transforms to γ-Al_2O_3 at 300–500 °C. By further heating up to 1000 °C or at even higher temperature, γ-Al_2O_3 transformed to stable α-Al_2O_3 [7]. For the present work, the as-made material showed a mixture of boehmite and bayerite as shown in Fig. 2(1), whereas the dry gel sintered at 600–700 °C for several hours displayed only pure γ-Al_2O_3 (Fig. 2(2)). A TEM micrograph of the γ-Al_2O_3 powders of Fig. 3 shows spherical shaped particles with a narrow size distribution ranging from about 5 to 10 nm. No agglomerate particles have been found.

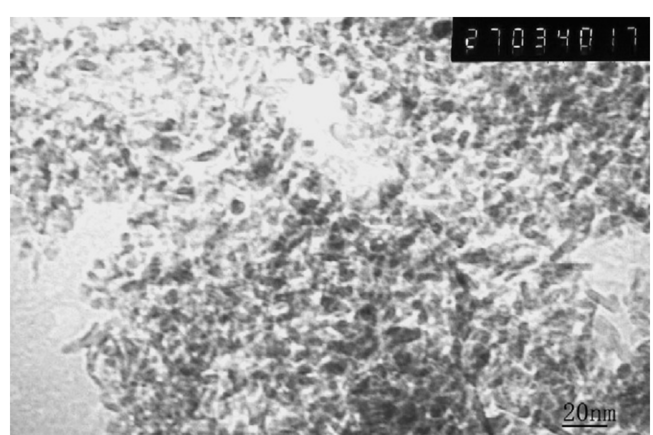

Fig. 3. TEM micrograph of γ-Al_2O_3 powders.

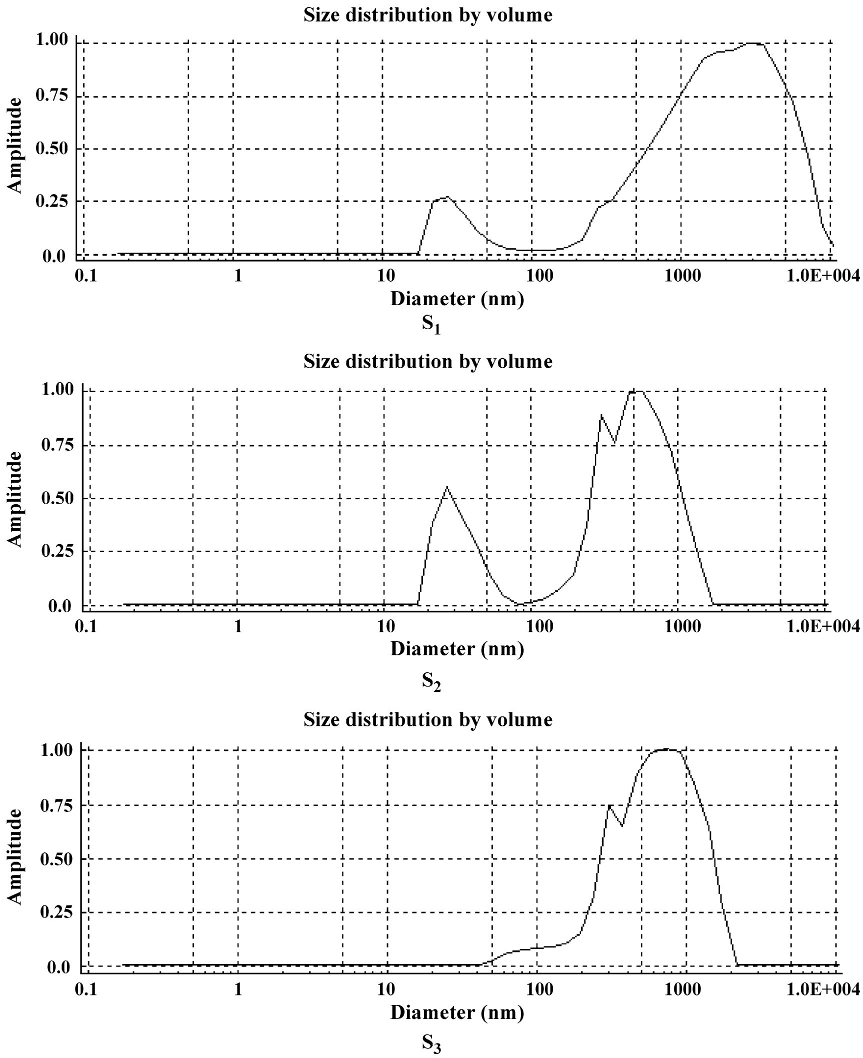

Fig. 4. Size distribution of γ-Al_2O_3 slurry: (S_1) grinding for two cycles; (S_2) grinding for three cycles; (S_3) grinding for four cycles.

3.2. Dispersion of γ-Al_2O_3 particles in the slurry

For their high surface area and surface energy, nanosized particles tend to agglomerate when mixed with water or an organic vehicle with particle size larger than 1 μm (Fig. 4(S_1)). So, in this work, dispersers were introduced and a high speed sand grinder was used in order to prepare a highly homogeneous and stable slurry.

For the given slurry containing the disperser, sand grinding conditions showed an evident effect on the dispersion state of the γ-Al_2O_3 particles in the slurry. As shown in Fig. 4, after grinding for two cycles, γ-Al_2O_3 particles in the water-based slurry were poorly dispersed. Except for a few particles which were under 100 nm, or larger than 1 μm, the average particle size was about 500 nm (Fig. 4(S_1)). By three-cycle grinding, however, the dispersion state improved with the average particle size decreasing to 200 nm (Fig. 4(S_2)). After four cycles grinding, the concentration of smaller γ-Al_2O_3 particles decreased while the average size of particles increased (Fig. 4(S_3)). This might be due to both agglomeration and dispersion processes taking place during the grinding treatment. Although the high speed sand grinding played the role of disintegrating the agglomerated particles, it also increased the probability of collision among the particles. Therefore, there exists an optimal grinding condition corresponding to the highest homogeneity and stability of the slurry.

3.3. Properties of the alumina film

SEM micrographs of γ-Al_2O_3 films prepared from the γ-Al_2O_3 slurry which was subject to high speed sand grinding are shown in Fig. 5. Improved dispersion of γ-Al_2O_3 particles in the slurry affects positively the film microstructure as observed in Fig. 5(F_1, F_2 and F_3) up to three cycles sand grinding.

Transmittance of γ-Al_2O_3 films in the visible region is one of the main properties for application as a protective coating on the inside surface of a fluorescent lamp. Fig. 6 shows the visible light transmission spectra of the γ-Al_2O_3 films. Because visible light is scattered by agglomerated particles, the average visible light transmission of the γ-Al_2O_3 film prepared from the slurry grinding for one cycle is very low (about 50%) (Fig. 6(F_1)). With an increase in sand grinding cycles which causes more

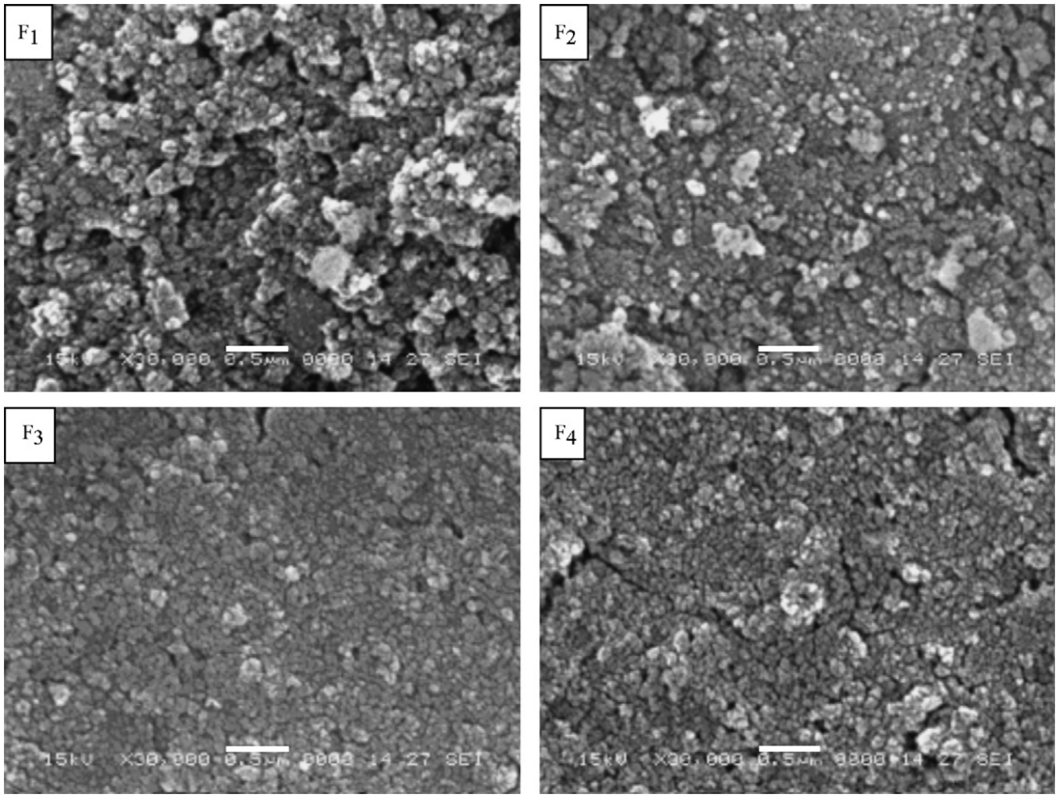

Fig. 5. SEM micrograph of γ-Al_2O_3 films: (F_1) prepared from the slurry grinding for one cycle; (F_2) prepared from S_1; (F_3) prepared from S_2; (F_4) prepared from S_3.

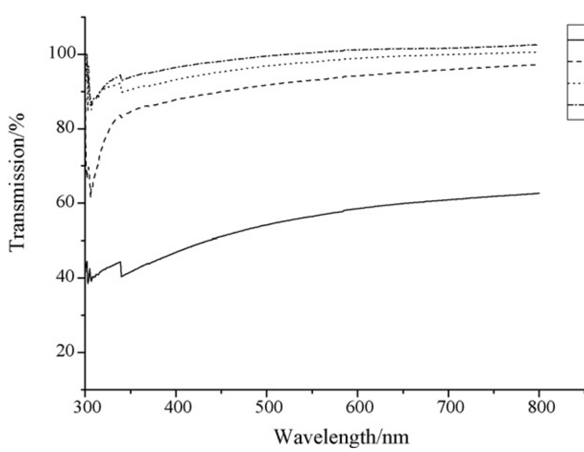

Fig. 6. Visible light transmission spectra of γ-Al_2O_3 films.

uniformly dispersed agglomerated particles in the slurry, the transmission of γ-Al_2O_3 films increases up to 95% for the sample F_3. Further increasing the grinding cycles to four did not deteriorate the transmittance of γ-Al_2O_3 films (Fig. 6(F_4)). This may possibly be attributed to the less continuous and adherent coating (Fig. 5(F_4)) caused by the lower homogeneity and stability of the slurry of the four grinding cycles.

4. Conclusions

Pure nanosized γ-Al_2O_3 particles having an average grain size from about 5 to 10 nm were prepared by the sol–gel method. With these γ-Al_2O_3 particles, a highly homogeneous and stable slurry could be obtained after being ground in high speed sand mill for three cycles. The average grain size of the agglomerated particles in this slurry is about 200 nm. The slurry was spin coated on glass pieces, and a smooth, continuous and adherent γ-Al_2O_3 film with 95% visible light transmission was prepared by heating the coating at 80 °C.

Acknowledgement

The authors gratefully acknowledge the financial support from Science and Technology Office of Zhejiang province, China (Grant no. 2004C11019).

References

[1] D.K. Moore, K. Wieder, I.L. Ericson, US Patent 4,670,688, (1987).
[2] D.J. Yusko, D. Hamadi, C.F. Ruoff, F.P. Craig, US Patent 5,113,118, (1992).
[3] K. Yatsui, T. Yukawa, C. Grigoriu, M. Hirai, W.H. Jiang, Synthesis of ultrafine γ-Al_2O_3 powders by pulsed laser ablation, J. Nanoparticle Res. 2 (2000) 75–83.
[4] J. Wrzyszcz, W. Mista, D. Hreniak, W. Strek, M. Zawadzki, H. Grabowska, Preparation and optical properties of nanostructured europium-doped γ-Al_2O_3, J. Alloy Compd. 341 (2002) 358–361.
[5] S. Kureti, W. Weisweiler, A new route for the synthesis of high surface area γ-aluminum oxide xerogel, Appl. Catal. A: Gen. 225 (2002) 251–259.
[6] M.I.F. Macedo, C.C. Osawa, C.A. Bertran, Sol–gel synthesis of transparent alumina gel and pure gamma alumina by urea hydrolysis of aluminum nitrate, J. Sol–Gel Sci. Technol. 30 (2004) 135–140.
[7] Y.H. Kim, C. Kim, P. Kim, J. Yi, Effect of preparation conditions on the phase transformation of mesoporous alumina, J. Non-Cryst. Solids 351 (2005) 550–556.